A DFT study of the tautomerism of 1H-benzo[de]cinnolines and their protonated forms

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Abstract
1H-Benzo[de]cinnolines and 1H-indeno[6,7,1-def]cinnolines have been studied theoretically at the B3LYP/6-311++G(d,p) level in the gas-phase and in water solution (PCM model); gas-phase geometries were used to calculate absolute shieldings (GIAO) that were transformed into chemical shifts using empirical equations. The annular tautomerism of neutral species and of protonated cations have been determined, and the most stable cations coincide with those determined experimentally.

Keywords 1H-Benzo[de]cinnolines · Tautomerism · Protonation · 1H NMR · GIAO · MEP · HOMO

1 Introduction

In comparison to perimidines [1–3], 1H-benzo[de]cinnolines have been much less studied; they have a similar relationship as that between benzimidazoles and indazoles (Fig. 1). According to different databases, the number of items of perimidines and benzo[de]cinnolines is very different; the same happens for benzimidazoles and indazoles. This is partly due to the fact that o-phenylenediamine and 1,8-diaminonaphthalene are cheap and convenient starting materials; note however that the difference is much larger in the perimidine/benzo[de]cinnoline pair than in the benzimidazole/indazole pair, as a consequence that benzo[de]cinnolines have been reported with different names, such as diazaphenalenenes, peridazines, etc. Trying to correct this imbalance, we started the present theoretical study.

Simple 1H-benzo[de]cinnolines, 1–4, have been prepared by Lacy and Smith [4, 5], as well as by Aksenov, Aksenova et al. [6] see Fig. 2.

Previous theoretical studies are due to Pozharskki and Malysheva in 1970 using the HMO approximation and concluding that there is a shift of electrons from the pyridazine ring to the naphthalene [7] and a much more recent paper by Mezheritskii et al. [8] where B3LYP/6-31(d,p) calculations on the tautomerism of the protonated forms of a derivative of 1H-benzo[de]cinnoline (5, 1-ethyl-3-methyl-1H-indeno[6,7,1-def]cinnoline) has been reported. Finally, there are two papers by Tsoungas et al. [9, 10] on the aromaticity of 1H-benzo[de]cinnolines and related heterocycles based on NICS calculations.

2 Computational details

All calculations correspond to B3LYP/6-311++G(d,p) [11, 12] and were carried out using the Gaussian 16 set of programs [13] including general solvent effects, PCM [14].

To confirm that the optimized structures were minima, vibrational frequencies were calculated at the same level of theory as geometry optimizations, and it was verified that they had only real frequencies. Fukui function [15–17] for electrophilic attack, f-, has been calculated as the difference of the density of the neutral system and the radical cation computed at B3LYP/6-311++G(d,p) level. The atomic contributions to this functions have been obtained using the NBO-6 [18] charges of the neutral and radical cation molecules.

NMR chemical shifts were calculated with the gauge-independent atomic orbital (GIAO) method [19, 20] at the B3LYP/6-311++G(d,p) level of theory in the gas phase.

The following equations [21, 22] were used to transform absolute shieldings into chemical shifts:

$$\delta^1H = 31.0 - 0.97 \times \sigma^1H, \quad \text{reference TMS, 0.00 ppm}.$$
\[ \delta^{13}C = 175.7 - 0.963 \times \sigma^{13}C, \quad \text{(reference TMS, 0.00 ppm)}. \]

\[ \delta^{15}N = -152.0 - 0.946 \times \sigma^{15}N, \quad \text{(reference MeNO}_2, \ 0.00 \text{ ppm)}. \]

These equations are based on \( \sigma \) values calculated in the gas phase and \( \delta \) values measured in solution.

### 3 Results and discussion

#### 3.1 Annular tautomerism 1H-benzo[de]cinnolines

In the case of the benzimidazole/perimidine pair, there is a perfect similitude, both presenting annular tautomerism of the class called degenerate or autotrope, indicating that both tautomers are identical [23]. In the case of indazole, both annular tautomers, the 1\( H \) and the 2\( H \), are of different energy [24, 25] (Fig. 3).

In the case of benzo[de]cinnoline 1, the transfer of the proton from N1 to N2 leads to a zwitterionic compound (in blue in Fig. 3). Similarly to all other compounds of Fig. 2 (2–4), 1\( H \)-benzo[de]cinnoline have also CH tautomers that are much less stable because the aromaticity or part of the aromaticity is lost. The tautomer with the proton on C9aa has a very high energy, in the gas phase 252.5 kJ mol\(^{-1}\) (\( \mu = 5.2 \) D), and it will no longer be considered; its instability is due to the destruction of the aromaticity of two benzene rings.

We have represented in Fig. 4 the seven tautomers of the parent compound 1. Energies and dipole moments are reported in Table 1. The position of the tautomeric proton was used to name the tautomers. In red, the most stable tautomer, 1-1\( H \), that serves as reference compound in Table 1.

An analysis of Table 1 energetic results lead to the following conclusions:

1. Water vs. gas: water = \( - (2 \pm 4) + (0.88 \pm 0.06) \) gas, \( n = 7, \ R^2 = 0.975 \)

Since the intercept is not significant, we impose intercept = 0:

\[ \text{Water} = (0.85 \pm 0.02) \text{ gas}, \quad n = 7, \quad R^2 = 0.996. \]

This equation shows that the solvation by water leads to values roughly proportional to the gas values.
2. The zwitterion, \(2H\), although highly unstable compared with the \(1H\) tautomer is still more stable than any CH tautomer.

3. The two most stable CH tautomers are \(1-7H\) and \(1-9H\). The dipole moments are also linearly related, \(\text{water} = (1.45 \pm 0.02) \, \text{gas} \), \(n = 7, \, R^2 = 0.999\).

3.2 Annular tautomerism of protonated \(1H\)-benzo[\(de\)]cinnolines

Lacy and Smith, \([4, 5]\) demonstrated, using \(^1\)H NMR spectroscopy (see Sect. 3.3), that dissolving compounds 1 and 2 in trifluoroacetic acid cations protonated on C7 were obtained, \(1-1,7H\) and the corresponding 3-methyl derivative \(2-1,7H^+\). To illustrate that these cations have several resonance forms, two of the most representative of cation \(1-1,7H\) are represented in Fig. 5.

Table 2 contains the relative energies of the twelve tautomers obtained by protonation of \(1H\) and \(2H\) tautomers. Very unstable \(1-1,5H\) (137.8 \(\text{kJ mol}^{-1}\)) and \(1-1,8H\) tautomers (138.4 \(\text{kJ mol}^{-1}\)) will not discussed, and these cations are non-classical carbocations with the positive charge on C9aa.

The discussion of Table 2 results leads to the following conclusions:

1. The effect of water is more disperse than in the case of neutral molecules: \(\text{water} = -(0.7 \pm 3.0) + (0.90 \pm 0.08) \, \text{gas} \), \(n = 12, \, R^2 = 0.936\). Without intercept, \(\text{water} = (0.89 \pm 0.04) \, \text{gas} \), \(n = 12, \, R^2 = 0.975\).

2. In agreement with literature results (see Sect. 3.2), the most stable cation is the \(1-1,7H\).

3. Protonation of the most stable tautomer, \(1H\), on N2 leads to the zwitterion \(1-1,2H\) that occupies the eighth place in stability.

4. After the \(1-1,7H\) tautomer, the next most stable are \(1-2,7H\), \(1-1,9H\) and \(1-2,9H\) that is protonated on positions 7 and 9.

5. The last column of Table 2 contains the data of the protonated N1-methyl derivatives; they are related to the NH ones by the following relationship: \(\text{NMe} = (0.84 \pm 0.03) \, \text{NH} \), \(n = 6, \, R^2 = 0.996\). The worst point, as expected, corresponds to the \(2-1,2H\) tautomer that deviates by 6.8 kJ \(\text{mol}^{-1}\).

Mezheritskii et al. \([8]\) reported B3LYP/6-31(d,p) calculations on the tautomerism of the protonated forms of compound \(5\) (\(1H\)-indenol[6,7-\(de\)]cinnoline). Only four tautomers were considered (Fig. 6). The most stable cation is the \(5-6H\) that corresponds to the structure found experimentally.

There is a relationship between both series of values: \(5 = (1.71 \pm 0.25) \, 1, \, n = 4, \, R^2 = 0.94\).

3.3 \(^1\)H NMR results of \(1H\)-benzo[\(de\)]cinnolines

NMR literature data on the simple \(1H\)-benzo[\(de\)]cinnolines of Fig. 2 concerns exclusively \(^1\)H NMR (Table 3).

GIAO calculations of the same compounds but including \(^{13}\)C and \(^{15}\)N nuclei are reported in Table 4. Calculated chemical shifts of the other compounds discussed in this work are gathered in the Electronic supplementary material.
The experimental $^1$H NMR data, the only available (Table 3), correlate quite well with the calculated ones (Table 4): Exp. = $(0.21 \pm 0.16) + (0.98 \pm 0.02) + (0.80 \pm 0.15)$ \text{ppm}, $n=48$, $R^2 = 0.976$. The three NH protons need a correction of 0.80 ppm due to specific solvent effects.

### 3.4 The structure of the cations resulting from the protonation of $1H$-benzo[de]cinnolines

To discuss the protonation of $1H$-benzo[de]cinnolines is useful to collect a series of proton affinities, PA, values both calculated and experimental, Table 5.
The C7 position of 1\(H\)-benzo[de]cinnoline (1) is more basic than the N2 position (difference 33.3 kJ mol\(^{-1}\)); actually, the basicity of the carbon atom is the same than the N atom of pyridine while the basicity of N2 is close to that of indazole, a compound having also a H–N1–N2=\(\text{C}\) sequence of atoms where protonation took place on N2 [27]. Compared with protonation on C4 of aniline, 880.7 kJ mol\(^{-1}\), the benzo[de]cinnoline 1 is a much stronger carbon base, +47.1 kJ mol\(^{-1}\); as N bases, benzo[de]cinnoline 1 is a stronger carbon base, +22.5 kJ mol\(^{-1}\).

We have calculated some properties of the parent compound 1 to explain the protonation site.

The MEP (molecular electrostatic potential also abbreviated as MESP) is usually a good guide in assessing the molecules reactivity toward positively or negatively charged reactants; however, it does not take into account the charge transfer to the proton and a major redistribution of electron density, which becomes polarized toward the protonation

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**Fig. 6** Four tautomers of the cations of 1-ethyl-3-methyl-1\(H\)-indenophenyl[6,7,1-def]cinnoline 5. Relative energies, gas phase, in kJ mol\(^{-1}\) are also reported

**Table 3** Experimental \(^1\)H NMR chemical shifts (\(\delta\), ppm) and \(^1\)H–\(^1\)H coupling constants (Hz)

|   | 1\(H\) | 2\(^a\) | 3 | 4 | 1-1,7\(H\) | 2-1,7\(H\) |
|---|--------|--------|---|---|------------|------------|
| R\(^1\) | H      | H      | H | CH\(_3\) | H          | H          |
| R\(^3\) | H      | CH\(_3\) | C\(_6\)H\(_5\) | CH\(_3\) | H          | CH\(_3\) |
| References | [5]    | [6]    | [6] | [5] | [5] | [5] |
| 1 | 8.16   | 8.28 (br) | 8.26 (br) | 3.40 | N.o | N.o |
| 3 | 7.0–7.3 | 2.16 | b  | 2.15 | 9.4 | 3.1 |
| 4 | 7.0–7.3 | 7.38, \(J\)\(_{45}\) = 7.5 | 7.31, \(J\)\(_{45}\) = 7.6 | 7.1–7.4 | 8.3 | 8.3 |
| 5 | 7.0–7.3 | 7.12 | 7.12 | 7.1–7.4 | 8.3 | 8.3 |
| 6 | 6.8, \(J\) = 1.5, 9.0 | 6.87, \(J\)\(_{56}\) = 8.1 | 6.92, \(J\)\(_{56}\) = 8.2 | 6.90 (\(J\) = 8) | 8.3 | 8.3 |
| 7 | 6.6, \(J\) = 2.5, 6.0 | 6.65, \(J\)\(_{78}\) = 7.3 | 6.74, \(J\)\(_{78}\) = 7.3 | 6.70 (\(J\) = 7) | 4.5 (br) | 4.5 (br) |
| 8 | 7.0–7.3 | 7.12 | 7.12 | 7.1–7.4 | 7.6, \(J\)\(_{89}\) = 10.0, \(J\)\(_{78}\) = 4.0 | 7.5, \(J\)\(_{99}\) = 10.0, \(J\)\(_{89}\) = 4.0 |
| 9 | 6.1, \(J\) = 1.0, 7.0 | 6.21, \(J\)\(_{99}\) = 7.0 | 6.23, \(J\)\(_{99}\) = 7.0 | 6.05 (\(J\) = 7) | 7.3, \(J\)\(_{99}\) = 1.0 | 7.3 |

\(^a\)Also reported in Ref. [4] but probably with a lower field apparatus (not given) than that used more recently (200 MHz) [6]

\(^b\)3-Phenyl signals: 7.45 (3H, \(m\)-H, \(p\)-H), 7.56 (d, 2H, \(o\)-H, \(J\) = 6.9)
Table 4  GIAO/B3LYP/6-311++G(d,p) calculated NMR chemical shifts (δ, ppm)

\[
\begin{array}{cccccc}
\text{1H} & 2^* & 3 & 4 & 1.7H & 3\text{Me 2-1H} \\
R^1 & H & H & H & CH_3 & H & H \\
R^3 & H & CH_3 & C_6H_5 & CH_3 & H & CH_3 \\
H1 & 7.26 & 7.38 & 7.50 & 3.34 (Me) & 10.14 & 9.99 \\
H3 & 7.06 & 2.03 (Me) & (Ph)^a & 2.08 (Me) & 9.06 & 3.02 (Me) \\
H4 & 6.37 & 6.82 & 6.77 & 6.54 & 8.18 & 8.24 \\
H5 & 7.05 & 7.14 & 7.04 & 7.21 & 8.52 & 8.50 \\
H6 & 7.09 & 7.20 & 7.17 & 7.27 & 8.35 & 8.30 \\
H7 & 6.74 & 6.84 & 6.81 & 6.93 & 4.57, 4.57 & 4.52, 4.52 \\
H8 & 6.97 & 7.06 & 7.01 & 7.20 & 7.84 & 7.74 \\
H9 & 5.92 & 6.02 & 5.99 & 5.95 & 6.90 & 6.85 \\
C3 & 138.4 & 143.8 & 148.3 & 142.5 & 151.9 & 163.8 \\
C3a & 127.8 & 127.4 & 127.8 & 127.0 & 126.4 & 126.8 \\
C4 & 111.9 & 110.4 & 113.0 & 110.2 & 126.8 & 124.7 \\
C5 & 128.3 & 128.1 & 127.8 & 127.8 & 140.3 & 139.7 \\
C6 & 123.2 & 123.5 & 123.8 & 123.0 & 135.6 & 134.6 \\
C6a & 135.9 & 135.7 & 136.3 & 135.6 & 140.3 & 140.6 \\
C7 & 114.5 & 113.8 & 114.7 & 114.3 & 36.3 & 36.2 \\
C8 & 128.4 & 128.1 & 128.0 & 128.2 & 161.3 & 159.1 \\
C9 & 96.6 & 96.5 & 96.5 & 97.0 & 116.9 & 116.7 \\
C9a & 139.6 & 139.4 & 139.5 & 139.6 & 151.0 & 150.1 \\
C9aa & 127.7 & 126.4 & 128.0 & 126.8 & 122.0 & 121.4 \\
N1 & -222.0 & -230.3 & -228.1 & -230.5 & -187.8 & -188.5 \\
N2 & -63.8 & -72.3 & -66.5 & -59.6 & -60.5 & -69.7 \\
\end{array}
\]

\(^a3\text{-Phenyl group: } Ho = 7.61, Hm = 7.40, Hp = 7.35; Ci = 138.6, Co = 128.4, Cm = 127.9, Cp = 128.0\)

Table 5  Proton affinities (in kJ mol\(^{-1}\)) of several compounds

| Compound | Protonation site | Calculated | Experimental, NIST [26] |
|----------|-----------------|------------|-------------------------|
| Pyridine |                 | 928.2      | 930                     |
| Indazole |                 | 902.0      | 900.8                   |
| Aniline  | Protonated on the NH\(_2\) | 872.0 |                         |
| Aniline  | Protonated on C\(_{para}\) | 880.7 | 882.5                   |
| 1H-benzo\(_{de}\)cinnoline (I) | Protonated on N2 | 894.5 |                         |
| 1H-benzo\(_{de}\)cinnoline (I) | Protonated on C7 | 927.8 (+33.3*) |                         |
Fig. 7  a Left, MEP of compound 1: in red zones of maximum electronic density. 
b Center side, HOMO map of compound 1. c Right, Fukui for electrophilic attack, f-, at a value of ~ 0.004 au with indication of atomic contribution with hydrogen summed into heavy atoms (e).

site.[28] That represented in Fig. 7, red zones, indicates that toward the proton the preferred sites of attack are N2 (− 116.6 a.u.) > C7 (− 62.7 a.u.) > C6 (− 56.4 a.u.) based on the MEP. This is satisfactory as C7 is better than C6 but not as N2 is much better because this lead to the very unstable 1-1,2H cation. In the cited work of Tsoungas et al. [9], they analyzed the MEP as indicating that the reactivity of electrophiles toward 1 will occur at positions 3, 6 and 9.

The unsatisfactory result obtained by the analysis of the MEP leads us to calculate the HOMO and Fukui index for electrophilic attack on 1. Several authors have published results that indicate that the HOMOs of a given molecule are related to the protonation position [28–32]. The central structure of Fig. 7 shows that the HOMO on N2 is very small while those on C4 and C7 are important; although position 4 is never protonated, nitration occurs on it after position 7 [33]. The Fukui index for electrophilic attack (Fig. 7 right) shows the most negative values for the atoms involved in the two most stable tautomers of the protonated 1-1H system, 1-1,7H and 1-1,9H (− 0.23 and − 0.21 e, respectively). A recent article shows the complexity of the analysis of protonation sites that sometimes is associated with electrostatic (hard-hard interaction) while in others cases it is related to the formation of the new X–H bond involving the orbitals of the neutral molecule (soft–soft interaction) [34].

4 Concluding remarks

This work has shed light on the structures of neutral and protonated simple 1H-benzo[de]cinnolines like 1 and 1H+. There is no a clear relationship between reactivity and aromaticity nor between protonation and MEP. On the other hand, the HOMO favors position 4 and 7 and the Fukui function favors positions 7 and 9. Since the calculated chemical shifts agree well with the experimental results for 1H NMR, the calculated chemical shifts for 13C and 15N should be considered a good estimation for future experimental studies on simple molecules of the classes 1H-benzo[de] cinnoline and 1H-indeno[6,7,1-de]cinnoline. Besides their predictive character, the results obtained in the present work indicate that benzo[de]cinnolines are attractive molecules that deserve more attention since they are important cornerstones in the building of a consistent view of heterocyclic chemistry.

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