1. Introduction

"Acylation differs from alkylation in being virtually irreversible" [Olah, 1973], free of rearrangements and isomerizations [Wang, 2009; Norman & Taylor, 1965]. This authoritative exposition of the state of the art of Friedel–Crafts chemistry in 1973 close to the centennial of the invention of the Friedel–Crafts reaction has been long recognized and not without reason. The difference in behavior between Friedel–Crafts acylation and Friedel–Crafts alkylation was attributed to the resonance stabilization existing between the acyl group and the aromatic nucleus [Buehler & Pearson, 1970], which may serve as a barrier against rearrangements and reversible processes. However, if the acyl group is tilted out of the plane of the aromatic nucleus, e.g., by bulky substituents, the resonance stabilization is reduced and the pattern of irreversibility of Friedel–Crafts acylation may be challenged [Buehler & Pearson, 1970; Pearson & Buehler, 1971; Gore, 1974]. Under these conditions deacylations and acyl rearrangements become feasible [Buehler & Pearson, 1970; Pearson & Buehler, 1971; Gore, 1974].

Fig. 1. The Friedel–Crafts acyl rearrangement of 1- and 2-benzoynaphthalenes in PPA

The concept of reversibility in Friedel–Crafts acylations [Gore, 1955, 1964] was put forward in 1955 by Gore, who proposed that "the Friedel–Crafts acylation reaction of reactive hydrocarbons is a reversible process" [Gore, 1955]. Gore concluded that "Reversibility is an important factor in acylation reactions" [Gore, 1955]. The reversibility studies have been
focused mainly on unusual aspects of selectivity, including deacylations, one-way rearrangements and kinetic versus thermodynamic control [Gore, 1974]. Under classical Friedel–Crafts conditions (e. g., AlCl₃ and a trace of water), the pattern of irreversibility (e. g., in the naphthalene series) has been highlighted [Gore, 1964, 1974; Andreou et al., 1978; Dowdy et al., 1991].

The incursion of reversibility in Friedel–Crafts acylations was revealed by Agranat, et al. in the benzylation of naphthalene in polyphosphoric acid (PPA) at elevated temperatures (Fig. 1) [Agranat et al., 1974]. The kinetically controlled 1-benzylnaphthalene rearranged to the thermodynamically controlled 2-benzylnaphthalene (PPA, 140 °C) (vide infra). The reversibility concept was then applied to the synthesis of linearly annelated polycyclic aromatic ketones by intramolecular Friedel–Crafts rearrangements of their angularly annelated constitutional isomers [Agranat & Shih, 1974a; Heaney, 1991]. The Haworth synthesis of PAHs, which previously had allowed access to angularly annelated PAHs could thus be applied to the synthesis of linearly annelated PAHs [Agranat & Shih, 1974b]. Further experimental evidence in support of true reversibility of Friedel–Crafts acylation is limited [Frangopol et al., 1964; Balaban, 1966; Nenitzescu & Balaban, 1964; Effenberger et al., 1973; Levy et al., 2007; Mala’bi et al., 2009; Titinchi et al., 2008; Adams et al., 1998; Okamoto & Yonezawa, 2009]. Notable cases are the report by Balaban [Frangopol et al., 1964; Balaban, 1966; Nenitzescu & Balaban, 1964] on the reversibility of Friedel–Crafts acetylation of olefins to β-chloroketones, the report by Effenberger [Effenberger et al., 1973] of the retro-Fries rearrangement of phenyl benzoates (CF₃SO₂H, 170 °C) and the reversible ArS₅E₅aroylation of naphthalene derivatives [Okamoto & Yonezawa, 2009]. Additional examples are the acyl rearrangements of acetylphenanthrenes [Levy et al., 2007] and acetylanthracenes [Mala’bi et al., 2009] in PPA, the acetylation of fluorene [Titinchi et al., 2008], the disproportionation of 9-acetylanthracene into 1,5- and 1,8-diacetylanthracenes in an ionic liquid systems [Adams et al., 1998]. Complete reversibility of Friedel–Crafts acylation was established in the intramolecular para ←→ ortho acyl rearrangements of fluorofluorenones in PPA (Fig. 2) [Agranat et al., 1977]. Friedel–Crafts acyl rearrangement of polycyclic aromatic ketones (PAKs) has been referred to as the Agranat–Gore rearrangement [Levy et al., 2007; Mala’bi et al., 2009]. The Friedel–Crafts acylation can be adjusted to give a kinetically controlled ketone or a thermodynamically controlled ketone [Buehler & Pearson, 1970]. Acyl rearrangements and reversibility in Friedel–Crafts acylations have been associated with thermodynamic control [Pearson & Buehler, 1971; Andreou et al., 1978; Agranat et al., 1977]. The contributions of kinetic control vs. thermodynamic control in Friedel–Crafts acyl rearrangements remain an open question, in spite of the rich chemistry of Friedel–Crafts acylations. We have recently shown that kinetic control wins out over thermodynamic control in the Friedel–Crafts acyl rearrangement of diacetylanthracenes in PPA [Mala’bi et al., 2011].

Fig. 2. The Friedel–Crafts intramolecular acyl rearrangements of fluorofluorenones in PPA

A plausible mechanism of the Friedel–Crafts acyl rearrangement of 1-benzoynaphthalene (1-BzNA) into 2-benzoynaphthalene (2-BzNA) in PPA, is presented in Fig. 3. The
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mechanism involves the two dibenzoylnaphthalenes, their O-protonates and their $\sigma$-complexes. In the kinetically controlled pathway $1\sigma$-BzNAH$^+$ is more stable than $2\sigma$-BzNAH$^+$ and by virtue of the Hammond–Leffler postulate [Muller, 1994] the transition state leading to $1\sigma$-BzNAH$^+$ is lower in energy than the transition state leading to $2\sigma$-BzNAH$^+$. Thus, 1-BzNA is the kinetically controlled product. By contrast, in the thermodynamically controlled pathway, 1-BzNAH$^+$ and 1-BzNA are less stable than 2-BzNAH$^+$ and 2-BzNA, respectively. Therefore, 2-BzNA is the thermodynamically controlled product. Under conditions of thermodynamic control, the relative stabilities of the constitutional isomers of a given PAK are detrimental to the products of the Friedel–Crafts acyl rearrangement of the PAK and of the Friedel–Crafts acylation of the corresponding PAH.

![Figure 3](image_url)

Fig. 3. The mechanism of the Friedel–Crafts acyl rearrangement of representative PAKs 1- and 2-benzoylnaphthalenes.

2. Structures of monoacetylanthracenes and diacetylanthracenes

Anthracene (AN) is essentially a planar PAH. Due to its $D_{2h}$ symmetry, three constitutional isomers of acetylanthracenes (AcAN) are possible: 1-acetylanthracene (1-AcAN), 2-acetylanthracene (2-AcAN), and 9-acetylanthracene (9-AcAN) (see Fig. 4). These isomers differ in the position of the acetyl substituent at the anthracene ring system. The three constitutional isomers of AcAN can be categorized, depending on the degree of their overcrowding: (i) the non-overcrowded isomer 2-AcAN, in which the acetyl group is flanked by two ortho-hydrogens ($H^1$, $H^3$); (ii) the overcrowded isomer 1-AcAN, in which the overcrowding is due to the presence of one hydrogen atom ($H^3$) peri to the acetyl group; (iii) the severely overcrowded isomer 9-AcAN (assuming the planar conformation), in which the overcrowding is due to the presence of two peri-hydrogens ($H^1$, $H^8$) to the acetyl group. The
overcrowding in 1-AcAN and 9-AcAN should result in significant deviations of the acetyl groups from the plane of the anthracene nucleus, which is expected to encourage reversibility and rearrangements.

![Diagram of constitutional isomers](attachment:fig4.png)

**Fig. 4.** Constitutional isomers of monoacetylanthracenes (E and Z stereodescriptors are omitted)

There are 15 constitutional isomers of diacetylanthracenes (Ac$_2$AN), shown in Fig. 5. These isomers differ in the position of the acetyl substituents at the anthracene ring system. The present study encompasses the three monoacetylanthracenes 1-AcAN, 2-AcAN, 9-AcAN and the following eleven diacetylanthracenes: 1,5-Ac$_2$AN, 1,6-Ac$_2$AN, 1,7-Ac$_2$AN, 1,8-Ac$_2$AN, 1,9-Ac$_2$AN, 1,10-Ac$_2$AN, 2,6-Ac$_2$AN, 2,7-Ac$_2$AN, 2,9-Ac$_2$AN, 2,10-Ac$_2$AN and 9,10-Ac$_2$AN. The remaining diacetylanthracenes, 1,2-Ac$_2$AN, 1,3-Ac$_2$AN, 1,4-Ac$_2$AN and 2,3-Ac$_2$AN were not included in the present study. These constitutional isomers are not expected to be formed in the Friedel–Crafts acylations of 1-AcAN and 2-AcAN, due to the deactivation effect of the electron-withdrawing acetyl group towards further acetylation. This effect is not necessarily operating with respect to the "remote" unsubstituted benzene ring.

In 1-AcAN and 2-AcAN, the E- and Z-diastereomers should be considered. E and Z are the stereodescriptors applied to monoacetylanthracenes and diacetylanthracenes with a fractional bond order of the bond between the carbonyl carbon and the corresponding aromatic carbon [Moss, 1996]. In diacetylanthracenes, four diastereomers should be considered: ZZ, ZE, EZ and EE. Depending on the symmetry of a given diacetylanthracene, ZE and EZ diastereomers could be equivalent. 9,10-AcAN is a special case: only one stereodescriptor, Z or E, is required. In this case, Z or E refers to whether the carbonyl bonds lie on the same or on the opposite sides of the plane containing the C$_9$–C$_{11}$ and C$_{10}$–C$_{12}$ bonds and perpendicular to the aromatic plane.

Acetylanthracene 2-AcAN and diacetylanthracenes 1,5-Ac$_2$AN, 1,6-Ac$_2$AN, 1,7-Ac$_2$AN, 1,8-Ac$_2$AN, 2,7-Ac$_2$AN and 9,10-Ac$_2$AN have been synthesized in the present study and their crystal structures have been determined. Ketones 2-Ac$_2$AN, 1,5-Ac$_2$AN and 1,8-Ac$_2$AN have been prepared by the Friedel–Crafts acetylation of anthracene. Ketones 1,6-Ac$_2$AN, 1,7-Ac$_2$AN and 2,7-Ac$_2$AN have been prepared by the Friedel–Crafts acetylation of 2-AcAN. Ketone 9,10-Ac$_2$AN has been synthesized by methylation (MeLi) of 9,10-dicarboxymethoxyanthracene (prepared from 9,10-dibromoanthracene via 9,10-anthracenedicarboxylic acid). Ketones 1,7-Ac$_2$AN and 2,7-Ac$_2$AN are reported here for the first time.

The present study encompasses the crystal and molecular structures of monoacetylanthracenes (AcANs) and diacetylanthracenes (Ac$_2$ANs), the results of a systematic DFT study of the structures and the conformational spaces of AcANs and Ac$_2$ANs, as well as the comparison between the calculated and the experimental structures of these PAKs.
2.1 Molecular and crystal structure of monoacetylanthracenes and diacetylanthracenes

Of the three monoacetylanthracenes and eleven diacetylanthracenes included in the present study, only the crystal structures of 1-AcAN [Langer & Becker, 1993], 9-AcAN [Anderson et al., 1984; Zouev et al., 2011] and 1,5-AcAN [Li & Jing, 2006] have previously been described. The molecular and crystal structures of 2-AcAN, 1,6-Ac2AN, 1,7-Ac2AN, 1,8-Ac2AN, 2,7-Ac2AN and 9,10-Ac2AN are reported here for the first time, along with the previously reported structures.

2.1.1 Geometries of monoacetylanthracenes and diacetylanthracenes

Table 1 shows the crystallographic data for 2-AcAN, 1,5-Ac2AN, 1,6-Ac2AN, 1,7-Ac2AN, 1,8-Ac2AN, 2,7-Ac2AN and 9,10-Ac2AN.1 The ORTEP diagrams of 2-AcAN and of the six diacetylanthracenes as determined by X-ray crystallography are presented in Fig. 6–10. Ketones 2-AcAN, 1,5-Ac2AN, 1,8-Ac2AN and 2,7-Ac2AN crystallize in the monoclinic space groups P21/n, P21/c, P2/n and I2/a, respectively. The unit cell dimensions of the crystal structure of 1,5-Ac2AN are essentially identical to those reported in the literature [Li & Jing, 2006]. Ketone 1,6-Ac2AN and 1,7-Ac2AN crystallize in the triclinic space group P-1. Ketone 9,10-Ac2AN crystallizes in the orthorhombic space group Pnna21. Table 2 gives selected geometrical parameters derived from the X-ray crystal structures of the mono- and diacetylanthracenes under study. The following geometrical parameters were considered: the twist angles τ(Carom–Carom–Carb–O) (divided into τ1, τ2 and τ0 depending on the position of the acetyl group) and ψ(Carom–Carom–Carb–O) around the anthracenyl-carbonyl bond; the dihedral angle θ between the least-square planes of the carbonyl group and the anthracene system; the dihedral angle φ between the least-square planes of two side rings of the anthracene system; the pyramidalization angles χ at Carom and Carb. Table 3 gives the bond lengths in the mono- and diacetylanthracenes under study, as compared with the parent anthracene.

The data presented in Table 3 indicate the considerable variation in bond lengths in mono- and diacetylanthracenes. The bond lengths may be classified into several types: four C1–C2 or α-β bonds (134.2–137.7 pm), two C2–C3 or β-β bonds (138.7–144.4 pm), four C1–C9a bonds (141.8–145.5 pm), four C9a–C9 bonds (138.3–140.9 pm), and two C4a–C9a bonds (142.8–145.3 pm). These values are in the same range as the respective bond lengths in the X-ray crystal structure of anthracene, which are 136.1, 142.8, 143.4, 140.1 and 143.6 pm [Brock & Dunitz, 1990]. It has previously been shown that the bond lengths in anthracene are in agreement with the superposition of its four Kekulé structures and with the free valence numbers [Sinclair et al., 1950]. Table 3 also shows that the bonds adjacent to the acetyl group are elongated as compared to the respective bonds in anthracene, e.g. the C2–C3 bond in 2-AcAN (143.2 pm vs. 142.8 pm), the C1–C2 bonds in 1,5-Ac2AN and 1,8-Ac2AN (137.5 pm vs. 136.1 pm), the C9a–C9 bonds in 1,6-Ac2AN (137.0 pm vs. 136.1 pm), the C7–C8 bond in 1,7-Ac2AN (137.4 pm vs. 136.1 pm) and the C2–C3 bond in 2,7-Ac2AN (144.4 pm vs. 142.8 pm). This elongation effect stems from the contributions of dipolar Kekulé structures, in which the anthracene bonds adjacent to the acetyl group are necessarily single. This effect, however, is not noticeable in 9,10-Ac2AN, because the carbonyl groups are almost perpendicular to the aromatic plane and are hardly conjugated with the anthracene system.
Fig. 5. Constitutional isomers of diacetylanthracenes (E and Z stereodescriptors are omitted)
Table 1. Crystallographic data for acetylanthracenes 2-AcAN, 1,5-AcAN, 1,6-AcAN, 1,7-AcAN, 1,8-AcAN, 2,7-AcAN and 9,10-AcAN.
| Compound     |  \( t^a \)  |  \( \psi^b \) |  \( \theta^c \) |  \( \varphi^c \) |  \( C_{\text{carb}}^\text{C-arom} \) |  \( C_{\text{carb}}^\text{C-anc} \) |  \( \chi(C_{\text{arom}}) \) |  \( \chi(C_{\text{carb}}) \) |  \( O-H \) |  \( CH_3-H \) |
|--------------|------------|------------|------------|------------|-----------------|-----------------|-----------------|-----------------|-----------|-----------|
| 1-AcAN      | 27.1       | -152.7     | 28.6       | 3.2        | 149.3           | -0.1            | -0.2            | 223.4           | H\(^1\)   | 223.4     | H\(^2\)   |
| 2-AcAN      | 173.1      | -5.3       | 5.9        | 0.4        | 148.6           | -1.6            | 0.4             | 249.2           | H\(^1\)   | 244.3     | H\(^1\)   |
| 9-AcAN      | 87.9       | -91.8      | 89.2       | 5.8        | 150.4           | 0.3             | -0.8            | 294.0           | H\(^1\)   | 263.1     | H\(^8\)   |
| 1,5-Ac\(_2\)AN | 20.0       | -156.8     | 22.7       | 0.0        | 149.4           | -3.2            | 3.4             | 226.9           | H\(^9\)   | 243.7     | H\(^2\)   |
| 1,6-Ac\(_2\)AN | 30.0       | -147.1     | 32.2       | 1.3        | 150.1           | -2.9            | 3.0             | 228.8           | H\(^9\)   | 230.0     | H\(^2\)   |
| 1,7-Ac\(_2\)AN | -15.2      | 162.9      | 16.0       | 2.3        | 149.8           | 1.9             | -1.9            | 221.3           | H\(^9\)   | 229.2     | H\(^2\)   |
| 1,8-Ac\(_2\)AN | -176.6     | 3.7        | 4.5        |           | 149.0           | 0.3             | -0.6            | 247.9           | H\(^9\)   | 229.5     | H\(^8\)   |
| 2,7-Ac\(_2\)AN | -34.0      | 145.4      | 36.0       | 0.3        | 149.3           | 0.6             | 0.3             | 228.2           | H\(^9\)   | 231.1     | H\(^2\)   |
| 9,10-Ac\(_2\)AN | 0.9        | -178.5     | 2.0        |           | 148.9           | 0.7             | -1.3            | 225.9           | H\(^9\)   | 226.4     | H\(^3\)   |
|             | 85.0       | 94.0       | 86.7       | 1.6        | 151.3           | -1.0            | -1.2            | 288.2           | H\(^9\)   | 257.4     | H\(^1\)   |
|             | 87.0       | -93.7      | 86.5       |           | 151.5           | -0.6            | 0.1             | 290.5           | H\(^9\)   | 264.4     | H\(^5\)   |

\(^a\) \( t(C_8-C_1-C_{11}-O^{13}) \) for 1-AcAN, 1,5-Ac\(_2\)AN, 1,6-Ac\(_2\)AN, 1,7-Ac\(_2\)AN and 1,8-Ac\(_2\)AN, \( t(C_1^-C_2^-C_{11}^-O^{13}) \) for 2-AcAN and 2,7-Ac\(_2\)AN, \( t(C_3^-C_2^-C_{11}^-O^{10}) \) for 1,6-Ac\(_2\)AN, \( t(C_2^-C_7^-C_{13}^-O^{10}) \) for 1,7-Ac\(_2\)AN, \( t(C_8^-C_9^-C_{11}^-O^{13}) \) for 9-AcAN and 9,10-Ac\(_2\)AN.

\(^b\) \( \psi(C_2^-C_1^-C_{11}^-O^{13}) \) for 1-AcAN, 1,5-Ac\(_2\)AN, 1,6-Ac\(_2\)AN, 1,7-Ac\(_2\)AN and 1,8-Ac\(_2\)AN, \( \psi(C_8^-C_9^-C_{11}^-O^{13}) \) for 2-AcAN and 2,7-Ac\(_2\)AN, \( \psi(C_5^-C_6^-C_{13}^-O^{10}) \) for 1,6-Ac\(_2\)AN and 2,7-Ac\(_2\)AN, \( \psi(C_8^-C_7^-C_{13}^-O^{10}) \) for 1,7-Ac\(_2\)AN, \( \psi(C_8^-C_9^-C_{11}^-O^{13}) \) for 9-AcAN and 9,10-Ac\(_2\)AN.

\(^c\) \( \varphi(C_1^-C_{11}^-) \) for 1-AcAN, 1,5-Ac\(_2\)AN, 1,6-Ac\(_2\)AN, 1,7-Ac\(_2\)AN and 1,8-Ac\(_2\)AN, \( \varphi(C_2^-C_1^-C_{11}^-) \) for 2-AcAN and 2,7-Ac\(_2\)AN, \( \varphi(C_5^-C_6^-C_{13}^-) \) for 1,6-Ac\(_2\)AN and 2,7-Ac\(_2\)AN, \( \varphi(C_8^-C_7^-C_{13}^-) \) for 1,7-Ac\(_2\)AN, \( \varphi(C_8^-C_9^-C_{11}^-) \) for 9-AcAN and 9,10-Ac\(_2\)AN.

Table 2. Selected geometrical parameters of the X-ray molecular structures of acetylanthracenes 2-AcAN, 1,5-Ac\(_2\)AN, 1,6-Ac\(_2\)AN, 1,7-Ac\(_2\)AN, 1,8-Ac\(_2\)AN, 2,7-Ac\(_2\)AN and 9,10-Ac\(_2\)AN.
Fig. 6. ORTEP drawing of the crystal structure of 2-AcAN, scaled to enclose 50% probability

Fig. 7. ORTEP drawings of the crystal structures of 1,5-Ac₂AN (left) and 1,6-Ac₂AN (right), scaled to enclose 50% probability
Fig. 8. ORTEP drawings of the crystal structures of 1,7-Ac₂AN (left) and 1,8-Ac₂AN (right), scaled to enclose 50% probability.

Fig. 9. ORTEP drawings of the crystal structure of 2,7-Ac₂AN, scaled to enclose 50% probability.
### Table 3. Bond lengths (pm) in the X-ray structures of anthracene, monoacetylanthracenes and diacetylanthracenes.

|       | C\(^1\)–C\(^2\) | C\(^2\)–C\(^3\) | C\(^3\)–C\(^4\) | C\(^4\)–C\(^4\) | C\(^4\)–C\(^8\) | C\(^4\)–C\(^10\) |
|-------|-----------------|-----------------|-----------------|-----------------|---------------|-----------------|
| AN\(^a\) | 136.1           | 142.8           | 136.1           | 143.4           | 143.6         | 140.1          |
| 1-AcAN\(^b\) | 137.6(3)       | 138.7(3)       | 134.6(3)       | 143.1(3)       | 143.1(3)     | 139.2(3)       |
| 2-AcAN     | 136.4(4)       | 143.2(4)       | 134.6(4)       | 144.1(4)       | 143.0(4)     | 138.7(4)       |
| 9-AcAN\(^c\) | 134.9(3)       | 141.2(3)       | 135.0(3)       | 142.9(3)       | 143.2(3)     | 138.8(3)       |
| 1,5-Ac\(^2\)AN | 137.5(2)       | 141.4(2)       | 135.6(2)       | 142.9(2)       | 143.8(2)     | 139.9(2)       |
| 1,6-Ac\(^2\)AN | 136.9(2)       | 142.0(2)       | 135.5(2)       | 142.7(2)       | 144.1(2)     | 140.0(2)       |
| 1,7-Ac\(^2\)AN | 137.7(2)       | 141.5(2)       | 135.6(2)       | 143.0(2)       | 144.0(2)     | 140.0(2)       |
| 1,8-Ac\(^2\)AN | 137.3(2)       | 141.4(3)       | 135.5(2)       | 142.8(2)       | 143.7(2)     | 139.2(2)       |
| 9-Ac\(^2\)AN | 137.5(2)       | 141.2(3)       | 135.2(3)       | 142.9(2)       | 143.7(2)     | 139.2(2)       |
| 1,5-Ac\(^2\)AN | 137.1(3)       | 144.4(3)       | 134.2(4)       | 142.5(3)       | 144.6(3)     | 138.3(3)       |
| 9,10-Ac\(^2\)AN | 136.3(3)       | 141.8(4)       | 134.6(4)       | 142.7(3)       | 143.8(3)     | 140.9(3)       |

|       | C\(^1\)–C\(^10\) | C\(^10\)–C\(^8\) | C\(^10\)–C\(^5\) | C\(^5\)–C\(^6\) | C\(^8\)–C\(^7\) | C\(^7\)–C\(^8\) | C\(^8\)–C\(^9\) |
|-------|-----------------|-----------------|-----------------|-----------------|---------------|---------------|---------------|
| AN\(^a\) | 140.1           | 143.6           | 143.4           | 136.1           | 142.8         | 136.1         | 143.4         |
| 1-AcAN\(^b\) | 139.5(3)       | 142.8(3)       | 134.0(3)       | 134.6(3)       | 140.8(3)     | 135.1(3)     | 142.2(3)     |
| 2-AcAN     | 139.3(4)       | 143.6(4)       | 142.4(4)       | 136.1(4)       | 141.3(4)     | 135.0(4)     | 143.0(4)     |
| 9-AcAN\(^c\) | 139.1(3)       | 142.9(3)       | 142.4(3)       | 134.5(3)       | 140.4(3)     | 135.6(3)     | 142.7(3)     |
| 1,5-Ac\(^2\)AN | 139.7(2)       | 143.8(2)       | 145.0(2)       | 137.5(2)       | 141.4(2)     | 135.6(2)     | 142.9(2)     |
| 1,6-Ac\(^2\)AN | 139.2(2)       | 143.7(2)       | 142.5(2)       | 137.0(2)       | 143.9(2)     | 135.5(2)     | 143.1(2)     |
| 1,7-Ac\(^2\)AN | 139.0(2)       | 142.8(2)       | 143.3(2)       | 135.6(2)       | 142.8(2)     | 137.4(1)     | 142.7(1)     |
| 1,8-Ac\(^2\)AN | 139.2(2)       | 143.7(2)       | 142.8(2)       | 135.5(2)       | 141.4(3)     | 137.3(2)     | 144.4(2)     |
| 9-Ac\(^2\)AN | 139.4(3)       | 144.3(3)       | 142.3(3)       | 134.9(3)       | 142.8(3)     | 136.6(3)     | 141.8(3)     |
| 9,10-Ac\(^2\)AN | 139.4(3)       | 143.8(3)       | 143.3(3)       | 135.2(4)       | 141.1(4)     | 136.5(4)     | 143.0(3)     |

|       | C\(^9\)–C\(^9\) | C\(^9\)–C\(^9\) | C\(^9\)–C\(^1\) | C\(^1\)–C\(^1\) | C\(^1\)–C\(^1\) | C\(^1\)–C\(^1\) | C\(^1\)–C\(^1\) |
|-------|-----------------|-----------------|-----------------|-----------------|---------------|---------------|---------------|
| AN\(^a\) | 140.1           | 140.1           | 143.4           | -               | -             | -             | -             |
| 1-AcAN\(^b\) | 139.0(3)       | 138.9(3)       | 144.8(3)       | 149.3(3)       | 148.8(3)     | 121.7(3)     | -             |
| 2-AcAN     | 139.3(4)       | 139.7(4)       | 142.3(4)       | 148.6(4)       | 149.5(4)     | 121.5(3)     | -             |
| 9-AcAN\(^c\) | 140.3(3)       | 140.2(3)       | 142.4(3)       | 150.3(3)       | 148.5(3)     | 120.8(2)     | -             |
| 1,5-Ac\(^2\)AN | 139.9(2)       | 139.7(2)       | 145.0(2)       | 149.4(2)       | 150.9(2)     | 121.8(2)     | -             |
| 1,6-Ac\(^2\)AN | 139.5(2)       | 140.0(2)       | 144.6(2)       | 150.1(2)       | 150.5(2)     | 121.7(2)     | -             |
| 1,7-Ac\(^2\)AN | 140.5(1)       | 140.1(1)       | 145.5(1)       | 149.8(2)       | 151.6(2)     | 121.7(1)     | -             |
| 1,8-Ac\(^2\)AN | 140.1(2)       | 140.1(2)       | 144.4(2)       | 149.3(2)       | 151.2(2)     | 121.5(2)     | -             |
| 9,10-Ac\(^2\)AN | 140.0(3)       | 140.1(3)       | 142.9(3)       | 151.4(3)       | 149.4(3)     | 121.3(3)     | -             |

\(^a\) Brock & Dunitz, 1990; averaged bonds lengths

\(^b\) Langer & Becker, 1993

\(^c\) Zouev et al., 2011
Fig. 10. ORTEP drawings of the crystal structure of 9,10-Ac₂AN, scaled to enclose 50% probability

Ketone 2-AcAN crystallizes in the E conformation with a small twist angle of $\tau_2(C^1-C^2-C^{11}O^{13})=173.1^\circ$ and a small dihedral angle $\theta=5.9^\circ$. There are two pairs of enantiomeric molecules in the unit cell of 2-AcAN. The structure does not contain any short contact distances. Ketone 1,5-Ac₂AN adopts the Z,Z conformation with large twist angles, $\tau_1(C^{9b}-C^1-C^{11}O^{15})=20.0^\circ$, $\tau_2(C^{10a}-C^5-C^{13}O^{16})=-20.0^\circ$. The O$^{15}$H$^9$ and O$^{16}$H$^{10}$ contact distances are 226.9 pm, which is slightly shorter (7% penetration) than the sum of the respective van der Waals radii of hydrogen (115 ppm) and oxygen (129ppm) [Zefirov, 1997]. There are two identical molecules of 1,5-Ac₂AN in the unit cell, each possessing the C$_i$ symmetry. Ketone 1,6-Ac₂AN crystallizes in the Z,E conformations, with a large twist angle of the Z carbonyl group, $\tau_1(C^{9a}-C^1-C^{11}O^{15})=30.0^\circ$ and a small twist of the E carbonyl group, $\tau_2(C^5-C^6-C^{13}O^{16})=178.6^\circ$. The O$^{15}$H$^9$ contact distance is 228.8 pm (6% penetration), while the O$^{16}$H$^7$ contact distance is 249.9 pm. There are two enantiomeric molecules in the unit cell of 1,6-Ac₂AN. Ketone 1,7-Ac₂AN also crystallizes in the Z,E conformations, with the twist angles of $\tau_1(C^{9a}-C^1-C^{11}O^{15})=-15.2^\circ$ and $\tau_2(C^8-C^7-C^{15}O^{16})=-176.6^\circ$. The O$^{15}$H$^9$ contact distance is 221.3 pm (9% penetration). There are two enantiomeric molecules in the unit cell of 1,7-Ac₂AN. Ketone 1,8-Ac₂AN adopts the Z,Z conformation with two large twist angles, due to the repulsive peri-interactions O$^{15}$H$^9$ and O$^{16}$H$^9$ (225.9 and 228.2 pm) between two carbonyl oxygens and the same aromatic hydrogen. There are two enantiomeric pairs of non-equivalent molecules, A and B, in the unit cell of 1,8-Ac₂AN, each of them possessing the C$_2$ symmetry. The respective twist angles are $\tau_1(C^{9a}-C^1-C^{11}O^{15})=-34.0^\circ$ (A) and $\tau_1(C^{9a}-C^1-C^{11}O^{15})=-32.4^\circ$ (B). Ketone 2,7-Ac₂AN adopts the E,Z conformation, which is similar to
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those of 1,6-Ac$_2$AN and 1,7-Ac$_2$AN but with a larger twist of the E-acetyl group, $\tau_2(C_1^0-C_2-C_{11}^0-O_{15}^0)=171.9^\circ$, and a smaller twist of the Z-acetyl group, $\tau_2(C_6^0-C_7-C_{12}^0-O_{16}^0)=0.9^\circ$. There are four pairs of enantiomeric molecules in the unit cell of 1,5-Ac$_2$AN. Ketone 9,10-Ac$_2$AN crystallizes in the Z-conformation with a twist angle of $\tau_9(C_{9a}^0-C_9-C_{11}^0-O_{13}^0)=-85.0^\circ$. There are two pairs of enantiomeric molecules in the unit cell of 9,10-Ac$_2$AN. According to the literature structure [Langer & Becker, 1993], 1-AcAN crystallizes in the Z-conformation with a twist angle of $\tau_1(C_{9a}^0-C_9-C_{11}^0-O_{13}^0)=27.1^\circ$. The carbonyl group of ketone 9-AcAN [Zouev2011] is nearly orthogonal to the aromatic plane, $\tau_9(C_1-C_2-C_{11}^0-O_{13}^0)=87.9^\circ$. None of the mono- and diacetylanthracenes under study adopts a planar conformation in their crystal structures. The absolute values of the twist angles in the mono- and diacetylanthracenes vary, depending on the position of substitution and on the conformation of the acetyl groups: $|\tau_1|=15.2–34.0^\circ$ for the 1Z-acetyl groups, $|\tau_2|=0.9^\circ$ for the 2Z-acetyl group, $|\tau_2|=171.9–178.6^\circ$ for the 2E-acetyl groups, and $|\tau_1|=85.0–87.9^\circ$. The higher twist angles of the 1Z-acetyl groups are caused by the repulsive interactions between the carbonyl oxygen and the respective peri-hydrogen. The acetyl groups themselves are nearly planar (excluding the methyl hydrogens), and the pyramidalization angles $\chi$ at the carbonyl carbon atom are small, 0.1–3.4°. The dihedral angles $\theta$ between the plane of the carbonyl group and the aromatic plane are very close to the respective twist angles $\tau$ (Table 2). The anthracene systems in the mono- and diacetylanthracenes under study are also essentially planar: the dihedral fold angles $\Phi$ between the side six-membered rings of the anthracene unit are 0.0–5.8°. The pyramidalization angles $\chi$ at the carbon atom bonded to the acetyl substituent are small, 0.1–4.7°. Thus, the twist of the acetyl group(s) is the main feature of non-planarity in the mono- and diacetylanthracenes.

The diacetylanthracenes under study can be arranged in the order of decreasing twist angles $\tau$:

9,10-Ac$_2$AN $\gg$ 1,8-Ac$_2$AN $>$ 1,6-Ac$_2$AN $>$ 1,5-Ac$_2$AN $> 1,7$-Ac$_2$AN $> 2,7$-Ac$_2$AN.

The magnitude of the twist angle of the acetyl group is important. It has been shown that if an acyl group is tilted out of the plane of the aromatic ring of an aromatic ketone by neighboring bulky groups, the resonance stabilization is reduced and the pattern irreversibility of Friedel–Crafts acylation may be challenged, allowing decylation, transacylation and acyl rearrangements [Buehler & Pearson, 1970; Gore, 1974; Mala’bi, et al., 2011]. Thus, the twist angle $\tau$ may define the ability of diacetylanthracenes to undergo deacylations and rearrangements according to Agranat-Gore rearrangement.

Another factor that may influence the tilting of the acetyl group and, as a consequence, the feasibility of acyl rearrangements, is the overcrowding. Its main source is the short contact distances between the carbonyl oxygen and the peri-hydrogen, or between the methyl group and peri-hydrogen. The intramolecular O–H distances in the crystal structures of the mono- and diacetylanthracenes under study are not particularly short, 221–246 pm, for the Z-acetyl groups, which corresponds to 0–9% penetration. There are no close contact distances caused by the E-acetyl groups.

2.1.2 Intermolecular interactions in monoacetylanthracenes and diacetylanthracenes

Aromatic–aromatic interactions are non-covalent intermolecular forces similar to hydrogen bonding [Janiak, 2000]. Aromatic systems may be arranged in three principal configurations:
• A stacked (S) configuration, or a π–π interaction, in which aromatic rings are face-to-face aligned, with the interplanar distances of about 3.3–3.8 Å [Janiak, 2000]. This configuration has the maximal overlap but it is rarely observed in real systems containing aromatic rings [Sinnokrot & Sherrill, 2006].
• The T-shaped configuration (T), or a C–H–π interaction, where one aromatic ring points at the center of another ring.
• The parallel displaced (D), or offset stacked, configuration; it is reached from the stacked configuration by the parallel shift of one aromatic ring relative to the other [Sinnokrot & Sherrill, 2006], and features both π–π and C–H–π interactions. The T- and D-type configurations are often observed in small aromatic compounds [Dahl, 1994] and proteins [Hunter et al., 1991].

The crystal structure of the parent anthracene (AN) has been studied [Brock & Dunitz, 1990; Sinclair et al., 1950; Murugan & Jha, 2009]. It crystallizes in the monoclinic space group P21/a. Within the unit cell, the anthracene molecules are packed in a “herringbone” pattern, similar to the parent PAH naphthalene [Desiraju & Gavezzotti, 1989]. In this motif, the C–C non-bonded interactions are between non-parallel nearest neighbor molecules. The herringbone packing is one of four basic structural types for PAH, which are defined depending on the shortest cell axis and the interplanar angle [Desiraju & Gavezzotti, 1989]. The structures with herringbone packing, “sandwich herringbone” packing and γ packing obtain crystal stabilization mainly from C–C interactions, but also from C–H interactions [Desiraju & Gavezzotti, 1989]. The “graphitic”, or β, packing characterized by strong C–C interactions without much contribution from C–H contacts [Desiraju & Gavezzotti, 1989] is never observed in real systems containing aromatic rings [Sinnokrot & Sherrill, 2006].

The selected geometric parameters of aromatic interactions in the mono- and diacetylanthracenes under study are presented in Table 4. Cg1 is the centroid for the C1–C2–C3–C4a–C6a–C10a ring, Cg2 is the centroid for the C4a–C10a–C11a–C8–C9–C10 ring and Cg3 is the centroid for the C5–C6–C7–C8a–C10a ring; Cg4–6 are the respective centroids of the second non-equivalent molecule in the unit cell, if it exists. Interplanar angle is the angle between the planes of adjacent molecules. Slippage distance is distance of one centroid from the projection of another centroid. Displacement angle is the angle between the ring normal and the centroid vector.

The molecules of 2-AcAN are packed in a “herringbone” pattern, with the interplanar angle of 51.0°. The anthracene moieties in the crystal structure of 2-AcAN adopt the T-configuration with the shortest centroid-centroid separation of 464.7 pm. The shortest distances between the centroids of one molecule and the carbon atoms of the other molecule are Cg3–C1=343.7 pm, Cg2–C8=351.2 pm, Cg2–C10=351.2 pm, Cg3–C9=357.6 pm and Cg1–C5=358.2 pm. The respective centroid–hydrogen distances are Cg3–H4=271.5 pm, Cg2–H8=283.3 pm, Cg2–H10=280.8 pm, Cg3–H9=288.2 pm and Cg1–H5=287.9 pm. The π–π interactions in 2-AcAN are very weak despite close lying parallel planes, as reflected in very long distances between the respective centroids (>584 pm). Thus, the aryl C–H–π interactions dominate in the crystal structure of 2-AcAN. The unit cell of 2-AcAN is shown in Figure 11.

The molecules of 1,5-Ac2AN are packed in a “herringbone” pattern, with the interplanar angle of 56.2°. The anthracene moieties in the crystal structure of 1,5-Ac2AN adopt the T-configuration with the shortest centroid-centroid separation of 462.9 and 470.5 pm. The shortest distances between the centroids of one molecule and the carbon atoms of the other molecule are Cg1–C4=341.9 pm, Cg1–C3=353.6 pm and Cg2–C4=376.3 pm. The respective centroid–hydrogen distances are Cg1–H4=264.3 pm, Cg1–H3=293.7 pm and Cg2–H4=342.9 pm. Thus, the aryl C–H–π interactions dominate in the crystal structure of 1,5-Ac2AN, while...
the π-π interactions are not possible due to very long distances between molecules lying in the parallel planes (>600 pm). The unit cell of 1,5-Ac\textsubscript{2}AN is shown in Figure 12.

![Fig. 11. The unit cell of 2-AcAN (view along c axis)](image1)

![Fig. 12. The unit cell of 1,5-Ac\textsubscript{2}AN (view along special axis 1,0,1)](image2)

The molecules of 1,6-Ac\textsubscript{2}AN are packed by β type, forming a layered structure made up of “graphitic” planes with zero interplanar angle. From the point of view of aromatic-aromatic interactions, the anthracene moieties in the crystal structure of 1,6-Ac\textsubscript{2}AN are stacked by the D-type, with the centroid-centroid separation of 359.2 and 385.6 pm. The slippage distances
of the centroids are relatively short, 94.0 and 107.1 pm. The shortest contact distances between the aromatic carbons in 1,6-Ac$_2$AN are C$_5$–C$_7'$=355.1 and C$_6$–C$_8a'$=358.5. The unit cell of 1,6-Ac$_2$AN is shown in Figure 13.

Fig. 13. The unit cell of 1,6-Ac$_2$AN (view along c axis)

The molecules of 1,7-Ac$_2$AN are also packed by β type. The anthracene moieties in the crystal structure of 1,7-Ac$_2$AN adopt the D-configuration, with the shortest centroid-centroid separation of 370 pm. Despite the longer slippage distance between centroids (154.4–154.8 pm), the contact distances in 1,7-Ac$_2$AN are shorter than those in 1,6-Ac$_2$AN: C$_3$–C$_8'$=333.3, C$_4a$–C$_9'$=336.4, C$_8$–C$_9'$=337.1 and C$_1$–C$_10'$=340.9. In both 1,6-Ac$_2$AN and 1,7-Ac$_2$AN the aromatic interactions are mainly those of the π–π type. The unit cell of 1,7-Ac$_2$AN is shown in Figure 14.

The molecules of 1,8-Ac$_2$AN are packed in a “herringbone” pattern, with the interplanar angle of 34.7°. The centroids of the anthracene molecules lying onto the parallel planes are separated by 580–581 pm. These distances together with the slippage distance of 493–494 pm render the aromatic interactions of either S- or D-type impossible. The T-type interactions in 1,8-Ac$_2$AN are too weak to be of any importance, due to the long distances between centroids (546–562 pm). However, the plane of the acetyl group (containing C$_1$, C$_{11}$, C$_{13}$, O$_{15}$) of molecule A forms the angle of 4.0° with the aromatic plane of molecule B. Analogously,
the plane of the acetyl group (containing C'1, C'11, C'13, O'15) of molecule B is nearly parallel to the aromatic plane of molecule A, 3.8°. The distances between the anthracene systems and the carbonyl group are sufficiently small to consider the intermolecular π–π interactions: Cg4'–O1=353.8 pm, Cg4'–C11=384.3 pm, Cg3–O1=363.3 pm and Cg3–C11=398.2 pm. Thus, the crystal structure of 1,8-Ac$_2$AN features π–π-interactions not between two aromatic systems, but between the aromatic system and the carbonyl π-bond. The unit cell of 1,8-Ac$_2$AN is shown in Figure 15.

Fig. 14. The unit cell of 1,7-Ac$_2$AN (view along b axis)

Fig. 15. The unit cell of 1,8-Ac$_2$AN (view along b axis)
The molecules of 2,7-Ac$_2$AN are packed in a “herringbone” pattern. The anthracene moieties in the crystal structure of 2,7-Ac$_2$AN adopt the T-configuration, similarly to 1,5-Ac$_2$AN. The planes of the adjacent molecules form the angle of 58.1°. The shortest distances between the centroids and the carbon atoms are Cg3–C4=358.4 pm and Cg1–C5=375.5 pm on the one side of the anthracene system, and Cg3–C9=374.0 pm, Cg2–C8=374.8 pm on the other side. The respective shortest centroid-aryl hydrogen distances are Cg1–H5=299.3 pm and Cg3–H4=283.5 pm. The D-type interactions in 2,7-Ac$_2$AN are very weak due to the large separation of centroids (420–433 pm) and large slippage distances (226–242 pm). The unit cell of 2,7-Ac$_2$AN is shown in Figure 16.
The anthracene moieties in the crystal structure of 9,10-Ac$_2$AN adopt the T-configuration, similarly to 1,5-Ac$_2$AN and 2,7-Ac$_2$AN. The planes of the adjacent molecules form the angle of 73.6°. The shortest distances between the centroids and the carbon atoms are C$_{g2}$-C$^\text{7}=356.1$ pm, C$_{g2}$-C$^\text{8}=379.6$ pm and C$_{g1}$-C$^\text{8}=384.7$ pm. The respective shortest centroid-aryl hydrogen distances are C$_{g2}$-H$^\text{7}=287.9$ pm, C$_{g2}$-H$^\text{8}=329.4$ pm and C$_{g1}$-H$^\text{8}=294.4$ pm. The D-type interactions in 9,10-Ac$_2$AN are non-existent. The molecules lying in the parallel planes are separated by >720 pm, probably due to the considerable twist angles of the acetyl group in 9,10-Ac$_2$AN (~85.0° and 87.0°), making the tighter arrangement impossible. The unit cell of 9,10-Ac$_2$AN is shown in Figure 17.

| Centroid | Centroid | Centroid centroid distance pm | Interplanar distance pm | Interplanar angle deg | Slippage distance pm | Displacement angle deg |
|----------|----------|-------------------------------|-------------------------|-----------------------|----------------------|-----------------------|
| 2-AcAN   | C$_{g1}$ | C$_{g3}^\text{a}$            | 464.7                   | 51.0                  | 110.8                | 13.8                  |
|          | C$_{g1}$ | C$_{g3}^\text{b}$            | 477.2                   | 51.0                  | 103.6                | 12.5                  |
|          | C$_{g1}$ | C$_{g3}^\text{c}$            | 499.5                   | 51.0                  | 209.7                | 24.8                  |
|          | C$_{g1}$ | C$_{g3}^\text{d}$            | 511.1                   | 51.0                  | 205.9                | 23.8                  |
|          | C$_{g1}$ | C$_{g2}^\text{e}$            | 584.5                   | 251.6                 | 544.4                | 64.5                  |
| 1,5-AcAN | C$_{g2}$ | C$_{g1}^\text{f}$            | 462.9                   | 56.2                  | 526.4                | 61.1                  |
|          | C$_{g1}$ | C$_{g1}^\text{g}$            | 470.5                   | 56.2                  |                      |                       |
|          | C$_{g2}$ | C$_{g1}^\text{h}$            | 601.5                   | 292.2                 |                      |                       |
| 1,6-AcAN | C$_{g3}$ | C$_{g2}^\text{b}$            | 601.5                   | 292.2                 | 525.8                | 60.9                  |
|          | C$_{g3}$ | C$_{g3}^\text{i}$            | 359.2                   | 346.1                 | 94.0                 | 15.2                  |
|          | C$_{g1}$ | C$_{g1}^\text{j}$            | 385.6                   | 370.4                 | 107.1                | 16.1                  |
| 1,7-AcAN | C$_{g1}$ | C$_{g3}^\text{j}$            | 370.1                   | 335.9                 | 154.6                | 24.7                  |
|          | C$_{g1}$ | C$_{g2}^\text{k}$            | 370.4                   | 335.9                 | 154.8                | 24.7                  |
|          | C$_{g2}$ | C$_{g2}^\text{l}$            | 370.2                   | 335.9                 | 154.4                | 24.7                  |
| 1,8-AcAN | C$_{g1}$ | C$_{g4}^\text{k}$            | 546.4                   | 34.7                  |                      |                       |
|          | C$_{g1}$ | C$_{g4}^\text{l}$            | 561.5                   | 34.7                  |                      |                       |
|          | C$_{g1}$ | C$_{g4}^\text{m}$            | 580.5                   | 307.2                 | 492.6                | 58.1                  |
|          | C$_{g1}$ | C$_{g4}^\text{n}$            | 580.9                   | 305.9                 | 493.9                | 58.2                  |
| 2,7-AcAN | C$_{g2}$ | C$_{g3}^\text{n}$            | 419.8                   | 354.6                 | 226.2                | 32.6                  |
|          | C$_{g3}$ | C$_{g3}^\text{n}$            | 432.7                   | 354.6                 | 241.8                | 35.2                  |
|          | C$_{g1}$ | C$_{g3}^\text{o}$            | 481.0                   | 58.1                  |                      |                       |
|          | C$_{g2}$ | C$_{g3}^\text{o}$            | 486.6                   | 58.1                  |                      |                       |
| 9,10-AcAN| C$_{g2}$ | C$_{g3}^\text{p}$            | 475.5                   | 73.6                  |                      |                       |
|          | C$_{g2}$ | C$_{g1}^\text{q}$            | 481.8                   | 73.6                  |                      |                       |
|          | C$_{g3}$ | C$_{g2}^\text{r}$            | 721.2                   | 478.0                 | 540.1                | 48.5                  |
|          | C$_{g2}$ | C$_{g1}^\text{r}$            | 722.3                   | 478.0                 | 541.5                | 48.6                  |
|          | C$_{g3}$ | C$_{g1}^\text{r}$            | 724.2                   | 478.0                 | 544.0                | 48.7                  |

Symmetry codes: $^\text{a}$0.5-x, 0.5+y, 1.5-z; $^\text{b}$0.5-x, -0.5+y, 1.5-z; $^\text{c}$1.5-x, 0.5+y, 1.5-z; $^\text{d}$1.5-x, -0.5+y, 1.5-z; $^\text{e}$-1+x, y, z; $^\text{f}$x, 0.5-y, 0.5-z; $^\text{g}$1-x, 0.5+y, 0.5-z; $^\text{h}$x, 1+y, 1+z; $^\text{i}$1-x, 1-y, 1-z; $^\text{j}$1-x, -y, -z; $^\text{k}$1.5-x, 1+y, 1.5-z; $^\text{l}$-1-x, -y, 1-z; $^\text{m}$0.5+x, -y, -0.5+z; $^\text{n}$0.5-x, 0.5-y, 0.5-z; $^\text{o}$-x, 0.5+y, 0.5-z; $^\text{p}$-0.5+x, 1.5-y, 1.5-z; $^\text{q}$0.5+x, 0.5-y, z; $^\text{r}$x, -1+y, z.

Table 4. Aromatic interactions in monoacetylanthracenes and diacetylanthracenes
Thus, the monoacetylanthracenes and diacetylanthracenes under study may be divided into two groups, based on the aromatic–aromatic interactions in their crystal structures. The anthracene units in 1,6-Ac$_2$AN and 1,7-Ac$_2$AN are offset stacked (the D-type arrangement) and feature aromatic–aromatic π–π interactions. The anthracene molecules in ketones 2-AcAN, 1,5-Ac$_2$AN, 2,7-Ac$_2$AN and 9,10-Ac$_2$AN adopt the T-type arrangement, and feature aryl C–H–π interactions. The analysis of the literature crystal structures of 1-AcAN and 9-AcAN shows that these ketones also adopt the T-type arrangement. In 1-AcAN, 9-AcAN, 1,5-Ac$_2$AN and 9,10-Ac$_2$AN the considerable twist angles of the acetyl groups prevents the molecules from being arranged in close lying parallel planes. The exception is the crystal structure of 1,8-Ac$_2$AN, which features π–π-interactions between the aromatic system and the carbonyl π-bond. Most likely the methyl groups are the reason for the lack of more examples of slipped-stacking and also in some cases the competing ketone–π system as well.

It should be noted, however, that the centroid–centroid analysis can be misleading, and its limitations should not be overlooked.

Another kind of intermolecular interactions that could exist in acetylanthracenes is hydrogen bonds. No particular strong intermolecular aryl C–H–O bonds have been found in the diacetylanthracenes under study. The shortest contact distances between an oxygen and an aromatic hydrogen are O$_{15}$–H$_5$=242.2 pm (9,10-Ac$_2$AN), O$_{15}$–H$_1$=247.4 pm and O$_{16}$–H$_9$=259.4 pm (2,7-Ac$_2$AN), O$_{15}$–H$_3$=255.6 pm (1,6-Ac$_2$AN), O$_{16}$–H$_a$=256.4 pm and O$_{15}$–H$_4$=260.7 pm (1,7-Ac$_2$AN), O$_{15}$–H$_2$=260.5 pm (1,8-Ac$_2$AN), O$_{15}$–H$_2$=284.6 pm (1,5-Ac$_2$AN). The shortest contact distances between an oxygen and a methyl hydrogen are of a similar magnitude: O$_{15}$–H$_{14c}$=240.8 pm (2,7-Ac$_2$AN), O$_{16}$–H$_{12c}$=254.7 pm (1,6-Ac$_2$AN), O$_{16}$–H$_{12b}$=257.5 pm (1,7-Ac$_2$AN), O$_{15}$–H$_{12c}$=259.4 pm (1,5-Ac$_2$AN), O$_{15}$–H$_{12c}$=265.9 pm (9,10-Ac$_2$AN).

### 2.2 NMR Study of monoacetylanthracenes and diacetylanthracenes

The structure of a compound in crystal is not necessarily the same as that in solution. More often, in the case of substances that are not conformationally homogeneous, e.g., diacetylanthracenes, the crystal has a unique conformation and the conformational heterogeneity appears in fluid phases [Elie! & Wilen, 1994]. An insight into the conformations of mono- and diacetylanthracenes in solution may be gained from the chemical shifts of the aromatic protons adjacent to the carbonyl groups. The magnetic shielding (or deshielding) effect on the chemical shifts of protons that lie in or near the plane of the carbonyl group is well known. The McConnell equation [McConnel, 1957] predicts shielding for protons lying above the center of a carbon–oxygen double bond and deshielding for protons located within a cone aligned with the carbon–oxygen bond axis.

The McConnell model, however, takes into account only the effect of magnetic anisotropy. Recently, more detailed shielding model has been proposed [Martin et al., 2003]. According to this model, shielding is predicted for protons located in the region from over the center of the carbon–oxygen double bond to beyond the carbon atom; deshielding is predicted for protons located above and beyond the oxygen atom. Table 5 gives $^1$H-NMR chemical shifts for the monoacetylanthracenes and diacetylanthracenes under study, together with the chemical shifts in parent anthracene (AN).

The data presented in Table 5 show that the protons at ortho-positions to an acetyl group are considerably deshielded as compared with the protons of unsubstituted anthracene. The magnitudes of the low field shifts of the ortho-protons are similar among
monoacetylanthracenes and diacetylanthracenes: \( \Delta \delta (H^1, \text{ppm}) = 0.70 \) (2-AcAN), 0.72 (2,7-Ac\(_2\)AN); \( \Delta \delta (H^2, \text{ppm}) = 0.59 \) (1-AcAN), 0.63 (1,6-Ac\(_2\)AN), 0.67 (1,5-Ac\(_2\)AN), 0.67 (1,7-Ac\(_2\)AN), 0.73 (1,8-Ac\(_2\)AN); \( \Delta \delta (H^3, \text{ppm}) = 0.61 \) (2-AcAN), 0.65 (2,7-Ac\(_2\)AN); \( \Delta \delta (H^5, \text{ppm}) = 0.62 \) (1,6-Ac\(_2\)AN); \( \Delta \delta (H^6, \text{ppm}) = 0.63 \) (1,7-Ac\(_2\)AN), 0.65 (2,7-Ac\(_2\)AN), 0.67 (1,5-Ac\(_2\)AN); \( \Delta \delta (H^7, \text{ppm}) = 0.58 \) (1,6-Ac\(_2\)AN), 0.73 (1,8-Ac\(_2\)AN); \( \Delta \delta (H^8, \text{ppm}) = 0.72 \) (2,7-Ac\(_2\)AN), 0.77 (1,7-Ac\(_2\)AN).

The protons at peri-positions to an acetyl group are deshielded with even greater magnitudes: \( \Delta \delta (H^9, \text{ppm}) = 1.06 \) (1,6-Ac\(_2\)AN), 1.08 (1-AcAN), 1.17 (1,5-Ac\(_2\)AN), 1.27 (1,7-Ac\(_2\)AN), 1.78 (1,8-Ac\(_2\)AN). The latter case is special because of the presence of two acetyl groups at peri-positions to H\(^9\), which nearly double its low field chemical shift. Note that in 2-AcAN, 1,6-Ac\(_2\)AN, 1,7-Ac\(_2\)AN and 2,7-Ac\(_2\)AN both protons ortho to the acetyl groups demonstrate similar low field shifts, suggesting that these protons are located above the plane of the carbonyl group and near the oxygen atom [Martin et al., 2003]. Thus, the twist angles of the acetyl groups of mono- and diacetylanthracenes are small, in accordance with their respective X-ray crystal structures, and E,Z-diastereomerizations of the acetyl groups at both \( \alpha \) (1, 5, 8) and \( \beta \) (2, 6, 7) positions are swift on the NMR time scale.

|        | H\(^1\) | H\(^2\) | H\(^3\) | H\(^4\) | H\(^5\) | H\(^6\) | H\(^7\) | H\(^8\) | H\(^9\) | CH\(_3\) | CH\(_3\) |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| AN     | 7.95   | 7.41   | 7.41   | 7.95   | 7.95   | 7.41   | 7.41   | 7.95   | 8.40   | 8.40   |        |
| 1-AcAN | 7.998  | 7.469  | 8.169  | 7.998  | 7.528  | 7.528  | 8.083  | 9.482  | 8.446  | 2.810  |        |
| 2-AcAN | 8.646  | 8.054  | 8.054  | 8.054  | 7.467  | 7.467  | 8.054  | 8.573  | 8.432  | 2.763  |        |
| 9-AcAN | 7.859  | 7.556  | 7.556  | 8.027  | 8.027  | 7.556  | 7.556  | 7.859  | 8.473  | 2.822  |        |
| 1,5-Ac\(_2\)AN | 8.083 | 7.530 | 8.262  | 8.083 | 7.530  | 8.262 | 9.570  | 9.570  | 2.818  | 2.818  |        |
| 1,6-Ac\(_2\)AN | 8.040 | 7.490 | 8.153  | 8.570  | 7.994  | 8.064 | 9.457  | 8.523  | 2.796  | 2.730  |        |
| 1,7-Ac\(_2\)AN | 8.080 | 7.559 | 8.199  | 8.036  | 8.036  | 8.719 | 9.673  | 8.460  | 2.836  | 2.773  |        |
| 1,8-Ac\(_2\)AN | 8.140 | 7.514 | 7.964  | 7.964  | 7.514  | 8.140 | 10.175 | 8.471  | 2.840  | 2.840  |        |
| 2,7-Ac\(_2\)AN | 8.670 | 8.063 | 8.063  | 8.063  | 8.063  | 8.670 | 8.718  | 8.449  | 2.775  | 2.775  |        |
| 9,10-Ac\(_2\)AN | 7.881 | 7.571 | 7.571  | 7.881  | 7.881  | 7.571 | 7.571  | 7.881  | 2.816  | 2.816  |        |
| 7.845 | 7.537 | 7.537  | 7.845  | 7.845  | 7.537 | 7.537  | 7.845  |        |        |        |

Table 5. The \(^1\)H-NMR chemical shifts (\( \delta \), ppm) of aromatic and methyl protons in anthracene (AN), monoacetylanthracenes and diacetylanthracenes under study.

Ketones 9-AcAN and 9,10-Ac\(_2\)AN differ from the rest of the mono- and diacetylanthracenes. The protons at peri-positions to the acetyl groups of 9-AcAN and 9,10-Ac\(_2\)AN are slightly shielded: \( \Delta \delta (H^1, \text{ppm}) = -0.09 \) (9-AcAN), -0.09 (9,10-Ac\(_2\)AN). This suggests that the carbonyl groups in 9-AcAN and 9,10-Ac\(_2\)AN are turned away of the protons at peri-positions, and these protons are located near the carbonyl carbon atoms, which implies high twist angles of the acetyl groups. It corresponds well to the respective X-ray crystal structures of 9-AcAN and 9,10-Ac\(_2\)AN.
2.3 DFT computational study of monoacetylanthracenes and diacetylanthracenes

DFT methods are capable of generating a variety of isolated molecular properties quite accurately, especially via the hybrid functional, and in a cost-effective way [deProft & Geerlings, 2001, Koch & Holthausen, 2000]. The B3LYP hybrid functional was successfully employed to treat overcrowded BAEs [Biedermann et al., 2001, Pogodin et al., 2006] and overcrowded naphthologues of BAEs-1, i.e. mono-bridged tetraarylethylenes [Assadi et al., 2009]. The monoacetylanthracenes and diacetylanthracenes under study were subjected to a systematic computational DFT study of their conformational spaces and of their relative stabilities. The B3LYP/6-31G(d) relative energies of the global minima conformations of certain diacetylanthracenes have been previously reported [Mala’bi et al., 2011]. The total and relative B3LYP/6-31G(d) energies (\(E_{\text{Tot}}\) and \(\Delta E_{\text{Tot}}\)) and Gibbs free energies (\(\Delta G_{298}\) and \(\Delta \Delta G_{298}\)) of the acetylanthracenes are presented in Table 6. Selected calculated geometrical parameters of the acetylanthracenes are also given in Table 6. The following geometrical parameters were considered: the twist angles \(\tau_1\), \(\tau_2\) and \(\tau_9\) and the respective twist angles \(\nu\) around the anthracenyl-carbonyl bond; the dihedral angle \(\theta\) between the least-square planes of the carbonyl group and the anthracene system; the dihedral angle \(\varphi\) between the least-square planes of two side rings of the anthracene system; the pyramidalization angles \(\chi\) at \(C_1\), \(C_2\) and \(C_9\).

2.3.1 Conformational space of monoacetylanthracenes and diacetylanthracenes

Monoacetylanthracenes may adopt two conformations, \(Z\) and \(E\), defined by the twist angle of the carbonyl group. Diacetylanthracenes may adopt four conformations, i.e. \(ZZ\), \(ZE\), \(EZ\) and \(EE\); in certain cases, \(ZE\) is identical to \(EZ\). In addition, the oxygen atoms of two carbonyl groups may be located on the same side of the aromatic plane, or on the opposite sides, potentially resulting in \(\text{syn-ZZ}, \text{syn-ZE}, \text{syn-EZ}\) and \(\text{syn-EE}\) conformations, respectively. Depending on the symmetry constraints and the twist angle \(\tau\), not all of the above-mentioned conformations exist for a given diacetylanthracene. The possible conformations of diacetylanthracene are shown in Fig. 18.

![Fig. 18. Schematic representation of the eight possible conformations of a diacetylanthracene (view along the aromatic plane).](image-url)
| Structure  | E<sub>tot</sub>  | ΔE<sub>tot</sub>  | ΔG<sub>298</sub>  | ΔΔG<sub>298</sub>  | τ<sup>a</sup>  | τ<sup>b</sup>  | θ  | Ψ  | C<sub>11</sub>–C<sub>arom</sub>  | χ  |
|------------|----------------|----------------|----------------|----------------|-------|-------|----|----|----------------|----|
| 1-AcAN     | -692.17301155  | 14.66          | 15.79          | 0.00           | 0.0   | 180.0 | 0.0 | 0.0 | 149.9          | 0.0 |
| 1-AcAN<sup>d</sup> | -621.16815672  | 27.41          | 28.80          | 13.01          | 27.1  | -152.28 | 3.2 | 149.3–0.1 |
| 1-AcAN     | -692.17859715  | 0.00           | 0.00           | 0.00           | 180.0 | 0.0   | 0.0 | 0.0 | 149.6          | 0.0 |
| 1-AcAN<sup>d</sup> | -621.16815672  | 27.41          | 28.80          | 13.01          | 173.1 | 5.3   | 0.4 | 149.6–1.6 |
| 9-AcAN     | -692.16381815  | 38.80          | 36.94          | 0.00           | -67.0 | 113.9 | 69.8| 151.3          | 1.0 |
| 9-AcAN<sup>d</sup> | -621.16815672  | 27.41          | 28.80          | 13.01          | 87.9  | -91.89 | 5.8 | 150.4          | 0.3 |
| 1,5-Ac<sub>C</sub><sup>2</sup>AN | -844.81621983  | 24.25          | 27.69          | 0.00           | 0.0   | 180.0 | 0.0 | 0.0 | 149.8          | 0.0 |
| 1,5-Ac<sub>C</sub><sup>d</sup>AN | -844.81074449  | 38.62          | 40.48          | 12.79          | 152.4 | -29.34 | 3.8 | 150.6          | 1.6 |
| 1,5-Ac<sub>C</sub><sup>2</sup>AN | -844.80527143  | 52.99          | 55.06          | 27.36          | 150.6 | -30.9 | 3.8 | 150.8          | 1.5 |
| 1,5-Ac<sub>C</sub><sup>2</sup>AN | -844.8059961  | 52.13          | 55.74          | 28.05          | 151.9 | -29.35 | 7.6 | 150.7          | 1.7 |
| 1,6-Ac<sub>C</sub><sup>2</sup>AN | -844.82056764  | 12.83          | 13.45          | 0.00           | 0.0   | 180.0 | 0.0 | 0.0 | 150.0          | 0.0 |
| 1,6-Ac<sub>C</sub><sup>d</sup>AN | -844.82055388  | 14.18          | 15.14          | 1.69           | 178.6 | -0.7 | 1.3 | 149.3          | -0.7 |
| 1,5-Ac<sub>C</sub><sup>2</sup>AN | -844.81569542  | 25.63          | 27.03          | 13.57          | 150.6 | -31.3 | 3.6 | 150.8          | 1.7 |
| 1,5-Ac<sub>C</sub><sup>2</sup>AN | -844.81493981  | 27.61          | 28.88          | 15.43          | 179.9 | -0.1 | 1.4 | 149.8          | 0.1 |
| 1,7-Ac<sub>C</sub><sup>2</sup>AN | -844.82110775  | 11.42          | 12.34          | 0.00           | 150.6 | -31.2 | 3.6 | 150.7          | 1.7 |
| 1,7-Ac<sub>C</sub><sup>d</sup>AN | -844.82055388  | 14.18          | 15.14          | 1.69           | 178.6 | -0.7 | 1.3 | 149.3          | -0.7 |
| 1,7-Ac<sub>C</sub><sup>2</sup>AN | -844.81569542  | 25.63          | 27.03          | 13.57          | 179.6 | -0.5 | 1.7 | 149.8          | 0.0 |
| 1,8-Ac<sub>C</sub><sup>2</sup>AN | -844.81112929  | 37.66          | 38.89          | 0.00           | 150.8 | -31.0 | 3.5 | 150.9          | 1.7 |
| 1,8-Ac<sub>C</sub><sup>d</sup>AN | -844.81126554  | 37.26          | 39.25          | 0.35           | 1.5  | 178.3 | 2.6 | 150.0          | 0.2 |
| 1,8-Ac<sub>C</sub><sup>2</sup>AN | -844.80423404  | 55.72          | 56.49          | 17.60          | 147.9 | -33.8 | 2.7 | 150.7          | 1.7 |
| 1,9-Ac<sub>C</sub><sup>2</sup>AN | -844.79904569  | 69.34          | 70.32          | 0.00           | 50.9  | 120.3 | 69.8| 150.4          | 0.3 |
| 1,9-Ac<sub>C</sub><sup>2</sup>AN | -844.78990701  | 93.33          | 96.19          | 25.88          | 44.8  | 128.4 | 81.3| 151.1          | 6.8 |
| 1,10-Ac<sub>C</sub><sup>2</sup>AN | -844.80536578  | 52.75          | 49.45          | 0.00           | 0.2   | -180.0| 1.8 | 150.1          | 0.2 |
| 1,10-Ac<sub>C</sub><sup>d</sup>AN | -844.80575464  | 51.73          | 50.43          | 0.98           | -108.0| 73.0 | 7.5 | 151.6          | -1.0 |

*Note: Values are given in kJ/mol.*
| Compound          | Energy (kcal/mol) | Geometric Parameters | 
|-------------------|-------------------|----------------------|
| 1,10-AcAN         | -844.80066416     | 65.09 63.37 13.91    |
| E/Zanti C1        |                   |                      |
| 1,10-AcAN         | -844.80064430     | 65.14 63.38 13.92    |
| E/Eanti C1        |                   |                      |
| 1,10-AcAN         | -844.80035871     | 65.89 63.70 14.25    |
| E/Esyn C1         |                   |                      |
| 9,10-AcAN         | -844.79648217     | 76.07 71.57 0.00     |
| E/E C1            |                   |                      |
| 9,10-AcAN         | -844.79616186     | 76.91 71.63 0.06     |
| Z/E C2            |                   |                      |
| 9,10-AcAN         | -844.79637404     | 76.35 72.55 0.99     |
| E/E C2            |                   |                      |
| 9,10-AcAN         | -844.79619082     | 76.84 73.69 2.13     |
| Z/E C2            |                   |                      |
| 2,6-Ac2AN         | -844.82603788     | -1.53 0.40 0.00      |
| EE C2             |                   |                      |
| 2,6-Ac2AN         | -844.82517129     | 0.75 0.79 0.40       |
| ZE C2             |                   |                      |
| 2,6-Ac2AN         | -844.82448815     | 2.54 4.19 3.79       |
| ZZ C2             |                   |                      |
| 2,7-Ac2AN         | -844.82545585     | 0.00 0.00 0.00       |
| EZ C2             |                   |                      |
| 2,7-Ac2AN         | -844.82612845     | -1.77 0.20 0.20      |
| d EZ C1           |                   |                      |
| 2,7-Ac2AN         | -844.82444406     | 2.66 4.29 4.29       |
| ZZ C2             |                   |                      |
| 2,9-Ac2AN         | -844.81120818     | 37.41 32.29 0.00     |
| EE C1             |                   |                      |
| 2,9-Ac2AN         | -844.81178130     | 35.90 35.90 3.61     |
| EZ C1             |                   |                      |
| 2,9-Ac2AN         | -844.81042981     | 39.45 37.37 5.08     |
| ZE C1             |                   |                      |
| 2,10-Ac2AN        | -844.81146291     | 36.74 34.49 0.00     |
| EE C1             |                   |                      |
| 2,10-Ac2AN        | -844.81128488     | 37.21 34.81 0.32     |
| EZ C1             |                   |                      |
| 2,10-Ac2AN        | -844.81074527     | 38.62 36.64 2.15     |
| ZE C1             |                   |                      |
| 2,10-Ac2AN        | -844.81084444     | 38.36 38.36 3.87     |
| ZZ C2             |                   |                      |

Table 6. Total energies ($E_{tot}$), relative energies ($\Delta E_{tot}$) and Gibbs free energies ($\Delta G_{298}$) and selected geometric parameters of mono- and diacetylanthracenes.

Ketone 1-AcAN adopts a C$_z$-Z conformation as its global minimum. The planar (excluding the methyl hydrogens) C$_1$-1Z-AcAN is overcrowded due to the short O$_{13}$–H$_{19}$ contact distance (the O$_{13}$–H$_{19}$ distance is 215 pm, 14% penetration, based on the sum of the van-der-Vaals...
radii of oxygen and hydrogen, 244 pm [Zefirov, 1997]). The non-planar $C_1$-$1E$-AcAN conformation (the twist angle $\tau_1(C^{\alpha\beta}_{10}-C^{\beta\gamma}_{13}-O^{\alpha\beta}_{13})=150.8^\circ$) is higher in energy by 13.0 kJ/mol. The energy barrier for the $E,Z$-diastereomerization $C_r$-$1Z$-AcAN$\rightarrow$-$C_r$-$1E$-AcAN by the rotation of the acetyl group via a nearly orthogonal transition state is 19.5 kJ/mol. As mentioned above, 1-AcAN [Langer1993] crystallizes as the $Z$-diastereomer, which is correctly described by the calculated structure of $C_r$-$1Z$-AcAN. However, the carbonyl group in the crystal structure of 1-AcAN is considerably twisted out of the plane of the anthracene ring system, $\tau_1=27.1^\circ$. As a result, the calculated $C_r$-$1Z$-AcAN structure is more overcrowded than the X-ray structure (in the latter the O$^{13}$-H$^9$ distance is 223 pm).

Ketone 2-AcAN adopts a $C_r$-$E$ conformation as its global minimum. Its local minimum $C_r$-$2Z$-AcAN conformation is 2.2 kJ/mol higher in energy. Both conformations are not overcrowded, lacking any peri-interactions. The energy barrier for the $E,Z$-diastereomerization $C_r$-$2E$-AcAN$\rightarrow$-$C_r$-$2Z$-AcAN by the rotation of the acetyl group via a nearly orthogonal transition state is 31.5 kJ/mol. The calculated $C_r$-$2E$-AcAN conformation corresponds well to the $E$-conformation of the crystal structure. The latter, however, features a small twist angle of $\tau_2(C^{\alpha\beta}_{13}-C^{\beta\gamma}_{11}-O^{\alpha\beta}_{13})=173.1^\circ$, in contrast to the planar (excluding the methyl hydrogens) calculated structure.

In the global minimum conformation of 9-AcAN the twist angle $\tau_9(C^{\alpha\beta}_{10}-C^{\beta\gamma}_{13}-O^{\alpha\beta}_{13})$ is $-67.0^\circ$. This conformation cannot be defined as either $E$ or $Z$, and no other minimum conformation was located. Comparing the calculated structure of 9-AcAN with the crystal structure of 9-AcAN reported in the literature [Zouev2011], the carbonyl group in the latter is almost orthogonal to the plane of the anthracene ring system: the twist angle $\tau_9(C^{\alpha\beta}_{10}-C^{\beta\gamma}_{13}-O^{\alpha\beta}_{13})=87.9^\circ$ is considerably larger than the twist angle predicted by the DFT calculations. The energy barrier for the enantiomerization of 9-AcAN via the orthogonal $[C_r,9-AcAN]$ transition state is only 3.6 kJ/mol. The low enantiomerization barrier as compared to the diastereomerization barriers in 1-AcAN and 2-AcAN is due to an already high twist angle in 9-AcAN.

Ketone 1,5-Ac$_2$AN adopt a $C_{2h}$-$1Z,5Z$ conformation as its global minimum. The geometry optimizations under $C_2$ or $C_1$ symmetry constraints converged to the $C_{2h}$ symmetry structure. $C_{2h}$-$1Z,5Z$-Ac$_2$AN is considerably overcrowded due to the short O$^{15}$-H$^9$/O$^{16}$-H$^{10}$ contact distances (14\% penetration). The $C_{2h}$-$1Z,5Z$-Ac$_2$AN conformation corresponds to the $Z,Z$ X-ray structure of 1,5-Ac$_2$AN. However, the calculated structure is planar (excluding the methyl hydrogens), while the X-ray structure has the twist angle $\tau_1(C^{\alpha\beta}_{10}-C^{\beta\gamma}_{13}-O^{\alpha\beta}_{13})=20.0^\circ$ and the dihedral angle $\theta=22.7^\circ$, and, as a result, is less overcrowded. In addition to the global minimum, there are three local minima conformations of 1,5-Ac$_2$AN: $C_1$-$1Z,5E$-Ac$_2$AN, $C_r$-$1E,5E$-anti-Ac$_2$AN and $C_r$-$1E,5E$-syn-Ac$_2$AN. The four conformations of 1,5-Ac$_2$AN undergo diastereomerizations by the rotation of one of the acetyl groups via “nearly orthogonal” transition states, in which the rotating acetyl group has the twist angle of $\tau=85-97^\circ$, and the other acetyl group retains its $E$- or $Z$-conformation. The rotation of an acetyl group of $C_{2h}$-$1Z,5Z$-Ac$_2$AN via $[C_r$-$1Z,90-Ac$_2$AN] leads to the $C_1$-$1Z,5E$-Ac$_2$AN conformation, which is 12.8 kJ/mol higher in energy than the global minimum. The $E$-orientation of the acetyl group at the 5-position and the peri-interactions of its methyl hydrogens with H$^{10}$ force the acetyl group out of the aromatic plane, thus decreasing the conjugation. Due to the twist angle $\tau_1(C^{\alpha\beta}_{10}-C^{\beta\gamma}_{13}-O^{\alpha\beta}_{10})=152.4^\circ$ which differs from either $0^\circ$ or $180^\circ$, rotation of the $1Z$-acetyl group of $C_1$-$1Z,5E$-Ac$_2$AN may be realized in either anti- (via $[C_r$-$90,5E$-anti-Ac$_2$AN]) or in syn-direction (via $[C_1$-$90,5E$-syn-Ac$_2$AN]) relative to the 5E-acetyl group. These processes lead to the different local minima $C_r$-$1E,5E$-anti-Ac$_2$AN and $C_r$-$1E,5E$-syn-Ac$_2$AN conformations, respectively, which are 27.4 and 28.0 kJ/mol higher in
energy than C21r-1Z,5Z-Ac2AN, due to both acetyl groups being forced out of the aromatic plane: \( \tau_1(C^{9a}-C^{1}-C^{11}-O^{15}) = 150.6^\circ \) and 151.9\(^\circ\), respectively. In addition, the C1r-1E,5E-anti-Ac2AN and C2r-1E,5E-syn-Ac2AN conformations may undergo syn,anti-diastereomerization via the \([C_1r-1E,5E_{180r}-Ac2AN]\) transition state. It is a “nearly planar” transition state of a different type than the “nearly orthogonal” one; the twist angle of the rotating acetyl group is close to zero, and the other acetyl group retains its E- or Z-conformation. The \([C_1r-1E,5E_{180r}-Ac2AN]\) transition state is considerably strained due to the short O\(^{16r}\)-H\(^{10r}\) distance (205.3 pm) and the distorted \(sp^2\) angles C\(^{15r}\)-C\(^{5}\)-C\(^{10}\) (127.9\(^\circ\)) and C\(^{13}\)-C\(^{5}\)-C\(^{6}\) (113.4\(^\circ\)). The diastereomerization processes in 1,5-Ac2AN are shown in Fig. 19.

![Diagram of conformational interconversion](image)

Fig. 19. The interconversion of conformations of 1,5-Ac2AN and their relative Gibbs free energies (\(\Delta G_{298}\), kJ/mol)

Ketone 1,6-Ac2AN adopts a C\(_r\)-1Z,6E conformation as its global minimum. Like C21r-1Z,5Z-Ac2AN, it is overcrowded due to the short O\(^{15r}\)-H\(^{9}\) contact distance (14% penetration). The C1r-1Z,6E-Ac2AN conformation corresponds to the Z,E X-ray structure of 1,6-Ac2AN. As in the case of 1,5-Ac2AN, the DFT calculations predict a planar structure for 1,6-Ac2AN, while the X-ray geometry features the twisted 1Z-acetyl group: the twist angle \(\tau_1(C^{9a}-C^{1}-C^{11}-O^{15}) = 30.0^\circ\) and the dihedral angle \(\theta = 32.2^\circ\). The 6E-acetyl group remains in the aromatic plane in both calculated and the X-ray geometries. The rotation of the 1Z-acetyl group leads from C1r-1Z,6E-Ac2AN via \([C_1r-90,6E-Ac2AN]\) to the local minimum C1r-1E,6E-Ac2AN, which is 13.6 kJ/mol higher in energy. The 6E-acetyl group, in contrast to the 1E-acetyl group, lies in the aromatic plane: \(\tau_1(C^{9a}-C^{1}-C^{11}-O^{15}) = 150.6^\circ\) and \(\tau_1(C^{9a}-C^{6}-C^{13}-O^{16}) = 179.9^\circ\). The rotation of the 6E-acetyl group of C1r-1E,6E-Ac2AN may be realized either via \([C_1r-1E,90-syn-Ac2AN]\) or via \([C_1r-1E,90-anti-Ac2AN]\) transition states; both pathways lead to C1r-1E,6Z-anti-Ac2AN, which is 15.4 kJ/mol higher in energy than the global minimum. The rotation of the 6E-acetyl group in C1r-1Z,6E-Ac2AN via \([C_1r-1Z,90-Ac2AN]\) leads to the local minimum C1r-1Z,6Z-Ac2AN, which is only 1.7 kJ/mol higher in energy than the global minimum. The rotation of the 1E-acetyl group in C1r-1E,6Z-Ac2AN via \([C_1r-90,6Z-Ac2AN]\) also leads to C1r-1Z,6Z-Ac2AN. The diastereomerization processes in 1,6-Ac2AN are shown in Fig. 20.

Ketone 1,7-Ac2AN, similarly to 1,6-Ac2AN, adopts a C\(_r\)-1Z,7E conformation as its global minimum. It is overcrowded due to the short O\(^{15r}\)-H\(^{9}\) contact distance (15% penetration). The C1r-1Z,7E-Ac2AN conformation corresponds to the Z,E X-ray structure of 1,7-Ac2AN. The differences between the geometries of the planar DFT calculated structure of C1r-1Z,7E-Ac2AN and the twisted X-ray structure of 1,7-Ac2AN are smaller than in 1,5-Ac2AN and 1,6-Ac2AN. In the X-ray structure of 1,7-Ac2AN the twist angles are \(\tau_1(C^{9a}-C^{1}-C^{11}-O^{15}) = 15.2^\circ\)
and $\tau_3(C^8-C^7-C^{13}-O^{16})=-176.6$. The relative stabilities of the conformations of $1,7$-Ac$_2$AN and its conformational space are very similar to those of $1,6$-Ac$_2$AN, both being $\alpha,\beta$-diacetylanthracenes. The local minima conformations $C_1$-$1Z,7E$-Ac$_2$AN, $C_1$-$1E,7E$-Ac$_2$AN and $C_1$-$1E,7Z$-anti-Ac$_2$AN are higher in energy than the global minimum by 3.5, 14.5, and 16.6 kJ/mol, respectively. The diastereomerization processes in $1,7$-Ac$_2$AN are shown in Fig. 21.

![Fig. 20. The interconversion of conformations of $1,6$-Ac$_2$AN and their relative Gibbs free energies ($\Delta G_{298}$, kJ/mol)](image)

![Fig. 21. The interconversion of conformations of $1,7$-Ac$_2$AN and their relative Gibbs free energies ($\Delta G_{298}$, kJ/mol)](image)

The most interesting diacetylanthracene is $1,8$-Ac$_2$AN. Peri-interactions $O^{15}$-$H^9$ and $O^{16}$-$H^9$ tilt both carbonyl groups out of the aromatic plane, rendering a planar conformation such as $C_2$-$1Z,5Z$-Ac$_2$AN energetically highly unfavorable. Ketone $1,8$-Ac$_2$AN adopts a $C_2$-$1Z,8Z$-anti conformation as its global minimum. It is overcrowded due to the short $O^{15}$-$H^9$ contact distance (12% penetration). The $C_2$-$1Z,8Z$-anti-Ac$_2$AN conformation corresponds to the $Z,Z$ X-ray structure of $1,8$-Ac$_2$AN. Both structures feature twisted carbonyl groups; however, in the X-ray structure the twist angles are more pronounced ($\tau_1(C^{9a}-C^{1}-C^{11}-O^{15})=-32.4^\circ$ and $34.0^\circ$, $\theta=35.4^\circ$ and $36.0^\circ$) than in the calculated structure ($\tau_1(C^{9a}-C^{1}-C^{11}-O^{15})=-17.3^\circ$, $\theta=19.3^\circ$).

Although the conformational space of $1,8$-Ac$_2$AN resembles that of another $\alpha,\alpha$-diacetylanthracene, $1,5$-Ac$_2$AN, it is more complicated. There are three local minima conformations of $1,8$-Ac$_2$AN: $C_1$-$1Z,8E$-Ac$_2$AN, $C_1$-$1E,8E$-syn-Ac$_2$AN and $C_1$-$1E,8E$-anti-Ac$_2$AN. Rotation of an acetyl group of $C_2$-$1Z,8Z$-Ac$_2$AN via $[C_1$-$1Z,90$-Ac$_2$AN] leads to the $C_1$-$1Z,8E$-Ac$_2$AN conformation, which is only 0.4 kJ/mol higher in energy. The tilting of the $8E$-acetyl group ($\tau_3(C^{8a}-C^{8}-C^{13}-O^{16})=150.4^\circ$) allows the $1Z$-acetyl group to align itself with the aromatic plane ($\tau_1(C^{9a}-C^{1}-C^{11}-O^{15})=1.5^\circ$), restoring the conjugation and thus stabilizing this conformation. The rotation of the $1Z$-acetyl group of $C_1$-$1Z,8E$-Ac$_2$AN may be realized.
in either syn- (via \([C_1\text{-}90,8\text{-}syn\text{-}Ac_{2}AN]\)) or in anti-direction (via \([C_1\text{-}90,8\text{-}anti\text{-}Ac_{2}AN]\)) relative to the 8E-acetyl group. These pathways lead to the local minima \(C_r\text{-}1E,8E\text{-}syn\text{-}Ac_{2}AN\) and \(C_2\text{-}1E,8E\text{-}anti\text{-}Ac_{2}AN\) conformations, respectively, which are 17.6 and 17.7 kJ/mol higher in energy than the global minimum. These two conformations undergo interconversion via the \([C_1\text{-}1E,8E_{180}\text{-}Ac_{2}AN]\) transition state. The diastereomerization processes in 1,8-Ac_{2}AN are shown in Fig. 22.

![Chemical Structure Diagram](image)

**Fig. 22.** The interconversion of conformations of 1,8-Ac_{2}AN and their relative Gibbs free energies (\(\Delta G_{298}\), kJ/mol)

Ketone 2,7-Ac_{2}AN adopts a \(C_r\text{-}2E,7Z\) conformation as its global minimum. It is not overcrowded, lacking peri-interactions. The \(C_r\text{-}(2E,7Z)\text{-}Ac_{2}AN\) conformation corresponds well to the E,Z X-ray structure of 2,7-Ac_{2}AN. The differences between the geometries of the planar DFT calculated structure of \(C_r\text{-}2E,7Z\text{-}Ac_{2}AN\) and the twisted X-ray structure of 2,7-Ac_{2}AN are not large: in the latter structure the twist angles are \(\tau_2(C_1\text{-}C_2\text{-}C_{11}\text{-}O_{10})=171.9^\circ\) and \(\tau_2(C_{8}\text{-}C_{7}\text{-}C_{13}\text{-}O_{10})=0.9^\circ\) (\(\theta=9.8^\circ\) and 1.6\(^\circ\), respectively). There are only two local minima conformations of 2,7-Ac_{2}AN, both are planar like the global minimum. Due to the twist angles \(\tau_2\) being either 0\(^\circ\) or 180\(^\circ\), no anti-, syn-conformations are possible. The rotation of the 7Z-acetyl group in \(C_r\text{-}2E,7Z\text{-}Ac_{2}AN\) via \([C_1\text{-}2E,90\text{-}Ac_{2}AN]\) leads to \(C_{2r}\text{-}2E,7E\text{-}Ac_{2}AN\) conformation, which is only 0.2 kJ/mol higher in energy. The rotation of the 2E-acetyl group of \(C_r\text{-}2E,7Z\text{-}Ac_{2}AN\) via \([C_1\text{-}90,7Z\text{-}Ac_{2}AN]\) leads to the \(C_{2r}\text{-}2Z,7Z\text{-}Ac_{2}AN\) conformation, which is 4.3 kJ/mol higher in energy than the global minimum. The diastereomerization processes in 2,7-Ac_{2}AN are shown in Fig. 23.

![Chemical Structure Diagram](image)

**Fig. 23.** The interconversion of conformations of 2,7-Ac_{2}AN and their relative Gibbs free energies (\(\Delta G_{298}\), kJ/mol)

The conformational space of 2,6-Ac_{2}AN is similar to that of 2,7-Ac_{2}AN. The global minimum is the \(C_{2r}\text{-}2E,6E\text{-}Ac_{2}AN\) conformation. Rotation of the 6E-acetyl group leads to \(C_r\text{-}2E,6Z\text{-}Ac_{2}AN\) conformation, which is only 0.4 kJ/mol higher in energy than the global minimum. The rotation of the 2E-acetyl group in \(C_r\text{-}2E,6Z\text{-}Ac_{2}AN\) leads to \(C_{2r}\text{-}2Z,6Z\text{-}Ac_{2}AN\) conformation, which is 3.8 kJ/mol higher in energy than the global minimum. The diastereomerization processes in 2,6-Ac_{2}AN are shown in Fig. 24.
Polycyclic Aromatic Ketones – A Crystallographic and Theoretical Study of Acetyl Anthracenes

Ketone 9,10-Ac$_2$AN stands out of the other diacetylanthracenes by virtue of its acetyl groups being each flanked by two peri-hydrogens. In order to avoid short non-contact distances to H$_1$/H$_4$/H$_5$/H$_8$, the acetyl groups in all the conformations of 9,10-Ac$_2$AN are considerably twisted. Another mode for the relief of the steric strain in 9,10-Ac$_2$AN is elongation of the C$_{11}$–C$_9$ and C$_{12}$–C$_{10}$ carbonyl bonds, 151.6 pm, as compared to 149.7 pm in planar C$_r$-(2E,7Z)-Ac$_2$AN and 149.8 pm in C$_r$-(2E,6E)-Ac$_2$AN. The global minimum of 9,10-Ac$_2$AN is a C$_i$-E conformation, with the twist angles $\tau_9$(C$_9a$–C$_9$–C$_{11}$–O$_{15}$)=$-72.6^\circ$, $\tau_9$(C$_{10a}$–C$_{10}$–C$_{13}$–O$_{16}$)=$72.6^\circ$ and the dihedral angle $\theta$=74.7°. It corresponds well to the X-ray structure, which features even higher twist angles $\tau_9$=-85.0°, 87.0° and the dihedral angles $\theta$=86.7°, 86.5°. The local minima conformations of 9,10-Ac$_2$AN are C$_s$-Z (0.1 kJ/mol), C$_2$-E (1.0 kJ/mol) and C$_2$-Z (2.1 kJ/mol). They all have high twist angles, ±71.8°, 75.4° and –71.9°, respectively. The similarity of the energies and the geometries of the four conformations of 9,10-Ac$_2$AN stems from the fact that in 9,10-Ac$_2$AN, each of the Z and E conformations is defined relative to the other acetyl group, and not by the twist angles of the carbonyl groups relative to the anthracene system, which are very similar for all four conformations of 9,10-Ac$_2$AN. The C$_r$-E global minimum undergoes diastereomerization to the C$_2$-E conformation via [C$_9$-(9E,10E$_{180}$)] transition state, in which one of the carbonyl groups lies in the aromatic plane. The C$_r$-Z and C$_2$-Z conformations interconvert via the analogous [C$_1$-(9Z,10Z$_0$)] transition state. The C$_r$-E conformation diastereomerizes to the C$_2$-Z conformation and the C$_2$-E conformation diastereomerizes to the C$_r$-Z conformation via the pair of transition states [C$_1$-90-syn] and [C$_1$-90-anti], in which one of the carbonyl groups is orthogonal to the aromatic plane. The diastereomerization processes in 9,10-Ac$_2$AN are shown in Fig. 25.

$$C_{2h} (2Z, 6Z) \overset{3.8}{\longleftrightarrow} [C_1-(90, 6Z)] \overset{0.4}{\longleftrightarrow} C_{5h} (2E, 6Z) \overset{0.0}{\longleftrightarrow} [C_1-(2E, 90)] \overset{4.4}{\longleftrightarrow} C_{2h} (2E, 6E)$$

Fig. 24. The interconversion of conformations of 2,6-Ac$_2$AN and their relative Gibbs free energies (Δ$G_{298}$, kJ/mol)

$$C_2Z \overset{0.1}{\longleftrightarrow} [C_1-(9Z, 10Z_0)] \overset{2.1}{\longleftrightarrow} C_2Z$$

$$[C_1-90\text{-syn}] \overset{4.4}{\longleftrightarrow} [C_1-90\text{-anti}] \overset{3.7}{\longleftrightarrow} C_2E \overset{1.0}{\longleftrightarrow} [C_1-(9E, 10E_{180})] \overset{0.0}{\longleftrightarrow} C_1E$$

Fig. 25. The interconversion of conformations of 9,10-Ac$_2$AN and their relative Gibbs free energies (Δ$G_{298}$, kJ/mol)
Ketone 1,9-Ac$_2$AN has never been isolated. Recently, 1,9-Ac$_2$AN has been claimed to be a putative intermediate in the Friedel–Crafts acyl rearrangements of 1,5-Ac$_2$AN, 1,8-Ac$_2$AN, and 9,10-Ac$_2$AN in PPA to give 3-methylbenz[de]anthracen-1-one [Mala’bi et al., 2011]. Ketone 1,9-Ac$_2$AN adopts a $C_1$-1Z,9Z-anti conformation as its global minimum. Both acetyl groups are considerably twisted because of their mutual peri-positions: $\tau_1$(C$^{9a}$–C$^1$–C$^{11}$–O$^{15}$)=–50.9°, $\tau_9$(C$^{9a}$–C$^9$–C$^{13}$–O$^{16}$)=–59.6°. The local minimum conformation $C_1$-1E,9Z-syn-Ac$_2$AN is considerably higher in energy than the global minimum, 25.9 kJ/mol. Potentially, two more conformations may exist due to the twist angles $\tau_1$ and $\tau_9$ being different from 0° or 180°, i.e. $C_1$-1Z,9Z-syn-Ac$_2$AN and $C_1$-1E,9Z-anti-Ac$_2$AN. However, the search after these conformations has not resulted in any additional stationary points. The $C_1$-1Z,9E-Ac$_2$AN and $C_1$-1E,9E-Ac$_2$AN conformations have also not been found in the conformational space of 1,9-Ac$_2$AN, probably due to the considerable steric strain caused by the peri-interactions between the methyl of the 9E-acetyl group and the 1-acetyl group.

Ketone 1,10-Ac$_2$AN (which has never been synthesized [Mala’bi et al., 2011]) adopts a $C_1$-1Z,10E conformation as its global minimum. Contrary to 1,9-Ac$_2$AN, its acetyl groups do not affect directly each other. Hence, their twist angles, $\tau_1$(C$^{9a}$–C$^1$–C$^{11}$–O$^{15}$)=0.2°, $\tau_9$(C$^{4a}$–C$^{10}$–C$^{13}$–O$^{16}$)=–108.0°, are very close to the twist angles of the lone acetyl groups in $C_s$-1Z-AcAN (0.0°) and $C_1$-9-AcAN (–67.0°), respectively. Another consequence of the non-interacting acetyl groups in 1,10-Ac$_2$AN is the abundance of conformations – six minima conformations have been identified. The local minimum $C_1$-1Z,10Z-Ac$_2$AN conformation is only 1.0 kJ/mol less stable than the global minimum, and differs from it in the twist angle $\tau_9$(C$^{4a}$–C$^{10}$–C$^{13}$–O$^{16}$)=–65.9°. There are four 1E conformations of 1,10-Ac$_2$AN, which have the twist angles $\tau_1$(C$^{9a}$–C$^1$–C$^{11}$–O$^{15}$) of 148–150° and the relative energy of 13.9–15.3 kJ/mol. The conformational behavior of 1,10-Ac$_2$AN is complicated. Depending on the rotational direction of the
1Z-acetyl group, the C1-1Z,10E-Ac2AN conformation may undergo diastereomerization to either C1-1E,10E-anti-Ac2AN or C1-1E,10E-syn-Ac2AN via the respective “nearly orthogonal” transition states. Analogously, the C1-1Z,10Z-Ac2AN may undergo diastereomerization to either C1-1E,10Z-anti-Ac2AN or C1-1E,10Z-syn-Ac2AN. The C1-1E,10E-anti-Ac2AN and C1-1E,10Z-anti-Ac2AN conformations are interconnected via the [C1-1E,90-anti-Ac2AN] transition state, while C1-1E,10E-syn-Ac2AN and C1-1E,10Z-syn-Ac2AN are interconnected via the [C1-1E,90-syn-Ac2AN] transition state. Finally, C1-1E,10E-anti-Ac2AN is interconnected with C1-1E,10E-syn-Ac2AN and C1-1E,10Z-anti-Ac2AN is interconnected with C1-1E,10Z-syn-Ac2AN via the “nearly planar” transition states [C1-1E,10E180-Ac2AN] and [C1-1E,10Z0-Ac2AN], respectively. The diastereomerization processes in 1,10-Ac2AN are shown in Fig. 26.

Ketone 2,9-Ac2AN (which has never been synthesized) adopts a C1-2E,9E conformation as its global minimum. The acetyl groups in 2,9-Ac2AN do not affect directly another one, and twist angles are similar to the respective twist angles in 2-AcAN and 9-AcAN: \(\tau_2(C1-C2-C11-O13)=-178.9^\circ\) and \(\tau_0(C4a-C10-C13-O16)=-106.9^\circ\). There are two local minima conformations of 2,9-Ac2AN, C1-2E,9Z-Ac2AN (3.6 kJ/mol above the global minimum) and C1-2Z,9E-Ac2AN (5.1 kJ/mol). Surprisingly, the search after the C1-2Z,9Z-Ac2AN conformation was not successful. The acetyl groups in the putative C1-2Z,9Z-Ac2AN conformation are not expected to cause a steric hindrance more severe than in the C1-1Z,9Z-anti-Ac2AN conformation. Nevertheless, the latter conformation exists and even was found to be a global minimum, while the former does not seem to exist. The global minimum C1-2E,9E-Ac2AN conformation may diastereomerize either to the C1-2E,9Z-Ac2AN conformation via the [C1-2E,90-Ac2AN] transition state, or to the C1-2Z,9E-Ac2AN conformation via the [C1-90,9E-Ac2AN] transition state. The diastereomerization processes in 2,9-Ac2AN are shown in Fig. 27.

\[
C_1\{2E,9Z\} \rightleftharpoons [C_1\{2E,90\}] \rightleftharpoons C_1\{2E,9E\} \rightleftharpoons [C_1\{90,9E\}] \rightleftharpoons C_1\{2Z,9E\}
\]

3.6 \hspace{1cm} 0.0 \hspace{1cm} 5.1

Fig. 27. The interconversion of conformations of 2,9-Ac2AN and their relative Gibbs free energies (\(\Delta G_{298}\), kJ/mol)

Ketone 2,10-Ac2AN (which has never been synthesized) adopts a C1-2E,10E conformation as its global minimum. The twist angles are \(\tau_2(C1-C2-C11-O13)=179.9^\circ\) and \(\tau_0(C4a-C10-C13-O16)=-113.9^\circ\). The global minimum C1-2E,10E-Ac2AN conformation may diastereomerize either to the C1-2Z,10E-Ac2AN conformation (the relative energy of 2.1 kJ/mol) via the [C1-90,10E-Ac2AN] transition state, or to the C1-2E,10Z-Ac2AN conformation (0.3 kJ/mol) via the [C1-2E,90-Ac2AN] transition state. Both these local minima configurations undergo diastereomerization to the C1-2Z,10Z-Ac2AN conformation (3.9 kJ/mol) via the [C1-2Z,90-Ac2AN] and [C1-90,10Z-Ac2AN] transition states, respectively. The diastereomerization processes in 2,10-Ac2AN are shown in Fig. 28.

The comparison between the X-ray structures of mono- and diacetylanthracenes and their respective calculated geometries deserves a brief discussion. The absolute values of the twist angles of the B3LYP/6-31G(d) calculated conformations (including the local minima conformations) of mono- and diacetylanthracenes may be summarized as follows: \(|\tau_1|=0.0-17.3^\circ\) for the 1Z-acetyl groups, \(|\tau_1|=141.2-152.4^\circ\) for the 1E-acetyl groups, \(|\tau_2|=0.0-1.8^\circ\) for the 2Z-acetyl groups, and \(|\tau_2|=51.9^\circ\) due to the steric strain caused by its interaction with the peri 9Z-acetyl group. The mutual peri-positions of the acetyl groups lead to an enhanced degree of overcrowding.
Current Trends in X-Ray Crystallography

\[ C_1^{-}(2Z,10Z) \rightleftharpoons [C_1^{-}(2Z,90)] \rightleftharpoons C_1^{-}(2Z,10E) \]
3.9
\[ \downarrow \]
\[ [C_1^{-}(90,10Z)] \rightleftharpoons [C_1^{-}(90,10E)] \]
2.1
\[ \downarrow \]
\[ C_1^{-}(2E,10Z) \rightleftharpoons [C_1^{-}(2E,90)] \rightleftharpoons C_1^{-}(2E,10E) \]
0.3
\[ \downarrow \]
0.0

Fig. 28. The interconversion of conformations of 2,10-Ac\(_2\)AN and their relative Gibbs free energies (\(\Delta G_{298}, \text{kJ/mol}\))

the 2Z-acetyl groups, \(|\tau_2|=178.9–180.0^\circ\) for the 2E-acetyl groups, and \(|\tau_9|=44.8–75.4^\circ\) (180–
\(|\varphi_9|>90^\circ\)). The respective twist angles derived from the X-ray structures are
\(|\tau_1|=15.2–34.0^\circ\) for the 1Z-acetyl groups, \(|\tau_2|=0.9^\circ\) for the 2Z-acetyl group,
\(|\tau_2|=177.9–178.6^\circ\) for the 2E-acetyl groups, and \(|\varphi_9|=85.0–87.9^\circ\). There is no X-ray structure
of acetylanthracenes featuring a 1E-acetyl group, and such conformations are always found
to be local minima by the DFT calculations. The B3LYP/6-31G(d) calculations seem to
underestimate the twist angles of the 1Z- and 9-acetyl groups in mono- and
diacetylanthracenes. In a number of cases it leads to predicting planar and more
overcrowded conformations than the respective twisted X-ray geometries. There is a
limited number of reports in the literature that DFT methods, including B3LYP,
could overstabilize planar conformations of biphenyl and related heteroaromatic compounds [Viruela et al.,
1997; Karpfen et al., 1997]. As in the X-ray structures, the acetyl groups and the anthracene
systems in the mono- and diacetylanthracenes under study are essentially planar. Thus,
B3LYP/6-31G(d) satisfactorily predicts the overall conformations of mono- and
diacetylanthracenes under study, i.e. the Z-conformation of 1-AcAN, the E-conformation
of 2-AcAN, the twisted conformation of 9-AcAN, the Z,Z conformations of 1,5-Ac\(_2\)AN and 1,8-
Ac\(_2\)AN, the Z,E conformations of 1,6-Ac\(_2\)AN, 1,7-Ac\(_2\)AN and 2,7-Ac\(_2\)AN, and the E,E
conformation of 9,10-Ac\(_2\)AN. It has not escaped our mind, however, that the packing
interactions in crystals can readily dominate and suppress any preference for one
conformation or another, especially in the cases of low diastereomerization barriers and low
energy differences. We also note the limitations of the DFT calculations in the gas phase and
in the comparison of the computational results with the crystal structures.

The relative free Gibbs energies of the diacetylanthracenes under study are given in Table 6.
It should be noted that 1,5-Ac\(_2\)AN is 11.2 kJ/mol more stable than its constitutional isomer
1,8-Ac\(_2\)AN. The acetyl groups of 1,5-Ac\(_2\)AN are attached to a starred and an unstarred
aromatic carbons of alternant anthracene, while the acetyl groups of 1,8-Ac\(_2\)AN are both
attached to starred aromatic carbons. Simple resonance considerations would favor the
stabilization of 1,8-Ac\(_2\)AN over 1,5-Ac\(_2\)AN, due to the better delocalization of the partial
positive charge in the dipolar Kekulé structures. However, the twist angle of the acetyl
groups in 1,8-Ac\(_2\)AN are notably larger than that in 1,5-Ac\(_2\)AN, in both the crystal
structures (32.4°/34° vs. 20.0°) and the DFT calculated geometries (17.3° vs. 0.0°). This
increased twist angle decreases the conjugation between the acetyl group and the aromatic
system, thus destabilizing 1,8-Ac\(_2\)AN relative to 1,5-Ac\(_2\)AN.
The order of stabilities of the global minima of the diacetylanthracenes is 2,7-Ac$_2$AN ≈ 2,6-Ac$_2$AN > 1,7-Ac$_2$AN > 1,5-Ac$_2$AN > 2,9-Ac$_2$AN > 2,10-Ac$_2$AN > 1,8-Ac$_2$AN > 1,10-Ac$_2$AN > 1,9-Ac$_2$AN > 9,10-Ac$_2$AN. The acetyl groups at positions 1, 5 and 8 destabilize the diacetylanthracenes, while acetyl groups at positions 9 and 10 cause even greater destabilization. The destabilization of the 1, 5, 8, 9 and 10-substituted diacetylanthracenes relative to their 2, 6 and 7-substituted constitutional isomers stems from the overcrowding due to repulsive non-bonding interactions between the carbonyl oxygen/methyl group and the aromatic hydrogens in peri-positions, and from the decreased resonance stabilization between the carbonyl and the aromatic system. Thus, the acetyl groups in 9,10-Ac$_2$AN, 1,9-Ac$_2$AN, 1,10-Ac$_2$AN and 1,8-Ac$_2$AN, being considerably tilted out of the aromatic plane, reduce the relative stabilities of these diacetylanthracenes, potentially allowing deacylation, transacylation and acyl rearrangements. By contrast, 2,7-Ac$_2$AN and 2,6-Ac$_2$AN are not expected to undergo the Friedel–Crafts acyl rearrangements.

2.3.2 Activation barriers
As noted above, monoacetylanthracenes and diacetylanthracenes may undergo E,Z-diastereomerizations and syn,anti-diastereomerizations by rotation of their acetyl groups. The diastereomerization of the first type connects an E-diastereomer with a Z-diastereomer and proceeds via a “nearly orthogonal” transition state, in which the acetyl group, rotating around the C$_{arom}$-C$_{carb}$ bond, has the twist angle of τ=85–97° (the other acetyl group in diacetylanthracenes retains its E- or Z-orientation). The diastereomerization of the second type occurs only in diacetylanthracenes and connects either an E-syn-diastereomer with an E-anti-diastereomer, or a Z-syn-diastereomer with a Z-anti-diastereomer. It proceeds via a “nearly planar” transition states, in which the twist angle of the rotating acetyl group is close to either 180° (E-diastereomer) or zero (Z-diastereomer), and the other acetyl group retains its E- or Z-orientation. Fig. 29 and Fig. 30 show the E,Z-diastereomerization and syn,anti-diastereomerization on the example of 1,8-Ac$_2$AN.

Table 7 gives the energy barriers for the E,Z-diastereomerization and syn,anti-diastereomerization in the monoacetylanthracenes and diacetylanthracenes under study by rotation of the acetyl groups via the respective nearly orthogonal or nearly planar transition states. The E,Z-diastereomerization energy barriers may be divided into three groups, depending on the position of the acetyl group that undergoes rotation and on its conformation. E-Acetyl groups at positions 1, 5 and 8 and acetyl groups at positions 9 and 10 have the lowest energy barriers, 3.6–9.5 kJ/mol, due to their already significant twist angles (τ=141–152° for E-acetyl groups at positions 1, 5 and 8 and τ=67–73° for acetyl groups at positions 9 and 10). Z-Acetyl groups at the same positions 1, 5 and 8 have medium energy barriers, 19.5–23.5 kJ/mol. The twist angles of these acetyl groups are smaller (τ=0–17°), but the E,Z-diastereomerization in this case is facilitated by the steric strain due to repulsive peri-interactions between the carbonyl oxygen and aromatic H$_9$/H$_{10}$ hydrogens. Finally, both E- and Z-acetyl groups at positions 2, 6 and 7 have the highest energy barriers for diastereomerization, 27.3–31.6 kJ/mol, due to the lack of steric strain and negligible twist angles (less than 1°). For comparison, the experimental rotational energy barrier for methyl 1-(2-methylnaphthyl) ketone is 33.9 kJ/mol (~110 °C, [Wolf, 2008]). Table 8 gives the relative Gibbs free energies of the global minima and the most stable local minima of the acetylanthracenes whose crystal structures have been determined in this study or reported in the literature, i.e. 1-AcAN, 2-AcAN, 9-AcAN, 1,5-Ac$_2$AN, 1,6-Ac$_2$AN, 1,7-Ac$_2$AN, 1,8-Ac$_2$AN, 2,7-Ac$_2$AN and 9,10-Ac$_2$AN, as well the energy barriers for their E,Z-
diastereomerizations. The energy barriers are in the range of 20–32 kJ/mol (relative to the respective global minima) for the rotation of the acetyl groups at 1, 2, 5, 6 and 7 positions. The lower energy barrier in 1,8-Ac$_2$AN (9.8) may be rationalized by destabilization of the global minimum due to the larger twist of the acetyl groups. This effect is even more pronounced in the case of 9-AcAN and 9,10-Ac$_2$AN, which have large twist values (67° and 73°, respectively) and remarkably low $E,Z$-diastereomerization barriers (less than 4 kJ/mol).

All these barriers are sufficiently low to allow a swift $E,Z$-diastereomerizations on the NMR time scale (at room temperature), in accordance with the results of the NMR experiments (vide supra). The differences in the relative energies of the global minimum and the most stable local minimum of these acetylanthracenes are relatively small, 0.06-3.5 kJ/mol (with the exception of 1-AcAN and 1,5-Ac$_2$AN), which suggests the presence of both $E$- and $Z$-diastereomers in equilibrium mixture at ambient temperature.
| E,Z diastereomerization or syn,anti-diastereomerization | ΔG° (kJ/mol) | Transition state | E_{Tot} (Hartree) |
|-------------------------------------------------------|--------------|-----------------|------------------|
| 1Z-AcAN→1E-AcAN                                       | 19.52        | [1-AcAN]        | -692.16527547    |
| 1E-AcAN→1Z-AcAN                                       | 6.51         |                 |                  |
| 2Z-AcAN→2E-AcAN                                       | 29.28        | [2-AcAN]        | -692.16644237    |
| 2E-AcAN→2Z-AcAN                                       | 31.52        |                 |                  |
| 9-AcAN→9-AcAN*                                        | 3.64a        | [9-AcAN]        | -692.16355087    |
| 1Z,5Z-Ac2AN→1Z,5E-Ac2AN                               | 19.93        | [1Z,90-Ac2AN]   | -844.80776475    |
| 1Z,5E-Ac2AN→1Z,5Z-Ac2AN                               | 7.14         |                 |                  |
| 1E,5E-syn-Ac2AN→1E,5E-anti-Ac2AN                      | 7.54         | [1E,5E_{180}-Ac2AN] | -844.80415197    |
| 1E,5E-anti-Ac2AN→1E,5E-syn-Ac2AN                       | 8.22         |                 |                  |
| 1Z,5Z-Ac2AN→1Z,5E-syn-Ac2AN                           | 20.93        | [90,5E-syn-Ac2AN] | -844.80261144    |
| 1E,5E-syn-Ac2AN→1Z,5E-Ac2AN                           | 5.67         |                 |                  |
| 1Z,5E-Ac2AN→1E,5E-anti-Ac2AN                          | 21.01        | [90,5E-anti-Ac2AN] | -844.80259178    |
| 1E,5E-anti-Ac2AN→1Z,5E-Ac2AN                          | 6.44         |                 |                  |
| 1Z,6Z-Ac2AN→1Z,6E-Ac2AN                               | 28.66        | [1Z,90-Ac2AN]   | -844.80884650    |
| 1Z,6E-Ac2AN→1Z,6Z-Ac2AN                               | 30.35        |                 |                  |
| 1Z,6Z-Ac2AN→1E,6Z-Ac2AN                               | 19.86        | [90,6Z-Ac2AN]   | -844.81218832    |
| 1E,6Z-Ac2AN→1Z,6Z-Ac2AN                               | 6.13         |                 |                  |
| 1Z,6E-Ac2AN→1E,6E-Ac2AN                               | 19.86        | [90,6E-Ac2AN]   | -844.81289093    |
| 1E,6E-Ac2AN→1Z,6E-Ac2AN                               | 6.29         |                 |                  |
| 1E,6Z-Ac2AN→1E,6E-Ac2AN                               | 29.02        | [1E,90-anti-Ac2AN] | -844.80381925    |
| 1E,6E-Ac2AN→1E,6Z-Ac2AN                               | 30.88        |                 |                  |
| 1E,6Z-Ac2AN→1E,6E-Ac2AN                               | 29.16        | [1E,90-syn-Ac2AN] | -844.80371345    |
| 1E,6E-Ac2AN→1E,6Z-Ac2AN                               | 31.01        |                 |                  |
| 1Z,7Z-Ac2AN→1Z,7E-Ac2AN                               | 28.05        | [1Z,90-Ac2AN]   | -844.80879074    |
| 1Z,7E-Ac2AN→1Z,7Z-Ac2AN                               | 31.54        |                 |                  |
| 1Z,7Z-Ac2AN→1E,7Z-Ac2AN                               | 19.95        | [90,7Z-Ac2AN]   | -844.81202172    |
| 1E,7Z-Ac2AN→1Z,7Z-Ac2AN                               | 6.83         |                 |                  |
| 1Z,7E-Ac2AN→1E,7E-Ac2AN                               | 20.72        | [90,7E-Ac2AN]   | -844.81303091    |
| 1E,7E-Ac2AN→1Z,7E-Ac2AN                               | 6.26         |                 |                  |
| 1E,7Z-Ac2AN→1E,7E-Ac2AN                               | 28.53        | [1E,90-anti-Ac2AN] | -844.80384032    |
| 1E,7E-Ac2AN→1E,7Z-Ac2AN                               | 30.69        |                 |                  |
| 1E,7Z-Ac2AN→1E,7E-Ac2AN                               | 29.29        | [1E,90-syn-Ac2AN] | -844.80370612    |
| 1E,7E-Ac2AN→1E,7Z-Ac2AN                               | 31.45        |                 |                  |
| 1Z,8Z-anti-Ac2AN→1Z,8E-Ac2AN                          | 9.81         | [1Z,90-Ac2AN]   | -844.80732674    |
| 1Z,8E-Ac2AN→1Z,8Z-anti-Ac2AN                          | 9.46         |                 |                  |
Table 7. Energy barriers (ΔG‡, kJ/mol) for diastereomerizations of monoacetylanthracenes and diacetylanthracenes

| Reaction                                      | ΔG‡ 298 | ΔΔG 298 | ΔG‡  |
|-----------------------------------------------|---------|---------|------|
| 1E,8E-anti-Ac$_2$AN→1Z,8E-Ac$_2$AN             | 4.15    |         | -844.80278079 |
| 1Z,8E-Ac$_2$AN→1E,8E-anti-Ac$_2$AN             | 21.46   |         | -844.80231227 |
| 1E,8E-syn-Ac$_2$AN→1Z,8E-Ac$_2$AN              | 6.22    |         | -844.80296243 |
| 1Z,8E-Ac$_2$AN→1E,8E-syn-Ac$_2$AN              | 23.46   |         | -844.80926430 |
| 1E,8E-syn-Ac$_2$AN→1E,8E-anti-Ac$_2$AN         | 9.49    |         | -844.80926430 |
| 1E,8E-anti-Ac$_2$AN→1E,8E-syn-Ac$_2$AN         | 9.42    |         | -844.80926430 |
| C$_r$-E-9,10-Ac$_2$AN→C$_r$-Z-9,10-Ac$_2$AN     | 3.73    | [C$_r$-90-anti-9,10-Ac$_2$AN] | -844.79633239 |
| C$_r$-Z,9,10-Ac$_2$AN→C$_r$-E-9,10-Ac$_2$AN     | 3.67    |         | -844.79605863 |
| C$_r$-E-9,10-Ac$_2$AN→C$_r$-Z-9,10-Ac$_2$AN     | 3.44    | [C$_r$-90-syn-9,10-Ac$_2$AN] | -844.79605863 |
| C$_r$-Z,9,10-Ac$_2$AN→C$_r$-E-9,10-Ac$_2$AN     | 4.36    |         | -844.79605863 |
| C$_r$-2E,7Z-Ac$_2$AN→C$_r$-2Z,7Z-Ac$_2$AN       | 31.63   | [C$_r$-90,7Z-Ac$_2$AN] | -844.81338779 |
| C$_s$-2Z,7Z-Ac$_2$AN→C$_s$-2E,7Z-Ac$_2$AN       | 27.34   |         | -844.81338779 |

Table 8. Relative energies (ΔG$_{298}$ and ΔΔG$_{298}$, kJ/mol) of selected monoacetylanthracenes and diacetylanthracenes and respective energy barriers for E,Z-diastereomerizations (ΔG‡, kJ/mol)
3. Conclusions

The monoacetylanthracenes and diacetylanthracenes under study adopt non-planar conformations in their crystal structures. The twist angles are maximal for the 9-acetyl groups (|\(\tau_9\)| = 85.0–87.9°) and significant for the 1Z-acetyl groups (|\(\tau_1\)| = 15.2–34.0°), but very small for 2-acetyl groups. The conformations in solution are in agreement with the X-ray crystal structure conformations, according to the NMR data. The crystal structures are stabilized by intermolecular interactions: aromatic–aromatic \(\pi\)–\(\pi\) interactions (1,6-Ac\(_2\)AN and 1,7-Ac\(_2\)AN), C–H–\(\pi\) interactions (2-AcAN, 1,5-Ac\(_2\)AN, 2,7-Ac\(_2\)AN and 9,10-Ac\(_2\)AN), or \(\pi\)–\(\pi\) interactions between the anthracene unit and the carbonyl bond (1,8-Ac\(_2\)AN). The B3LYP/6-31G(d) calculated conformations of the monoacetylanthracenes and diacetylanthracenes are in good agreement with the X-ray crystal structures. The acetyl groups in the crystal structures and the B3LYP/6-31G(d) calculated global minima of the monoacetylanthracenes and diacetylanthracenes preferentially adopts 1\(Z\) and 2\(E\) conformations. The order of stabilities of the diacetylanthracenes under study is 2,7-Ac\(_2\)AN > 1,7-Ac\(_2\)AN = 1,6-Ac\(_2\)AN > 1,5-Ac\(_2\)AN > 1,8-Ac\(_2\)AN > 9,10-Ac\(_2\)AN. The acetyl groups at positions 1, 5 and 8 destabilize the diacetylanthracenes because of the repulsive interactions between the carbonyl oxygen/methyl group and the aromatic \textit{peri}-hydrogens, and because of the decreased resonance stabilization. This effect is even more pronounced for the acetyl groups at positions 9 and 10. The B3LYP/6-31G(d) calculated energy barriers for the \(E,Z\)-diastereomerizations show that the \(E,Z\)-diastereomerizations is swift on the NMR time scale (at room temperature), in accordance with the results of the NMR experiments. The present results of the crystallographic and theoretical study of monoacetylanthracenes and diacetylanthracenes contribute to our understanding of the motifs of reversibility and thermodynamic control in the Friedel–Crafts acyl rearrangements of these representative PAKs.

4. Experimental section

Table 9 summarizes the applied methods of preparation of the monoacetylanthracenes and diacetylanthracenes. Melting points are uncorrected. All NMR spectra were recorded with Bruker DRX 500 MHz spectrometer. \(^1\)H-NMR spectra were recorded at 500.13 MHz using CDCl\(_3\) as solvent and as internal standard, \(\delta\)(CDCl\(_3\))=7.263 ppm. \(^13\)C-NMR spectra were recorded at 125.75 MHz using CDCl\(_3\) as a solvent with internal standard, \(\delta\)(CDCl\(_3\))=77.008 ppm. Complete assignments were made through 2-dimensional correlation spectroscopy (COSY, HSQC, HBMC and NOESY). Anthracene and nitrobenzene were obtained from Sigma-Aldrich; acetyl chloride and aluminum chloride were obtained from Acros. All the solvents were AR grade. Chloroform and dichloromethane were distilled before use. Single crystal X-ray diffraction was carried out on a Bruker SMART APEX CCD X-ray diffractometer, equipped with graphite monochromator and using MoK\(_\alpha\) radiation (\(\lambda\)=0.71073 Å). Low temperature was maintained with a Bruker KRYOFLEX nitrogen cryostat. The diffractometer was controlled by a Pentium-based PC running the SMART software package [Bruker AXS GmbH, 2002a]. Immediately after collection, the raw data frames were transferred to a second PC computer for integration and reduction by the SAINT program package [Bruker AXS GmbH, 2002b]. The structures were solved and refined by the SHELXTL software package [Bruker AXS GmbH, 2002c].
Table 9. Summary of methods of preparation of monoacetylanthracenes and diacetylanthracenes.

| Compound | Method of preparation | Solvent | Melting point °C | Lit. melting point °C | Solvent of recryst. | Reference |
|----------|-----------------------|---------|------------------|-----------------------|---------------------|-----------|
| 1-AcAN   | Anthracene AlCl₃, Acetyl chloride | CH₂Cl₂ | 110              | 109                   | EtOH                | Bassilios, 1962, Mala’bi et al., 2009 |
| 2-AcAN   | Anthracene AlCl₃, Acetyl chloride | C₆H₅NO₂ | 177              | 174-178              | MeCO₂Et            | Bassilios, 2009, Bassilios, 1966 |
| 9-AcAN   | Anthracene AlCl₃, Acetyl chloride | CH₂Cl₂ | 78               | 75-76                | MeCO₂Et            | Bassilios, 1962, Bassilios, 1962 |
| 1,5-Ac₂AN| Anthracene AlCl₃, Acetyl chloride | CH₂Cl₂ | 215              | 213                   | CHCl₃               | Bassilios, 1963 |
| 1,6-Ac₂AN| 2-AcAN AlCl₃, Acetyl chloride | CIC₅H₅Cl | 170-172         | 171-172              | MeCO₂Et            | Gore, 1966 |
| 1,7-Ac₂AN| 2-AcAN AlCl₃, Acetyl chloride | CIC₅H₅Cl | 102-103         | -                     | EtOH                | -         |
| 1,8-Ac₂AN| Anthracene AlCl₃, Acetyl chloride | CH₂Cl₂ | 179              | 174-176              | CHCl₃               | Sarobe & Jenneskens, 1997 |
| 2,7-Ac₂AN| 2-AcAN AlCl₃, Acetyl chloride | C₆H₅NO₂ | 156-157         |                       | iPrOH               | -         |
| 9,10-Ac₂AN| 9,10-dicarbomethoxy-anthracene, MeLi | Et₂O | 247              | 249-250              | CH₂Cl₂              | Duerr, 1988 |

The quantum mechanical calculations were performed using the Gaussian03 [Frisch et al., 2004] package. Becke's three parameter hybrid density functional B3LYP [Becke, 1993], with the non-local correlation functional of Lee, Yang, and Parr [Lee et al., 1988] was used. The split valence 6-31G(d) basis set [Hariharan & Pople, 1973] was employed. All structures were fully optimized using symmetry constraints as indicated. Vibrational frequencies were computed at the same level of theory to verify the nature of the stationary points. For calculating the thermal corrections to Gibbs' free energy, the zero point energies were scaled by 0.9804 [Bauschlicher & Partridge, 1995].

5. References

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