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Crystal Structure of *o*-(*p*-N,N-dimethylaminobenzoyl)benzoic Acid

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Ortho-benzoylbenzoic acids provide the key intermediates in the synthesis of a wide variety of phthalein[1,2] and fluoran dyes.[3] The structural chemistry of these acids has drawn much interest because of their properties of the ring-chain tautomerism in solution[4] and the polymorphism in the crystals state.[5] Lalancette et al. reported that the simplest acid, *o*-benzoylbenzoic acid (BBA) crystallizes in the two polymorphic, hydrous and anhydrous, forms.[5] In the anhydrous form of BBA, the molecules form dimers through the intermolecular hydrogen bondings between the carboxylic groups of adjacent molecules whereas the keto oxygen is not involved in the hydrogen bonding. This hydrogen bonding pattern is characterized by the IR bands at 1693 and 1676 cm^{-1}, which are assigned to the C=O stretching vibrations of the dimeric acid and the free ketone moieties respectively. In the course of our study on a new class of phthalein dyes we prepared *o*-(*p*-N,N-dimethylaminobezoyl)benzoic acid (DMABBA). Interestingly, the carboxylic acid and ketone C=O bands are observed at 1732 and 1627 cm^{-1} respectively. These frequencies are deviated to a higher and a lower frequency by 39 and 49 cm^{-1}, respectively, from those of BBA. We have undertaken the X-ray analysis of DMABBA in order to clarify the structural features causing the IR frequency changes.

N,N-Dimethylaniline was allowed to react with phthalic anhydride in the presence of anhydrous aluminum chloride in carbon disulfide. The reaction mixture was separated by decantation from the solvent and decomposed with diluted sulfuric acid. The insoluble solid was filtered off, and the filtrate was neutralized to pH 2-3 with 10% sodium hydroxide aqueous solution. The crude *o*-(*p*-N,N-dimethylaminobenzoyl)benzoic acid was obtained as greenish yellow solid and recrystallized from aqueous ethanol (mp 201.5 °C).

A prism with approximate dimensions of 0.36 mm x 0.29 mm x 0.18 mm was mounted on a glass rod. The detailed measurement conditions and crystal data are listed in Table 1. The neutral atomic scattering factors were taken from Cromer and Waber.[7] Anomalous dispersion effects were included in Fcalc[8]: the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[9] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[10] All calculations were performed using the program teXsan crystallographic software package of molecular Structure Corporation.[11]

The final atomic parameters are listed in Table 2. The molecular structure is shown in Fig. 1, together with the atomic labeling scheme. Selected bond distances, bond angles and torsion angles are listed in Table 3.

As shown in Fig. 2, the carboxylic acid OH group of a DMABBA molecule is intermolecularly hydrogen bonded to the ketone oxygen of an adjacent molecule and forms catemeric chains along the *a* axis. [O1...O3^{i} 2.707(4) Å, O1-H...O3^{i} 166(5)°, symmetry code (i): 1/2+x, 3/2-y, 1 -z] The carboxylic acid C=O group does not participate in either inter- or intramolecular hydrogen bonding. This hydrogen bonding pattern differs distinctly from that of BBA and other BBA derivatives[12], where the carboxylic acid groups form centrosymmetric dimer through intermolecular hydrogen bondings and the ketone C=O group is free from such interactions. Differences in the intermolecular hydrogen bonding patterns are reflected in both the molecular geometry and the conformation. Thus the C=O bond of the carboxyl and the ketone groups are shorter and longer, respectively, for DMABBA than those for BBA. [O2-C1 is 1.179(5) Å for DMABBA and 1.223(3) Å for BBA; O3-C8 is 1.229(5) Å for DMABBA and 1.208(3) Å for BBA] These differences in the C=O bond lengths correspond to differences in the bond order and influence the IR frequencies.

The carbonyl group in the DMABBA molecule is coplanar with the *p*-N,N-dimethylaminobenzene ring [O3-C8-C9-C10 -0.5(5)°] but this palne is twisted by 60° from the benzoic acid ring [O3-C8-C7-C2 62.1(5)°]. The carboxylic acid plane is tilted by about 30° with respect to the adjacent ring [O1-C1-C2-C3 32.8(5)°] for DMABBA, whereas that for BBA is almost coplanar. The two C-C bonds adjacent to the keto carbonyl group display significantly different bond lengths [C8-C9 1.450(4) Å and C7-C8 1.509(4) Å]. This result suggests that the π-conjugation is possible for the ketone C=O and the *p*-N,N-dimethylaminobenzene ring, but is disrupted for the ketone C=O and the benzoic acid ring. Furthermore, the C10-C11 and the C13-C14 bonds [1.365(5) and 1.367(5) Å respectively] are significantly shorter than the C9-C10, the C11-C12, the C12-C13 and the C14-C9 bonds [1.403(4), 1.406(5), 1.405(4) and 1.393(4) Å

respectively]. This finding indicates that the *p*-N,N-dimethylaminophenyl ring has a quinoid nature because of the π-conjugation.

Another interesting conformational feature is the orientation of the carbonyl C=O group with respect to the keto C=O group in the ortho position. The carboxylic O2 atom points to the ketone C8 atom with a short contact [O2...C8 2.768(6) Å]. This carboxylic group conformation implies that the chain-to-ring tautomerism may occur through the nucleophilic attack of the carboxyl O2 atom to the ketone C8 carbon atom.

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Table 1 Crystal and experimental data

Formula: $C_{16}H_{15}NO_3$
Formula weight: 269.30
Crystal system: orthorhombic
Space group: $P2_12_12_1$ Z= 4
Radiation: Mo Kα
T = 296 K
a= 8.643(1) Å
b= 12.1464(7) Å
c= 13.2515(2) Å
V= 1391.1(2) $Å^3$
$Dcalc$= 1.286 g/cm^3
R=0.0431, R_w=0.0570
No. of reflections used= 1157 ($F^2>3.0\sigma(F^2)$)
No. of parameters: 236
Goodness-of-fit: 1.234
$(\Delta/\sigma)_{max}$: 0.0025
$(\Delta/\rho)_{max}$: 0.29 $eÅ^{-3}$
$(\Delta/\rho)_{min}$: -0.21 $eÅ^{-3}$
Measurement: Quantum CCD/Rigaku AFC7
Program system: TEXSAN
Structure determination: direct method
Refinement: full-matrix least-squares

Table 2 Fractional coordinates of non-hydrogen atoms and equivalent Isotropic displacements ($Å^2$).

Atom	x	y	z	B_{eq}
O1	1.2493(5)	0.7796(2)	0.3850(2)	6.97(8)
O2	1.1949(6)	0.6442(3)	0.4869(2)	9.7(1)
O3	0.8523(5)	0.6218(2)	0.4445(2)	7.54(8)
N	0.9409(4)	0.1693(2)	0.6808(2)	5.38(7)
C1	1.1927(5)	0.6833(3)	0.4055(3)	5.26(9)
C2	1.1356(4)	0.6220(3)	0.3139(2)	3.86(6)
C3	1.2051(5)	0.6333(3)	0.2204(2)	4.53(7)
C4	1.1624(5)	0.5671(3)	0.1413(2)	4.98(8)
C5	1.0507(4)	0.4891(3)	0.1535(2)	4.66(8)
C6	0.9774(4)	0.4761(3)	0.2459(3)	4.25(7)
C7	1.0185(4)	0.5438(3)	0.3262(2)	3.64(6)
C8	0.9278(4)	0.5392(3)	0.4234(2)	4.46(7)
C9	0.9301(4)	0.4415(3)	0.4861(2)	3.81(6)
C10	0.8439(4)	0.4391(3)	0.5758(2)	4.57(8)
C11	0.8470(4)	0.3508(3)	0.6395(2)	4.63(8)
C12	0.9357(4)	0.2571(3)	0.6161(2)	4.13(7)
C13	1.0195(4)	0.2582(3)	0.5254(2)	4.39(7)
C14	1.0175(4)	0.3484(3)	0.4635(2)	4.08(7)
C15	0.8732(8)	0.1793(6)	0.7808(4)	7.0(1)
C16	1.0214(7)	0.0703(4)	0.6540(4)	7.2(1)

$B_{eq}=(8/3)\pi^2[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos\gamma+2U_{13}aa^*cc^*\cos\beta+2U_{23}bb^*cc^*\cos\alpha]$.

Table 3 Selected bond lengths (Å), bond angles (°) and torsion angles (°)

Atom	Atom	Distance	Atom	Atom	Distance
O1	C1	1.296(5)	C5	C6	1.388(5)
O2	C1	1.179(5)	C6	C7	1.391(4)
O3	C8	1.229(5)	C7	C8	1.509(4)
N	C12	1.369(4)	C8	C9	1.450(4)
N	C15	1.454(6)	C9	C10	1.403(4)
N	C16	1.433(6)	C9	C14	1.393(4)
C1	C2	1.506(5)	C10	C11	1.365(5)
C2	C3	1.384(4)	C11	C12	1.406(5)
C2	C7	1.398(4)	C12	C13	1.405(4)
C3	C4	1.373(5)	C13	C14	1.367(5)
C4	C5	1.362(6)			

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O1	C1	O2	123.2(4)	O3	C8	C7	116.1(3)
O1	C1	C2	113.7(3)	O3	C8	C9	123.0(3)
O2	C1	C2	122.9(4)	C7	C8	C9	120.8(3)
C1	C2	C3	122.0(3)	C8	C9	C10	119.7(3)
C1	C2	C7	118.7(3)	C8	C9	C14	123.3(3)
C3	C2	C7	119.1(3)	C10	C9	C14	117.0(3)
C2	C3	C4	120.6(3)	C9	C10	C11	122.0(3)
C3	C4	C5	120.5(3)	C10	C11	C12	120.7(3)
C4	C5	C6	120.5(3)	N	C12	C11	120.7(3)
C5	C6	C7	119.4(3)	N	C12	C13	121.7(3)
C2	C7	C6	119.9(3)	C11	C12	C13	117.5(3)
C2	C7	C8	120.0(3)	C12	C13	C14	120.9(3)
C6	C7	C8	120.0(3)	C9	C14	C13	121.9(3)

Atom	Atom	Atom	Atom	Angle
O1	C1	C2	C3	32.8(5)
O1	C1	C2	C7	-153.3(3)
O2	C1	C2	C3	-142.5(5)
O2	C1	C2	C7	31.4(6)
O3	C8	C7	C2	62.1(5)
O3	C8	C7	C6	-112.7(4)
O3	C8	C9	C10	-0.5(5)
O3	C8	C9	C14	-178.8(4)
C1	C2	C7	C8	13.4(5)
C2	C7	C8	C9	-118.7(4)
C3	C2	C7	C8	-172.5(3)
C6	C7	C8	C9	66.4(4)
C7	C8	C9	C10	-179.5(3)
C7	C8	C9	C14	2.1(5)
C11	C12	N	C15	-9.2(6)
C11	C12	N	C16	175.2(4)
C13	C12	N	C15	169.9(4)
C13	C12	N	C16	-5.7(6)

Estimated standard deviations in the least significant figure are given in parentheses.

Figure Captions

Fig. 1 Molecular structure with the numbering of the atoms
Thermal ellipsoids of the non-hydrogen atoms scaled to enclose 50 % probability.
The spheres of the hydrogen atoms are drawn in an arbitrary scale.

Fig. 2 Molecular packing and intermolecular hydrogen bondings

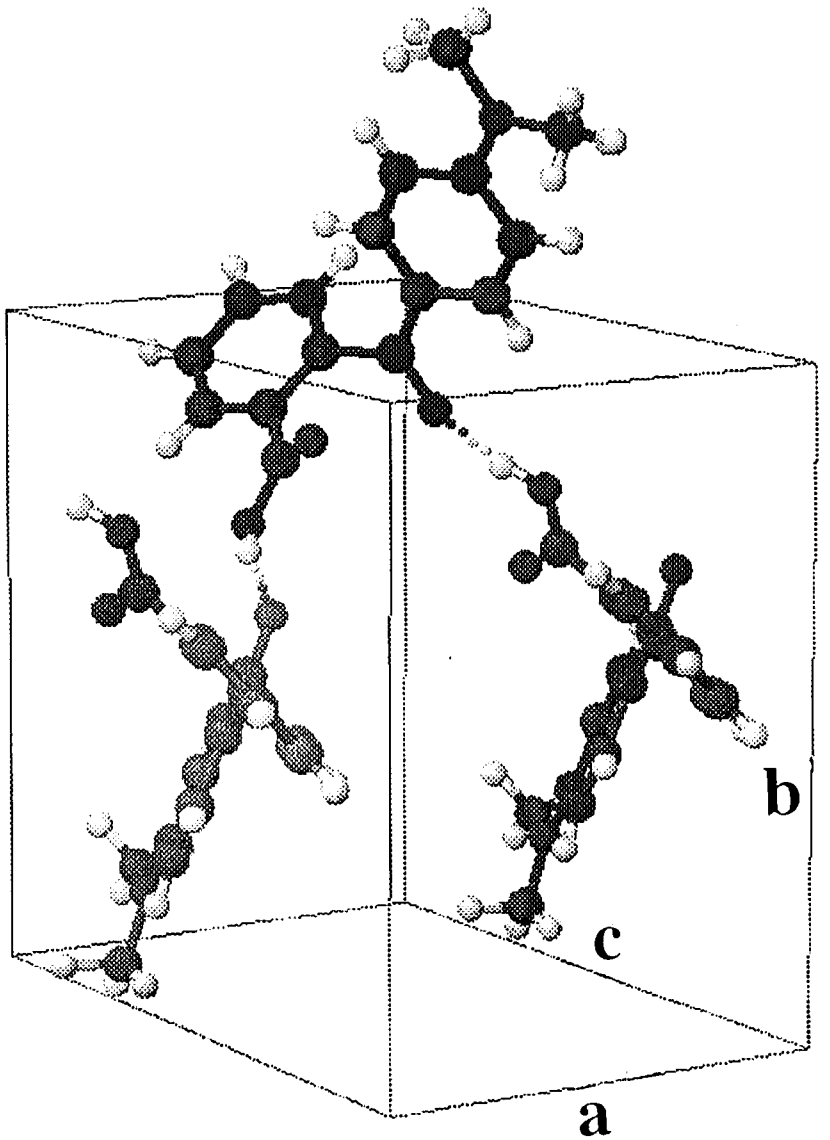


Fig. 2

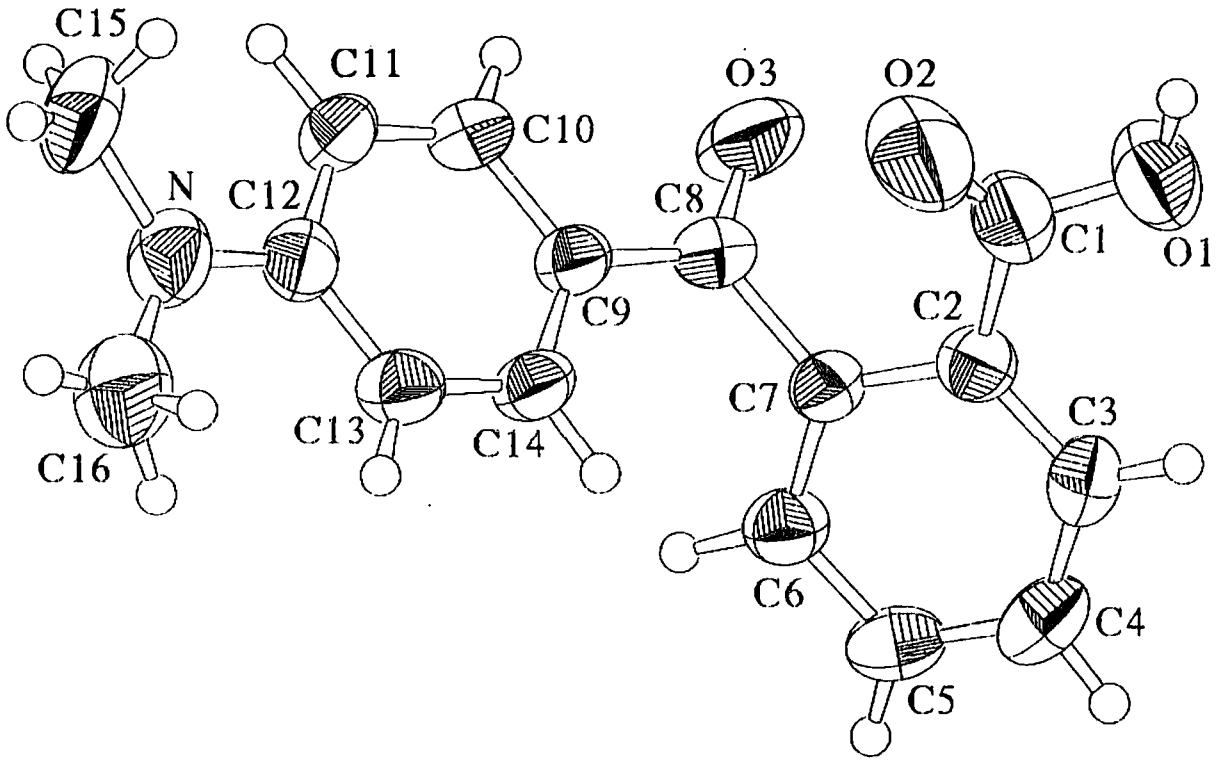


Fig. 1

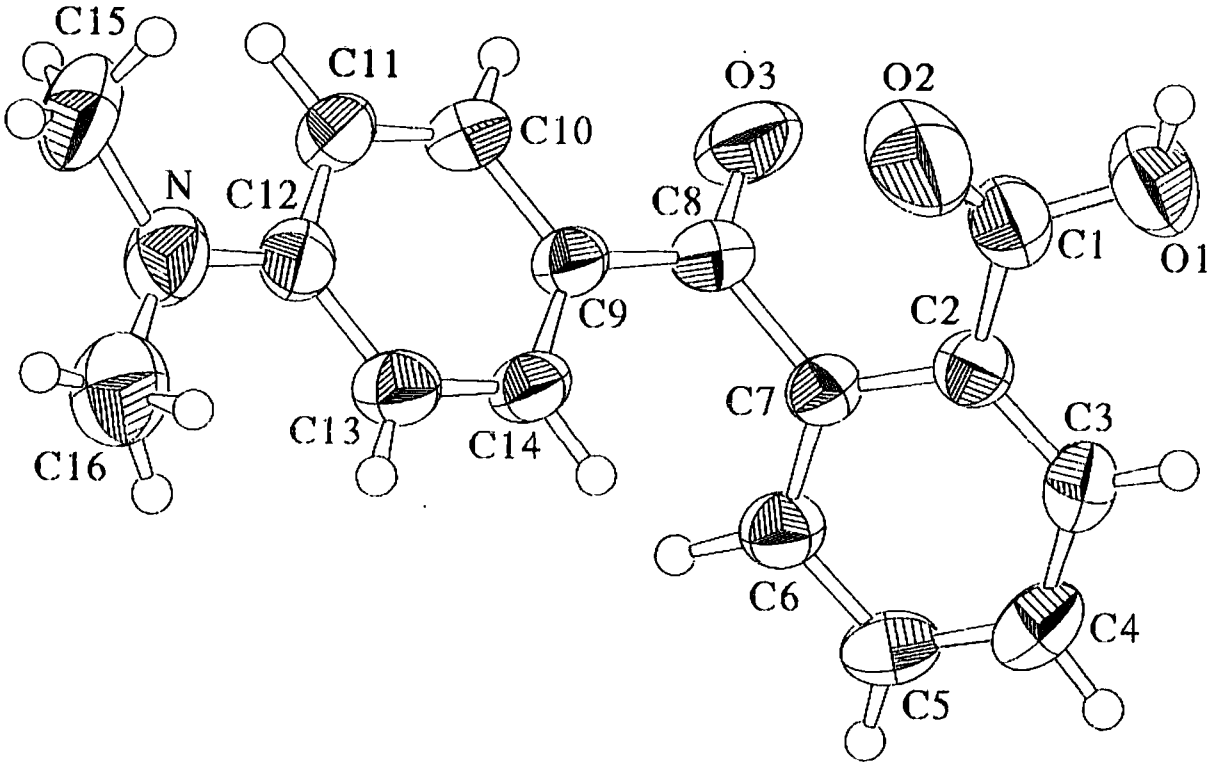


Fig. 1

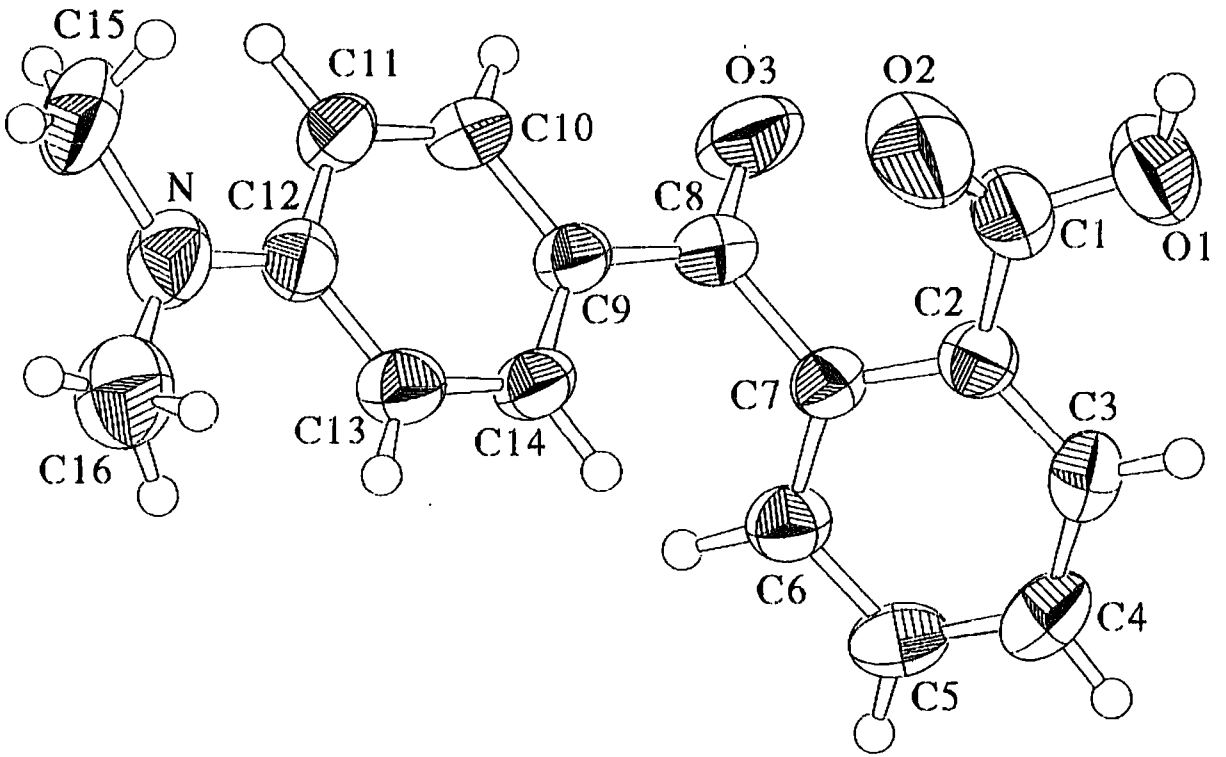


Fig. 1

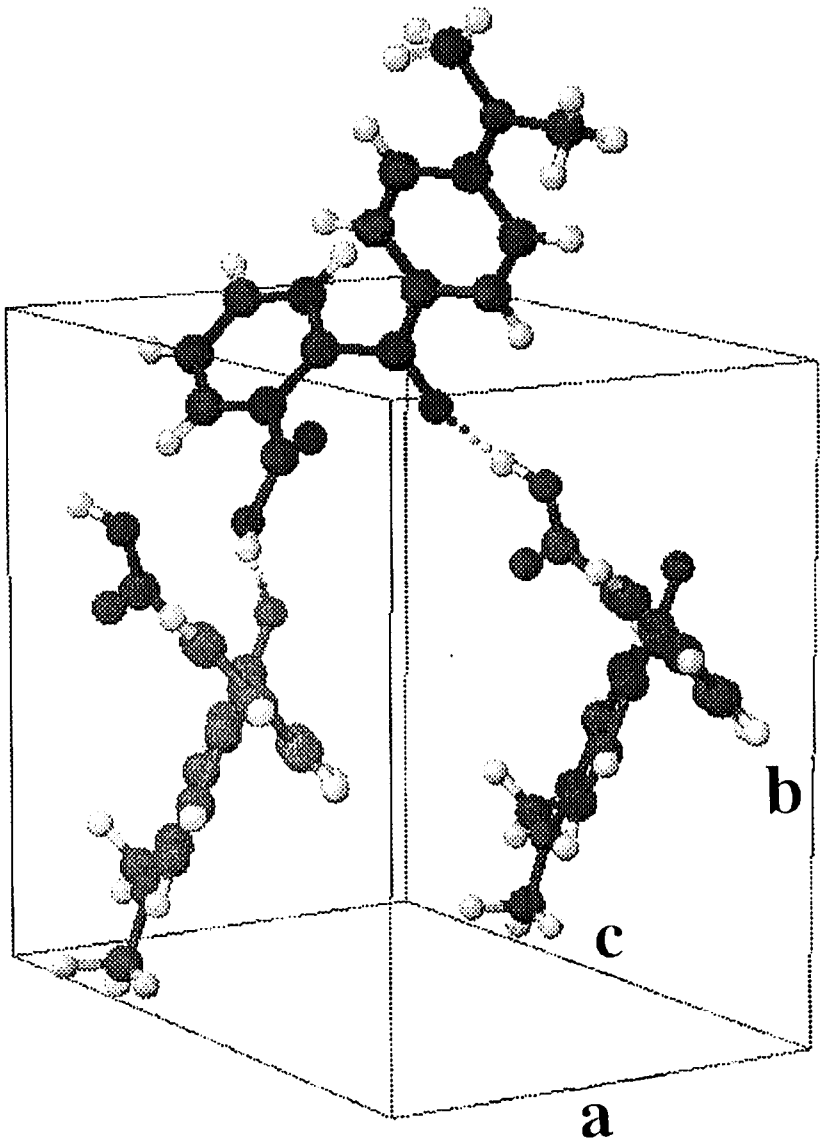
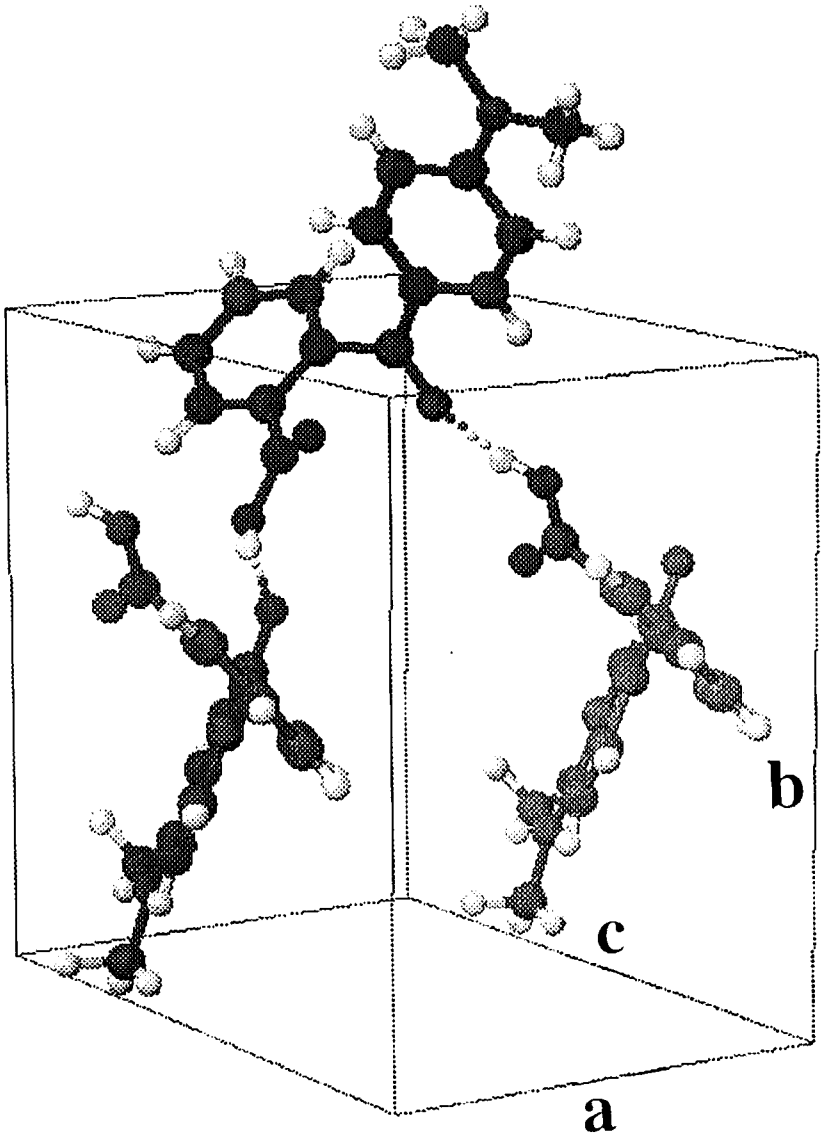


Fig. 2



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