

Structural Studies of Curcuminoids IV.* Crystal Structure of 1,7-Diphenyl-4-butyl-1,6-heptadien-3,5-dione (DPBHDD)**

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The crystal and molecular structure of 1,7-diphenyl-4-butyl-1,6-heptadien-3,5-dione has been determined at 121 K by X-ray crystallographic methods using 2357 reflections observed by counter methods. The crystals are orthorhombic, space group $Pca2_1$ with unit cell dimensions $a=11.675(2)$ Å, $b=21.399(3)$ Å and $c=7.378(1)$. The structure was refined to a conventional R -factor of 0.040. Estimated standard deviations in interatomic distances are $3 \cdot 10^{-3}$ Å and in angles 0.2° when hydrogen atoms are not involved. The enol ring is found to be asymmetric.

The present work is a part of a series of X-ray crystallographic investigations in order to study

* Part III, see Ref. 3.

** For simplicity this name is used even if the title compound does exist in the enol form in the crystals.

the conformational properties of curcuminoid molecules in general and the geometry of the inherent enol-ring in particular.¹⁻³ The molecules also present an opportunity to study the possible influence of the crystal environment on the aromatic character of the enol-ring as well as the packing interactions of aromatic moieties in general.

EXPERIMENTAL

Synthetic and crystallization procedure⁴ gave a sample of strongly yellow coloured needleformed crystals with melting point 135-40 °C. One such crystal of dimensions 0.6×0.4×0.3 mm was used for the X-ray crystallographic experiments. The experimental data is given in the table below. Cell parameters were determined by a least

EXPERIMENTAL CONDITIONS

Instrument
Radiation

Crystal dimension (mm)
Scanning mode
Scan speed ($^\circ\text{min}^{-1}$)
Scan range ($^\circ$)
Background counts

Temperature (K)
 2θ range ($^\circ$)

Number of reflections measured
Number of unique reflections with $I > 2.5(I)$
Number of standard reflections
Number of reflections between standard reflections

SYNTEX P1
Graphite Crystal
Monochromated $\text{MoK}\alpha$
 $\lambda=0.71069$ Å
0.6×0.4×0.3
 $\theta/2\theta$
2.0-4.0
 $2\theta_{a1}-0.9$ to $2\theta_{a2}+1.1$
For 0.35 of scan time
at scan limits
121
2.5-60.0
2476
2357
3
57

squares fit to the diffractometer settings for 15 general reflections. Standard deviations in the measured intensities were calculated as $\delta(I) = |C_T + (0.02C_N)^2|^{1/2}$ where C_T is the total number of counts and C_N is the scan count minus the background count. The intensity data were cor-

rected for Lorentz and polarization effects. The variation of the test reflections were less than 2% and no correction was made on this basis. Scattering factors used were those of Doyle and Turner⁵ for oxygen and carbon, and of Stewart, Davidson and Simpson⁶ for hydrogen atoms.

Table 1. Fractional atomic coordinates for DPBHDD. Estimated standard deviations in parentheses.

ATOM	X	Y	Z
O1	.6801(1)	.3088(0)	.4987(9)
O2	.6859(1)	.1948(0)	.4899(9)
C1	.9569(2)	.6078(1)	.5452(10)
C2	.9944(2)	.5587(1)	.5981(10)
C3	.9508(1)	.4988(1)	.5950(9)
C4	.8466(1)	.4859(0)	.5066(10)
C5	.7890(2)	.5552(1)	.4259(9)
C6	.8559(2)	.5955(1)	.4265(10)
C7	.7970(1)	.4229(0)	.4988(10)
C8	.8444(1)	.5707(1)	.5691(10)
C9	.7861(1)	.5095(0)	.5472(10)
C10	.8483(1)	.2528(1)	.5745(10)
C11	.7923(2)	.1961(1)	.5597(9)
C12	.8490(1)	.1551(1)	.5500(10)
C13	.8028(1)	.0886(0)	.4778(10)
C14	.8515(1)	.0206(0)	.4788(10)
C15	.7925(1)	-.0277(1)	.5918(9)
C16	.8557(2)	-.0881(1)	.5882(10)
C17	.9583(2)	-.1019(1)	.4756(10)
C18	.9973(2)	-.0547(1)	.5628(10)
C19	.9557(1)	.0058(1)	.5649(9)
C20	.9745(1)	.2563(1)	.6552(10)
C21	1.0572(1)	.2729(1)	.4847(10)
C22	1.0798(2)	.2203(1)	.5525(10)
C23	1.1757(2)	.2568(1)	.2211(10)
H1	.967(1)	.652(1)	.516(3)
H2	1.062(2)	.570(1)	.661(3)
H3	.992(1)	.468(0)	.657(3)
H4	.745(2)	.527(0)	.558(3)
H5	.794(1)	.631(0)	.562(4)
H6	.726(1)	.449(0)	.459(3)
H7	.946(2)	.569(1)	.654(4)
H12	.927(2)	.155(1)	.607(3)
H13	.750(1)	.090(0)	.424(3)
H15	.722(2)	-.019(0)	.535(3)
H16	.792(1)	-.121(1)	.528(3)
H17	.969(2)	-.145(1)	.471(4)
H18	1.068(2)	-.068(1)	.622(4)
H19	.997(2)	.058(1)	.626(3)
H201	.993(2)	.220(1)	.687(4)
H202	.976(2)	.287(1)	.752(3)
H211	1.152(2)	.284(1)	.540(3)
H212	1.053(2)	.308(1)	.444(4)
H221	1.009(2)	.245(1)	.279(4)
H222	1.101(2)	.176(1)	.420(4)
H231	1.192(2)	.206(1)	.152(4)
H232	1.251(2)	.249(0)	.294(4)
H233	1.158(2)	.274(1)	.153(3)
HO	.666(0)	.248(0)	.489(0)

CRYSTAL DATA

1,7-diphenyl-4-butyl-1,6-heptadiene-3,5-dione.
 $C_{23}O_2H_{24}$, orthorhombic, $a=11.676(2)$ Å,
 $b=21.399(3)$ Å, $c=7.378(1)$ Å $V=1843$ Å³,
 $M=333.23$, $Z=4$, $F(000)=712$, space group
 $Pca2_1$ M.p. 135–40 °C $D_o=1.201$ g cm⁻¹

STRUCTURE DETERMINATION

The structure was solved by direct methods using the program assembly MULTAN.⁷ Successive Fourier syntheses indicated the positions of all the non hydrogen atoms and the hydrogen atoms, except that connected to the enol ring, were introduced from stereochemical considerations. All positional parameters, anisotropic temperature factors for the heavy atoms and isotropic temperature factors for the hydrogen atoms were refined by least squares methods. At these stages a difference map served to locate the hydrogen atom belonging to the enol-ring system and the structure further refined to a conventional R-factor of 0.040 and a goodness of fit $S=(\sum w\Delta^2/m-n)^{1/2}=2.0$.

The final coordinates are given in Table 1. Temperature factors as well as tables of observed and calculated structure factors are available from the authors.

DESCRIPTION AND DISCUSSION

A drawing of the DPBHDD molecule and the numbering of the atoms are given in Fig. 1. Bond

lengths, angles and some torsional angles are given in Table 2. In the present structure the enol-ring is clearly not symmetric, the two C–O distances as well as the distances C9–C10 and C10–C11 being significantly different. Accordingly the hydrogen atom HO is found to be closer to the oxygen atom (O2) that have the longest C–O bond, the O2–H distance being 1.16 Å as compared to the O1–H distance of 1.31 Å. (e.s.d. of the O–H bonds are 0.04 Å). The geometry of the enol-ring, including the position of the hydrogen atom as found by the least squares refinements, is depicted in Fig. 2 which also indicates the electron density in the area between the two oxygen atoms as found by a difference synthesis in the enol-ring plane. The temperature factor (B) for the HO-atom is 10.0 as compared to the temperature factors for the rest of the hydrogen atoms varying between 1.9 and 4.9.

The present results concerning the enol-ring are different from those found in DPHDD³ but in accordance with the crystal structure of pentane-2,4-dione.⁸ In all these three crystal structures the enol-ring is undisturbed by intermolecular hydrogen bonds. In the structure of pentane-2,4-dione also the bonds extending from the enol-ring appear to be included in the asymmetry, whereas this has not been found in any of the curcuminoid structures. In fact the molecular structure of DPBHDD is remarkably symmetric on each side of the enol-ring, as reflected by bond lengths, angles and conformation.

None of the atoms in the enol-ring, the hydrogen atom being included, deviates signifi-

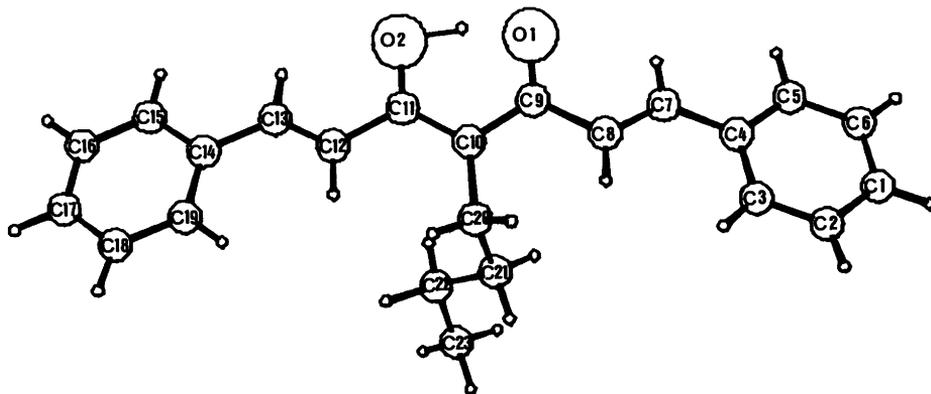


Fig. 1. Drawing of the DPBHDD molecule with the numbering of the atoms.

Table 2. Bond lengths, angles and some torsional angles as found in the DPBHDD molecule. Estimated standard deviations in parentheses. The C-H distances is found to vary between 1.09 and 0.90 Å with a mean value of 0.98 Å, and estimated standard deviation of 0.03–0.04 Å.

DISTANCE	(Å)	DISTANCE	(Å)
C1 - C2	1.388(5)	C2 - C3	1.390(5)
C3 - C4	1.408(5)	C4 - C5	1.392(5)
C5 - C6	1.395(5)	C6 - C1	1.384(5)
C4 - C7	1.468(5)	C7 - C8	1.356(5)
C8 - C9	1.476(5)	C9 - O1	1.278(5)
C9 - C10	1.454(5)	C10 - C11	1.405(5)
C11 - O2	1.348(5)	C11 - C12	1.466(5)
C12 - C13	1.358(5)	C13 - C14	1.462(5)
C14 - C15	1.398(5)	C15 - C16	1.388(5)
C16 - C17	1.386(4)	C17 - C18	1.388(5)
C18 - C19	1.394(5)	C19 - C14	1.409(5)
C10 - C20	1.509(5)	C20 - C21	1.536(4)
C21 - C22	1.545(5)	C22 - C23	1.522(4)
ANGLE	(°)	ANGLE	(°)
C1 - C2 - C3	120.6(2)	C2 - C3 - C4	120.6(2)
C3 - C4 - C5	118.2(2)	C3 - C4 - C7	122.6(2)
C7 - C4 - C5	119.1(2)	C4 - C5 - C6	120.9(2)
C5 - C6 - C1	120.1(2)	C6 - C1 - C2	119.6(2)
C4 - C7 - C8	126.8(2)	C7 - C8 - C9	121.9(2)
C8 - C9 - O1	117.9(2)	C8 - C9 - C10	120.5(2)
O1 - C9 - C10	124.6(2)	C9 - C10 - C20	119.4(2)
C20 - C10 - C11	122.9(2)	C10 - C20 - C21	114.7(2)
C20 - C21 - C22	114.1(2)	C21 - C22 - C23	111.5(2)
C9 - C10 - C11	117.8(2)	C10 - C11 - O2	124.2(2)
C10 - C11 - C12	125.4(2)	O2 - C11 - C12	115.4(2)
C11 - C12 - C13	122.0(2)	C12 - C13 - C14	126.8(2)
C13 - C14 - C15	119.1(2)	C13 - C14 - C19	125.1(2)
C14 - C15 - C16	124.2(2)	C15 - C16 - C17	120.3(2)
C16 - C17 - C18	119.3(2)	C19 - C14 - C15	117.8(2)
C18 - C19 - C14	120.6(2)	C17 - C18 - C19	120.8(2)
DIHEDRAL ANGLE	(°)	DIHEDRAL ANGLE	(°)
C5 - C4 - C7 - C8	179.4(2)	C7 - C8 - C9 - C10	161.4(2)
C4 - C7 - C8 - C9	-177.9(2)	C5 - C4 - C7 - C8	-7(4)
C7 - C8 - C9 - C10	161.4(2)	C7 - C8 - C9 - O1	-16.8(4)
C5 - C4 - C7 - C8	-7(4)	O1 - C9 - C10 - C11	2.4(3)
C7 - C8 - C9 - O1	-16.8(4)	O1 - C9 - C10 - C20	-178.9(3)
O1 - C9 - C10 - C11	2.4(3)	C10 - C11 - C12 - C13	-164.5(2)
O1 - C9 - C10 - C20	-178.9(3)	C9 - C10 - C11 - O2	-2.4(4)
C10 - C11 - C12 - C13	-164.5(2)	O2 - C11 - C12 - C13	15.6(4)
C9 - C10 - C11 - O2	-2.4(4)	C11 - C12 - C13 - C14	179.6(7)
O2 - C11 - C12 - C13	15.6(4)	C12 - C13 - C14 - C15	-178.2(3)
C11 - C12 - C13 - C14	179.6(7)	C12 - C13 - C14 - C19	2.3(4)
C12 - C13 - C14 - C15	-178.2(3)	C9 - C10 - C20 - C21	-77.9(3)
C12 - C13 - C14 - C19	2.3(4)	C11 - C10 - C20 - C21	100.9(3)
C9 - C10 - C20 - C21	-77.9(3)	C10 - C20 - C21 - C22	-75.7(3)
C11 - C10 - C20 - C21	100.9(3)	C20 - C21 - C22 - C23	-175.1(2)
C10 - C20 - C21 - C22	-75.7(3)		
C20 - C21 - C22 - C23	-175.1(2)		

cantly from a least squares plane through the five non-hydrogen atoms, and this plane makes an angle of 18° with the two phenyl rings. As judged from the torsional angles alone, the molecule

appears to be fairly planar, but in fact it is bent in such a way as to induce an angle of about 22° between the two phenyl ring planes. The packing of the molecules in the crystal is illustrated in Fig.

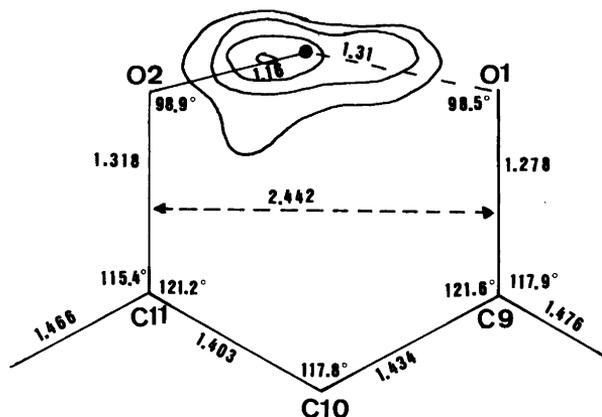


Fig. 2. The geometry of the enol-ring in the DPBHDD molecule. The electron density as found from a difference synthesis in the enol-ring plane is also given. The lines are drawn through electron densities of 0.10, 0.20, 0.30 and 0.40 electrons \AA^{-3} .

3, where it may be seen that there are no intermolecular hydrogen bonds and as in the structure of DPHDD, the molecules are kept together by interactions between the aromatic moieties. In the present structure the closest contacts are found between the enol-rings in neighbour molecules, and the crystal structure is characterized by a stacking of glide plane related molecules along the direction of the *c*-axis. The angle between the enol ring planes in these stacks

is 33.4° and the shortest contacts are 3.326 \AA (O2-C10') and 3.333 \AA (O2-C11'). The respective distances from O1 are 3.367 \AA (O1-C10') and 3.356 \AA (O1-C9').

The interaction between the phenyl rings appears to be less than that described for the enol rings. Thus the shortest distances between these moieties are 3.783 \AA (C5-C3') (HC5-C3': 2.81 \AA , HC5-C4': 2.84 \AA) and 3.631 \AA (C15-C14') (HC15-C14': 2.88 \AA , HC15-C19': 2.92 \AA). It is

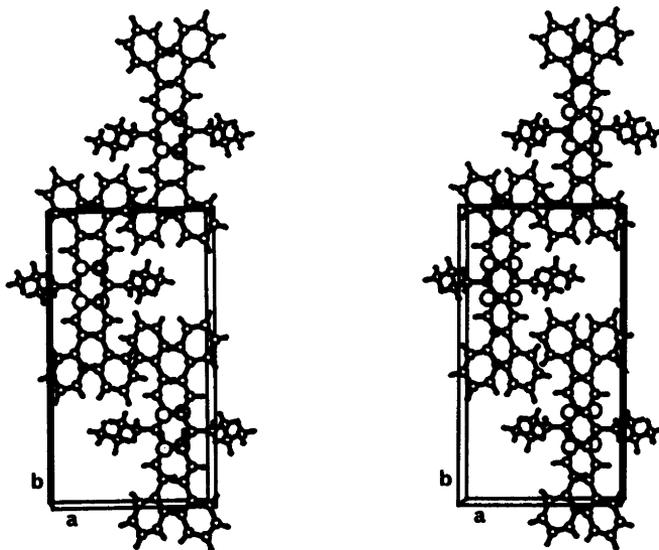


Fig. 3. Packing of the DPBHDD molecules in the crystal as seen along the *c*-axis.

interesting to notice that the interactions are almost exactly the same between the two pairs of phenyl rings and that the two bonds C3–C4 and C14–C19 which are involved in the phenyl-phenyl interaction also are the longest bonds in the respective phenyl rings. The angles between the planes of the interacting phenyl rings are in both pairs close to 60°.

Also the shortest contacts between neighbouring molecular stacks seem to involve the oxygen atoms as 3.361 Å (O1–C1') (O1–H1': 2.63 Å) and 3.492 Å (O2–C17') (O2–HC17': 2.72 Å) and all other contacts being longer than 3.5 Å (3.3 Å for C–H). In all it appears that the asymmetry in the enol-ring is reflected in an asymmetry in the interactions of the respective oxygen atoms with the neighbour molecules.

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