Structural Studies of Curcuminoids. VIII. Crystal and Molecular Structure of 4-Benzyl-1,7-diphenyl-1,6-heptadiene-3,5-dione

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4-Benzyl-1,7-diphenyl-1,6-heptadiene-3,5-dione, (DPBZHDD) $C_{26}H_{22}O_2$, $M = 366.5$, crystallizes in the monoclinic space group $P2_1/c$ (No. 14). The unit cell dimensions are: $a = 5.888(3)$, $b = 8.664(5)$, $c = 40.110(18)$ Å, $\beta = 92.93(4)°$ and $V = 2043.4(5)$ Å^3. The calculated density is 1.19 g cm^{-3} and $Z = 4$. The X-ray data were collected at room temperature ($T = 293$ K) using Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å); the intensities of 1003 unique reflections with $I > 3.0\sigma(I)$ were used in the refinement procedure. The structure was refined to a conventional R-factor of 0.040 ($R_w = 0.035$) giving e.s.d. in bond lengths and angles not involving hydrogen atoms of about 0.01 Å and 0.7°, respectively.

The interactions between the aromatic moieties are discussed and a hydrogen bond of the type C_{arom}–H---O is suggested.

In the course of our study of curcuminoid molecules, the title compound was investigated by X-ray crystallographic methods. The molecule is similar to 1,7-diphenyl-1,6-heptadiene-3,5-dione,[1] 1,7-diphenyl-4-(2-propenyl)-1,6-heptadiene-3,5-dione[2] and 4-butyl-1,7-diphenyl-1,6-heptadiene-3,5-dione,[3] the only difference being the substituent at the C10 atom. The derivative having a 2-propenyl group at the C10 atom crystallizes with a mirror plane bisecting the molecule, and it was of interest to examine whether the compound with a phenyl group at this position would display similar symmetry. Furthermore, the crystal structure of the title compound is of interest with regard to the interactions between aromatic moieties.

Experimental

The compound was synthesized according to Lawesson et al.[4] Recrystallization from Me$_2$SO resulted in soft colourless or faintly yellow crystals. Intensity data were collected on a NICOLET P3/F diffractometer at room temperature. The unit cell dimensions were determined by a least-squares fit of 25 general reflections (2θ: 10–17°) The intensity data collection was monitored by measuring three test reflections at intervals of 100 measurements. No loss of intensity in the test reflections during the experiment was observed. Standard deviations in the measured intensities were calculated as $\sigma(I) = [C_T + (0.02C_N)^2]^{1/2}$, were 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, but not for absorption.

Table 1. Crystal data and the experimental conditions.

Compound	4-Benzyl-1,7-diphenyl-1,6-heptadiene-3,5-dione
Formula	$C_{26}O_2H_{22}$
Crystal system	Monoclinic
a/Å	5.888(3)
b/Å	8.664(5)
c/Å	40.110(18)
$\beta/°$	92.93(4)
Cell volume/Å^3	2043.4
Experimental temp./K	293
Space group	$P2_1/c$ (No. 14)
M/D	366.5
Z	4
λ/Å	0.71069 Mo-Kα
D/g cm^{-1} (calc.)	1.19
Crystal dimensions/mm	0.3×0.2×0.2
Apparatus	NICOLET P3/F
Scan mode	ω
Scan speed/° min^{-1}	3.0–20.0
Scan range/°	0.5–0.6
Background count time/scan time	0.7
2θ range	2.5–50.0
No. indep. meas.	2569
No. observed [$I > 3.0\sigma(I)$]	1003
Test reflections	3
Corr. for absorption	None
Corr. for sec. ext.	None
Method of structure det.	MITHRIL
Method of refinement	Fourier/LSR
$R = \Sigma\|F_o\|-\|F_c\|/\Sigma\|F_o\|$	0.040
$R_w = [\Sigma_w(\|F_o\|-\|F_c\|)^2/\Sigma wF_o^2]^{1/2}$	0.035
$S = [\Sigma w(\|F_o\|-\|F_c\|)^2/(n-m)]^{1/2}$	1.80[a]

[a] w is the inverse of the variance of observed structure factors.

Table 2. Fractional atomic coordinates and equivalent temperature factors with estimated standard deviations for non-hydrogen atoms.

Atoms	x	y	z	U_{eq} [a]
O(1)	0.1842(6)	0.4621(5)	0.5733(1)	0.083
O(2)	0.4325(6)	0.4910(4)	0.6219(1)	0.075
C(1)	−0.7417(14)	0.1759(10)	0.4755(2)	0.099
C(2)	−0.5756(15)	0.2674(10)	0.4632(2)	0.101
C(3)	−0.3992(13)	0.3201(9)	0.4842(2)	0.087
C(4)	−0.3873(11)	0.2792(7)	0.5179(2)	0.064
C(5)	−0.5585(12)	0.1871(9)	0.5299(2)	0.081
C(6)	−0.7344(13)	0.1346(9)	0.5087(2)	0.099
C(7)	−0.1987(11)	0.3369(7)	0.5397(2)	0.070
C(8)	−0.1521(11)	0.3128(7)	0.5719(2)	0.066
C(9)	0.0512(10)	0.3764(7)	0.5893(2)	0.063
C(10)	0.0984(10)	0.3415(6)	0.6239(1)	0.055
C(11)	0.2934(10)	0.4050(7)	0.6392(1)	0.058
C(12)	0.3649(11)	0.3805(8)	0.6743(2)	0.063
C(13)	0.5485(11)	0.4474(8)	0.6882(2)	0.064
C(14)	0.6469(10)	0.4322(7)	0.7225(2)	0.064
C(15)	0.8468(11)	0.5119(8)	0.7315(2)	0.084
C(16)	0.9425(14)	0.4974(12)	0.7642(2)	0.105
C(17)	0.8394(17)	0.4099(11)	0.7873(2)	0.111
C(18)	0.6443(18)	0.3320(11)	0.7783(2)	0.118
C(19)	0.5474(12)	0.3431(9)	0.7462(2)	0.088
C(20)	−0.0688(11)	0.2462(9)	0.6424(1)	0.057
C(21)	−0.0807(12)	0.0760(10)	0.6345(1)	0.051
C(22)	−0.2720(12)	−0.0057(13)	0.6431(1)	0.068
C(23)	−0.2922(16)	−0.1611(14)	0.6367(2)	0.089
C(24)	−0.1233(19)	−0.2377(11)	0.6220(2)	0.088
C(25)	0.0681(15)	−0.1617(13)	0.6125(2)	0.083
C(26)	0.0871(12)	−0.0036(13)	0.6188(2)	0.068
HC(1)	−0.877(8)	0.151(6)	0.460(1)	0.11(2)
HC(2)	−0.575(10)	0.300(9)	0.440(2)	0.17(3)
HC(3)	−0.271(9)	0.378(7)	0.474(1)	0.13(3)
HC(5)	−0.549(7)	0.149(6)	0.554(1)	0.09(2)
HC(6)	−0.852(9)	0.071(7)	0.520(1)	0.13(3)
HC(7)	−0.096(6)	0.392(5)	0.528(1)	0.03(2)
HC(8)	−0.258(7)	0.244(5)	0.585(1)	0.07(2)
HC(12)	0.273(7)	0.308(5)	0.687(1)	0.06(2)
HC(13)	0.634(6)	0.510(5)	0.675(1)	0.05(2)
HC(15)	0.925(8)	0.577(7)	0.713(1)	0.12(2)
HC(16)	1.081(9)	0.560(7)	0.769(1)	0.13(3)
HC(17)	0.902(10)	0.392(8)	0.810(2)	0.17(3)
HC(18)	0.573(11) ·	0.276(9)	0.794(2)	0.16(4)
HC(19)	0.393(8)	0.285(6)	0.741(1)	0.10(2)
HC(201)	−0.232(8)	0.296(5)	0.638(1)	0.08(2)
HC(202)	−0.0315(5)	0.257(4)	0.667(1)	0.03(1)
HC(22)	−0.387(8)	0.059(6)	0.655(1)	0.08(2)
HC(23)	−0.452(11)	−0.225(8)	0.642(1)	0.17(3)
HC(24)	−0.134(8)	−0.343(6)	0.617(1)	0.07(2)
HC(25)	0.202(9)	−0.216(7)	0.601(1)	0.12(3)
HC(26)	0.224(7)	0.051(5)	0.613(1)	0.06(2)
HO(2)	0.385(18)	0.516(17)	0.606(3)	1.07(8)

[a] $U_{eq} = (U11 + U22 + U33)/3$ for anisotropic atoms.

As the crystals were small and ill-formed, and the experimental temperature was 20°C, only 1003 reflections had intensities above the limit of $3\sigma(I)$.

The structure was solved by using the program system MITHRIL and refinements were performed with least-squares calculations. Hydrogen atomic positions, except that for the enol hydrogen atom, were introduced from geometrical considerations and included in the refinements which proceeded with anisotropic temperature factors for the heavier atoms and isotropic temperature factors for hydrogen atoms. The refinement converged at an R-factor of 0.040. The experimental conditions are summarized in Table 1. Computer programs used are described in Refs. 5 and 6.

Description and discussion

The atomic parameters are listed in Table 2 and a drawing of the molecule with the numbering of the atoms is
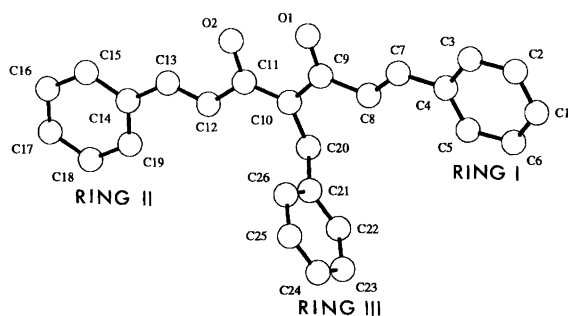
Fig. 1. Drawing of the DPBZHDD molecule showing the numbering of the rings and the atoms.

given in Fig. 1. Bond distances and angles are given in Table 3 and some torsion angles in Table 4. Even if the present structure is studied at room temperature and with rather low accuracy, bond lengths and angles indicate a geometry corresponding to that of related molecules,[1-3] and conform with the bond lengths given by Allen *et al.*[6]

with a higher fidelity than might be expected from the e.s.d.

The main part of the molecule is almost planar, the angle between the terminal phenyl groups being only 4.1°, and the largest deviations from a plane through atoms C1 to C19 (including O1 and O2) are 0.094 Å (C2), 0.066 Å (C3) and 0.072 Å (C8), respectively, the rest of the atoms being situated less than 0.005 Å out of this plane. C20 is 0.14 Å out of the plane and the angle between the main molecular plane and that through the phenyl ring C21–C26 is 81.3°. The angles formed by the terminal phenyl rings I and II and the enol ring are 3.3° and 2.1°, respectively.

The most interesting feature in the present structure is the molecular packing which is dominated by a C_{arom}–H---O hydrogen bond and by interactions between aromatic moieties. The latter interaction seems to involve aryl hydrogen atoms and π-electrons in the aromatic systems. The structure is depicted in the stereogram in Fig. 2 as it appears looking down the *x*-axis. Ring II is embedded in a pocket of seven aromatic rings where ring III in

Table 3. Bond lengths (Å) and angles (°) for non-hydrogen atoms in DPBZHDD molecules. Estimated standard deviations in parentheses. The bond lengths involving hydrogen atoms are between 1.07 and 0.91 Å except the O2–H bond which is found to be 0.71 Å. The e.s.d in these bonds are about 0.06 Å.

Bond	$d/\text{Å}$	Bond	$d/\text{Å}$
O(1)–C(9)	1.275(8)	C(12)–C(13)	1.324(9)
O(2)–C(11)	1.328(7)	C(13)–C(14)	1.470(9)
C(1)–C(2)	1.371(13)	C(14)–C(15)	1.396(9)
C(1)–C(6)	1.376(12)	C(14)–C(19)	1.379(10)
C(2)–C(3)	1.382(12)	C(15)–C(16)	1.405(12)
C(3)–C(4)	1.393(9)	C(16)–C(17)	1.364(14)
C(4)–C(5)	1.391(10)	C(17)–C(18)	1.365(15)
C(4)–C(7)	1.468(9)	C(18)–C(19)	1.384(12)
C(5)–C(6)	1.383(11)	C(20)–C(21)	1.508(12)
C(7)–C(8)	1.320(10)	C(21)–C(22)	1.389(11)
C(8)–C(9)	1.463(9)	C(21)–C(26)	1.383(11)
C(9)–C(10)	1.436(9)	C(22)–C(23)	1.374(17)
C(10)–C(11)	1.387(9)	C(23)–C(24)	1.355(15)
C(10)–C(20)	1.507(9)	C(24)–C(25)	1.376(15)
C(11)–C(12)	1.466(9)	C(25)–C(26)	1.396(16)

Bonds	$\theta/°$	Bonds	$\theta/°$
C(2)–C(1)–C(6)	120.8(8)	C(11)–C(12)–C(13)	121.9(6)
C(1)–C(2)–C(3)	119.9(8)	C(12)–C(13)–C(14)	128.9(6)
C(2)–C(3)–C(4)	120.4(7)	C(13)–C(14)–C(15)	118.9(6)
C(3)–C(4)–C(5)	118.7(7)	C(13)–C(14)–C(19)	122.3(6)
C(3)–C(4)–C(7)	119.4(6)	C(15)–C(14)–C(19)	118.7(6)
C(5)–C(4)–C(7)	121.9(6)	C(14)–C(15)–C(16)	119.3(7)
C(4)–C(5)–C(6)	120.6(7)	C(15)–C(16)–C(17)	120.8(9)
C(1)–C(6)–C(5)	119.6(8)	C(16)–C(17)–C(18)	119.6(9)
C(4)–C(7)–C(8)	130.0(7)	C(17)–C(18)–C(19)	120.8(9)
C(7)–C(8)–C(9)	122.0(6)	C(14)–C(19)–C(18)	120.7(8)
O(1)–C(9)–C(8)	119.3(6)	C(10)–C(20)–C(21)	117.2(6)
O(1)–C(9)–C(10)	121.0(6)	C(20)–C(21)–C(22)	118.4(7)
C(8)–C(9)–C(10)	119.7(6)	C(20)–C(21)–C(26)	123.8(7)
C(9)–C(10)–C(11)	117.3(6)	C(22)–C(21)–C(26)	117.8(9)
C(9)–C(10)–C(20)	119.5(6)	C(21)–C(22)–C(23)	121.1(8)
C(11)–C(10)–C(20)	123.2(6)	C(22)–C(23)–C(24)	120.1(9)
O(2)–C(11)–C(10)	120.7(5)	C(23)–C(24)–C(25)	121.0(10)
O(2)–C(11)–C(12)	115.4(5)	C(24)–C(25)–C(26)	118.7(9)
C(10)–C(11)–C(12)	123.9(6)	C(21)–C(26)–C(25)	121.2(8)

Table 4. Selected torsional angles in the DPBZHDD molecule.

Bonds	θ/°	Bonds	θ/°
HO(2)–O(2)–C(11)–C(10)	14.3(110)	C(9)–C(10)–C(20)–C(21)	73.0(7)
HO(2)–O(2)–C(11)–C(12)	– 167.2(110)	C(20)–C(10)–C(11)–O(2)	– 178.5(9)
C(2)–C(3)–C(4)–C(7)	– 179.8(11)	C(20)–C(10)–C(11)–C(12)	3.2(6)
C(3)–C(4)–C(7)–C(8)	– 179.4(11)	C(11)–C(10)–C(20)–C(21)	– 110.3(8)
C(7)–C(4)–C(5)–C(6)	179.9(11)	O(2)–C(11)–C(12)–C(13)	3.8(6)
C(5)–C(4)–(7)–C(8)	2.0(7)	C(10)–C(11)–(12)–C(13)	177.7(10)
C(4)–C(7)–C(8)–C(9)	177.6(11)	C(11)–C(12)–C(13)–C(14)	178.1(11)
C(7)–C(8)–C(9)–O(1)	2.4(6)	C(12)–C(13)–C(14)–C(15)	178.5(11)
C(7)–C(8)–C(9)–C(10)	– 177.5(10)	C(12)–C(13)–C(14)–C(19)	–2.2(7)
O(1)–C(9)–(10)–C(11)	0.1(6)	C(13)–C(14)–C(15)–C(16)	– 179.7(10)
O(1)–C(9)–C(10)–C(20)	177.0(9)	C(13)–C(14)–C(19)–(18)	– 179.7(11)
C(8)–C(9)–C(10)–C(11)	– 179.9(9)	C(10)–C(20)–C(21)–C(22)	– 161.4(10)
C(8)–C(9)–C(10)–C(20)	– 3.1(6)	C(10)–(20)–C(21)–C(26)	17.1(7)
C(9)–C(10)–C(11)–O(2)	– 1.7(6)	C(20)–C(21)–C(22)–C(23)	– 179.6(12)
C(9)–C(10)–C(11)–C(12)	179.9(9)	C(20)–C(21)–C(26)–C(25)	179.1(12)

a neighbouring molecule (screw axis related) represents the bottom of the pocket. The six rings forming the walls of the pocket are illustrated in Fig. 3(b) where the distances to neighbouring rings are also given. The angle between interacting rings is 75.8°.

The C17-H bond in ring II points almost to the centre of Ring III, the distances from HC17 to the carbon atoms in ring III varies between 2.89 and 3.17 Å. The angle between these rings is 79.6° [Fig. 3(a)]. Furthermore, molecules displaced one unit along the *y*-axis are in direct contact with each other through the ring III–enol ring interaction depicted in Fig. 3(c) where it may be seen that the HC25 is at an equal distance to the two oxygen atoms and that HC24 is almost at the apex of a trigonal pyramid where C8,C10 and O1 constitute the base. The figure also displays the contact between ring III and the enol ring in a molecule displaced one unit along both the *x* and the *y* axes. The phenyl rings are at an angle of 81.7° to the enol ring. These interactions keep together stacks of molecules in the *a* and *b* direction. The contacts between molecules in different stacks occurs over a centre of symmetry [Fig. 3(d)] and between ring I and ring III as

shown in Fig. 3(a). The angle between rings I and III is 78.8°.

Using values of van der Waals' radii of 1.54 Å for O,[7] 1.70 and 1.77 Å for C_{aliph} and C_{arom}, respectively,[8] and
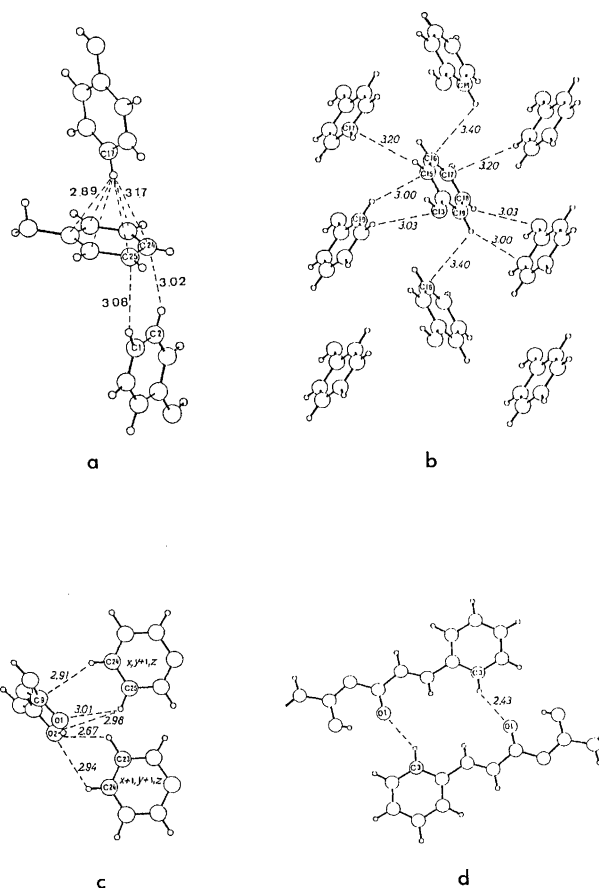

a

b

c

d

Fig. 3. The geometry of the intermolecular contacts. (A) The contacts between ring I and III and between II and III, the longest and the shortest distances are indicated. (b) The aromatic environment of ring II. (c) The interaction between the enol ring and ring III. (D) Contacts between molecules related by a centre of symmetry.
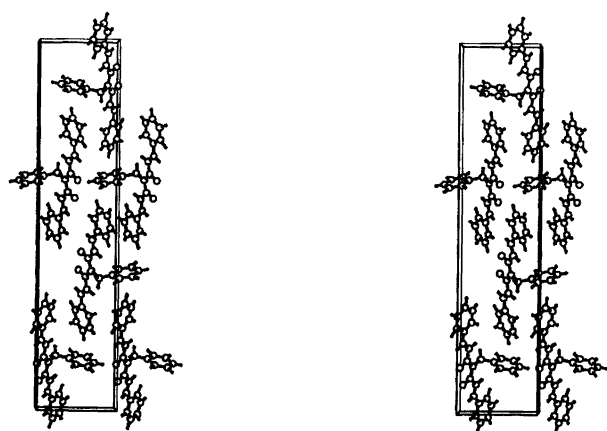

Fig. 2. Stereoscopic view of the packing of the BDPZHDD molecules as seen down the *a*-axis.

1.20 Å for H,[9] contacts between H and O are expected at a distance of 2.74 Å, between H and C_{aliph} at 2.97 Å and between H and C_{arom} at 2.90 Å. From these criteria, the only contacts between neighbouring molecules occur between ring II and ring III (HC17–C21: 2.89), ring III and enol rings (HC24–C9:2.91 Å and HC23–O2: 2.67 Å) and ring I and enol ring (HC3–O1: 2.43 Å), the latter being the strongest interaction indicating a formal hydrogen bond.

In conclusion, the molecules seem to be held together in the crystal by weak interactions only. This is also indicated by the only slight deviation from a planar conformation expected for a conjugated molecule. The structure underlines the tendency of aromatic units to pack at angles of 60–90° with one or two C–H bonds pointing onto, and imbedded in, the π-electron density of a neighbouring aromatic unit. This feature is also present in the related structures II, III and IV.

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