

Article

Synthesis and Structural Studies of Two New Anthracene Derivatives

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Abstract: Anthracene derivatives are an interesting class of compounds and modifications in the anthracene ring, producing different compounds with different properties. Structural analysis of anthracene derivatives with modifications in position 9,10 of the aromatic ring is necessary in order to obtain information about its properties. The introduction of groups with polar substituents increases the possibility to modify the molecule lipophilicity, corroborating its use as bioimaging probes. Anthracene derivatives are used in many biochemical applications. These compounds can react with molecular singlet oxygen [$O_2 (^1\Delta_g)$], a reactive oxygen species, through the Diels–Alder reaction [4 + 2] to form the respective endoperoxide and to be used as a chemical trap in biological systems. Thus, the structural and crystalline characterizations of two anthracene derivatives are presented in this work to obtain information about their physical-chemical properties. The compounds were characterized by Fourier-transform infrared spectroscopy, thermogravimetric analyses and scanning electron microscopy. The molecular structures of the compounds were studied by the Density Functional Theory, M06-2X/6-311++G(d,p) level of theory in the gas phase. From the results obtained for the frontier molecular orbitals, HOMO and LUMO, and from the Molecular Electrostatic Potential map, it was possible to predict the chemical properties of both compounds. The supramolecular arrangements were also theoretically studied, whose molecules were kept fixed in their crystallographic positions, through the natural bonding orbitals analysis to check the stability of interactions and the quantum theory of atoms in molecules to verify the type of intermolecular interaction between their molecules, as well as how they occur.

Keywords: anthracene derivatives; structural characterization; fluorescence; singlet molecular oxygen

1. Introduction

Anthracene and its derivatives are an important class of compounds and have been extensively investigated in different areas. Some anthracene derivatives exhibit interesting properties in the materials science area, which are involved in the composition of electronic

and photonic devices. Bimolecular photochemical reactions of anthracenes are of special interest, especially because it also possesses photochromic properties. These properties are based on the photodimerization reaction and can be used in the design of optical, electronic, or magnetic switches incorporated in mesophases, polymers, films, or crystals [1–4]. Anthracene derivatives have also been widely used in many biochemical applications because of their fluorescent properties and their ability to react with singlet molecular oxygen [$O_2(^1\Delta_g)$]—a reactive oxygen species (ROS) capable of causing damage in DNA biomolecules, proteins, and lipids. Anthracene derivatives show higher fluorescence quantum yield according to modifications at the 9,10 ring positions. The change in substituents may also provide compounds with lipophilic properties, which can be used as probes in biological systems. This ability to alter the structure of anthracene can provide different molecules especially for use in bioimaging and chemical uptake of $O_2(^1\Delta_g)$, forming an endoperoxide via the Diels–Alder [4 + 2] reaction [5–11].

Anthracene alone does not react with $O_2(^1\Delta_g)$, and the direct binding of electron-attractive groups to the aromatic ring would decrease its reactivity. Thus, at least one or, preferably, two donor groups of electrons must be present at the 9,10 ring positions to allow cycloaddition [4 + 2] and stabilize the endoperoxide. Thus, the methyl groups of 9,10-dimethylantracene or bromo in the 9,10-dibromoanthracene provide a suitable position for substituent entry, since the alkyl chain enables a good separation between the hydrophilic group and the anthracene ring [5–11]. In addition, the modifications in the 9,10 positions of the ring give molecules with different spectroscopic properties, such as fluorescence intensity, solubility, reactivity and capacity to be used in biological systems [12].

The synthesis of new compounds with less time and steps to be used in biological systems has been a challenge. In recent years, an anthracene derivative—the 3,3'-(9,10-anthracenediyl) bisacrylate (DADB) with fluorescent properties—was synthesized using the Heck reaction and shown to be able to cross the plasma membrane. However, the reduction of the double bonds of DADB produces a derivative, the diethyl 9,10-anthracenedipropionate (DEADP) (Figure 1), with higher fluorescence intensity and better reactivity with $O_2(^1\Delta_g)$, by the difference in the reactivity constant, k_t (2.20×10^6 and $2.65 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) [13,14].

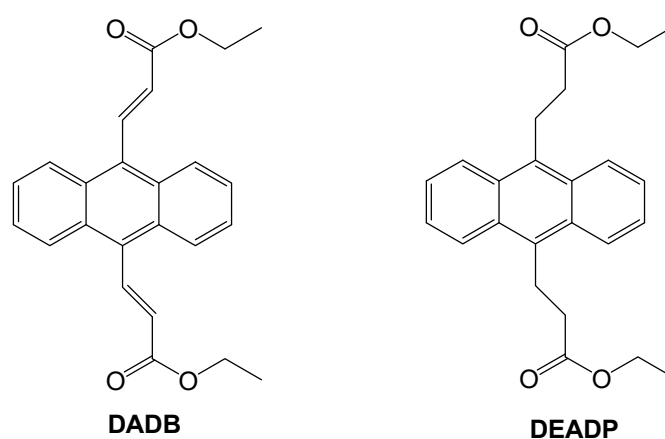


Figure 1. Chemical structure of anthracene derivatives diethyl-(2E,2'E)-3,3'-(anthracene-9,10-diyl)di(prop-2-enoate) (DADB) and diethyl-(2E,2'E)-3,3'-(anthracene-9,10-diyl)di(prop-2-enoate) (DEADP).

With that in mind, the study of the properties of anthracene derivatives and their crystallographic characterization will be useful in understanding the characteristics of these compounds and the properties to be used as an $O_2(^1\Delta_g)$ chemical trap and in assisting the development of other compounds with modifications in the anthracene ring to be used in biological systems. Thus, this work aims to analyze the structure of two anthracene

derivatives with ideal characteristics for use as a fluorescent probe related to its reactivity toward O_2 ($^1\Delta_g$) in biological systems.

2. Experimental and Computational Procedures

2.1. Synthesis and Spectroscopic Analysis

Anthracene derivatives diethyl-(2E,2'E)-3,3'-(anthracene-9,10-diyl)di(prop-2-enoate) (DADB) and diethyl-(2E,2'E)-3,3'-(anthracene-9,10-diyl)di(prop-2-enoate) (DEADP) were synthesized by the methodology presented by Oliveira et al. [13,14]. Spectroscopic analysis by Fourier-Transform Infrared (FTIR). (PerkinElmer, Anápolis, GO, Brazil) was carried out in a Frontier Perkin Elmer equipment in the region of $400\text{--}4000\text{ cm}^{-1}$, recording by 14 scans of accumulations using KBr pellets (PerkinElmer, Anápolis, GO, Brazil).

2.2. Thermogravimetric Analysis

A thermogravimetric analysis (TGA/DTG) of Pyris 1 Perkin Elmer (PerkinElmer, Anápolis, GO, Brazil) was used to obtain TGA curves. Sample masses were of 5.672 mg to DADB and 4.567 mg to DEADP, with a heating rate of $10\text{ }^\circ\text{C/min}$, a flow rate of 20 mL/min was used in a nitrogen atmosphere with a heating range of $30\text{ to }500\text{ }^\circ\text{C}$.

2.3. Scanning Electronic Microscopy

The DADB and DEADP crystals were analyzed by a Hitachi TM3030Plus Tabletop Microscope (Hitachi, Anápolis, GO, Brazil) attached to a carbon surface.

2.4. X-ray Crystallography

Single crystals of DADB and DEADP, suitable for X-ray study, were obtained by slow evaporation of a solution of hot methanol at room temperature $295(2)\text{ K}$. DADB and DEADP data collection was performed using the Kappa Apex II Duo diffractometer (Bruker-AXS, Goiânia, GO, Brazil) operating with $\text{Cu-K}\alpha$. Structure solutions were obtained using Direct Methods implemented in SHELXS [15] and the final refinement was performed with full matrix least-squares on F^2 using SHELXL [15]. The programs ORTEP-3 [16], SHELXS/SHELXL [15] were used within WinGX [16] software package. All hydrogen atoms were placed in calculated positions and refined with fixed individual displacement parameters [$\text{Uiso(H)} = 1.2\text{ or }1.5\text{ Ueq}$] following the riding model (C–H bond lengths of 0.97 and $0.96\text{ \AA}$ for aromatic and methyl groups, respectively). Geometric parameters of DADB and DEADP were validated and studied through Mercury [17] and Platon [18] softwares. Crystallographic information files for DADB and DEADP were deposited in the Cambridge Structural Database [19] under codes 2098280 and 2098281, respectively. Copies of data can be obtained free of charge at www.ccdc.cam.ac.uk (accessed on 3 August 2021).

2.5. Hirshfeld Surface Analysis

The supramolecular arrangements of DADB and DEADP were analyzed by Hirshfeld surface (HS). First, the intensity of the weaker $\text{C-H}\cdots\text{O}$ was studied through distance function d_{norm} available on Crystal Explorer software [20]. This function combines d_i (distance from an inner molecule to the surface) and d_e (distance from an outer molecule to the surface) contacts in a unique surface by normalizing them in the function of Van der Waals radii following Equation [21]:

$$d_{\text{norm}} = \frac{(d_i - r_i^{\text{vdW}})}{r_i^{\text{vdW}}} + \frac{(d_e - r_e^{\text{vdW}})}{r_e^{\text{vdW}}} \quad (1)$$

where r_i^{vdW} and r_e^{vdW} are the van der Waals radii. The shape index surface was used to study the $\pi\cdots\pi$ interactions involved in the crystal packings of both compounds. This function is based on concave or convex curvature observed in the molecule and indicates the places of interactions. Finally, d_i and d_e contacts were plotted in a 2D graph named fingerprints to quantify the percentage of each interaction.

2.6. Molecular Modeling Analysis

Density Functional Theory (DFT)—formulated initially in 1964 by Pierre Hohenberg, Walter Kohn and Lu Jeu Sham [22,23]—is among the most important methods used in the quantitative description of the properties of molecular systems. Modern implementations for DFT calculations offer the advantage of low computational cost and precision in the results of properties of molecular systems. Thus, in order to understand a little more about the molecular structures of DADB and DEADP, calculations were carried out at M06-2X/6-311G++(d,p) level of theory, in gas phase, implemented in the Gaussian09 software package [24]. The generated inputs were obtained from X-ray diffraction data.

Frontier molecular orbitals (FMO), where HOMO (highest occupied molecular orbital) and LUMO (lower unoccupied molecular orbital) are the most important, were obtained to describe molecular electronic structure, the stability and the reactivity in the compounds studied in this paper [25]. DFT methods provide a good theoretical basis for qualitative interpretation of molecular orbitals.

The molecular electrostatic potentials were calculated by potentials $V(\mathbf{r})$ at point $\mathbf{r}$ in space:

$$V(\mathbf{r}) = \sum_{\alpha}^N \frac{Z_{\alpha}}{|\mathbf{r}_{\alpha} - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}', \quad (2)$$

and the molecular electrostatic potentials (MEP) maps were obtained. In Equation (2), the Z_{α} variable is the charge on nuclei α at point $\mathbf{r}_{\alpha}$ and $\rho(\mathbf{r}')$ is the charge density at point $\mathbf{r}'$ [26]. The first term represents the electrostatic potential created by the nucleus and the second term is created by the electrons as a function of the electronic density [27]. Electronic isodensity surfaces are applied in several areas of theoretical chemistry, playing an important role in understanding the intermolecular interactions of compounds, molecular properties, reactivity, crystalline packaging, solvation, drug action and its chemical analogues, and so on.

The supramolecular arrangements in the crystals of DADB and DEADP compounds were theoretically studied in this paper aiming to understand the intermolecular interactions qualitatively and quantitatively. In this case, the molecular arrangements were constructed so that the atoms were kept fixed in their crystallographic positions. The complexation energies were analyzed at the level of theory DFT/M06-2X/6-311++G(d,p) and corrected by counterpoise theory [28], so that each of the interactions observed experimentally by diffraction X-ray were quantified. The heavy atoms of both compounds were kept fixed in their crystallographic positions, while the hydrogens remained free throughout the calculations. With the same level of theory, natural bonding orbitals (NBO) calculations [29,30] were carried out to check the stability of the interactions, through the measure of the intermolecular hyperconjugation between donor orbitals (Lewis type) and acceptor orbitals (non-Lewis type) estimated by the perturbation formula second order,

$$E_{i \rightarrow j}^2 = -n_{\sigma} \frac{\langle \sigma_i | \hat{F} | \sigma_j^* \rangle^2}{\varepsilon_{j^*} - \varepsilon_i} = -n_{\sigma} \frac{F_{ij}^2}{\varepsilon_{j^*} - \varepsilon_i}, \quad (3)$$

where $\langle \sigma | \hat{F} | \sigma \rangle^2$ or F_{ij}^2 is the Fock matrix element between the i and j natural bond orbitals. ε_{σ^*} is the energy of the antibonding orbital σ^* and ε_{σ} is the energy of the bonding orbitals σ . n_{σ} stands for the population occupation of the σ donor orbital.

Through analysis in the Quantum Theory of Atoms in Molecules (QTAIM), it was possible to determine the type of interaction present according to the critical points obtained by the topological properties of both crystal systems [31].

3. Results and Discussion

3.1. Spectroscopy Analysis

The DADB derivatives were synthesized by C–C coupling Heck reaction following the procedure described by Oliveira et al. [13,14]. In terms of this mechanism, it is important

to mention that the preference of structural form obtained is the trans-trans DADB. In the second step of synthesis, DEADP is obtained by reduction of double bonds, using KCOOH in the presence of catalyzed Pd. These compounds present different spectroscopy properties. The modifications in the substituent of the ring are of fundamental importance in obtaining derivatives with better properties to be used in biological systems.

As related by Oliveira et al. [13,14], the absorption and emission spectra of DEADP, gives three well-defined absorption bands at 356, 375 and 396 nm, and emission bands at 400, 424 and 449 nm, whereas DADB has a broad band of absorption and fluorescence spectra, due to the presence of the double bonds at the 9,10 position of the anthracene ring producing an electron delocalization in the structure, with a maximum absorption at 260 and 405 nm and a maximum fluorescence emission at 525 nm with excitation at 405 nm in acetonitrile. The quantum yield of fluorescence at room temperature to DADB and DEADP compared to Rhodamine B (at a concentration of $1 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ in MeCN; $\lambda_{\text{ex}} = 400 \text{ nm}$, $\Phi = 0.65$) was $\Phi = 0.230 \pm 0.002$ and 0.352 ± 0.01 in MeCN, respectively [13,14]

The infrared spectrum of the DADB derivative obtained is presented along with the spectrum of the DEADP derivative in Figure 2. The spectrum shows peaks in the region of $2900\text{--}3000 \text{ cm}^{-1}$ referring to the C–H and C=C groups and it is observed the influence of double bond in the intensity of signals in this region, the presence of the C=O at 1600 cm^{-1} and peaks in the 1200 cm^{-1} region characteristic of the C–O group. It is observed the higher contribution of signals characterized by C–H in the DEADP structure in the range of $1300\text{--}1400 \text{ cm}^{-1}$.

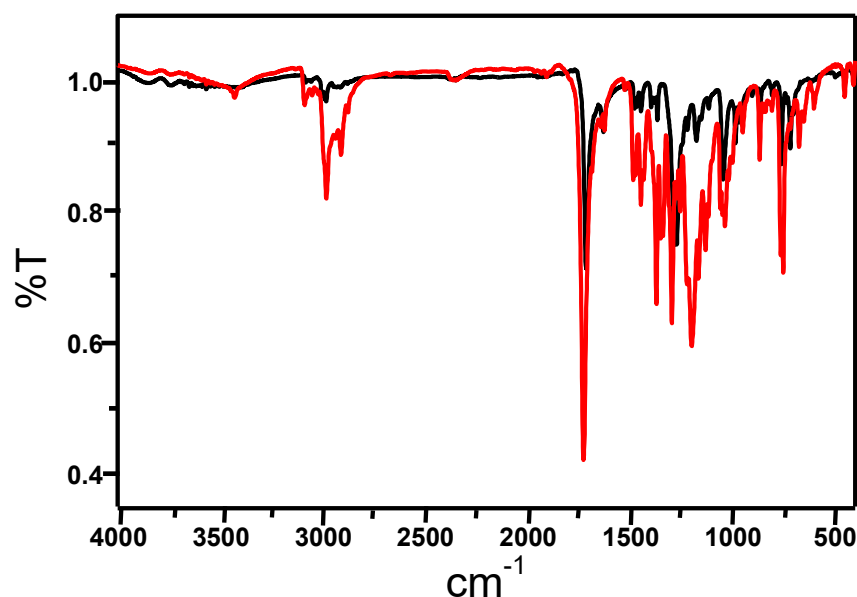


Figure 2. Infrared spectra of DADB (–) and DEADP (–).

3.2. Thermogravimetric Analysis

Thermal stability of the derivatives was analyzed by thermogravimetry under nitrogen atmosphere. Figure 3 shows the TGA/DTG curves for the DADB and DEADP derivatives. The curves show that the compounds are thermally stable up to 250°C . For the DADB derivative, the curve is well characterized by a mass loss of 80% defined by the DTG with maximum point of 350°C (Figure 3b). The DEADP derivative presents two mass losses of 55 and 36%, characterized by the DTG with maximum points of 300 and 330°C . This shows that the absence of the double bond favors the presence of two mass losses in the structure of the DEADP, by the change of the conjugation in the molecule.

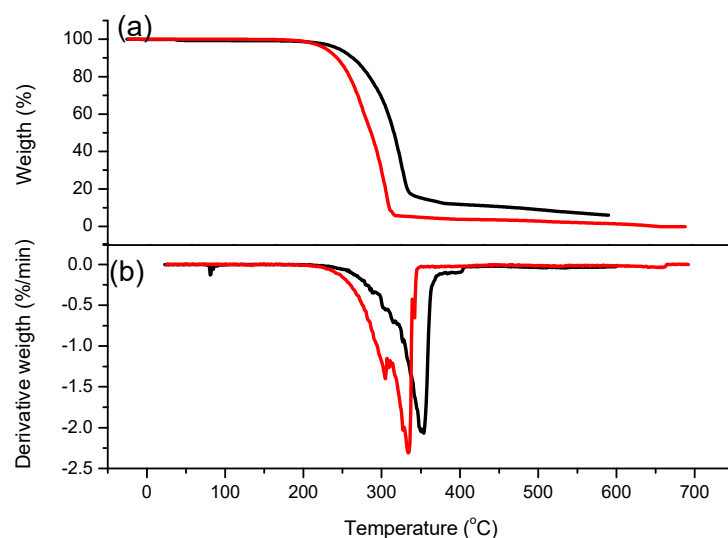


Figure 3. TGA (a) e DTG (b) analysis of DADB (–) and DEADP (–) in N₂ atmosphere at rate heating of 10 °C min^{−1}.

3.3. Scanning Electronic Microscopy

Figure 4 shows the micrograph imaging obtained for DADB (Figure 4a,b) and DEADP (Figure 4c,d) derivatives after recrystallization with methanol. A variation in morphology is observed from one derivative to another. In the DADB derivative, the crystal formation shows well-defined fine needles, whereas in the DEADP derivative, the formation of smaller crystals occurs but is also defined. The micrographs show the crystal formation of the two compounds analyzed.

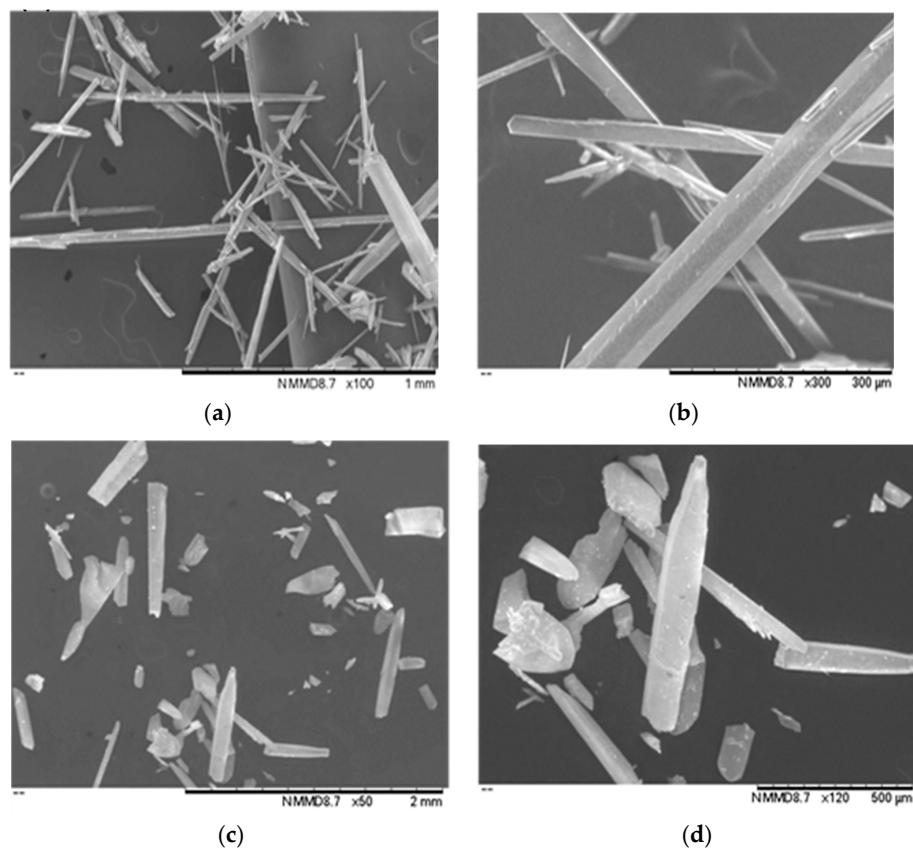


Figure 4. Micrographies (SEM) of the crystals after recrystallization with methanol of DADB (a) 100× and (b) 300×, and DEADP (c) 50× and (d) 300×.

3.4. Solid State Studies

DADB is an anthracene analogue in which two acrylate groups are *para*-bonded to aromatic ring B. This compound crystallized in the monoclinic crystal system and space group $P2_1/c$. Its unit cell measures $a = 13.0556(3)$ Å, $b = 4.03270(10)$ Å, $c = 18.0384(4)$ Å and $\beta = 90.7920(10)^\circ$. Besides crystallographic symmetry, DADB has molecular symmetry as an inversion center i above the gravity center of aromatic ring B. An Ortep diagram showing the atom displacement with 50% probability level and numbering scheme of DADB is presented in Figure 5a. DEADP is the result of the addition to the acrylate group, presenting two sp^3 carbons bound to ring B. DEADP crystallized in the centrosymmetric space group $C2/c$, with eight asymmetric units (AU) in the unit cell and half molecular unit per UA. The ORTEP representation of DEADP is shown in Figure 5b, as well as the numbering scheme used in the structural description. The refinement indicated that DEADP has a dynamic disorder in O_1 , O_2 , C_{11} and C_{12} atoms in which the dominant conformation corresponds to 85%. The main crystallographic data are tabulated in Table 1.

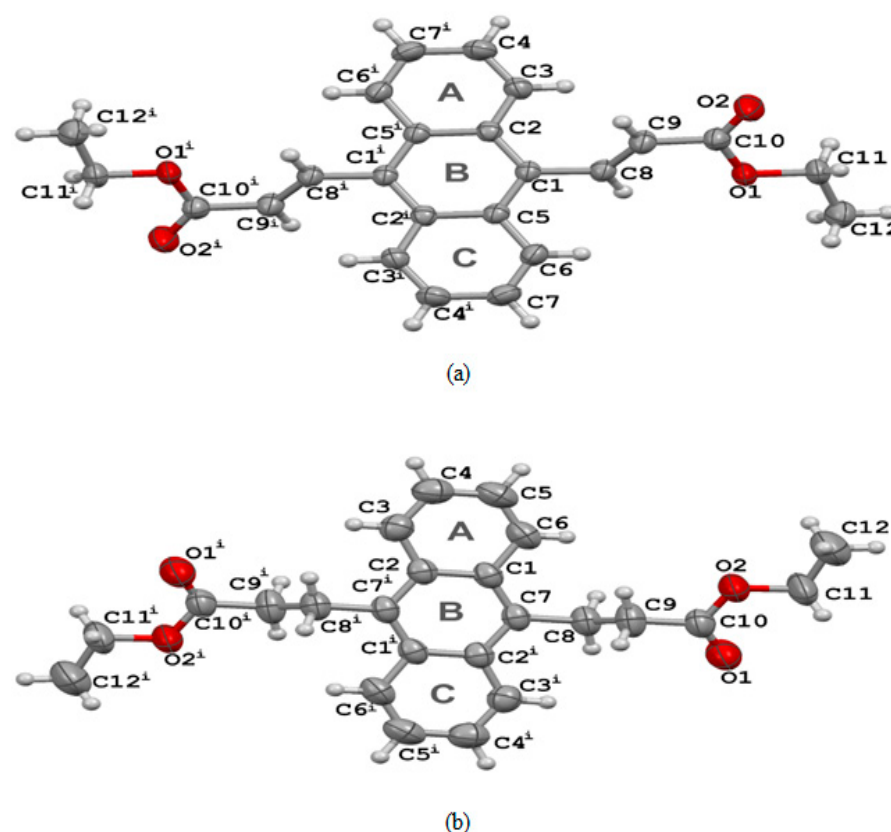


Figure 5. ORTEP view of DADB (a) and DEADP (b) with atom displacement ellipsoids drawn at 50% probability level.

Geometric parameters of DADB showed that it has a non-planar conformation by analyzing the angle formed between the planes of acrylate and anthracene groups ($\omega_1 = 48.72^\circ$). On the other hand, the acrylate portions can be considered planar since the unique planarity deviation is a slight twist around the σ -bond C_9-C_{10} ($\omega_1 = 12.09^\circ$). A conformational analysis was performed on two flexible dihedral angles $C_8-C_9-C_{10}-O_1$ (carbonyl and olefin groups) and $C_2-C_1-C_8-C_9$ (olefin and anthracene groups), indicating that carbonyl groups adopt an anti-periplanar conformation regarding olefin moiety, while the last one has a syn-clinal conformation regarding the anthracene group. Like DADB, the ethyl portion of DEADP is nonplanar to the anthracene group (the angle formed between the planes, ω_1 , is 25.38°).

Table 1. Crystal data and structure refinement for DADB and DEADP.

Empirical Formula	$C_{24}H_{22}O_4$ (DADB)		$C_{24}H_{26}O_4$ (DEADP)	
Formula weight	374.42		378.46	
Temperature	296(2) K		298(2) K	
Wavelength	1.54178 Å		1.54178 Å	
Crystal system, space group	Monoclinic; $P 2_1/c$		Monoclinic; $C 2/c$	
Unit cell dimensions	$a = 13.0556(3)$ Å	$\alpha = 90^\circ$	$a = 28.6843(10)$ Å	$\alpha = 90^\circ$
	$b = 4.03270(10)$ Å	$\beta = 90.7920(10)^\circ$	$b = 4.9458(2)$ Å	$\beta = 113.062(2)^\circ$
	$c = 18.0384(4)$ Å	$\gamma = 90^\circ$	$c = 15.8870(6)$ Å	$\gamma = 90^\circ$
Volume	949.62(4) Å ³		2073.71(14) Å ³	
Z, Density (calculated)	2; 1.309 Mg/m ³		1.212 Mg/m ³	
Absorption coefficient, $F(000)$	0.714 mm ^{−1} ; 396		0.654 mm ^{−1} ; 808	
Crystal size	0.071 × 0.138 × 0.372 mm ³		0.470 × 0.202 × 0.144 mm ³	
Theta range for data collection	3.385 to 68.159°		3.349 to 66.783°	
Index ranges	−15 ≤ h ≤ 15, −3 ≤ k ≤ 4, −21 ≤ l ≤ 21		−32 ≤ h ≤ 33, −5 ≤ k ≤ 3, −18 ≤ l ≤ 17	
Reflections collected; Independent reflections	5976; 1686 [R(int) = 0.0232]		6387; 1724 [R(int) = 0.0275]	
Completeness to theta	98.1%		92.20%	
Refinement method	Full-matrix least-squares on F^2		Full-matrix least-squares on F^2	
Data/restraints/parameters	1686/0/129		1724/3/141	
Goodness-of-fit on F^2	1.068		1.077	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0338$, $wR_2 = 0.0958$		$R_1 = 0.0450$, $wR_2 = 0.1423$	
R indices (all data)	$R_1 = 0.0384$, $wR_2 = 0.0992$		$R_1 = 0.0568$, $wR_2 = 0.1562$	
Extinction coefficient	0.0028(6)		0.0006(3)	
Largest diff. peak and hole	0.147 and −0.133 e [−] Å ^{−3}		0.235 and −0.206 e [−] Å ^{−3}	

For DADB, the carbonyl group often assists in aggregation via two weak C–H $\cdots$ O interactions. These interactions are responsible for assembling the acrylate groups as follows: the first one [C₁₁–H₁₁ $\cdots$ O_{2i}; $d_{(D-H)} = 0.970$ Å; $d_{(D-A)} = 3.137$ Å; $d_{(H \cdots A)} = 2.777$ Å; $\angle = 102.69^\circ$] gives rise to a 1D zigzag chain with C(13) motif, represented by the color green in Figure 6a. Then, the second one [C_{11i}–H_{11i} $\cdots$ O₂; same geometric parameters of C₁₁–H₁₁ $\cdots$ O_{2i}] forms a complementary 1D chain, also with C(13) motif that connects two green chains as a layer almost parallel to ($\bar{1}$ 0 3), represented by the color blue in Figure 6b,c. The crystal packing of DEADP is like that of DADB, since it is stabilized by two C–H $\cdots$ O interactions. The first interaction [C₅–H₅ $\cdots$ O_{1i}; $d_{(D-H)} = 0.931$ Å; $d_{(D-A)} = 3.541$ Å; $d_{(H \cdots A)} = 2.641$ Å; $\angle = 162.74^\circ$] forms a chain along the c axis, while the second interaction [C_{5i}–H_{5i} $\cdots$ O₁; $d_{(D-H)} = 0.931$ Å; $d_{(D-A)} = 3.541$ Å; $d_{(H \cdots A)} = 2.641$ Å; $\angle = 162.74^\circ$] links these chains to form a layer parallel to (100).

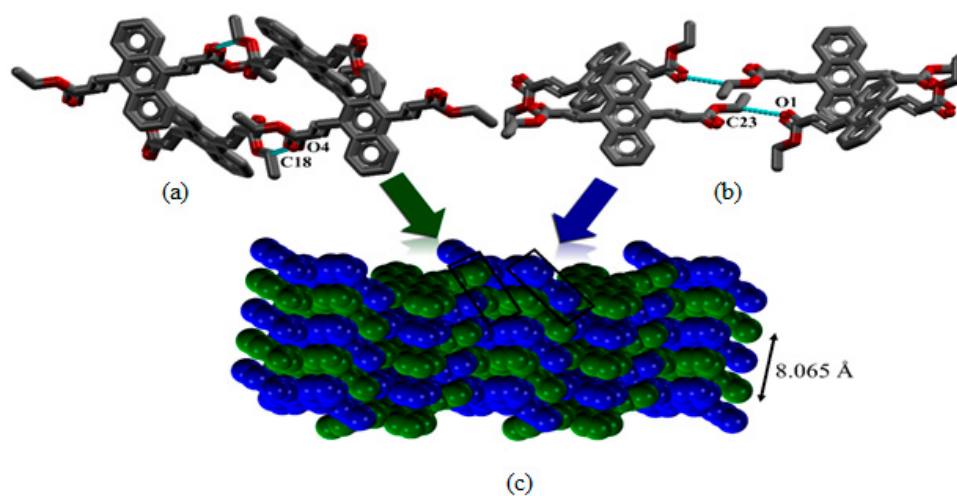


Figure 6. Two independent chains formed by weak intermolecular interactions of DADB (a,b); followed by the supramolecular arrangement in (c). Similar chains are separated by 8.065 Å, represented by the green and blue colors.

The supramolecular arrangements of DADB and DEADP were also evaluated from HS analysis. By combining d_i (distance from the inner molecule to the surface) and d_e (distance from the outer molecule to the surface) in the function of their Van der Waals radii, it is possible to generate a surface named d_{norm} . This surface is based on a scale color ranging from blue (less intense) to red (more intense). In this sense, the weak intermolecular interactions of DADB are shown as red dots on the surface, as seen in Figure 7a. The 2D fingerprint plot of O···H contacts is also shown, indicating their percentage. Although interactions (1) and (2) present high intensity on d_{norm} surface, the fingerprint indicates d_e and d_i around 1.5 Å as weak interactions. On the other hand, interactions (3) and (4), represented in both the HS and fingerprint plots of Figure 7b, presented d_e and d_i around 1.4 Å for DEADP.

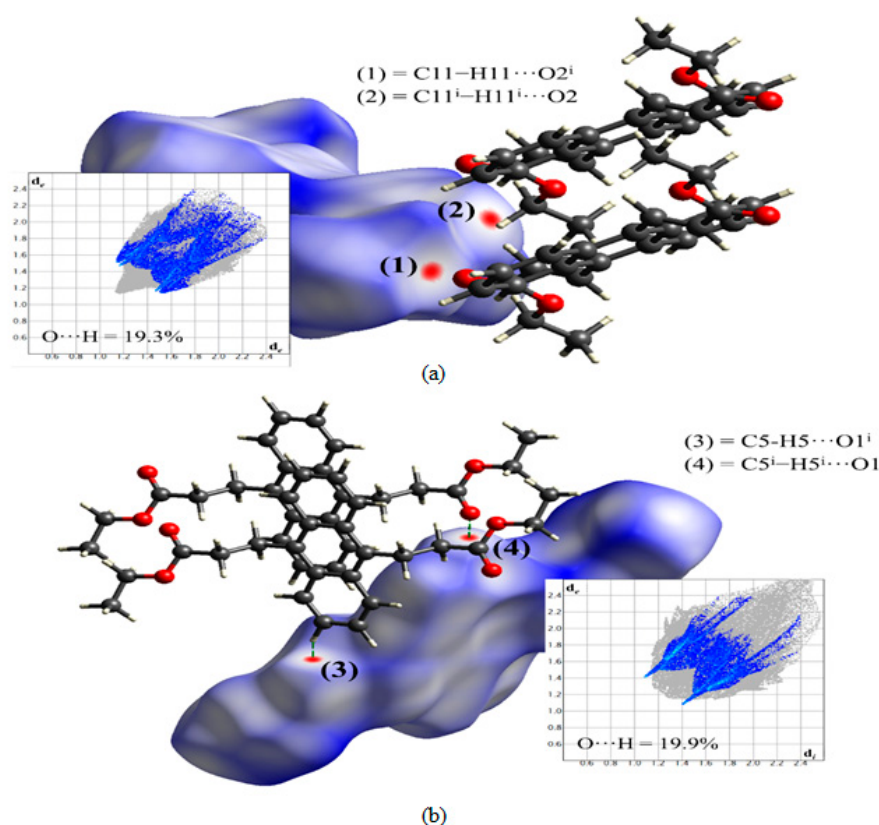


Figure 7. Hirshfeld surface d_{norm} confirming the intermolecular interactions of DADB (a) and the 2D fingerprint plot of O–H contacts (b).

The π delocalization presented on the anthracene portion provides a planar conformation to it. Hence, the crystal packing of DADB is also stabilized by $\pi \cdots \pi$, as represented in Figure 8a, and observed in all aromatic rings ($Cg \cdots Cg = 4.033$ Å). The confirmation of this interaction is given from the shape index surface (Figure 8b) as red and blue triangular shapes above aromatic rings, representing the places where two molecules meet each other.

In addition, $\pi \cdots \pi$ interactions have two specific features in the 2D fingerprint plots of C···C contacts: (a) a triangular shape around $2.2 \text{ Å} > d_e$ and $d_i > 1.7$ Å; and (b) high incidence of contacts with $d_e \approx d_i \approx 1.8$, concerning the stacking of aromatic rings. Even having as anthracene portion, DEADP adopts a conformation which stabilizes the DEADP crystal packing with C–H··· π interactions, shown in Figure 8c [$C_8-H_{8A} \cdots Cg_A$; $d(D-H) = 0.969$ Å; $d(D-A) = 3.628$ Å; $d(H \cdots A) = 2.987$ Å; $\angle = 124.67^\circ$; $C_8-H_{8B} \cdots Cg_B$; $d(D-H) = 0.969$ Å; $d(D-A) = 3.803$ Å; $d(H \cdots A) = 3.151$ Å; $\angle = 126.06^\circ$; $C_8-H_{8A} \cdots Cg_A$; $d(D-H) = 0.931$ Å; $d(D-A) = 3.937$ Å; $d(H \cdots A) = 3.256$ Å; $\angle = 131.75^\circ$]. These contacts are 21.2% of the total and are characterized both as red regions over aromatic rings A, B and C (acceptor regions) and blue regions over ethyl hydrogens (donor regions) (Figure 8d).

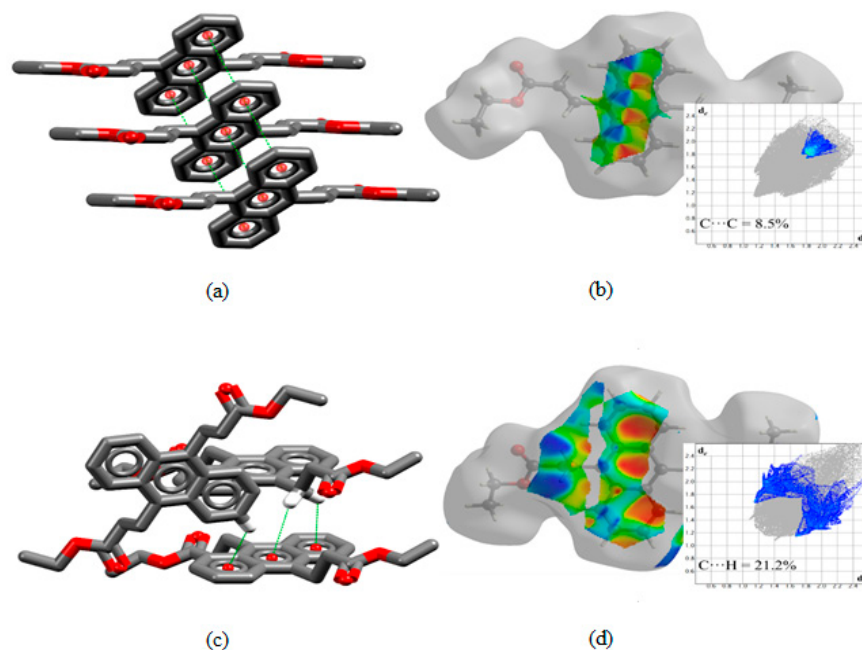


Figure 8. Representation of $\pi \cdots \pi$ interactions (a) and the shape index surface followed by 2D fingerprint plot (b) confirming the stacking of DADB; $C-H \cdots \pi$ interactions (c) and the shape index surface followed by 2D fingerprint plot (d) confirming the arrangement of DEADP.

3.5. Molecular Modeling Analysis

Molecular geometry plays an important role in understanding the chemical structure of the compounds. The lengths and angles bond molecules of the DADB and DEADP compounds are shown in Tables 2 and 3. The results obtained by DFT/M06-2X/6-311G++(d, p) level of theory agree with the experimental data, according to the correlation factor $R_{DADB} = 0.9825$ and $R_{DEADP} = 0.9816$ to bond lengths, and $R_{DADB} = 0.9339$ and $R_{DEADP} = 0.9786$ to angle and show by graphs present by Figures 9 and 10.

Table 2. Reactivity index of DADB and DEADP compounds.

Molecular Parameters	Dadb (kcal·mol ^{−1})	Deadp (kcal·mol ^{−1})
$\Delta E_{HOMO-LUMO}$	116.04	121.91
Electronegativity (χ)	157.31	152.40
Chemical Potential (μ)	−99.29	−91.44
Chemical Hardness (η)	58.02	61.00
Global Electrophilicity (ω)	61.86	65.44

The bond lengths obtained by theoretical calculations in the aromatic region of the compounds also agree with the values found for the anthracene molecule by measuring X-ray diffraction [32]. The average lengths of the $-C-O-$ and $-C=O$ bonds in the carboxyl group in both compounds correspond to 1.35 Å and 1.22 Å, respectively. Unsaturation in the vinyl group of DADB ($-C_8=C_9-$) has a length equal to 1.34 Å, whereas the saturation of the same carbon atoms in DEADP ($-C_8-C_9-$) has an average length of 1.53 Å. The aliphatic group covalently connected to the anthracene B ring through the $-C_1-C_8-$ bonds in the DADB with an average length of 1.48 Å and the $-C_7-C_8-$ bonds in the DEADP with an average length of 1.51 Å. The average length of $-C_1-C_8-$ bonds in DADB is 2.3% shorter than the equivalent $-C_7-C_8-$ bond in DEADP. In addition, the average length of $-C_9-C_{10}-$ bonds in DADB is 2.6% shorter than in DEADP. On the other hand, the average length of the $-C=O$ bonds of the carbonyls in DADB is 2.4% higher than in DEADP. The aforementioned differences are related to the presence of π electrons in the $-C_8=C_9-$ bonds of the DADB that resonate with the π electrons of the aromatic ring of anthracene. On the other hand,

the π electrons that resonate in this region result in the repulsion of the electrons from the C=O bond, causing its elongation.

Table 3. Second-order perturbation theory analysis in NBO basis obtained at M06-2X/6-311G(d,p) level of theory for DADB.

	Donor (<i>i</i>)	ED (<i>i</i>)	Acceptor (<i>j</i>)	ED (<i>j</i>)	E^2 (kcal·mol ^{−1})	$E_j - E_i$ (a.u.)	$F(i, j)$ (a.u.)
Frontal Interaction							
Unit 1 to 2	$\sigma(\text{C}_{11i}-\text{H})$	1.9855	$\sigma^*(\text{C}_{11}-\text{H})$	0.0211	0.10	1.08	0.009
	$\eta_1(\text{O}_{2i})$	1.9773	$\sigma^*(\text{O}_1-\text{C}_{11})$	0.0359	0.46	1.11	0.020
	$\eta_1(\text{O}_{2i})$		$\sigma^*(\text{C}_{12}-\text{H})$	0.0046	0.10	1.28	0.010
	$\eta_2(\text{O}_{2i})$	1.8649	$\sigma^*(\text{O}_1-\text{C}_{11})$	0.0359	0.13	0.67	0.008
Unit 2 to 1	$\sigma(\text{C}_{11}-\text{H})$	1.9852	$\sigma^*(\text{C}_{11i}-\text{H})$	0.0205	0.07	1.05	0.008
Axial Interaction							
Unit 1 to 2	$\pi(\text{C}_{3i}-\text{C}_{4i})$	1.7752	$\pi^*(\text{C}_{1i}-\text{C}_{2i})$	0.4056	0.13	0.37	0.007
			$\pi^*(\text{C}_1-\text{C}_5)$	0.3934	0.19	0.38	0.008
	$\pi(\text{C}_{2i}-\text{C}_5)$	1.5062	$\pi^*(\text{C}_{5i}-\text{C}_2)$	0.4979	0.06	0.33	0.004
			$\pi^*(\text{C}_1-\text{C}_5)$	0.3934	0.18	0.34	0.007
	$\sigma(\text{C}_{8i}-\text{H})$	1.9686	$\pi^*(\text{C}_{6i}-\text{C}_{7i})$	0.2097	0.13	0.67	0.009
	$\pi(\text{C}_{6i}-\text{C}_{7i})$	1.7806	$\pi^*(\text{C}_{6i}-\text{C}_{7i})$	0.2097	0.15	0.39	0.007
			$\pi^*(\text{C}_3-\text{C}_4)$	0.2028	0.20	0.40	0.008
	$\sigma(\text{C}_{11i}-\text{H})$	1.9853	$\sigma^*(\text{C}_{10i}-\text{H})$	0.0180	0.05	1.28	0.007
	$\sigma(\text{C}_{12i}-\text{H})$	1.9865	$\sigma^*(\text{C}_{11i}-\text{H})$	0.0210	0.06	1.04	0.007
	$\pi(\text{C}_1-\text{C}_2)$	1.6016	$\pi^*(\text{C}_3-\text{C}_4)$	0.2028	0.23	0.37	0.009
	$\pi(\text{C}_6-\text{C}_7)$	1.7848	$\sigma^*(\text{C}_8-\text{H})$	0.0225	0.18	0.83	0.011
			$\pi^*(\text{C}_6-\text{C}_7)$	0.2057	0.20	0.40	0.008
	$\sigma(\text{C}_9-\text{H})$	1.9741	$\sigma^*(\text{C}_3-\text{H})$	0.0155	0.06	1.12	0.007
	$\pi(\text{C}_{10}-\text{O}_2)$	1.9800	$\sigma^*(\text{C}_{11}-\text{H})$	0.0214	0.32	0.95	0.16
	$\sigma(\text{C}_{11}-\text{H})$	1.9857	$\sigma^*(\text{C}_{12}-\text{H})$	0.0096	0.07	1.07	0.008
	$\eta_2(\text{O}_{1i})$	1.8133	$\pi^*(\text{C}_{8i}-\text{C}_{9i})$	0.0158	0.07	0.48	0.005
			$\pi^*(\text{C}_{10i}-\text{O}_{2i})$	0.2290	0.07	0.45	0.005
	$\eta_2(\text{O}_1)$	1.8125	$\sigma^*(\text{C}_{12}-\text{H})$	0.0101	0.18	0.88	0.012
	$\pi(\text{C}_{1i}-\text{O}_{2i})$	1.6016	$\pi^*(\text{C}_{3i}-\text{O}_{4i})$	0.2029	0.23	0.37	0.009
			$\pi^*(\text{C}_{1i}-\text{O}_{5i})$	0.3933	0.18	0.34	0.007
	$\pi(\text{C}_{5i}-\text{O}_2)$	1.5061	$\pi^*(\text{C}_{2i}-\text{O}_5)$	0.4979	0.06	0.33	0.004
			$\sigma^*(\text{C}_{8i}-\text{H})$	0.0225	0.18	0.83	0.011
	$\pi(\text{C}_{6i}-\text{C}_{7i})$	1.7848	$\pi^*(\text{C}_{6i}-\text{C}_{7i})$	0.2056	0.20	0.40	0.008
			$\sigma^*(\text{C}_{9i}-\text{H})$	0.0155	0.06	1.12	0.007
	$\pi(\text{C}_{10i}-\text{O}_{1i})$	1.9800	$\sigma^*(\text{C}_{11i}-\text{H})$	0.0214	0.32	0.95	0.016
	$\sigma(\text{C}_{11i}-\text{H})$	1.9857	$\sigma^*(\text{C}_{12i}-\text{H})$	0.0096	0.07	1.07	0.008
	$\pi(\text{C}_3-\text{C}_4)$	1.7753	$\pi^*(\text{C}_{1i}-\text{C}_{5i})$	0.3933	0.19	0.38	0.008
			$\pi^*(\text{C}_1-\text{C}_2)$	0.4056	0.13	0.37	0.007
	$\sigma(\text{C}_8-\text{H})$	1.9686	$\pi^*(\text{C}_6-\text{C}_7)$	0.2098	0.13	0.67	0.009
			$\pi^*(\text{C}_{3i}-\text{C}_{4i})$	0.2029	0.20	0.40	0.008
	$\pi(\text{C}_6-\text{C}_7)$	1.7805	$\pi^*(\text{C}_6-\text{C}_7)$	0.2098	0.15	0.39	0.007
			$\sigma^*(\text{C}_{11}-\text{H})$	0.0180	0.05	1.28	0.007
	$\sigma(\text{C}_{12}-\text{H})$	1.9865	$\sigma^*(\text{C}_{11}-\text{H})$	0.0210	0.06	1.04	0.007
	$\eta_2(\text{O}_{1i})$	1.8125	$\sigma^*(\text{C}_{12i}-\text{H})$	0.0101	0.18	0.88	0.012
	$\eta_2(\text{O}_{1i})$	1.8133	$\pi^*(\text{C}_8-\text{C}_9)$	0.0568	0.07	0.48	0.005
			$\pi^*(\text{C}_{10}-\text{O}_2)$	0.2291	0.07	0.45	0.005
Unit 2 to 1	$\pi(\text{C}_{3i}-\text{C}_{4i})$	1.7752	$\pi^*(\text{C}_{1i}-\text{C}_{2i})$	0.4056	0.13	0.37	0.007
			$\pi^*(\text{C}_1-\text{C}_5)$	0.3934	0.19	0.38	0.008
	$\pi(\text{C}_{2i}-\text{C}_5)$	1.5062	$\pi^*(\text{C}_{5i}-\text{C}_2)$	0.4979	0.06	0.33	0.004
			$\pi^*(\text{C}_1-\text{C}_5)$	0.3934	0.18	0.34	0.007
	$\sigma(\text{C}_{8i}-\text{H})$	1.9686	$\pi^*(\text{C}_{6i}-\text{C}_{7i})$	0.2097	0.13	0.67	0.009
	$\pi(\text{C}_{6i}-\text{C}_{7i})$	1.7806	$\pi^*(\text{C}_{6i}-\text{C}_{7i})$	0.2097	0.15	0.39	0.007
			$\pi^*(\text{C}_3-\text{C}_4)$	0.2028	0.20	0.40	0.008
	$\sigma(\text{C}_{11i}-\text{H})$	1.9853	$\sigma^*(\text{C}_{10i}-\text{H})$	0.0180	0.05	1.28	0.007
	$\sigma(\text{C}_{12i}-\text{H})$	1.9865	$\sigma^*(\text{C}_{11i}-\text{H})$	0.0210	0.06	1.04	0.007
	$\pi(\text{C}_1-\text{C}_2)$	1.6016	$\pi^*(\text{C}_3-\text{C}_4)$	0.2028	0.23	0.37	0.009
	$\pi(\text{C}_6-\text{C}_7)$	1.7848	$\sigma^*(\text{C}_8-\text{H})$	0.0225	0.18	0.83	0.011
			$\pi^*(\text{C}_6-\text{C}_7)$	0.2057	0.20	0.40	0.008

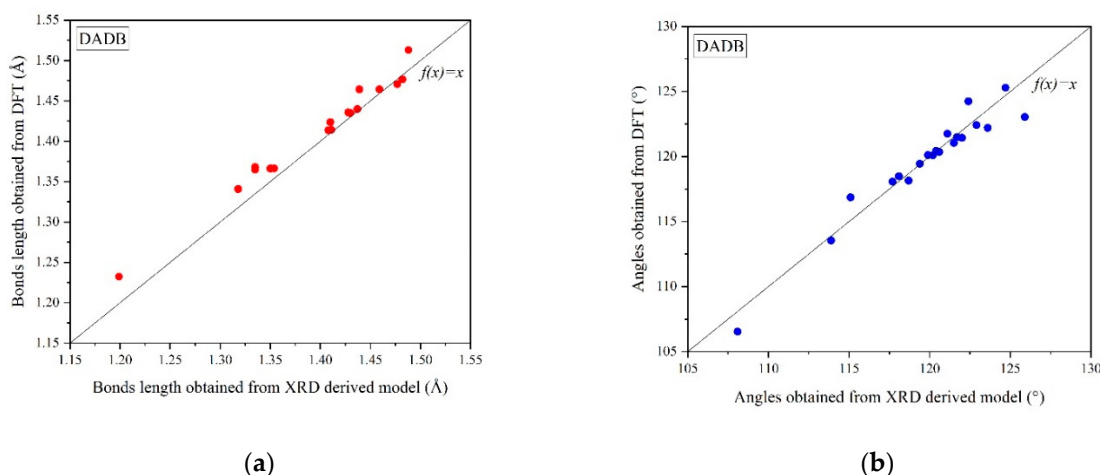


Figure 9. Comparison between the (a) bond lengths and (b) angles obtained using DFT method (M06-2X) and experimental result for DADB molecule.

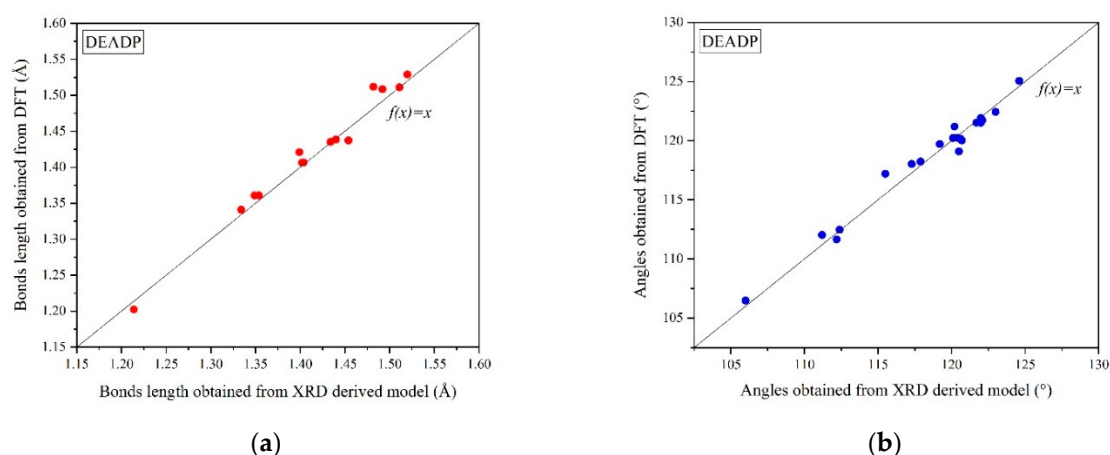


Figure 10. Comparison between the (a) bond lengths and (b) angles obtained using DFT method (M06-2X) and experimental result for DEADP molecule.

In fact, the largest deviations observed for the angles between the two compounds are found at the atoms of C₈ and C₉. The angles –C₁–C₈–C₉– and –C₈–C₉–C₁₀– are respectively 5.29° and 3.04° larger, compared to the 120° value of the plane trigonal geometry in the DADB. In the DEADP composite, the angles of the tetrahedral geometry are altered in relation to the value of 109.5°, which increase 2.53° and 2.44° in –C₇–C₈–C₉– and –C₈–C₉–C₁₀–, respectively. Both the anthracene aromatic ring and the aliphatic groups are coplanar in both compounds. However, these groups of molecules are in different planes when their dihedral angles are evaluated. In the DADB molecule, the aliphatic and aromatic groups are located at 56.60°, when we look at the dihedral angle –C₂–C₁–C₈–C₉–; on the other hand, in the DEADP molecule, these groups are at an average distance of 88.01°, when we look at the dihedral angle –C₂–C₇–C₈–C₉–.

The energies of the frontier molecular orbitals (HOMO and LUMO), obtained by the DFT calculations, for the compounds studied in this paper, are shown in Figure 11. These data are important parameters in the electronic description of the chemical compound, as they help in the understanding of chemical reactivity and kinetic stability of molecules. HOMO corresponds to the ability that the molecule must donate electrons, while LUMO, to receive electrons. and, thus, for large values of the difference between their $\Delta E_{\text{HOMO-LUMO}}$ energies, the molecule is highly stable, which means that the compound has low reactivity in chemical reactions, and vice versa. $\Delta E_{\text{HOMO-LUMO}}$ calculations showed that the DADB molecule is more reactive than the DEADP molecule. The differences between the energies

of the molecular orbitals, $\Delta E_{\text{HOMO-LUMO}}$, show that the DADB molecule is chemically less stable than the DEADP molecule. This is justified by the presence of π electrons located in the unsaturation between atoms C_8 and C_9 , in DADB. Furthermore, the energies of the frontier orbitals play an important role in describing the electronic structure, as well as the chemical reactivity of molecules. Important descriptors can be drawn from these values, such as electronegativity χ , chemical potential $\mu = -\chi$, hardness η and softness $\sigma = 1/\eta$, defined by the expressions

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(r)} = -\frac{I + A}{2} = -\chi, \quad \eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)} = \frac{I - A}{2} \quad \text{and} \quad \omega = \frac{\mu^2}{2\eta} \quad (4)$$

where E is the energy of the system, N is the number of electrons, $I = -E_{\text{HOMO}}$ is the ionization potential, $A = -E_{\text{LUMO}}$ is the electron affinity [33]. Table 2 brings the reactivity indexes for the DADB molecules and the DEADP molecule.

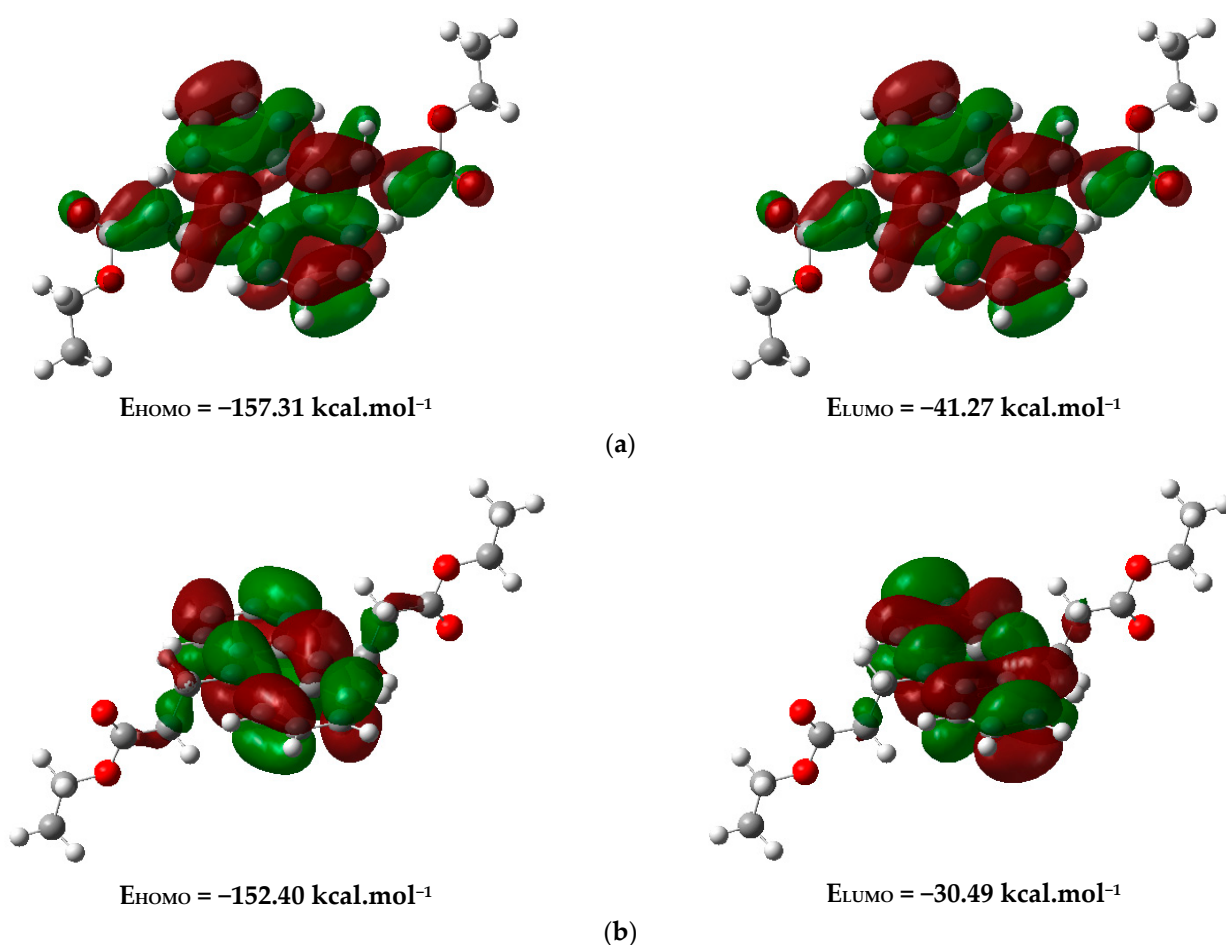


Figure 11. Frontier orbitals HOMO and LUMO for the (a) DADB and (b) DEADP molecule, obtained by DFT/M06-2X/6-311G++(2d, 2p) level of theory.

The electronic isodensities [25,29] for the DADB and DEADP molecules are shown in the electrostatic potential maps in Figure 12. The MEP maps show that the regions with the highest electron density are predominantly concentrated in the red regions of the molecules; that is, the oxygen atoms of the carbonyl groups are prone to electrophilic attacks.

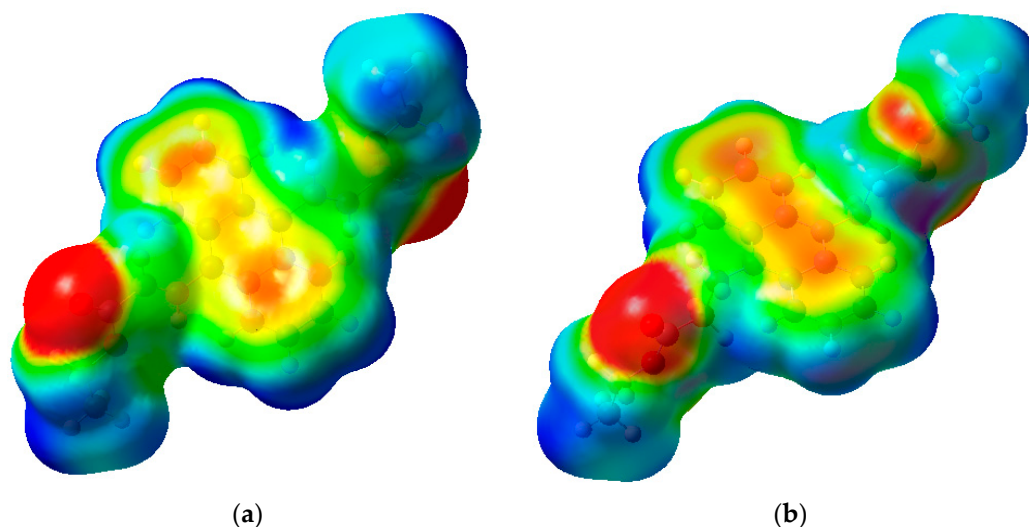


Figure 12. MEP surface at the $\rho(r) = 4.0 \times 10^{-4}$ electrons/bohr contour of the total SCF electronic density for the (a) DADB and (b) DEADP molecules, using M06-2X/6-311++G(2d,2p) level of theory.

The regions in blue, located on the hydrogen atoms, are the Van der Waals surfaces of lower electron density. The lowest potential values calculated on the electrophilic regions of the DADB and DEADP molecules are -31.39 and -29.96 kcal.mol $^{-1}$, respectively. Therefore, the carbonyl groups of both molecular structures are sites with high electronic density charge, which can exhibit Lewis base behavior in chemical processes.

3.6. Supramolecular Arrangement

DADB crystals are formed through two specific arrangements, observed experimentally: the first arrangement is a zig-zag structure, where the molecules are joined frontally through $-C=O \cdots C_{11}$ interactions; the second arrangement forms a second structure that interacts axially with the first (Figure 13a). The calculated values for the complexation energies in the frontal and axial interactions between molecules in the DADB crystals are -3.12 and -17.01 kcal.mol $^{-1}$, respectively, corrected by the counterpoise theory [30].

The first arrangement appears essentially between the region of higher electron density of a molecular unit, around the carbonyl group $-(CO)-$, with the region of low electron density of the second molecular unit, the ethyl group (Figure 13a). The second arrangement takes place with the axial contact between the molecules of the compound; its complexation energy is about 5.5 times more intense due to the large surface area of the structures in which contact occurs.

Similarly, the DEADP crystals are formed in two arrangements: the first in zig-zag and the second in layers (Figure 13b). In this case, the formation of the first arrangement occurs through the contact between the O atom of the carbonyl group with the H atom of the anthracene ring while the second also axially (Figure 13b). The theoretical calculation showed that the complexation energy of the frontal contact has an energy equal to -3.69 kcal.mol $^{-1}$ while the axial contact resulted in an energy of -12.69 kcal.mol $^{-1}$. The axial contact between DEADP molecules is justified by the large surface area, which is in contact with the crystals, resulting in an interaction 3.4 times greater compared to the frontal contact.

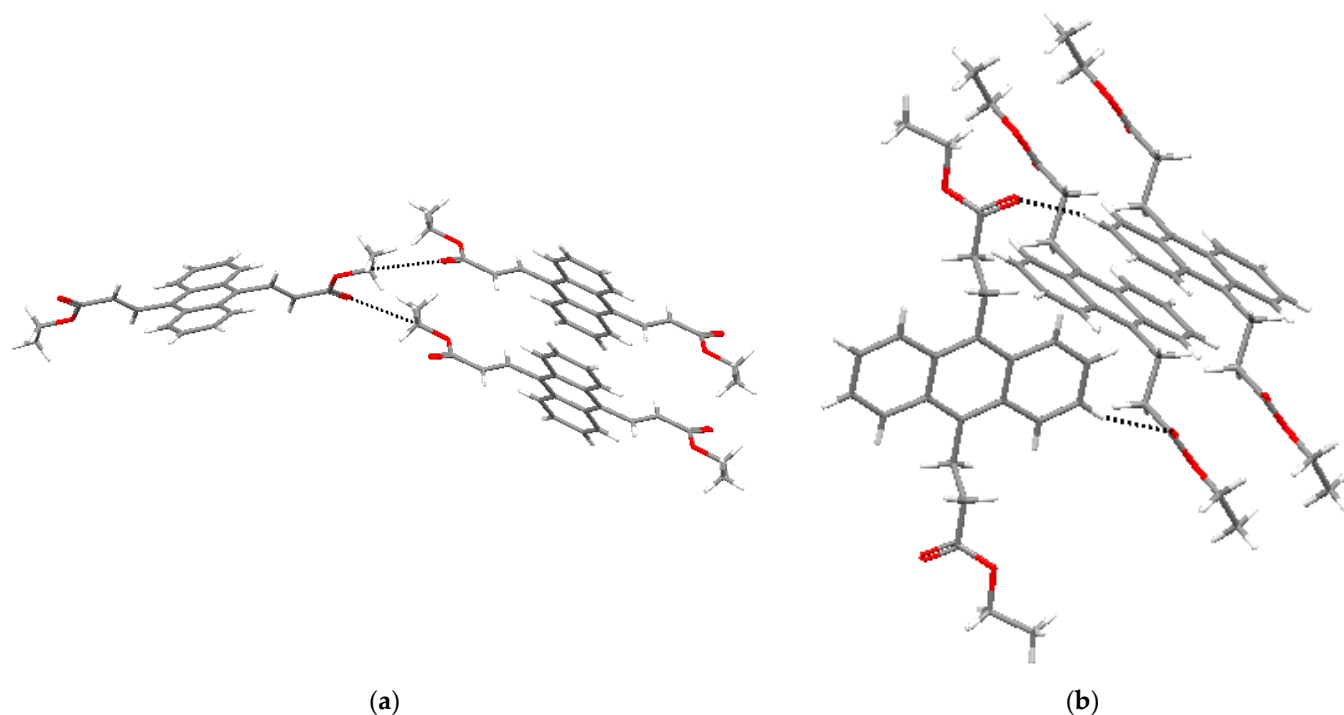


Figure 13. Arrangements observed in DADB (a) and DEADP (b) crystals.

Through NBO calculations, it was possible to determine the stabilizing interactions between the donor bonding orbitals (Lewis type) and acceptor antibonding (non-Lewis type) in the molecules of the crystals of DADB (Table 3) and DEADP (Table 4). The interactions present between the bonding orbitals (donors) and the antibonding orbitals (acceptors) have low hyperconjugation energies. The frontal contact between two DADB molecules showed that there are preferential hyperconjugations between the bonding σ orbitals the $C_{11}-H$ and $C_{11i}-H$ bonds—where the donor orbitals have an occupancy slightly higher than 1.98e, while the acceptor orbitals have an occupancy of 0.02e. The isolated pairs of electrons from the O atom of the carbonyl of a molecular unit also participate in this intermolecular interaction through hyperconjugation with antibonding σ^* orbitals of the O_1-C_{11} and $C_{12}-H$ bonds of the second molecular unit. In the axial contact between the DADB molecules, it is possible to observe a large amount of hyperconjugation between the binding π orbitals of one molecular unit with the antibonding π^* orbitals of the second molecular unit. These hyperconjugations have low energies, but in general, higher than $0.1 \text{ kcal}\cdot\text{mol}^{-1}$, especially in the interactions that occur in the region of the aromatic ring of anthracene. In DEADP crystals, frontal contact between molecular units occurs weakly through σ and π hyperconjugations, and through isolated pairs of electrons on the O atom of the carbonyls of one molecular unit with the antibonding orbitals of the other unit. The axial contact results in numerous interactions that are weakly stabilized thanks to the large contact surface in the planar region of the aromatic ring of the anthracene core. Hyperconjugations of the bonding π orbitals with the antibonding π^* orbitals have a greater stabilizing energy, as well as occur in the layered structure of DEADP crystals.

Table 4. Second-order perturbation theory analysis in NBO basis obtained at M06-2X/6-311G(d,p) level of theory for DEADP.

	Donor (<i>i</i>)	ED (<i>i</i>)	Acceptor (<i>j</i>)	ED (<i>j</i>)	E^2 (kcal·mol ^{−1})	$E_j - E_i$ (a.u.)	$F(i, j)$ (a.u.)
Frontal Interaction							
Unit 1 to 2	$\pi(C_3-C_4)$	1.7854	$\sigma^*(C_3-H)$	0.0156	0.08	0.85	0.008
			$\sigma^*(C_4-H)$	0.0163	0.24	0.84	0.013
	$\sigma(C_{9i}-H)$	1.96446	$\sigma^*(C_4-H)$	0.0163	0.06	1.10	0.007
	$\pi(C_{1i}-C_{7i})$	1.6120	$\pi^*(C_3-C_4)$	0.2058	0.06	0.01	0.001
	$\pi(C_3-C_4)$	1.7854	$\sigma^*(C_3-H)$	0.0156	0.07	0.45	0.015
			$\sigma^*(C_4-H)$	0.0163	0.06	0.45	0.014
Unit 2 to 1	$\sigma(C_3-H)$	1.9769	$\pi^*(C_3-C_4)$	0.0162	0.18	0.67	0.010
			$\pi^*(C_5-C_6)$	0.2054	0.07	0.67	0.006
	$\sigma(C_4-H)$	1.9770	$\pi^*(C_3-C_4)$	0.0162	0.08	0.66	0.007
	$\pi(C_{10i}-O_{1i})$	1.9931	$\sigma^*(C_5-H)$	0.0174	0.23	1.01	0.014
	$\eta_1(O_{1i})$	1.9769	$\sigma^*(C_5-H)$	0.0174	0.36	1.33	0.019
	$\eta_2(O_{1i})$	1.8664	$\sigma^*(C_5-H)$	0.0174	0.42	0.89	0.018
Axial Interaction							
Unit 1 to 2	$\pi(C_3-C_4)$	1.7794	$\pi^*(C_5-C_6)$	0.2098	0.22	0.39	0.008
	$\pi(C_5-C_6)$	1.7882	$\sigma^*(C_8-H)$	0.0169	0.13	0.80	0.010
	$\pi(C_{1i}-C_{7i})$	1.6098	$\pi^*(C_{1i}-C_{2i})$	0.5102	0.09	0.34	0.005
			$\pi^*(C_{3i}-C_{4i})$	0.2083	0.35	0.37	0.011
	$\pi(C_{5i}-C_{6i})$	1.7858	$\pi^*(C_{3i}-C_{4i})$	0.2083	0.12	0.40	0.006
	$\pi(C_{10i}-O_{1i})$	1.9928	$\sigma^*(C_{8i}-C_{9i})$	0.0158	0.05	0.92	0.006
			$\sigma^*(C_{9i}-H)$	0.0136	0.13	0.97	0.010
	$\eta_1(C_2)$	1.0084	$\pi^*(C_1-C_7)$	0.3825	0.35	0.18	0.009
			$\sigma^*(C_8-C_9)$	0.0162	0.09	0.55	0.009
	$\eta_1(O_2)$	1.9776	$\sigma^*(C_{8i}-C_{9i})$	0.0158	0.10	1.23	0.010
	$\pi(C_1-C_7)$	1.6099	$\eta_1(C_2)$	1.0084	0.13	0.18	0.005
			$\pi^*(C_3-C_4)$	0.2082	0.35	0.37	0.011
Unit 2 to 1	$\pi(C_5-C_6)$	1.7858	$\pi^*(C_3-C_4)$	0.2082	0.12	0.40	0.006
	$\sigma(C_8-H)$	1.9758	$\pi^*(C_1-C_7)$	0.0302	0.06	0.64	0.006
	$\sigma(C_8-H)$	1.9762	$\eta_1(C_2)$	1.0084	0.05	0.46	0.006
	$\pi(C_{10}-O_1)$	1.9928	$\sigma^*(C_8-C_9)$	0.0158	0.05	0.92	0.006
			$\sigma^*(C_9-H)$	0.0136	0.13	0.97	0.010
	$\pi(C_{1i}-C_{2i})$	1.5094	$\pi^*(C_{1i}-C_{7i})$	0.3826	0.06	0.35	0.004
			$\sigma^*(C_{8i}-C_{9i})$	0.0162	0.10	0.71	0.009
	$\pi(C_{3i}-C_{4i})$	1.7793	$\pi(C_{5i}-C_{6i})$	0.2098	0.22	0.39	0.008
	$\pi(C_{5i}-C_{6i})$	1.7882	$\sigma^*(C_{8i}-H)$	0.0169	0.13	0.80	0.010
	$\eta_1(O_1)$	1.9776	$\sigma^*(C_8-C_9)$	0.0158	0.10	1.23	0.010

The topological parameters at the critical bond point between the nuclear attractors of the intermolecular interactions are shown in Tables 5 and 6 for compounds DADB and DEADP. The critical bond points, as well as the bond pathways, are represented by the

molecular graphs in Figures 14 and 15. The values of these parameters showed that the interactions between the molecules in the crystals of both compounds are of the *closed-shell* type. This means that the interactions that occurred present an electrostatic character due to the low electronic density between the nuclear regions of the molecular pairs.

Table 5. Topological properties calculated on the molecular interactions in DADB at the bond critical point.

Interaction	Electronic Density, $\rho(r)$ (a.u.)	Laplacian, $\nabla^2 \rho^2$ (a.u.)
Frontal Interaction		
(CO)–O $\cdots$ C ₁₁	0.023	0.037
C ₁₁ –H $\cdots$ H–C ₁₁	0.027	0.062
Axial Interaction		
C ₁₀ –O ₂ $\cdots$ H–C ₁₁	0.021	0.035
O ₁ $\cdots$ H–C ₁₂	0.025	0.057
C ₈ –H $\cdots$ C ₆	0.029	0.037
C ₉ –H $\cdots$ H–C ₃	0.042	0.005
C ₂ $\cdots$ C ₃	0.030	0.025

Table 6. Topological properties calculated on the molecular interactions in DEADP at the bond critical point.

Interaction	Electronic Density, $\rho(r)$ (a.u.)	Laplacian, $\nabla^2 \rho^2$ (a.u.)
Frontal Interaction		
C ₈ –H $\cdots$ H–C _{AR}	0.017	0.034
C _{AR} –H $\cdots$ H–C _{AR}	0.022	0.016
C _{AR} –H $\cdots$ O ₁ = C ₁₀	0.033	0.031
Axial Interaction		
C ₁₁ –H $\cdots$ H–C ₁₂	0.016	0.014
C ₁₀ = O ₁ $\cdots$ H–C ₈	0.021	0.045
C ₈ –H $\cdots$ C _{AR}	0.023	0.015
C _{AR} $\cdots$ C _{AR}	0.024	0.008
C _{AR} $\cdots$ H–C ₈	0.013	0.011
C ₉ –H $\cdots$ O ₁ = C ₁₀	0.020	0.037
C ₁₂ –H $\cdots$ H–C ₁₁	0.015	0.021

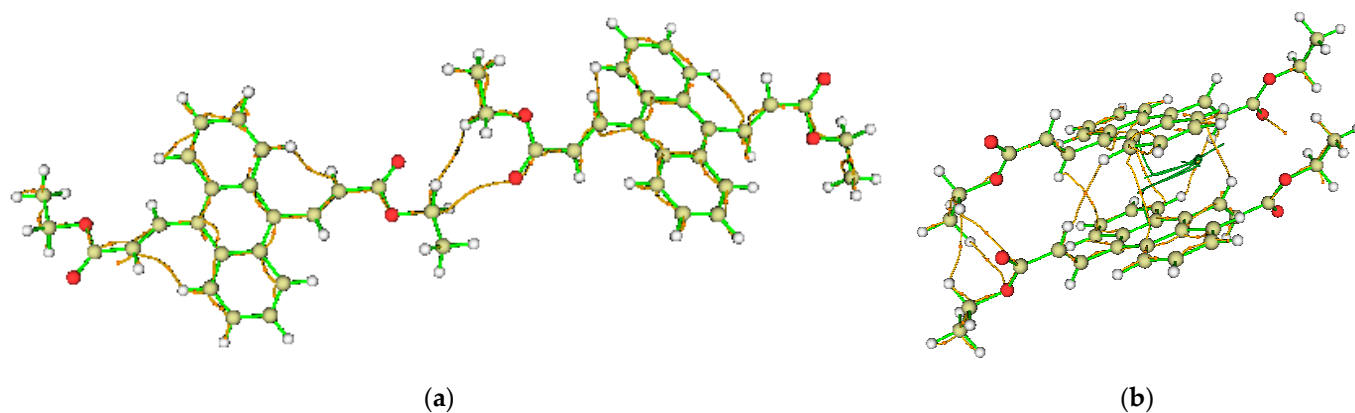


Figure 14. Molecular graph of the frontal (a) and axial (b) interactions between DADB molecules in the crystals, where the orange lines correspond to the bond path, and the small orange circles to the bond critical point.

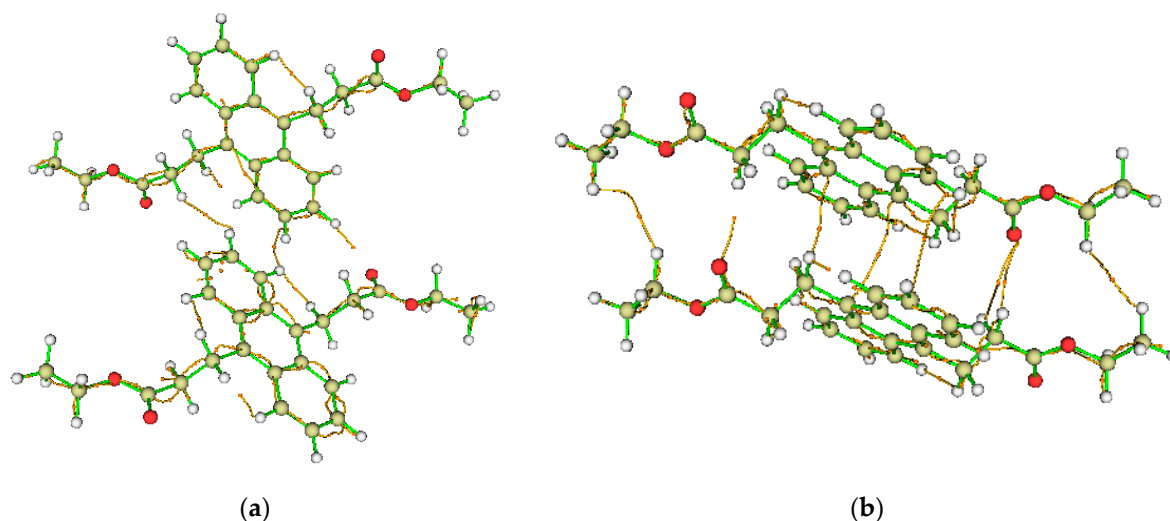


Figure 15. Molecular graph of the frontal (a) and axial (b) interactions between DEADP molecules in the crystals, where the orange lines correspond to the bond path, and the small orange circles to the bond critical point.

The frontal interaction between two DADB units is explained through two BCPs: the first, occurs exactly in the intranuclear region $-\text{C}=\text{O} \cdots \text{C}_{11}$; the second, in the $\text{C}_{11}-\text{H} \cdots \text{H}-\text{C}_{11}$ region. These two regions have a low electron density (<0.2 au). The axial interaction between two molecular units is observed through five BCP, all with low electron density. The larger contact surface between the molecules in the second case increases the number of interactions. In addition, the large number of delocalized π electrons in the region of the aromatic rings contributes to the weak interaction between the molecules of the compound in the crystal. Similarly, the interactions between molecules observed in DEADP interact, as shown in Figure 13b, being *closed-shell* interactions. Frontal contact between two molecules results in an interaction involving three BCP. The results showed that the electron density in the intranuclear regions $\text{C}_8-\text{H} \cdots \text{H}-\text{C}_{\text{AR}}$, $\text{C}_{\text{AR}}-\text{H} \cdots \text{H}-\text{C}_{\text{AR}}$ and $\text{C}_{\text{AR}}-\text{H} \cdots \text{O}_1=\text{C}_{10}$ are low, according to the values presented in Table 6.

The axial interaction between two molecules in the crystals of this compound is observed by several BCP, whose electron density is similarly low among nuclear attractors (Table 6). In this last contact, the interaction takes place at various points in the molecules due to the large contact surface. Therefore, the molecules of DADB and DEADP, interact in their respective crystals through low-intensity intermolecular forces.

4. Conclusions

Theoretical calculations showed that the geometric parameters obtained for the molecules of the studied compounds differ significantly, only in the C_8 and C_9 atoms. The differences only occurred due to the change in their hybridizations, as was in fact expected. The different groups, aromatic and aliphatic, configure flat structures; however, both molecular structures do not. Theoretical data showed that both compounds have electronically stable molecules, and DADB is chemically more reactive than DEADP due to the presence of the double bond in their acrylate groups. The molecules of both compounds are weakly complexed in the formation of their respective crystals, so that the donor orbitals and acceptor orbitals hyperconjugate with very low second-order energy. In addition, it was possible to show that the electronic charge density in the regions where the interactions occur is of the closed-shell type, configuring a low-intensity intermolecular contact.

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References

1. Becker, H.D. Unimolecular photochemistry of anthracenes. *Chem. Rev.* **1993**, *93*, 145–172. [\[CrossRef\]](#)
2. Bouas-Laurent, H.; Castellan, A.; Desvergne, J.P.; Lapouyade, R. Photodimerization of anthracenes in fluid solution: Structural aspects. *Chem. Soc. Rev.* **2000**, *29*, 43–55. [\[CrossRef\]](#)
3. Tomlinson, W.J.; Chandross, E.A.; Fork, R.L.; Pryde, C.A.; Lamola, A.A. Photodimerization of anthracenes in fluid solution: Structural aspects. *Appl. Opt.* **1972**, *11*, 533. [\[CrossRef\]](#)
4. Zehm, D.; Fudickar, W.; Hans, M.; Schilde, U.; Kelling, A.; Linker, T. 9,10-Diarylanthracenes as Molecular Switches: Syntheses, Properties, Isomerisations and Their Reactions with Singlet Oxygen. *Chem. Eur. J.* **2008**, *14*, 11429–11441. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Pierlot, C.; Aubry, J.M.; Briviba, K.; Sies, H.; Mascio, P. *Singlet Oxygen, UV-A, and Ozone*; Academic Press Inc.: San Diego, CA, USA, 2000.
6. Martinez, G.R.; Medeiros, M.H.G.; Mascio, P. Utilização de endoperoxidos de derivados de naftaleno como fontes químicas de oxigênio singlete em sistemas biológicos. *Quim. Nov.* **2000**, *23*, 686. [\[CrossRef\]](#)
7. Wasserman, H.H.; Wiberg, K.B.; Larsen, D.L.; Parr, J. Photooxidation of methylnaphthalenes. *J. Org. Chem.* **2005**, *70*, 105–109. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Wasserman, H.H.; Larsen, D.L. Formation of 1,4-endoperoxide from the dye-sensitized photooxygenation of alkyl naphthalenes. *J. Chem. Soc. Chem. Commun.* **1972**, *5*, 253–254. [\[CrossRef\]](#)
9. Pierlot, C.; Aubry, J.M.; Briviba, K.; Sies, H.; Mascio, P. Naphthalene endoperoxides as generators of singlet oxygen in biological media. *Methods Enzym.* **2000**, *319*, 3–20.
10. Pierlot, C.; Hajjam, S.; Barthelemy, C.; Aubry, J.-M. Water-soluble naphthalene derivatives as singlet oxygen (1O_2 , $^1\Delta_g$) carriers for biological media. *J. Photochem. Photobiol.* **1996**, *36*, 31–39. [\[CrossRef\]](#)
11. Dewilde, A.; Pellieux, C.; Pierlot, C.; Wattré, P.; Aubry, J.-M. Inactivation of intracellular and 3,3'-(1,4-Naphthylidene)dipropionate. Monomol and dimol photoemission and the effects of 1,4-diazabicyclo[2.2.2]octane. *Biol. Chem.* **1998**, *379*, 1377. [\[PubMed\]](#)
12. Klotz, O.; Pellieux, C.; Briviba, K.; Pierlot, C.; Aubry, J.-M.; Sies, H. Mitogen-activated protein kinase (p38-, JNK-, ERK-) activation pattern induced by extracellular and intracellular singlet oxygen and UVA. *Eur. J. Biochem.* **1999**, *260*, 917–922. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Oliveira, M.S.; Severino, D.; Prado, F.M.; Angeli, J.P.F.; Motta, F.D.; Baptista, M.S.; Medeiros, M.H.G.; Mascio, P. Di Singlet molecular oxygen trapping by the fluorescent probe diethyl-3,3'-(9,10-anthracenediyl)bisacrylate synthesized by the Heck reaction. *Photochem. Photobiol. Sci.* **2011**, *10*, 1546–1555. [\[CrossRef\]](#)
14. Oliveira, M.S.; Al, E. Heck reaction synthesis of anthracene and naphthalene derivatives as traps and clean chemical sources of singlet molecular oxygen in biological systems. *Photochem. Photobiol. Sci.* **2020**, *19*, 1590–1602. [\[CrossRef\]](#)
15. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8. [\[CrossRef\]](#)
16. Farrugia, L.J. WinGX and ORTEP for Windows: An update. *J. Appl. Crystallogr.* **2012**, *45*, 849–854. [\[CrossRef\]](#)
17. Macrae, C.F.; Edgington, P.R.; McCabe, P.; Pidcock, E.; Shields, G.P.; Taylor, R.; Towler, M.; van de Streek, J. Mercury: Visualization and analysis of crystal structures. *J. Appl. Crystallogr.* **2006**, *39*, 453–457. [\[CrossRef\]](#)
18. Spek, A.L. Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* **2003**, *36*, 7–13. [\[CrossRef\]](#)
19. Groom, C.R.; Allen, F.H. The Cambridge Structural Database in retrospect and prospect. *Angew. Chem. Int. Ed.* **2014**, *53*, 662–671. [\[CrossRef\]](#) [\[PubMed\]](#)

20. Spackman, P.R.; Turner, M.J.; McKinnon, J.J.; Wolff, S.K.; Grimwood, D.J.; Jayatilaka, D.; Spackman, M.A. CrystalExplorer: A program for Hirshfeld surface analysis, visualization and quantitative analysis of molecular crystals. *J. Appl. Cryst.* **2021**, *54*, 1006–1011. [[CrossRef](#)]
21. McKinnon, J.J.; Spackman, M.A.; Mitchell, A.S. Novel tools for visualizing and exploring intermolecular interactions in molecular crystals. *Acta Crystallogr. Sect. B Struct. Sci.* **2004**, *60*, 627–668. [[CrossRef](#)]
22. Hohenberg, P.; Kohn, W. Inhomogeneous electron gas. *Phys. Rev.* **1964**, *136*, B864. [[CrossRef](#)]
23. Kohn, W.; Sham, L.J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133–A1138. [[CrossRef](#)]
24. Frisch, M.; Trucks, G.; Schlegel, H.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. *Gaussian 09, revision E. 01*; Gaussian, Inc.: Wallingford, CT, USA, 2009.
25. Zhang, G.; Musgrave, C.B. Comparison of DFT methods for molecular orbital eigenvalue calculations. *J. Phys. Chem. A* **2007**, *111*, 1554–1561. [[CrossRef](#)]
26. Náray-Szabó, G.; Ferenczy, G.G. Molecular Electrostatics. *Chem. Rev.* **1995**, *95*, 829–847. [[CrossRef](#)]
27. Grant, G.H.; Richards, W.G. *Computational Chemistry*, 1st ed.; Oxford University Press: Oxford, UK, 1996.
28. Van Duijneveldt, F.B.; van Duijneveldt-van de Rijdt, J.G.C.M.; van Lenthe, J.H. State of the Art in Counterpoise Theory. *Chem. Rev.* **1994**, *94*, 1873–1885. [[CrossRef](#)]
29. Bader, R.F.W. Atoms in Molecules. *Acc. Chem. Res.* **1985**, *18*, 9–15. [[CrossRef](#)]
30. Matta, C.F.M.; Boyd, R.J. *The Quantum Theory of Atoms in Molecules*; Wiley-VCH: Weinheim, Germany, 2007; ISBN 9783527307487.
31. Matta, C.F.; Bader, R.F.W. Atoms-in-molecules study of the genetically encoded amino acids. III. Bond and atomic properties and their correlations with experiment including mutation-induced changes in protein stability and genetic coding. *Proteins Struct. Funct. Bioinform.* **2003**, *52*, 360–399. [[CrossRef](#)]
32. Allen, F.H.; Watson, D.; Brammer, L.; Orpen, A.G.; Taylor, R. Typical interatomic distances: Organic compounds. *Int. Tables Crystallogr.* **2006**, *C*, 790–811. [[CrossRef](#)]
33. Duarte, H.A. Chemical reactivity indexes from density functional theory: Formalism and perspectives. *Quim. Nova* **2001**, *24*, 501–508. [[CrossRef](#)]