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Structural Studies of Curcuminoids. III. Crystal Structure of 1,7-Diphenyl-1,5-heptadiene-3,5-dione

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The crystal and molecular structure of the curcumin derivative 1,7-diphenyl-1,6-heptadiene-3,5-dione has been determined at 121 K by X-ray crystallographic methods using 1553 reflections observed by counter methods. The crystals are orthorhombic, space group *P*bca with unit cell dimensions $a=36.903(25)$ Å, $b=13.998(8)$ Å and $c=5.686(3)$ Å.

The structure was refined to a conventional *R*-factor of 0.068. Estimated standard deviations are 6×10^{-3} Å and 0.4° in interatomic distances and angles when hydrogen atoms are not involved. The enol-ring is found to be symmetric with complete delocalization of the double bonds.

Previous studies of the structure of the enol-ring in curcuminoids[1,2] indicate that the structure of these pseudoaromatic moieties may be very sensitive to intermolecular interactions such as hydrogen bonding.[2] In order to study this effect further the crystal structure determination of 1,7-diphenyl-1,6-heptadiene-3,5-dione (BPHDD)*, where the possibilites of intermolecular hydrogen bond formation are restricted as far a possible, has been carried out.

EXPERIMENTAL

The synthetic and crystallization procedures[3] resulted in a sample of strongly yellow coloured needle-formed crystals with melting point 425 K. One of these crystals was used for the X-ray crystallographic experiments, details of which are described under experimental conditions. Cell parameters were determined by least squares fit to the diffractometer settings for 15 general reflections. The standard deviation in the measured intensities were calculated as $\sigma(I)=|C_T+(0.02C_N)^2|^{\frac{1}{2}}$ where C_T is the total number of counts and C_N is the scan count minus the background count. The intensity data were corrected for Lorentz and polarization effects. No corrections were made on the basis of test reflection variation which was less than 2 %. Scattering factors were those of Doyle and Turner[4] for oxygen and carbon atoms, and of Stewart, Davidson and Simpson[5] for hydrogen atoms.

EXPERIMENTAL CONDITIONS

Instrument	SYNTEX P$\bar{1}$
Radiation	Graphite Crystal Monochromated Mo*Kα*, $\lambda=0.71069$ Å
Crystal dimensions (mm)	0.4×0.2×0.1
Scanning mode	ω
Scan speed (° min^{-1})	3.0
Scan range (°)	1.5
Background counts	For 0.35 of scan time at scan limits
Temperature (K)	121
2θ range (°)	3.0–50.0
Number of reflections measured	1968

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

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Number of reflections with I>2.5σ(I)	1553
Number of standard reflections	3
Number of reflections between standard reflections	57

CRYSTAL DATA

1,7-Diphenyl-1,6-heptadien-3,5-dione, $C_{19}O_2H_{16}$, orthorhombic, a=36.903(25) Å, b=13.998(8) Å, c=5.686(3) Å, V=2937 Å^3, M=276.19, Z=8, F_{000}=1168, space group *Pbca*.

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

ATOM	X	Y	Z
O1	.3550(0)	.3809(1)	.0561(5)
O2	.4220(0)	.3803(1)	.0119(5)
C1	.1750(1)	.3833(2)	−.3769(7)
C2	.2015(1)	.3419(2)	−.5209(8)
C3	.2372(1)	.3414(2)	−.4499(7)
C4	.2480(1)	.3816(2)	−.2360(6)
C5	.2210(1)	.4226(2)	−.0926(7)
C6	.1851(1)	.4247(2)	−.1655(7)
C7	.2857(1)	.3815(2)	−.1492(7)
C8	.3155(1)	.3566(2)	−.2705(8)
C9	.3520(1)	.3616(2)	−.1671(7)
C10	.3830(1)	.3498(2)	−.3075(7)
C11	.4177(1)	.3620(2)	−.2094(7)
C12	.4505(1)	.3587(2)	−.3582(8)
C13	.4834(1)	.3864(2)	−.2779(7)
C14	.5179(1)	.3875(2)	−.4059(6)
C15	.5482(1)	.4312(2)	−.2983(7)
C16	.5816(1)	.4318(2)	−.4085(7)
C17	.5865(1)	.3860(2)	−.6218(7)
C18	.5566(1)	.3426(2)	−.7320(7)
C19	.5231(1)	.3435(2)	−.6233(7)
H1X	.388(1)	.383(3)	.098(10)
H1	.150(0)	.384(2)	−.438(6)
H2	.193(0)	.311(2)	−.669(6)
H3	.256(0)	.313(2)	−.555(6)
H5	.229(0)	.454(2)	.062(6)
H6	.166(0)	.456(2)	−.055(6)
H7	.289(0)	.407(2)	.015(7)
H8	.314(0)	.337(2)	−.427(7)
H10	.381(0)	.333(2)	−.470(7)
H12	.447(1)	.337(2)	−.523(7)
H13	.484(0)	.410(2)	−.107(6)
H15	.545(0)	.462(2)	−.140(6)
H16	.604(0)	.465(2)	−.319(6)
H17	.611(1)	.385(2)	−.705(7)
H18	.561(1)	.309(2)	−.888(7)
H19	.502(0)	.313(2)	−.707(6)

STRUCTURE DETERMINATION

The structure was solved by direct methods using the program assembly MULTAN.[6] Successive Fourier syntheses indicated the positions of

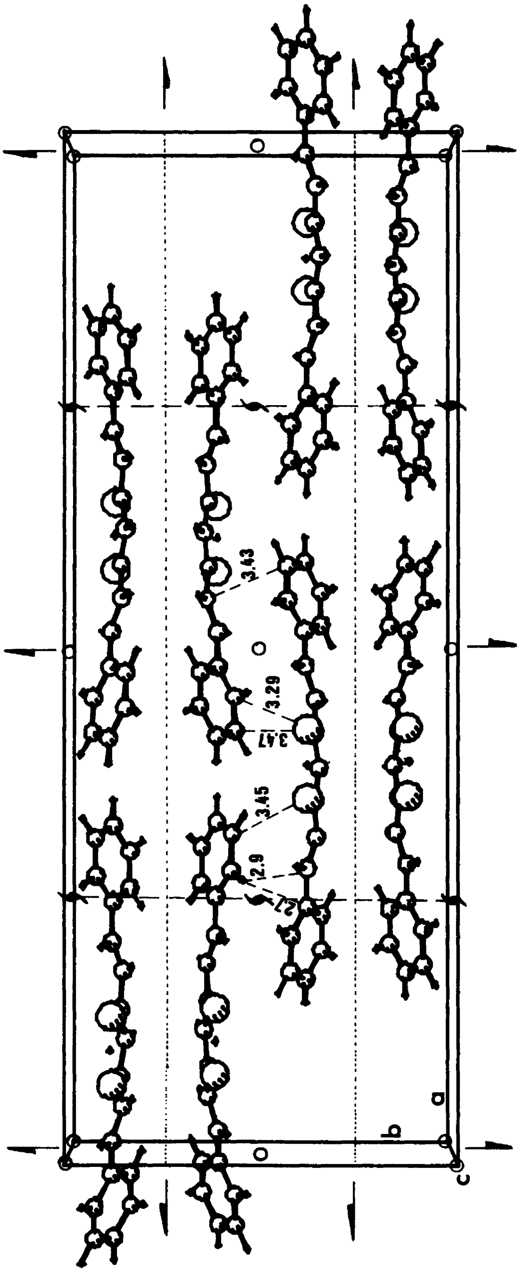

Fig. 1. Molecular packing in the BPHDD crystals as seen down the *c*-axis.

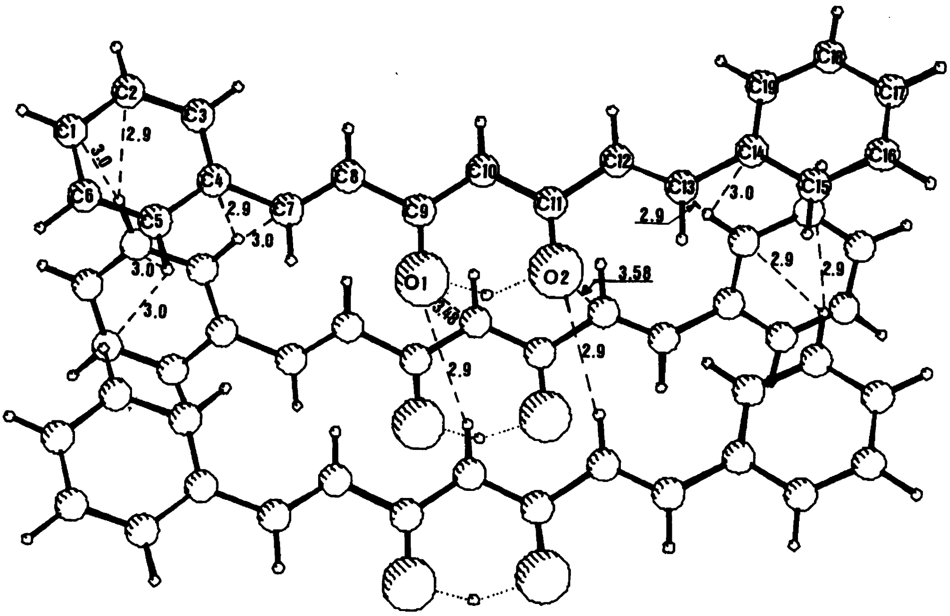

Fig. 2. Stacking of molecules in the BPHDD crystals.

Table 2. Bond lengths and angles in the BPHDD molecules.

DISTANCE	(Å)	DISTANCE	(Å)
C1 – C2	1.401(6)	C2 – C3	1.379(6)
C3 – C4	1.398(5)	C4 – C5	1.410(5)
C5 – C6	1.388(5)	C6 – C1	1.385(6)
C4 – C7	1.478(5)	C7 – C8	1.345(6)
C8 – C9	1.469(6)	C9 – O1	1.302(5)
C9 – C10	1.406(6)	C10 – C11	1.407(6)
C11 – O2	1.294(5)	C11 – C12	1.477(6)
C12 – C13	1.353(6)	C13 – C14	1.466(5)
C14 – C15	1.413(5)	C15 – C16	1.385(6)
C16 – C17	1.383(6)	C17 – C18	1.406(6)
C18 – C19	1.382(6)	C19 – C14	1.395(5)
C – H	1.01(4)		

ANGLE	(°)	ANGLE	(°)
C1 – C2 – C3	120.0(4)	C2 – C3 – C4	121.5(4)
C3 – C4 – C5	117.9(4)	C3 – C4 – C7	123.8(4)
C7 – C4 – C5	118.3(4)	C4 – C5 – C6	120.7(4)
C5 – C6 – C1	120.4(4)	C6 – C1 – C2	119.5(4)
C4 – C7 – C8	127.0(4)	C7 – C8 – C9	122.1(4)
C8 – C9 – O1	118.5(4)	C8 – C9 – C10	120.9(4)
O1 – C9 – C10	120.6(4)	C9 – C10 – C11	120.2(4)
C10 – C11 – O2	121.3(4)	O2 – C11 – C12	117.6(4)
C10 – C11 – C12	121.0(4)	C11 – C12 – C13	122.2(4)
C12 – C13 – C14	127.8(4)	C13 – C14 – C15	118.4(4)
C13 – C14 – C19	123.7(4)	C14 – C15 – C16	120.8(4)
C15 – C16 – C17	120.6(4)	C16 – C17 – C18	119.3(4)
C17 – C18 – C19	119.9(4)	C18 – C19 – C14	121.6(4)
C19 – C14 – C15	117.7(4)		

all the non-hydrogen atoms, and a difference synthesis after least squares refinement of the positions of the non-hydrogen atoms indicated the positions of 15 hydrogen atoms. All positional parameters, anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms were refined in the final least squares calculations giving a conventional R-factor of 0.068 and a goodness of fit $S=(\Sigma w\Delta^2/(m-n))^{\frac{1}{2}}=3.5$.

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

The packing of the molecules in the crystals of the present compound as seen down the c-axis is illustrated in Fig. 1. There are no intermolecular hydrogen bonds in these crystals and the molecular packing is thus governed by van der Waals' interactions. The glide planes in (0,1/4,0) and (0, 3/4, 0) give rise to molecular stacks as illustrated in Figs. 1 and 2 where the shortest intermolecular contacts are also given. The angle between the enol ring planes within these stacks is about 25° whereas the angles between the two pairs of phenyl ring planes are both close to 60°.

The numbering of the atoms is indicated in Fig. 2 whereas the bond lengths and angles are given in Table 2 and the values found to be in good agreement with those found in similar compounds.[1,2] This is also true for the molecular conformation as may be seen from the torsional angles given in Table 3.

Table 3. Some torsional angles in the BPHDD molecules in the crystal state.

DIHEDRAL ANGLE	(°)
C3 - C4 - C7 - C8	10.2(6)
C5 - C4 - C7 - C8	-171.4(4)
C4 - C7 - C8 - C9	178.4(4)
C7 - C8 - C9 - C10	169.8(4)
O1 - C9 - C10 - C11	-2.1(6)
O1 - C9 - C10 - O2	2.5(5)
C10 - C11 - C12 - C13	168.2(4)
C9 - C10 - C11 - O2	2.7(6)
O2 - C11 - C12 - C13	-9.0(6)
C11 - C12 - C13 - C14	-179.5(5)
C12 - C13 - C14 - C15	171.6(4)
C12 - C13 - C14 - C19	-11.9(6)

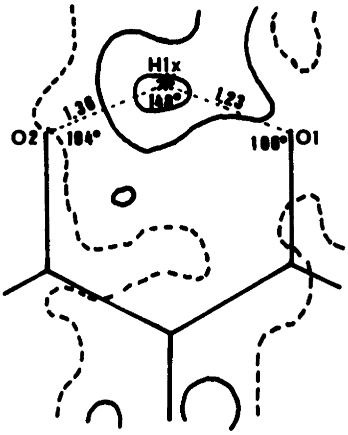

Fig. 3. Difference map in the enol-ring plane in the crystal structure of BPHDD. The solid lines represent the electron densities of 0.25 and 0.50, respectively. The position of the hydrogen atom is indicated.

The only hydrogen bond in the crystal structure of BPHDD is the intramolecular one between the two oxygen atoms in the enol-ring. In the two earlier structures in this series,[1,2] the hydrogen atom was found in one case to be statistically distributed between the two oxygen atoms and in the other to be bonded to one particular oxygen atom. In the present case the model giving the best fit to the data includes one hydrogen atom (H1X) about midway between the two oxygen atoms as illustrated in Fig. 3. However, an anisotropic refinement of the thermal vibrations of the H1X atom indicates a B-factor of about 18.0 in the O1−O2 direction and about 5.0 in the two other directions. Thus the data is also consistent with a statistical distribution of the H1X atom between two closely spaced positions.

The distance between the two oxygen atoms is 2.486 Å in the present structure. This is significantly longer than the respective distance found in the structure of curcumin[1] (2.446 Å) but shorter than that found in the B4HPDD-methanol complex.[2]

The geometry of the enol-ring in the present compound, however, is more like that found in curcumin; both the C−O distances being equal as are the two involved C−C distances.

The atoms C20 and C11 are found to be about 0.01 Å on each side of a least squares plane through the 5 heavy atoms of the enol-ring. The hydrogen atom H1X is situated less than 0.05 Å out of that plane.

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