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Structural investigation of (2*E*)-2-(ethoxycarbonyl)-3-[(4-methoxyphenyl)amino]prop-2-enoic acid: X-ray crystal structure, spectroscopy and DFT





Perumal Venkatesan ^a, Venkatachalam Rajakannan ^b, Natarajan S. Venkataramanan ^c, Andivelu Ilangovan ^{a, **}, Tom Sundius ^d, Subbiah Thamotharan ^{e, *}

^a School of Chemistry, Bharathidasan University, Tiruchirappalli, 620 024, Tamilnadu, India

^b Centre of Advanced Study in Crystallography and Biophysics, University of Madras, Chennai, 600 025, India

^c Centre for Computational Chemistry and Materials Science, SASTRA University, Thanjavur, 613 401, India

^d Department of Physics, University of Helsinki, P.O. Box 64, FIN-00014, Helsinki, Finland

^e Biomolecular Crystallography Laboratory, Department of Bioinformatics, School of Chemical and Biotechnology, SASTRA University, Thanjavur, 613 401, India

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ABSTRACT

The title compound, (2*E*)-2-(ethoxycarbonyl)-3-[(4-methoxyphenyl)amino]prop-2-enoic acid is characterized by means of X-ray crystallography, spectroscopic methods and quantum chemical calculations. The title compound crystallizes in centrosymmetric space group $P2_1/c$. Moreover, the crystal structure is primarily stabilized through intramolecular N–H···O and O–H···O and intermolecular N–H···O and C–H···O interactions along with carbonyl···carbonyl and C–H···C contacts. These intermolecular interactions are analysed and quantified by using Hirshfeld surface analysis, PIXEL energy, NBO, AIM and DFT calculations. The overall lattice energies of the title and parent compounds suggest that the title compound is stabilized by a 4.5 kcal mol⁻¹ higher energy than the parent compound. The additional stabilization force comes from the methoxy substitution on the title molecule, which is evident since the methoxy group is involved in the intermolecular C–H···O interaction as an acceptor. The vibrational modes of the interacting groups are investigated using both experimental and theoretical FT-IR and FT-Raman spectra. The experimental and theoretical UV–Vis spectra agree well. The time dependent DFT spectra show that the ligand-to-ligand charge transfer is responsible for the intense absorbance of the compound.

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1. Introduction

Ester hydrolysis is one of the most fundamental reactions in organic chemistry [1]. The reaction of partial hydrolysis of diesters generates half-esters, which consist of both a carboxylic acid and an ester moiety. Half-esters can be classified as geminal, vicinal, vinylic, aromatic and simple half-esters depending on the substitution positions of acid and ester moieties. Half-esters are versatile building blocks for a variety of natural products and biologically active compounds. Malonic acid half-esters, which belong to the geminal half-ester family, have numerous applications as intermediates in the synthesis of virantmycin [2], amino acids [3], β -hydroxy esters or β -amino esters [4] and tri-carbonyl compounds [5]. The synthesis of functionalized malonic acid half-ester derivatives has been reported by our group [6]. The crystal structures of these derivatives and the invariant and variable intermolecular interactions in them have been examined using Hirshfeld surfaces and PIXEL energy calculations [7]. We have also studied the crystal structure of the *L*-phenylalanine derivative (2*E*)-2-(ethoxycarbonyl)-3-[(1-methoxy-1-oxo-3-phenylpropan-2-yl) amino] prop-2-enoic acid, wherein we observed a push-pull network formed by the geminal methylene malonic acid and amine group at vicinal position of the double bond. The presence of a chiral center in the phenylalanine and the push pull environment helps to show good second harmonic generation (SHG) activity [8].

^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: ilangovanbdu@yahoo.com (A. llangovan), thamu@scbt.sastra. edu (S. Thamotharan).

In this work, we present the crystal and molecular structure of one of the malonic acid half-ester derivatives, (2E)-2-(ethoxycarbonyl)-3-[(4-methoxyphenyl) amino] prop-2-enoic acid. The structure of the title compound is optimized in the gas phase using the DFT level of theory with a 6-31+G(d) basis set. The harmonic vibrational frequencies are calculated for this compound at the same level of theory. The calculated spectra of this compound are compared with experimentally observed FT-IR and Raman spectra. Furthermore, the intermolecular interactions in the crystal structure of the title compound are visualized using a Hirshfeld surface diagram [9,10]. The relative contributions of various intermolecular interactions are quantified using decomposed two dimensional fingerprint plots [11,12]. Furthermore, we have used the PIXEL method [13–15] to quantify the strengths of the various intermolecular interactions present in the crystal structure of the title compound. Atoms-in-molecules (AIM) and natural bond orbitals (NBO) analysis shows the existence of various intra- and intermolecular interactions.

2. Experimental

2.1. Synthesis of (2E)-2-(ethoxycarbonyl)-3-[(4-methoxyphenyl) amino] prop-2-enoic acid

The title compound was prepared by BF3·OEt2 mediated hydrolysis of the geminal diester (Scheme 1) [6]. To a solution of diethyl 2-[(4-methoxyphenyl)amino] methylene malonate (1.0 g, 3.4 mmol, 1.0 equiv.) in CHCl₃ (3 \times w/v), BF₃·OEt₂ (856 μ L, 3.4 mmol, 1.0 equiv.) was added and stirred at 296 K and the progress of the reaction was monitored by TLC. The reaction mixture was quenched with water $(1 \times w/v)$ and extracted with chloroform (3 \times 10 mL). The combined organic layer was dried (anhydrous Na₂SO₄) and evaporated in a rotary evaporator under vacuum. The crude product obtained was passed through a short silica gel column using a hexane and ethyl acetate mixture (8:2, v/v)as eluent to obtain a yellow solid (mp: 110 °C, 0.80 g, yield 90%). The title compound recrystallized from ethanol by the slow evaporation method. ¹H NMR (400 MHz, CDCl₃) δ :1.37 (t, 3H, J = 7.2 Hz), 3.82 (s, 3H), 4.33 (q, 2H, J = 7.2 Hz), 6.94 (d, 2H, J = 12.0 Hz), 7.13 (d, 2H, J = 12.0 Hz), 8.39 (d, 1H, J = 13.6 Hz), 11.64 (d, 1H, J = 13.6 Hz), 13.01 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 14.3, 55.6, 61.3, 88.7, 115.1, 119.5, 131.9, 152.0, 157.9, 170.1, 170.8.

The infrared spectra of the title compound were recorded in the frequency region 4000–400 cm⁻¹ on the Perkin Elmer FT–IR spectrophotometer with a resolution of 1 cm⁻¹ using the KBr pellet technique. The Raman spectrum was recorded using the iRaman Plus Raman spectrometer (B &W Tek, USA) and the 532 nm laser line was used for excitation. The spectral resolution was 4 cm⁻¹. The ¹H (Fig. S1) and ¹³C NMR spectra (Fig. S2) for the title compound are presented in the supplementary information (SI) section. The UV–Vis absorption spectrum was recorded (200–700 nm) on a Eppendorf Biospectrophotometer in ethanol solvent.

2.2. Single crystal X-ray diffraction

X-ray intensity data were collected for the title compound at room temperature (296 K) using a Bruker SMART APEX-II CCD diffractometer (*MoK* α , $\lambda = 0.71073$ Å). The crystal structure of the title compound was solved by the SIR92 program [16] and all the non-hydrogen atoms were refined anisotropically using the SHELXL2014 program [17]. The positions of the amine and hydroxy hydrogen atoms were located from a difference Fourier map and refined freely along with their isotropic displacement parameters. The methyl hydrogen atoms were constrained to an ideal geometry (C-H = 0.98 Å), with $U_{iso}(H) = 1.5U_{eq}(C)$, but were allowed to rotate freely about the C-C bonds. The remaining H atoms were placed in idealized geometrical positions and constrained to ride on their parent atoms. The thermal ellipsoidal and crystal packing figures were produced using the programs PLATON [18] and MERCURY [19], respectively. CCDC 1438183 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.3. Computational details

All the density functional theory calculations were performed with the Gaussian 09 program package [20]. From the X-ray crystal structure analysis and PIXEL energy calculation, four different dimeric pairs were identified based on their interaction energies. These four dimers were further subjected to structural optimization without any geometrical constraints using a dispersion corrected M05-2X functional [21]. In previous studies, the use of the M05-2X functional has provided accurate prediction of the molecular geometries and binding energies for materials with hydrogen bonding interactions [22,23]. To include the effect of the ethanol solvent, we used the CPCM method, with sphere radii optimized for COSMO-RS, as proposed by Klamt [24]. In order to confirm the proper convergence to minima and to compute the IR spectra, vibrational frequencies were computed and we confirmed that no negative frequencies were present.

The interaction energy E_{int} was computed for four different dimers after incorporating the zero point vibrational energy (ZPVE) and counterpoise correction [25]. Partial charges were computed at the M05-2X/6-31+G(d) level of theory using the natural bond orbitals (NBO) program as implemented in Gaussian 09 program. The quantitative molecular electrostatic potentials (MESP) for all systems were computed on the 0.001 a.u. isodensity surface. AIM topological analysis was carried out using the AIM2000 package. For the optical part, the calculations of the properties have been carried out in the framework of time dependent-DFT (TDDFT) by extracting a minimum of 100 roots with the time dependent Kohn-Sham formalism [26]. For comparison, the calculated discrete spectra have been normalized and their peaks broadened with a Gaussian function of fwhm = 0.02 eV.



Scheme 1. Synthesis of malonic acid half-ester. Parent compound R = -H and title compound $R = -OCH_3$.

3. Results and discussion

3.1. Description of crystal structure

Single crystal X-ray analysis of the title compound reveals that the crystal has the space group $P2_1/c$ and belongs to the monoclinic system. The crystal data and refinement parameters are presented in Table 1. The hydrogen bonding interactions that stabilize the crystal structure are listed in Table 2. We have determined a series of crystal structures of malonic acid half-ester derivatives by X-ray crystallography earlier and analysed how different functional groups substituted at different positions on the phenyl ring alter the crystal packing in detail [7]. The malonic acid half-ester derivatives which include the title compound have a common skeletal framework consisting of acid and ester groups at the geminal position and an *N*-vinyl aniline moiety. In the title compound, a methoxy group is substituted at the *para*-position on *N*-vinyl aniline moiety.

The dihedral angles between the mean planes formed by different sets of atoms for the title molecule and its parent molecule are given in Table S1. Briefly, the phenyl ring is coplanar with the acid, ester and methoxy moieties. The dihedral angle is in the range of $2-5^{\circ}$. In the parent molecule, the phenyl ring is oriented at an angle of ~ 34° with both acid and ester moieties. This clearly indicates that the phenyl ring is undergoing a slight rotational movement. This observation is further supported by the variations of two torsion angles C7–N1–C1–C2 [177.97(14)° in the title compound and 147.45(11)° in the parent compound] and C7–N1–C1–C6 [$-2.3(2)^{\circ}$ in the title compound and $-32.44(16)^{\circ}$ in the structural superimposition of the title and the parent compounds is shown in Fig. S3.

In the crystal structure of the title compound, amine and hydroxy groups act as donors and carbonyl groups (atoms O2 and O3) of carboxylic acid and ester moieties act as acceptors for various intra-and intermolecular N–H···O, O–H···O and C–H···O hydrogen bonding interactions. The methoxy oxygen atom (O5) is also participating in an intermolecular C–H···O interaction. As observed in related malonic acid half-ester derivatives [7], two invariant intramolecular N–H···O and O–H···O hydrogen bonding interactions are seen in the crystal structure of the title molecule. As shown in the ORTEP diagram (Fig. 1), these intramolecular hydrogen bonding interactions are generating two fused pseudo six-membered rings. These rings can be described as S(6)–S(6) graph-set motifs [27].

In the crystal structure, molecules dimerize with R_2^2 (12) motif through an invariant intermolecular N-H...O hydrogen bonding interaction between the amine group and the carbonyl group of the carboxylic acid moiety as observed in the parent compound (Fig. 2(a)). This dimer is further stabilized by three additional noncovalent interactions. Two of them are intermolecular C-H--O interactions (C2-H2...O2 and C2-H2...O1) and a carbonyl···carbonyl (C=0···0=C) contact with a distance of 2.896 Å. This distance is slightly longer in the title compound when compared with its parent crystal structure (2.789 Å). Moreover, the intermolecular C2-H2···O2 and C2-H2···O1 interactions produce two independent $R_2^2(16)$ motif as shown in Fig. 2(b). The former intermolecular interaction is observed in the crystal structure of the parent molecule, while the latter interaction is only observed in the title molecule. The substitution of the 4-methoxy group on the phenyl ring provides an additional stabilization to the crystal structure. As mentioned earlier, the methoxy oxygen (O5) is involved in an intermolecular C6-H6...O5 interaction. This interaction links the molecules into a C(5) chain motif which runs parallel to the *b* axis as displayed in Fig. 3(c).

It is worthy to note that even though the title and its parent molecules superimpose well, there is a difference observed in these structures for the interconnection of N–H···O hydreon bonded dimeric molecules. In the parent crystal structure, adjacent dimers are interconnected by C11···O3 contacts. In contrast, this interaction is absent in the title molecule. However, dimeric molecules in one layer are interconnected by dimeric molecules in an adjacent layer by C11–H11A···C9 interactions. As shown in Fig. 3(a), this

Table	1
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The crystal data and refinement parameters of the title compound.

Empirical formula	C ₁₃ H ₁₅ N O ₅
Formula weight	265.26
Т (К)	296(2)
Wavelength (Á)	0.71073
Crystal system	Monoclinic
Space group	P21/c
a (Á)	7.7905(2)
b (Á)	7.3567(2)
c (Á)	23.7906(7)
α (°)	90
β(°)	98.358(2)
γ (°)	90
V (Å ³)	1349.01(6)
Z	4
Calculated density (Mg/m ³)	1.306
Absorption (mm ⁻¹)	0.101
F(0 0 0)	560
Crystal size (mm)	$0.25 \times 0.20 \times 0.20$
θ (°)	2.643-28.417
Limiting indices	$-10 \leqslant h \leqslant 9$, $-8 \leqslant k \leqslant 9$, $-31 \leqslant l \leqslant 31$
Reflections collected/unique, (R _{int})	3313/2261, (0.0241)
(θ°)/Completeness (%)	(25.42)/99.9
Refinement method	full-matrix least-squares on F ²
Data/restraints/parameters	3313/0/181
Goodness-of-fit (GOF) on F ²	1.054
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0449$, $wR_2 = 0.1280$
R indices (all data)	$R_1 = 0.0669, wR_2 = 0.1435$
Largest difference in peak and hole (e A^{-3})	0.157 and -0.147

Table 2

Various intra- and intermolecular interactions observed in the crystal structure of the title compound and key contacts visible on the HS are labelled.

D—H…A	D-H	Н…А	D····A	D-H···A	Symmetry	Label
01-H1003=C10	0.899(19)	1.70(2)	2.5466(19)	155.3(17)		
N1-H1N···O2=C9	0.875(16)	2.046(16)	2.6845(16)	129.0(13)		
N1-H1N···O2=C9	0.875(16)	2.608(17)	3.4122(19)	153.2(13)	−x+2, −y, −z	1
C2-H201-C9	0.93	2.62	3.441(2)	147.0	−x+2, −y, −z	2
C2-H2O2=C9	0.93	2.48	3.333(2)	153.3	−x+2, −y, −z	3
C9=02…02=C9			2.8958(17)		−x+2, −y, −z	4
C8…C9			3.3869(21)		−x+2, −y+1, −z	5
C11–H11A…C9	0.97	2.90	3.755(2)	147.5	−x+1, −y+1, −z	6
C6-H605	0.93	2.69	3.505(2)	146.6	-x+2, y+1/2, -z+1/2	7



Fig. 1. The ORTEP diagram and atomic labelling scheme of the title compound. The intramolecular N–H…O and O–H…O hydrogen bonding interactions are indicated by dashed lines.

interaction can be described as a $R_2^2(12)$ motif. The molecular dimers are arranged as layers and adjacent layers are further interconnected by C8····C9 contacts as observed in the parent compound (Fig. 3(b)).

3.2. Hirshfeld surface analysis and PIXEL energy calculation

The Hirshfeld surface (HS) and the two dimensional fingerprint plots are generated based on the d_e and d_i distances using Crystal Explorer 3.1 [28]. The former is the distance from the HS to the nearest atom outside the surface, while the latter is the distance from the nearest atom inside the surface. This analysis is used to identify the various intermolecular contacts and their relative contributions in the crystal structure. The HS diagram, decomposed two dimensional fingerprint plots and the relative contributions of the various intermolecular interactions to the HS area for the crystal structure of the title compound are displayed in Fig. 4. The result suggests that the intermolecular H···H contacts have a major contribution (42.8%) to the crystal packing of the title compound as observed in related structures [7]. These contacts are relatively comparable (44.2%) with that of the parent compound. The relative contributions of the O···H/H···O and C···H/H···C contacts are 29.2% and 18.9%, respectively. The relative contributions of the corresponding contacts are 27% and 18.6% in the parent compound. It is of interest to note that the O…H/H…O contacts are slightly increased (~2%) in the title compound. This increment is a consequence of the presence of the methoxy substitution on the phenyl ring. The other intermolecular contacts such as O···C/C···O, N···H/ H…N and C…C contacts are contributing 2.8, 2.3 and 1.9%, respectively to the crystal packing of the title compound. The relative contributions of the corresponding contacts in the parent compound are 2.9, 2.0 and 3.3%.

The intermolecular potential is evaluated using PIXEL method [13–15] which deals with the energy partitioned into Coulombic, polarization, dispersion and repulsion terms. The interaction energy is calculated for different pairs of molecules that are interconnected by various intermolecular interactions. The distances involving hydrogen atoms are moved to their neutron values before the calculation. The electron density of the molecule has been obtained at the MP2/6-31G** level of theory using Gaussian 09. The overall lattice energies of the title compound and its parent compound are summarized in Table 3. The lattice energies of these structures suggest that the title compound is stabilized by 4.5 kcal mol⁻¹ more than the parent compound. This additional stabilization is achieved by the involvement of methoxy substitution in the intermolecular interaction as mentioned earlier. It is also interesting to note that the dispersion contribution is nearly the same in both the title and parent crystal structures. However, there are variations (from 5.6 to 8.1 kcal mol^{-1}) in the energies of the Coulombic, polarization and repulsion energies observed in these crystal structures.

Various energy components for interacting molecular pairs along with the centroid-to-centroid distance between the interacting pair of molecules are listed in Table 4. As mentioned earlier, the invariant intermolecular N-H···O hydrogen bonding interaction along with additional C-H···O interactions forms a molecular dimer. The interaction energy $(-12.4 \text{ kcal mol}^{-1})$ for this dimer is found to be similar with a related structure where the methyl group is substituted at the para position on the phenyl ring [7]. Based on the energetics, this interaction makes a more significant contribution to the crystal packing when compared to other types of interactions observed in the crystal structure. As mentioned earlier, a non-covalent interaction is observed between atom C8 in one layer and atom C9 in the adjacent layer. The energy for this interaction is -10.5 kcal mol⁻¹. The second most significant contribution to the crystal packing comes from this interaction. The strength of this interaction is found to be similar to related structures [7]. Another interaction is (C11-H11A···C9), which links the adjacent layers in a similar way as the C8...C9 interaction (Fig. 3(b)). The interaction energy for the former is being -7.0 kcal mol⁻¹. It is worthy to note that this contact is not visible on the HS and the distance between the interacting atoms is slightly longer (the sum of the van der Waals radii+0.1 Å). The methoxy group is participating in an intermolecular C6–H6…O5 interaction. This interaction scores -6.1 kcal mol⁻¹. As can be seen from Table 4, the least contribution to the crystal packing comes from this interaction. However, this interaction provides an additional stabilization to the crystal structure.

3.3. DFT and wavefunction analysis

The bond lengths, angles and torsion angles derived from gas



Fig. 2. (a) Part of the crystal structure showing various intermolecular interactions forming a molecular dimer with $R_2^2(12)$ for N–H···O interaction. (b) Intermolecular C–H···O interaction forming a molecular dimer with $R_2^2(16)$ motif. (c) An intermolecular C–H···O interaction links the molecules into a C(5) chain motif.

phase DFT study are compared with the geometric parameters determined from X-ray analysis. The comparative geometric parameters are listed in Table S2. The structural overlay is performed in order to compare the experimental structure with that obtained from the gas phase geometry optimization (Fig. S4, SI). The RMSD between X-ray and optimized structures is 0.269 Å. It is of interest to note that the 4–OMe substituted phenyl ring shows a twist by ~30° when compared with the optimized structure. This larger deviation might be a consequence of the involvement of atom O5 in an intermolecular interaction in the crystal structure. Obviously, no such interaction exists in the isolated molecule. Two torsion angles (C7–N1–C1–C2 and C7–N1–C1–C6) indicate this deviation (Table S2, SI). Moreover, the inclusion of intrinsic solvent (ethanol) has only a marginal effect.

To understand the nature of interaction between the monomers (within dimers) and the relative strength of the four different dimeric pairs that were identified as mentioned earlier, they are subjected to complete optimization. The optimized structure of dimer-I is shown in Fig. S5(a), which is found to be stabilized by two N–H···O type hydrogen bonds, and four C–H···O type interactions as observed in the crystal structure. The dimer-II (Fig. S5(b)) is found to be 0.002 kcal mol⁻¹ higher in energy than the dimer-I and dimer-II is calculated to be 1.9 kcal mol⁻¹ using PIXEL method. Fig. S5(c and d) show the optimized geometries of dimer-II and dimer-IV, respectively. The former dimer is 0.803 kcal mol⁻¹ higher in energy than dimer-I, while the latter is

5.589 kcal mol⁻¹ higher in energy than dimer-I. The optimized structure of dimer-III has four intermolecular hydrogen bonding interactions, whereas dimer-IV has two interactions. Thus, it is evident that with the increase in the number of intermolecular interactions, and the interaction energy of the dimers increases.

Fig. S6(a) shows the molecular electrostatic potential (MEP) of the isolated monomer where the location of the various most positive and negative potentials is indicated, and the electrostatic potential maxima with the atom numbering and the values designated as Vs,max and Vs,min, are listed in Table 5. To understand the nature of interactions, and to identify the reason for the nearly isoenergetic geometries of dimer-I and dimer-II (Fig. S6(b and c)), we analysed the quantitative MEP. As shown in Table 5 and Fig. S6(a), the favourable sites for electrophilic attack are concentrated to the regions around the carboxylic group, the carbonyl group and on the oxygen atom. On the contrary, regions of positive electrostatic potential are found on the hydrogen atoms on the benzene ring and on the methyl group. The most striking feature of Fig. S6(b) is the positive electrostatic potential at the end benzene hydrogen atoms that are capped by the negative potentials of the carboxylic group with a large electronegative domain, thereby giving rise to a directional interaction. In dimer-II, we observed that the negative potentials on the carboxylic group are capped by the positive regions on the alkyl chain. Thus the dimers are formed by interactions of opposite electrostatic regions.

To contemplate the ESP results, we carried out AIM analysis on the dimer-I and dimer-II. The molecular graphs of these dimers



Fig. 3. (a) Part of the crystal structure showing an intermolecular C11–H11A···C9 interaction links the neighbouring molecular dimers with $R_2^2(12)$ motif. (b) The intermolecular C8···C9 and C11–H11A···C9 interactions links two adjacent layers.

show the existence of different types of bonding (Fig. 5). In dimer-I, we observed seven intermolecular bond critical bonds (BCP's). The computed topological electron density at the BCP's are in the range of 0.021–0.017 a.u. These values are comparable with those of predicted values for hydrogen bonding interactions [29]. Furthermore, an intermolecular BCP between the carbonyls (C=0···0=C) is observed with an electron density of 0.010 a.u. Thus in dimer-I, the major attractive interactions are the hydrogen bonds. In dimer-II, nine BCP's are observed which includes N···O, C···C, C···O types of bonds in addition to the hydrogen bonds. This accounts for the near degeneracy in the interaction energy between dimer-I and II. The existence of intermolecular C···C bonds which are rarely observed have been identified in this crystal structure.

Delocalization of the electron density between occupied bonds or lone pair NBO orbitals and unoccupied antibonding orbitals correspond to stabilizing donor-acceptor interactions. Furthermore, the larger the second-order perturbation $(E^{(2)})$ value, the more intensive is the interaction between the donor and the acceptor. The most important acceptor-donor interactions with high $E^{(2)}$ for dimer-I and II are presented in Table 6. In dimer-I, the highest interaction energy $(8.49 \text{ kcal mol}^{-1})$ is observed for the transfer of the lone pair electrons of the oxygen atom (O2) into the antibonding orbital of the amine hydrogen. We have also observed charge transfer from the lone pair electrons of the oxygen atom (O1) to the antibonding orbital of the hydrogen atom (H2) of the benzene ring with an interaction energy of 1.23 kcal mol⁻¹. It is worthy to note that these two intermolecular interactions are relatively more stabilizing dimer-I than other interactions. The optimized dimer-II is mainly stabilized by a C8...C9 intermolecular contact with an interaction energy of 1.36 kcal mol⁻¹, which supports what was found from the AIM analysis.

3.4. Spectral analysis

To understand the nature of interaction between the

monomer's in the crystal structure, we considered the most stable dimer-I and dimer-II for the simulation of IR and Raman spectra. The experimental and the simulated FT-IR and Raman spectra are displayed in Fig. 6. It is clearly visible from the figure that the simulated spectra resemble the experimental spectra. The secondary amine N-H stretching and carboxylic acid O-H vibrations are usually observed in the range of 3400-3250 and 3300-2500 cm⁻¹, respectively [30]. In the monomer, the computed N–H stretching is observed at 3437 cm⁻¹. The corresponding vibration is calculated at 3477 cm^{-1} in the dimer-I complex and at 3502 cm^{-1} in the dimer-II. The O-H stretching is calculated at 3409, 3348 3280 cm^{-1} in the monomer, dimer-I and dimer-II, respectively. In the FT-IR spectrum, a peak is observed at 3214 cm⁻¹, which could be assigned for N-H or O-H vibrations. It is of interest to note that both N-H and O-H groups are involved in intra-and intermolecular hydrogen bonding interactions. The spectral blue shift indicates the involvement of the band in hydrogen bond formation between the intermolecular species. The C2-H2 stretching is observed at 3070 cm⁻¹ in IR and at 3079 cm⁻¹ in Raman. The corresponding vibration is calculated at 3240 cm⁻¹ in the monomer and at 3265 cm^{-1} in the dimer-I. Again there is a spectral blue shift supporting the possible involvement of a hydrogen bonding interaction and an intermolecular C2-H2···O interaction in the dimer-I formation. The C8-C9 stretching is calculated at 1688, 1700 and 1692 cm⁻¹ in the monomer, dimer-I and dimer-II, respectively. There is a peak observed at 1603 cm^{-1} in Raman which could be assigned for this vibration. The computed stretching frequency for the C8–C9 in the monomer is at 1521 cm⁻¹, which gets red shifted to 1527 cm^{-1} in dimer-II. This shows that dimer-II, which is a part of the crystal structure is stabilized by a C8...C9 intermolecular interaction.

The absorption spectrum of the title compound is computed in ethanol solvent using the TDDFT method. In Fig. 7(a), we have plotted the experimental and theoretical spectra, which are in good agreement. The optical properties are governed by the frontier



Fig. 4. (a-c) Different orientations of Hirshfeld surface mapped with d_{norm} and potential intermolecular contacts are labelled (see Table 2). (d-j) Two dimensional fingerprint plots for various intermolecular interactions. Various reciprocal close contacts and their contributions are indicated. (k) The relative contributions (in %) of various intermolecular contacts.

Table 3

Lattice energies (kcal mol⁻¹) partitioned into Coulombic, polarization, dispersion and repulsion contributions for title and parent compounds.

Compound	E _{Coul}	$E_{\rm pol}$	E _{Disp}	E_{rep}	E _{Tot}
Parent compound [7]	-13.7	-4.4	-30.9	19.8	-29.3
Present study	-5.6	-11.0	-31.4	14.2	-33.8

molecular orbitals compositions and the HOMO and LUMO energy levels (Fig. 7(b)). The HOMO orbitals are localized over the phenyl rings, while the LUMO orbitals are localized over the alkyl and the carbonyl groups. The simulated spectra show an intense absorbance at the ultraviolet wavelength of 301 nm, which is mainly due to the transfer of charge from the HOMO orbital to the LUMO orbital

Table 4

PIXEL intermolecular interaction energies (kcal mol⁻¹) between molecular pairs related by a symmetry operation in the crystal structure.

Centroid-to-centroid distance of molecular pair	E _{coul}	Epol	Edisp	E _{rep}	E _{tot}	Symmetry	Important interactions	Label
7.175	-11.4	-4.4	-6.7	10.1	-12.4	−x+2, −y, −z	N1-H1N···02=C9 C2-H2···02=C9 C9=02···02=C9 C2-H2···01-C9	Dimer-I
5.615 8.349 7.793	-5.0 -3.1 -1.9	$-1.8 \\ -1.0 \\ -0.8$	-9.8 -5.7 -7.0	6.1 2.8 3.6	-10.5 -7.0 -6.1	-x+2, -y+1, -z -x+1, -y+1, -z -x+2, y+1/2, -z+1/2	C8…C9 C11—H11A…C9 C6—H6…O5	Dimer-II Dimer-III Dimer-IV

Table 5

Computed electrostatic potential maxima (Vs,max) and minima (Vs,min) on 0.001 a.u. molecular surface for the monomer.

Monomer			
Atom	V _{s,max}	Atom	V _{s,min}
H6	28.12	H12B	15.28
H13B	26.50	02	-46.2594
H1N	23.16	01	-28.7853
H2	19.78	05	-17.3296

with a 98% contribution. Furthermore, the calculated oscillator strengths are 0.696 for this charge transfer. The next absorption occurs at excitation energies of 188 and 177 nm with much lower oscillator strengths of 0.115 and 0.123, respectively, compared to the 301 nm excitation (Table S3, SI). Thus, in the title molecule the intense absorbance that occurs at 301 nm is mainly due to ligand-to-ligand charge transfer (LLCT).



Fig. 5. Molecular topography analysis obtained from AIM analysis for (a) dimer-I and (b) dimer-II. Bond critical points (BCP) are denoted by red dots. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 6

he intermolecular acceptor-donor interactions (E(i) - E(j)) and second order perturbation energies ($E^{(2)}$) (in kcal mol⁻¹) for Dimer-I and Dimer - II. The symbol ([§]) denotes atom-numbering of the second monomer in the dimer.

Donor (i)	Acceptor (j)	E ⁽²⁾	E(i) - E(j)	F(i,j)	Donor (i)	Acceptor (j)	E ⁽²⁾	E(i) - E(j)	F(i,j)
Dimer-I					Dimer-II				
σ(1)02-C9	RY*H1N ^{\$}	0.77	2.33	0.038	σ (2)02–C9	σ*(2)03 ^{\$} -C10 ^{\$}	0.63	0.48	0.017
LP(1)O1	σ* C2\$-H2\$	1.23	1.26	0.035	σ (2)C7–C8	σ*(2)O2 ^{\$} -C9 ^{\$}	1.39	0.37	0.020
LP(1)O2	σ* N1 ^{\$} -H1N ^{\$}	8.49	1.32	0.095	LP (1)01	σ*(1)C6 ^{\$} -H6 ^{\$}	0.72	1.23	0.027
LP(2)O2	σ* C2 ^{\$} -H2 ^{\$}	0.82	0.94	0.026	LP (2)01	σ*(2)C7 ^{\$} -C8 ^{\$}	0.96	0.42	0.019
σ(1)02 ^{\$} -C9 ^{\$}	RY*(1)H1N	0.77	2.33	0.038	σ (2)02 ^{\$} -C9 ^{\$}	σ*(2) 03-C10	0.65	0.48	0.017
LP(1)O1 ^{\$}	σ*(1) C2-H2	1.24	1.26	0.035	σ(2)C7 ^{\$} -C8 ^{\$}	σ*(2) 01–C9	1.36	0.37	0.020
LP(1)O2 ^{\$}	σ*(1) N1-H1N	8.38	1.32	0.094	LP (1)01 ^{\$}	σ*(1) C6–H6	0.72	1.23	0.027
LP(2)O2 ^{\$}	σ*(1) C2-H2	0.87	0.94	0.026	LP (2)01 ^{\$}	σ*(2)C7–C8	0.97	0.42	0.019

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Fig. 6. Spectra of the title molecule (a) FT-IR (b) FT-Raman.



Fig. 7. (a) The observed and calculated UV-Vis absorption spectra (b) HOMO and LUMO orbitals.

4. Conclusions

The title compound, one of the malonic acid half-ester derivatives, is synthesized and characterized by experimental and theoretical methods. The crystal structure of the 4-methoxy derivative is primarily stabilized by intramolecular N-H-O and O-H···O hydrogen bonds and intermolecular N-H···O, C-H···O interactions along with C-H···C, O···O and C···C contacts. The strengths of the various intermolecular interactions energies are calculated. We found that an invariant molecular dimer generated through intermolecular N-H1N···O2=C9, C2-H2···O2=C9, C9= 02...02=C9 and C1-H1...01-C9 interactions provides the highest contribution to the crystal-packing. Interestingly, the C···C interaction has a much higher contribution in comparison with some of the intermolecular C–H \cdots O interactions. The methoxy substitution on the phenyl ring gives an additional stabilization to the crystal structure as is evident from the involvement of methoxy group in the intermolecular C-H···O interaction. Furthermore, the overall lattice energies of the methoxy and the parent structures suggest that the methoxy structure is stabilized by 4.5 kcal mol⁻¹ higher energy than the parent crystal structure. AIM and NBO analysis show the presence of an intermolecular C…C contact in the dimer.

The experimental and computed IR and Raman spectra show the presence of $N-H\cdots O$ and $O-H\cdots O$ bonding in the crystals. The HOMO-LUMO diagram suggests that a charge transfer process is going on within the molecule.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2016.04.090.

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