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Synthesis and X-ray Crystal Structure of New Substituted 3-4′-Bipyrazole Derivatives. Hirshfeld Analysis, DFT and NBO Studies

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Citation: Boraei, A.T.A.; Haukka, M.; Sarhan, A.A.M.; Soliman, S.M.; Al-Majid, A.M.; Barakat, A. Synthesis and X-ray Crystal Structure of New Substituted 3-4′-bipyrazoles 2 and 3 were synthesized in high chemical yield from a reaction of pyran-2,4-diketone 1 with aryl hydrazines under thermal conditions in MeOH. Compound 2 was unambiguously confirmed by single-crystal X-ray analysis. It crystallizes in a triclinic crystal system and space group P-1. Its crystal structure was found to be in good agreement with the spectral characterizations. With the aid of Hirshfeld calculations, the H . . . H (54.8–55.3%) and H . . . C (28.3–29.2%) intermolecular contacts are the most dominant, while the O . . . H (5.8–6.5%), N . . . H (3.8–4.6%) and C . . . C (3.0–4.9%) are less dominant. The compound has a polar nature with a net dipole moment of 6.388 Debye. The BD(2)C31-C32→BD*(2)N4-C34 (27.10 kcal/mol), LP(1)N5→BD*(2)C31-C32 (36.90 kcal/mol), BD(1)C32-C34→BD*(1)C18-C31 (6.78 kcal/mol) and LP(1)N4→BD*(1)N5-C31 (7.25 kcal/mol) are the strongest π→π*, n→π*, σ→σ* and n→σ* intramolecular charge transfer processes, respectively.

Keywords: pyran-2,4-dione; bipyrazole; Hirshfeld analysis; NBO; DFT

1. Introduction

Pyranones are examples of ester-functional heterocyclic molecules which have been employed as a synthon for several targeted organic compounds [1]. These synthetic pyranones have been reported to have several applications related to medicine, including HIV protease inhibitors [2], anticonvulsants [3], antitumor [4,5], antifungal [3], and antimicrobial [6] agents, and as plant-growth regulators [2,7]. On the other hand, some other naturally occurring pyranones were reported to have interesting actions against bacteria, and also have cytotoxic effects (e.g., Marin natural product, Pectinatone) [8]. Another representative example works against inflammation and rheumatism (e.g., Bufalin) [9], and many others such as Pentlypyran-2-one [10] and Griseulin [11,12] exhibited antibiotic and mosquitocidal effects, respectively. These substituted pyranones scaffold have been studied extensively in the literature [13–15].

Heterocycles comprising five-membered rings with two adjacent nitrogen atoms are called pyrazoles, and these pharmacophore-containing heterocycles have been shown to have several therapeutic applications. They were reported to have interesting actions against different diseases, including cancer, inflammation, and bacterial infection, and can also be used as analgesic and antidepressant agents [16–18]. Pyrazolines are also
widely distributed in nature in the cells of animals and plants, and also exist in alkaloids, pigments, and vitamins [19]. Many approaches have been reported for the synthesis of pyrazoline scaffolds [20–26]. One representative common approach is a reaction of carbonyl compounds with hydrazines under thermal conditions [27], in addition to other reported methods for the synthesis of pyrazolines scaffold, such as the metal catalyzed approach [28].

In this context and continuation of our research program [29,30] here, we are reporting a facile and direct straightforward approach for the synthesis of substituted 3-4′-bipyrazoles in a catalyst free one-pot reaction, from pyran-2,4-dione and arylhydrazines. The structure of the newly synthesized 3-4′-bipyrazoles was confirmed by using different spectral characterizations. The X-ray structure of the bipyrazole 2 was further confirmed by single-crystal X-ray structure. Additionally, DFT calculations were used to predict its electronic parameters and calculate the different intramolecular charge transfer processes which stabilize the structure of 2.

2. Materials and Methods

2.1. General

Melting points were measured using a melting-point apparatus (SMP10) in open capillaries and are uncorrected. The progress of the reaction was observed by thin-layer chromatography (TLC), and detection was achieved by UV light. Nuclear magnetic resonance (1H- and 13C-NMR) spectra were determined in DMSO-d6 and were recorded on a Bruker AC 400 MHz spectrometer using tetramethylsilane as an internal standard. Chemical shifts are described in δ (ppm) and coupling constants are given in Hz. Elemental analysis was performed on a Flash EA-1112 instrument. X-ray crystallographic analysis was collected on a Rigaku Oxford Diffraction Supernova diffractometer using Cu Kα radiation. The UV-Vis electronic spectra were recorded in EtOH using a T90+UV/VIS spectrometer.

2.2. Synthesis of 2 and 3

A methanolic solution of pyran-2,4-dione 1 (1.0 mmol) was mixed with phenylhydrazine or 4-chlorophenylhydrazine HCl (2.2 mmol) in methanol (10 mL), then the mixture was refluxed for 4 h. The resulting solutions were cooled to room temperature. The formed precipitates were collected by filtration and dried. Purifications were performed by recrystallization from EtOH in case of 2 and DCM/MeOH in case of 3. Only good quality single crystals were obtained for 2, which were found to be suitable for single-crystal X-ray diffraction analysis.

2.2.1. 2,2′,5,5′-Tetraphenyl-1′,2′-Dihydro-2H,3′H-[3,4′-Bipyrazol]-3′-One (2)

Yield: 88%, m.p. 270–271 °C. 1H-NMR (400 MHz, DMSO-d6) δ 12.01 (s, 1H), 7.99 (d, J = 7.6 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.53 (t, J = 7.6 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.40–7.23 (m, 12H), 7.16 (s, 1H); 13C-NMR (101 MHz, DMSO-d6) δ 151.31, 140.28, 135.72, 133.33, 129.55, 129.30, 129.12, 128.79, 127.57, 127.47, 127.69, 126.59, 125.75, 124.21, 122.07, 108.40 (Figures S1 and S2 (Supplementary data)); CHN analysis for [C30H22N4O] C, 79.27; H, 4.88; N, 12.33; O, 3.52 found C, 79.38; H, 4.99; N, 12.21. UV-Vis (EtOH): 264 nm (Figure S7 (Supplementary data)).

2.2.2. 2,2′-Bis(4-Chlorophenyl)-5,5′-Diphenyl-1′,2′-Dihydro-2H,3′H-[3,4′-Bipyrazol]-3′-One (3)

Yield: 61%, m.p. 227–228 °C. 1H-NMR (400 MHz, DMSO-d6) δ 12.25 (s, 1H), 7.97 (d, J = 7.6 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.41–7.27 (m, 10H), 7.16 (s, 1H); 13C-NMR (101 MHz, DMSO-d6) δ 151.68, 138.97, 135.66, 133.04, 131.98, 130.34, 129.54, 129.33, 129.16, 129.04, 128.91, 128.83, 128.65, 126.67, 126.36, 125.80, 125.65, 123.35, 108.53 (Figures S3 and S4 (Supplementary data)); CHN analysis for
The chemical structure of the final compounds was assigned based on various spectroscopic techniques (\(^1\)H- and \(^{13}\)C-NMR, and CHN elemental analysis). Furthermore, compound 2 was unambiguously confirmed by single-crystal X-ray diffraction analysis.

Scheme 1. Synthesis and proposed mechanism for compounds 2 and 3 starting from pyran-2,4-diketone 1.
3.2. Crystal Structure Description of 2

The X-ray structure of 2 is shown in Figure 1. The structure agreed very well with the spectral analyses. The crystal data and structure refinement details are depicted in Table 1. The compound crystallized in the triclinic system and P-1 space group with unit cell parameters of \(a = 11.0023(4) \text{ Å}, b = 11.9332(5) \text{ Å}, c = 18.0128(7) \text{ Å}, \alpha = 85.276(3)^\circ, \beta = 84.517(3)^\circ \text{ and } \gamma = 85.240(3)^\circ\). The unit cell volume is 2339.40(16) \(\text{Å}^3\) and \(Z = 4\), and there are two molecules per asymmetric unit. Selected bond distances and angles are listed in Table 2.

![Figure 1. X-ray structure of 2. Atom thermal ellipsoids are drawn at 30% probability level.](image)

Table 1. Crystal Data for 2.

|                           | 2                                           |
|---------------------------|---------------------------------------------|
| CCDC no.                  | 2095217                                     |
| empirical formula         | \(\text{C}_{30}\text{H}_{22}\text{N}_{4}\text{O}\) |
| Fw                        | 454.51                                      |
| temp (K)                  | 120(2)                                      |
| \(\lambda\) (Å)           | 1.54184                                     |
| cryst syst                | Triclinic                                   |
| space group               | P-1                                         |
| \(a\) (Å)                 | 11.0023(4)                                  |
| \(b\) (Å)                 | 11.9332(5)                                  |
| \(c\) (Å)                 | 18.0128(7)                                  |
| \(\alpha\) (deg)          | 85.276(3)                                   |
| \(\beta\) (deg)           | 84.517(3)                                   |
| \(\gamma\) (deg)          | 85.240(3)                                   |
| \(V\) (Å\(^3\))          | 2339.40(16)                                 |
| \(Z\)                     | 4                                           |
| \(\rho_{\text{calc}}\) (Mg/m\(^3\)) | 1.290                                      |
| \(\mu\) (Mo K\(\alpha\)) (mm\(^{-1}\)) | 0.634                                      |
| No. reflns.               | 17900                                       |
| Unique reflns.            | 9577                                        |
| Completeness to \(\theta = 67.684^\circ\) (%) | 99.8                                      |
| GOOF (\(F^2\))           | 1.034                                       |
| \(R_{\text{int}}\)       | 0.0419                                      |
| \(R1\ a (I \geq 2\sigma) | 0.0485                                      |
| \(wR2 \ b (I \geq 2\sigma)| 0.1153                                      |

\(a\) \(R1 = \Sigma |F_o| - |F_c|/\Sigma |F_o|\). \(b\) \(wR2 = [\Sigma [w(F_o^2 - F_c^2) ]^2/\Sigma [w(F_o^2)]^2]^{1/2}\).
Table 2. Selected bond lengths [Å] and angles [°] for 2.

| Atoms       | Distance | Atoms       | Distance |
|-------------|----------|-------------|----------|
| O1–C7       | 1.249(2) | O1B–C7B     | 1.250(2) |
| N1–N2       | 1.377(2) | N1B–N2B     | 1.387(2) |
| N1–C7       | 1.385(2) | N1B–C7B     | 1.395(2) |
| N1–C6       | 1.422(2) | N1B–C6B     | 1.410(2) |
| N2–C9       | 1.360(2) | N2B–C9B     | 1.354(2) |
| N3–C18      | 1.332(3) | N3B–C18B    | 1.345(2) |
| N3–N4       | 1.361(2) | N3B–N4B     | 1.366(2) |
| N4–C16      | 1.370(2) | N4B–C16B    | 1.365(2) |
| N4–C25      | 1.425(2) | N4B–C25B    | 1.431(2) |

| Atoms Angle | Atoms Angle |
|-------------|-------------|
| N2–N1–C7   | 110.01(15)  | C5–C6–N1   | 118.42(17) |
| N2–N1–C6   | 121.68(15)  | O1–C7–N1   | 123.25(16) |
| C7–N1–C6   | 127.14(15)  | O1–C7–C8   | 131.41(17) |
| C9–N2–N1   | 107.80(15)  | N1–C7–C8   | 105.28(15) |
| C18–N3–N4  | 104.58(15)  | C9–C8–C7   | 107.45(16) |
| N3–N4–C16  | 112.08(15)  | C9–C8–C16  | 130.99(17) |
| N3–N4–C25  | 120.64(16)  | C7–C8–C16  | 121.41(16) |
| C16–N4–C25 | 127.25(16)  | N2–C9–C8   | 109.10(16) |
| C6–C1–C2   | 118.41(19)  | N2–C9–C10  | 119.81(16) |
| C3–C2–C1   | 120.4(2)    | C8–C9–C10  | 130.96(17) |
| C2–C3–C4   | 120.37(19)  | C15–C10–C11| 119.13(19) |
| C3–C4–C5   | 120.4(2)    | C15–C10–C9 | 120.99(17) |
| C4–C5–C6   | 118.60(19)  | C11–C10–C9 | 119.84(17) |
| C1–C6–C5   | 121.75(18)  | C12–C11–C10| 120.09(19) |
| C1–C6–N1   | 119.82(18)  |             |           |

The studied compound comprised six ring systems. The three rings B, D and E are twisted from the mean plane of ring C by 46.59, 36.61 and 30.90°, respectively. Similarly, rings A and F are twisted from ring B by 3.93 and 58.05°, respectively. The corresponding values of the second molecular unit are 58.02, 23.86, 24.74, 20.68 and 45.95°, respectively.

The molecules of 2 are connected with one another via strong N-H . . . O hydrogen bonding interactions. The hydrogen bond parameters are listed in Table 3 and presentation of the hydrogen bonding interactions among molecular units is shown in Figure 2 (upper part). In addition, the crystal structure of 2 comprised a large number of intra- and intermolecular π–π interactions. Summary of the short intra- and intermolecular C . . . C contacts are depicted in Table 4 and shown in the lower part of Figure 2.

Table 3. Hydrogen bonds for 2 [Å and °].

| D-H . . . A   | d(D-H) | d(H . . . A) | d(D . . . A) | <(DHA) |
|--------------|--------|-------------|-------------|--------|
| N2-H2 . . . O1B | 0.95(3) | 1.73(3)     | 2.681(2)    | 173(3) |
| N2B-H2B . . . O1 #1 | 1.01(3) | 1.65(3)     | 2.648(2)    | 166(3) |

#1 x + 1,y,z.
Table 4. The intra- and intermolecular π–π interactions for 2 [Å].

| Contact | Distance | Contact | Distance |
|---------|----------|---------|----------|
| C8 ... C30 | 3.195 | C8B ... C26B | 3.127 |
| C9 ... C25 | 3.287 | C9B ... C25B | 3.342 |
| C9 ... C30 | 3.316 | C9B ... C26B | 3.296 |
| C10 ... C25 | 3.307 | C10B ... C25B | 3.331 |
| C11 ... C16 | 3.303 | C15B ... C16B | 3.142 |
| C11 ... C26 | 3.335 | C15B ... C25B | 3.336 |
| C4 ... C26B | 3.264 | C4 ... C4 | 3.273 \(^{ii}\) |
| C24 ... C24 | 3.39 \(^{i}\) | C21 ... C14B | 3.369 \(^{iii}\) |

Symm. Codes: \(^{i}\) \(-1-x,-y,2-z\); \(^{ii}\) \(-x,1-y,1-z\); \(^{iii}\) \(-x,1-y,1-z\).

3.3. Analysis of Molecular Packing

The Hirshfeld surfaces, including the \(d_{\text{norm}}\), shape index and curvedness maps of 2 are shown in Figure 3. In the \(d_{\text{norm}}\) map, there are many short distance contacts appearing as red spots. In the studied crystal, there are two molecular units per asymmetric formula; hence, the Hirshfeld results are discussed for the two molecular units.
The decomposition of all possible contacts with the aid of fingerprint plots gave the percentages of all intermolecular interactions controlling the molecular packing of 2 (Figure 4). It is clear that the H . . . H and H . . . C interactions are the most dominant, which comprised 54.8–55.3% and 28.3–29.2% of the whole fingerprint area. The other contacts such as O . . . H (5.8–6.5%), N . . . H (3.8–4.6%) and C . . . C (3.0–4.9%) are less dominant in the crystal structure of 2. A summary of all possible contacts in both units are presented in Figure 5.

Figure 3. Hirshfeld surfaces for the molecular unit with atom numbering comprising B of 2. The results for the other unit are presented in Figure S5 (Supplementary data). A: O . . . H, B: H . . . H, C: C . . . C and D: H . . . C contacts.

Figure 4. Decomposed fingerprint plots for the molecular unit with atom numbering comprising B. The results for the other unit are presented in Figure S6 (Supplementary data).
ure 4). It is clear that the H⋯H and H⋯C interactions are the most dominant, which comprised 54.8–55.3% and 28.3–29.2% of the whole fingerprint area. The other contacts such as O⋯H (5.8–6.5%), N⋯H (3.8–4.6%) and C⋯C (3.0–4.9%) are less dominant in the crystal structure of 2. A summary of all possible contacts in both units are presented in Figure 5.

Figure 5. The percentages of all possible intermolecular interactions in the crystal structure of 2.

For simplicity, the most important short contacts are labelled A to D in the \( \text{d}_{\text{norm}} \) map shown in Figure 3. These red spots represent the intermolecular interactions with shorter distances than the van der Waals radii sum of the interacting atoms. The interaction distances of these short contacts are summarized in Table 5. The O⋯H hydrogen bonds are significantly shorter. The O1B⋯H2 and O1⋯H2B contacts have contact distances of 1.677 and 1.658 Å, respectively. In contrast, the H⋯C interactions are significantly longer with interaction distances ranging from 2.559 Å (H17⋯C21B) to 2.776 Å (H30⋯C4B). On the other hand, the shortest H⋯H and C⋯C contacts are H3⋯H11B and C4⋯C26B with interaction distances of 2.056 and 3.264 Å, respectively. These intermolecular interactions have an important role in the stability of the crystalline structure of the studied compound.

Table 5. Most important contacts and the corresponding shortest interaction distances.

| Contact      | Distance | Contact      | Distance |
|--------------|----------|--------------|----------|
| O1B⋯H2       | 1.677    | H30⋯C4B     | 2.776    |
| O1⋯H2B      | 1.658    | H2⋯C7B      | 2.613    |
| O1⋯H5B      | 2.465    | H12B⋯C28     | 2.761    |
| H23⋯C12     | 2.726    | H2B⋯C7      | 2.608    |
| H14B⋯C21    | 2.769    | H3⋯H11B     | 2.056    |
| H17⋯C21B    | 2.559    | C4⋯C26B     | 3.264    |

3.4. DFT Studies

The structure of 2 was optimized and the resulting minimum energy structure was shown in Figure 6. An overlay of the calculated structure with the experimental one is presented in the same figure. There are good agreements between the calculated bond distances and angles with the experimental ones (Table S1, Supplementary data). In Figure 7, there are excellent straight-line correlations (\( R^2 = 0.906–0.951 \)) between the calculated and experimental geometric parameters. Little variation between the calculated and experimental structures could be attributed to the crystal packing effects.
Table 5. Most important contacts and the corresponding shortest interaction distances.

| Contact          | Shortest Interaction Distance (Å) |
|------------------|-----------------------------------|
| H17…C21B         | 2.056                             |
| H14…H11B         | 2.056                             |
| H23…C12          | 2.056                             |
| O1…H5B           | 2.056                             |
| O1…H2B           | 2.056                             |
| O1…H2            | 2.056                             |
| O1B…H2           | 2.056                             |
| H2…C7B           | 2.056                             |
| H30…C4B          | 2.056                             |

The distribution of charges at the different atomic sites was predicted with the aid of natural population analysis (Figure 8). The results indicated the high electronegative nature of the nitrogen and oxygen atoms. Their natural charges were calculated to be $-0.6160$ and $-0.1673$ to $-0.4294$ e, respectively. Additionally, all carbons are negatively charged except those bonded to electronegative atoms. In contrast, all hydrogen atoms are electropositive. Of these atomic sites, the NH proton (0.427 e) and the carbonyl carbon (0.655 e) are the most electropositive. The studied molecule is highly polar with a net dipole moment of 6.388 Debye, and the direction of the dipole moment vector is presented in Figure 9.

In the MEP map shown in the right part of Figure 9, there is an intense red region found close to the carbonyl oxygen atom, while a blue region is close to the NH proton, which represent molecular sites with the highest and lowest electron density, respectively. Hence, the carbonyl oxygen atom and the NH proton are the most probable sites as hydrogen bond acceptors and donors, respectively. This analysis is in accord with the observed X-ray structure of the studied system. In Figure 9, the HOMO and LUMO levels are also presented. It is clear that the HOMO and LUMO are mainly located over the delocalized $\pi$ system of the compound. Hence, the HOMO–LUMO intramolecular charge transfer could be described as $\pi-\pi^*$ transition.
are the most electropositive. The studied molecule is highly polar with a net dipole moment of 6.388 Debye. Hence, the carbonyl oxygen atom and the NH proton are the most probable sites as hydrogen bond acceptor and donor sites with 0.608, 3.926, and 1.658 eV, respectively. It was believed that these electronic parameters have important role in the biomolecular reactivity.

3.5. NBO Analysis

Based on the HOMO and LUMO energies, the ionization potential (I = −E_{HOMO}), electron affinity (A = −E_{LUMO}), chemical potential (μ = −(I + A)/2), hardness (η = (I − A)/2), as well as electrophilicity index (ω = μ^2/2η) were calculated [31–37]. These reactivity indices are calculated to be 5.571, 1.645, −3.608, 3.926, and 1.658 eV, respectively. It was believed that these electronic parameters have important role in the biomolecular reactivity.

The results of the stabilization energies (E(2)) due to the different electron delocalization processes are summarized in Table 6. The compound is stabilized by a large number of π → π* intramolecular charge transfer (IMCT) processes. The strongest π → π* IMCT processes is BD(2)C31-C32 → BD*(2)N4-C34, which stabilized the structure by 27.10 kcal/mol. The structure is also stabilized by a number of strong n → π* IMCT processes which stabilized the system up to 36.90 kcal/mol for the LP(1)N5 → BD*(2)C31-C32 IMCT process. In contrast, the σ → σ* and n → σ* IMCT processes stabilized the system to weaker extents. The BD(1)C32-C34 → BD*(1)C18-C31 (6.78 kcal/mol) and LP(1)N4 → BD*(1)N5-C31 (7.25 kcal/mol) are the strongest σ → σ* and n → σ* IMCT in the studied molecule.
Table 6. The $E^{(2)}$ (kcal/mol) values for the IMCT interactions in $2^a$.

| NBO $^1$ | NBO $^1$ | $E^{(2)}$ | Donor NBO $^1$ | Acceptor NBO $^1$ | $E^{(2)}$ |
|----------|----------|-----------|----------------|-------------------|-----------|
| BD(1) C17–C18 | BD*(1) C19–C20 | 6.61 | BD(2) N4–C34 | BD*(2) C31–C32 | 12.59 |
| BD(1) C18–C31 | BD*(1) C18–C19 | 5.00 | BD(2) N4–C34 | BD*(2) C35–C36 | 9.42 |
| BD(1) C31–C32 | BD*(1) N5–C46 | 5.06 | BD(2) C6–C16 | BD*(2) C8–C10 | 20.71 |
| BD(1) C31–C32 | BD*(1) C34–C35 | 5.39 | BD(2) C6–C16 | BD*(2) C12–C14 | 17.34 |
| BD(1) C32–C34 | BD*(1) C18–C31 | 6.78 | BD(2) C8–C10 | BD*(2) C6–C16 | 19.45 |
| LP(1) N4 | BD*(1) N5–C31 | 7.25 | BD(2) C8–C10 | BD*(2) C12–C14 | 20.87 |
| LP(1) N4 | BD*(1) C32–C34 | 5.38 | BD(2) C12–C14 | BD*(2) C6–C16 | 21.86 |
| LP(1) N2 | BD*(2) C6–C19 | 29.57 | BD(2) C12–C14 | BD*(2) C8–C10 | 19.25 |
| LP(1) N3 | BD*(2) C18–C19 | 20.16 | BD(2) C12–C14 | BD*(2) C8–C10 | 19.25 |
| LP(1) N5 | BD*(2) N4–C34 | 28.45 | BD(2) C12–C14 | BD*(2) C8–C10 | 19.25 |
| LP(1) N5 | BD*(2) C31–C32 | 36.90 | BD(2) C12–C14 | BD*(2) C8–C10 | 19.25 |
| LP(1) N5 | BD*(2) C46–C55 | 17.17 | BD(2) C12–C14 | BD*(2) C8–C10 | 19.25 |

$^1$ Donor; $^1$ Acceptor.

4. Conclusions

In conclusion, newly substituted 3-4′-bipyrazoles were synthesized for the first time using a simple one-pot method from pyran-2,4-diketone and arylhydrazines. The structure of the newly synthesized compounds were elucidated using elemental analysis and spectroscopic techniques. The supramolecular structure of the crystallized compound $2$ was analyzed using Hirshfeld calculations. Moreover, the optimized geometry calculations showed good agreement with the experimental data. Different electron delocalization processes which stabilized the system through conjugation effects were also calculated using natural bond orbital calculations. HOMO, LUMO and MEP as well as the electronic reactivity descriptors were also presented and discussed.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/cryst11080953/s1, X-Ray single-crystal determination of $2$; Table S1: The calculated geometric parameters of $2$, Figure S1–S4. $^1$H- and $^{13}$C-NMR for compounds $2$ and $3$ in DMSO-$d_6$, Figure S5. Hirshfeld surfaces for the other molecular unit in the crystal structure of $2$; Figure S6. Decomposed fingerprint plots for the other molecular unit the crystal structure of $2$; Figure S7. Uv-Vis spectra of compounds $2$ and $3$.

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