Structural Studies of Curcuminoids. V. Crystal Structures of 1,7-Bis(3,4-dimethoxyphenyl)-4-benzyl-1,6-heptadiene-3,5-dione (DDBHDD) and 1,7-Bis(4-hydroxy-3-methoxy-phenyl)-4-(2-oxo-2-ethoxyethyl)-1,6-heptadiene-3,5-dione (DHMEDD)*

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The crystal and molecular structures of 1,7-bis(3,4-dimethoxyphenyl)-4-benzyl-1,6-heptadiene-3,5-dione (DDBHDD) and 1,7-di(4-hydroxy-3-methoxyphenyl)-4-(2-oxo-2-ethoxyethyl)-1,6-heptadiene-3,5-dione (DHMEDD) have been determined at 121 K by X-ray crystallographic methods using 3330 and 2288 reflections, respectively. The crystals of DDBHDD are monoclinic, space group $P2_1/n$ with unit cell dimensions $a = 9.139(2)$ Å, $b = 9.221(2)$ Å, $c = 29.681(5)$ Å, $\beta = 96.80(2)°$. DHMEDD crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 16.359(3)$ Å, $b = 6.221(1)$ Å, $c = 23.141(3)$ Å, $\beta = 104.55(1)°$. The structures were refined to conventional R factors of 0.034 and 0.039. Estimated standard deviations in interatomic distances and angles not involving hydrogen atoms, are 0.002 Å and 0.1–0.2° for DDBHDD and 0.004 Å and 0.3° for DHMEDD. In both molecules, the enol ring hydrogen atom is closer to one of the oxygen atoms, but only in DDBHDD is asymmetry apparent in the enol ring. A C−H····O intermolecular interaction appears to be present in the DHMEDD crystals.

Four curcuminoids have previously been subject to investigation by X-ray crystallographic methods.[1-4] They have shown different conformational properties and allowed studies of the inherent enol ring whose aromatic character may be influenced by the crystal environment as well as intramolecular interactions. It was also of interest to look at the packing interactions of the aromatic moieties in general. In order to study these effects further, crystal structure determinations of another two curcuminoids have been carried out.

Experimental

Synthetic and crystallization procedures for DDBHDD gave dark orange cube-shaped crystals with m.p. 136 °C, whereas the DHMEDD crystals were orange cube- to plate-shaped with m.p. 146 °C. The data collection procedure is described under experimental conditions.

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*These names are used even if the compounds exist in the enol form in the crystals and the DHMEDD molecule should be classified as an ester.

Experimental conditions

Instrument	Syntex P1	
Radiation	Graphite crystal	
	Monochromated MoKα	
	$\lambda = 0.71069$ Å	
Scanning mode	$\theta/2\theta$	
Scan speed ($^{\circ}min^{-1}$)	3.0	
Scan range ($^{\circ}$)	$2\theta_{\alpha 1} - 0.8$ to $2\theta_{\alpha 2} + 0.9$	
Background counts	For 0.35 of scan time at scan limits	
Temperature (K)	121	
2θ range	2.5–50.0	
	DDBHDD	**DHMEDD**
Crystal dimensions (mm)	$0.4 \times 0.3 \times 0.3$	$0.4 \times 0.3 \times 0.1$
Number of reflections measured	4498	2496
Number of reflections $I > 2.5 \, \sigma I$	3330	2288
Number of standard reflections	3	3
Number of reflections between standard reflections	97	57

Cell parameters were determined by a least-squares fit to the diffractometer settings for 15 general reflections. Standard deviations in the measured intensities were calculated as $\sigma I = (C_T + (0.02 C_N)^2)^{1/2}$ where C_T is the total number of counts and C_N is the scan count minus the background count. The intensities were corrected for Lorentz and polarization effects, but not for absorption. The variations of the test reflections were found to be less than 2 % for both sets of data, and no corrections were made on this basis. Atomic scattering factors for free heavy atoms and spherically bonded hydrogen atoms were taken from *International Tables for X-ray Crystallography*.[5]

Crystal data

1,7-Bis(3,4-dimethoxyphenyl)-4-benzyl-1,6-heptadiene-3,5-dione. $C_{30}H_{30}O_6$, monoclinic, $a = 9.139(2)$ Å, $b = 9.221(2)$ Å, $c = 29.681(5)$ Å, $\beta = 96.80(2)^{\circ}$, $V = 2483.6(9)$ Å^3, $M = 486.6$, $Z = 4$, $F_{000} = 1032$, space group $P2_1/n$, m.p. 136 °C, $D_0 = 1.301$ g cm^{-3}.

1,7-Bis(4-hydroxy-3-methoxyphenyl)-4-(2-oxo-2-ethoxyethyl)-1,6-heptadiene-3,5-dione. $C_{25}H_{26}O_8$, monoclinic, $a = 16.359(3)$ Å, $b = 6.221(1)$ Å, $c = 23.141(3)$ Å, $\beta = 104.55(1)^{\circ}$, $V = 2279.9(6)$ Å^3, $M = 454.5$, $Z = 4$, $F_{000} = 960$, space group $P2_1/c$, m.p. 146 °C, $D_0 = 1.324$ g cm^{-3}.

Structure determination

Both structures were solved by direct methods using the program assembly MULTAN.[6] Successive Fourier synthesis revealed the positions of all the non-hydrogen atoms. Positional parameters and isotropic temperature factors were refined by least-squares methods. At this stage, the hydrogen atoms of DDBHDD, except the one connected to the enol ring, were introduced from stereochemical considerations. After further least-squares refinement, a difference Fourier map served to locate the enol ring hydrogen atom. The positions of the hydrogen atoms of DHMEDD were all obtained from a difference synthesis.

All positional parameters, anisotropic temperature factors for C and O and isotropic temperature factors for H were refined by least-squares methods giving for DDBHDD $R = 0.034$, $R_w = 0.033$, goodness of fit $S = [\Sigma w \Delta^2 / (n-m)]^{1/2} = 1.69$, and for DHMEDD $R = 0.039$, $R_w = 0.040$, $S = 1.96$. The final parameters are given in Tables 1 and 2. The quantity minimized in the least-squares refinement was $\Sigma w (\Delta F)^2$, where w is the inverse of the variance of the observed structural factors. Description of the computer programs used is given in Ref. 7

Table 1. Fractional coordinates for DDBHDD; estimated standard deviations in parentheses

Atom	X	Y	Z	Atom	X	Y	Z
O1	.3744(1)	−.6447(1)	.6842(1)	C28	.0836(2)	−.4452(2)	.7521(1)
O2	.1935(1)	−.5299(1)	.7338(1)	C29	.3452(2)	.6827(2)	1.1626(1)
O3	.7257(1)	−.0516(1)	.8828(1)	C30	.0321(2)	.3170(3)	1.0442(1)
O4	.7205(1)	.1148(1)	.9467(1)	HO3	.749(3)	.029(3)	.911(1)
O5	.2713(1)	.5715(1)	1.1347(1)	H31	.315(2)	−.344(2)	.794(1)
O6	.1193(1)	.4038(1)	1.0771(1)	H51	.734(2)	−.375(2)	.759(1)
C1	.4356(2)	−.5463(2)	.7155(1)	H61	.649(2)	−.542(2)	.702(1)
C2	.3367(2)	−.4843(2)	.7432(1)	H71	.696(2)	−.235(2)	.824(1)
C3	.3860(2)	−.3847(2)	.7761(1)	H81	.412(2)	−.176(2)	.843(1)
C4	.5355(2)	−.3444(2)	.7832(1)	H121	.402(2)	.149(2)	.978(1)
C5	.6312(2)	−.4047(2)	.7551(1)	H131	.666(2)	.303(2)	1.004(1)
C6	.5818(2)	−.5044(2)	.7212(1)	H151	.673(2)	.469(2)	1.067(1)
C7	.5923(2)	−2444(2)	.8192(1)	H161	-553(2)	.589(2)	1.122(1)
C8	.5147(2)	−.1691(2)	.8466(1)	H191	.274(2)	.279(2)	1.020(1)
C9	.5819(2)	−.0724(2)	.8822(1)	H201	.322(2)	−.052(2)	.946(1)
C10	.5033(2)	−.0034(2)	.9134(1)	H202	.310(2)	−.118(2)	.897(1)
C11	.5806(2)	.0944(2)	.9455(1)	H221	.104(2)	.092(2)	.948(1)
C12	.5015(2)	.1742(2)	.9775(1)	H231	−.052(2)	.284(2)	.920(1)
C13	.5620(2)	.2785(2)	1.0049(1)	H241	−.005(2)	.412(2)	.853(1)
C14	.4879(2)	.3579(2)	1.0382(1)	H251	.196(2)	.332(2)	.814(1)
C15	.5665(2)	.4518(2)	1.0687(1)	H261	.347(2)	.140(2)	.842(1)
C16	.4977(2)	.5254(2)	1.1013(1)	H271	.408(2)	−.775(2)	.635(1)
C17	.3491(2)	.5073(2)	1.1039(1)	H272	.548(2)	−.764(2)	.673(1)
C18	.2666(2)	.4138(2)	1.0726(1)	H273	.514(2)	−.634(2)	.636(1)
C19	.3355(2)	.3419(2)	1.0404(1)	H281	−.012(2)	−.488(2)	.739(1)
C20	.3391(2)	−.0283(2)	.9146(1)	H282	.087(2)	−.337(2)	.743(1)
C21	.2408(2)	.0972(2)	.8971(1)	H283	.091(2)	−.451(2)	.787(1)
C22	.1226(2)	.1402(2)	.9195(1)	H291	.269(2)	.721(2)	1.179(1)
C23	.0328(2)	.2548(2)	.9033(1)	H292	.381(2)	.762(2)	1.144(1)
C24	.0587(2)	.3270(2)	.8641(1)	H293	.431(2)	.640(2)	1.183(1)
C25	.1743(2)	.2831(2)	.8411(1)	H301	−.069(2)	.329(2)	1.051(1)
C26	.2643(2)	.1696(2)	.8575(1)	H302	.066(2)	.208(2)	1.045(1)
C27	.4702(2)	−.7082(2)	.6548(1)	H303	.040(2)	.353(2)	1.012(1)

Description and discussion

Bond lengths, angles and some torsion angles are given in Tables 3–6. Drawings of the molecules with numbering of the atoms are given in Figs. 1 and 2.

The bond lengths in the conjugated chain are in good agreement with those found in similar compounds.[8] Bond angles along the chain are in general larger than 120°. This in particular holds true for angles at C3-C4-C7 and C4-C7-C8 which are opened to relieve the strain introduced by the short distance between the hydrogen atoms at C3 and C8. In an all 120° system, a severe clash of hydrogen atoms would occur with an H−H dis-

tance of about 1.78 Å compared to 2.17 to 2.29 Å found in DDBHDD and DHMEDD. It seems that the opening of these angles is energetically preferable to a loss in conjugational energy by a rotation about the $C_{arom}-C_{chain}$ bond.

The geometry of the respective enol rings is shown in Fig. 3. In DDBHDD the two C−O bond lengths are significantly different as are the two bonds C9−C10 and C10−C11. With the H atom being closer to O3, the ring has clearly adopted an asymmetric configuration. The isotropic temperature factor for HO3 is 7.3 Å^2 as compared to 1.3–4.3 Å^2 for the other H atoms. No such differences are found however in the DHMEDD molecule even if the hydrogen atom

Table 2. Fractional coordinates for DHMEDD; estimated standard deviations in parentheses

| Atom	X	Y	Z	Atom	X	Y	Z
O1	.2297(1)	.9633(4)	.2905(1)	C23	−.4012(3)	.0464(11)	.0577(2)
O2	.1466(1)	−.5929(3)	.2878(1)	C24	.0916(2)	−.4161(6)	.2912(2)
O3	−.1236(1)	−.6752(3)	−.0312(1)	C25	−.6454(2)	−.0421(6)	−.2600(2)
O4	−.2313(1)	−.4649(4)	−.0994(1)	H01	.225(2)	−.886(6)	.320(2)
O5	−.5963(1)	.5191(4)	−.1666(1)	H04	−.181(3)	−.587(7)	−.078(2)
O6	−.6219(1)	.1618(3)	−.2318(1)	H05	−.640(2)	.477(7)	−.194(2)
O7	−.2423(1)	−.2967(4)	.0969(1)	H31	.043(2)	−.514(5)	.181(1)
O8	−.2503(1)	.0559(4)	.0734(1)	H51	.096(2)	−1.063(5)	.097(1)
C1	.1749(2)	−.9000(5)	.2384(1)	H61	.197(2)	−1.156(5)	.191(1)
C2	.1294(2)	−.7062(5)	.2354(1)	H71	.000(2)	−.812(5)	.043(1)
C3	.0738(2)	−.6472(6)	.1825(1)	H81	−.059(2)	−.481(5)	.097(1)
C4	.0607(2)	−.7782(5)	.1320(1)	H121	−.268(2)	−.031(5)	−.046(1)
C5	.1068(2)	−.9687(5)	.1353(1)	H131	−.355(2)	−.232(5)	−.145(1)
C6	.1637(2)	−1.0278(6)	.1886(1)	H151	−.351(2)	.269(5)	−.069(1)
C7	−.0004(2)	−.7265(5)	.0761(1)	H161	−.456(2)	.527(5)	−.089(1)
C8	−.0553(2)	−.5631(5)	.0664(1)	H191	−.492(2)	−.108(5)	−.198(1)
C9	−.1149(2)	−.5238(5)	.0085(1)	H201	−.097(2)	−.168(5)	.069(1)
C10	−.1619(2)	−.3326(5)	−.0041(1)	H202	−.149(2)	−.017(5)	.020(1)
C11	−.2225(2)	−.3125(5)	−.0593(1)	H221	−.311(2)	−.012(5)	.137(1)
C12	−.2798(2)	−.1310(6)	−.0728(1)	H222	−.319(3)	.247(8)	.105(2)
C13	−.3455(2)	−.1197(6)	−.1201(1)	H231	−.448(2)	.078(6)	.075(1)
C14	−.4090(2)	.0503(5)	−.1330(1)	H232	−.406(3)	−.108(8)	.043(2)
C15	−.3994(2)	.2421(5)	−.1005(1)	H233	−.408(2)	.159(7)	.019(2)
C16	−.4620(2)	.3979(5)	−.1120(1)	H241	.112(2)	−.372(5)	.334(1)
C17	−.5350(2)	.3646(5)	−.1564(1)	H242	.095(2)	−.293(6)	.260(2)
C18	−.5458(2)	.1739(5)	−.1894(1)	H243	.033(2)	−.475(6)	.286(1)
C19	−.4833(2)	.0200(5)	−.1784(1)	H251	−.704(2)	−.016(6)	−.288(1)
C20	−.1506(2)	−.1491(6)	.0401(1)	H252	−.646(2)	−.153(6)	−.229(2)
C21	−.2190(2)	−.1427(6)	.0737(1)	H253	−.604(2)	−.076(5)	−.288(1)
C22	−.3199(3)	.0873(8)	.1020(2)				
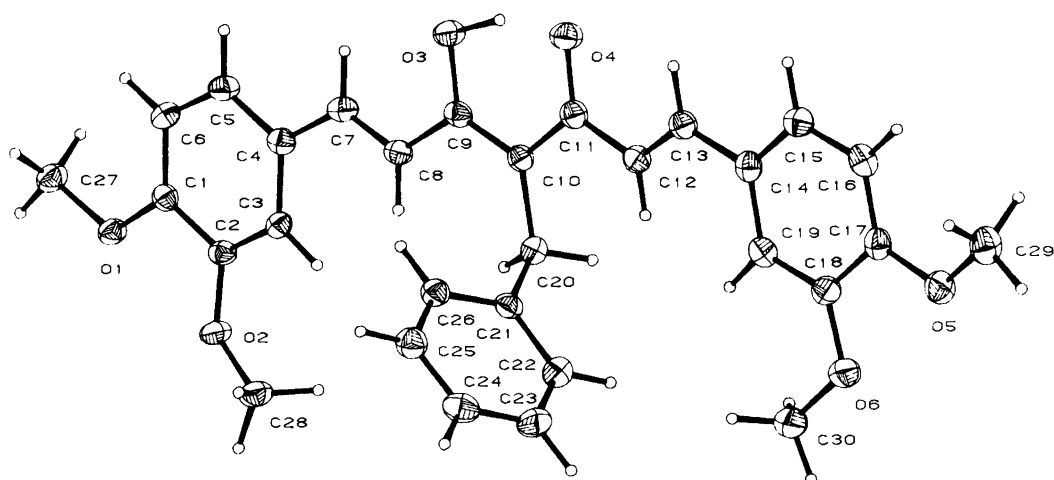
Fig. 1. Drawing of the DDBHDD molecule with numbering indicated.

Table 3. Bond lengths and angles in the DDBHDD molecule with e.s.d. in parentheses; the C—H distances vary between 0.93 and 1.05 Å (mean 0.99 Å) with e.s.d. 0.02 Å

Distance	(Å)	Distance	(Å)
O3– O4	2.445(2)	O1– C1	1.369(2)
O1–C27	1.432(2)	O2– C2	1.371(2)
O2–C28	1.429(2)	O3– C9	1.326(2)
O4–C11	1.289(2)	O5–C17	1.360(2)
O5–C29	1.436(2)	O6–C18	1.372(2)
O6–C30	1.431(2)	C1– C2	1.413(2)
C1– C6	1.381(2)	C2– C3	1.378(2)
C3– C4	1.408(2)	C4– C5	1.392(2)
C4– C7	1.460(2)	C5– C6	1.398(2)
C7– C8	1.336(2)	C8– C9	1.460(2)
C9–C10	1.393(2)	C10–C11	1.436(2)
C10–C20	1.522(2)	C11–C12	1.457(2)
C12–C13	1.338(2)	C13–C14	1.458(2)
C14–C15	1.390(2)	C14–C19	1.411(2)
C15–C16	1.392(2)	C16–C17	1.379(2)
C17–C18	1.417(2)	C18–C19	1.374(2)
C20–C21	1.519(2)	C21–C22	1.392(2)
C21–C26	1.388(2)	C22–C23	1.389(2)
C23–C24	1.385(3)	C24–C25	1.385(3)
C25–C26	1.383(2)	O3–HO3	1.12 (3)
O4–HO3	1.37 (3)		

Angle	(°)	Angle	(°)
C1– O1–C27	117.0(1)	C2– O2–C28	116.9(1)
C17– O5–C29	116.9(1)	C18– O6–C30	116.4(1)
O1– C1– C2	115.1(1)	O1– C1– C6	125.5(1)
C2– C1– C6	119.4(1)	O2– C2– C1	114.8(1)
O2– C2– C3	124.9(1)	C1– C2– C3	120.4(2)
C2– C3– C4	120.8(2)	C3– C4– C5	118.2(2)
C3– C4– C7	122.0(1)	C5– C4– C7	119.8(1)
C4– C5– C6	121.4(2)	C1– C6– C5	119.9(2)
C4– C7– C8	127.3(2)	C7– C8– C9	123.3(2)
O3– C9– C8	115.5(1)	O3– C9–C10	120.9(2)
C8– C9–C10	123.7(1)	C9–C10–C11	118.5(1)
C9–C10–C20	122.2(2)	C11–C10–C20	119.3(1)
O4–C11–C10	121.2(2)	O4–C11–C12	118.4(2)
C10–C11–C12	120.3(2)	C11–C12–C13	123.9(2)
C12–C13–C14	125.6(2)	C13–C14–C15	120.6(2)
C13–C14–C19	121.3(2)	C15–C14–C19	118.1(2)
C14–C15–C16	121.1(2)	C15–C16–C17	120.5(2)
O5–C17–C16	125.5(2)	O5–C17–C18	115.2(1)
C16–C17–C18	119.3(2)	O6–C18–C17	115.4(1)
O6–C18–C19	124.8(2)	C17–C18–C19	119.8(2)
C14–C19–C18	121.2(2)	C10–C20–C21	114.9(1)
C20–C21–C22	120.9(2)	C20–C21–C26	120.8(2)
C22–C21–C26	118.3(2)	C21–C22–C23	120.8(2)
C22–C23–C24	120.2(2)	C23–C24–C25	119.4(2)
C24–C25–C26	120.2(2)	C21–C26–C25	121.1(2)
C9– O3–HO3	102 (1)	C11– O4–HO3	100 (1)

Table 4. Some torsional angles in the DDBHDD molecule

Dihedral angle	(°)
C27– O1– C1– C2	178.8(1)
C28– O2– C2– C3	14.9(2)
C29– O5–C17–C16	9.4(2)
C30– O6–C18–C19	–3.1(3)
O1– C1– C2– O2	–1.3(2)
C3– C4– C7– C8	–6.6(3)
C4– C7– C8– C9	179.3(2)
C7– C8– C9– O3	6.7(2)
C7– C8– C9–C10	–174.3(2)
O3– C9–C10–C11	1.8(2)
C8– C9–C10–C11	–177.2(2)
C8– C9–C10–C20	2.8(2)
C9–C10–C11–C12	177.2(1)
C9–C10–C20–C21	–107.2(2)
C11–C10–C20–C21	72.8(2)
O4–C11–C12–C13	7.1(3)
C10–C11–C12–C13	–172.4(2)
C11–C12–C13–C14	–178.2(2)
C12–C13–C14–C15	172.2(2)
C13–C14–C19–C18	178.2(2)
O5–C17–C18– O6	1.5(2)
C10–C20–C21–C22	–137.5(2)

is observed to be positioned closer to the O4 atom. An analysis of the thermal vibrations of the enol ring atoms did not give reason to explain the symmetry as caused by disorder. It may also be noticed that the bond angles in the enol ring
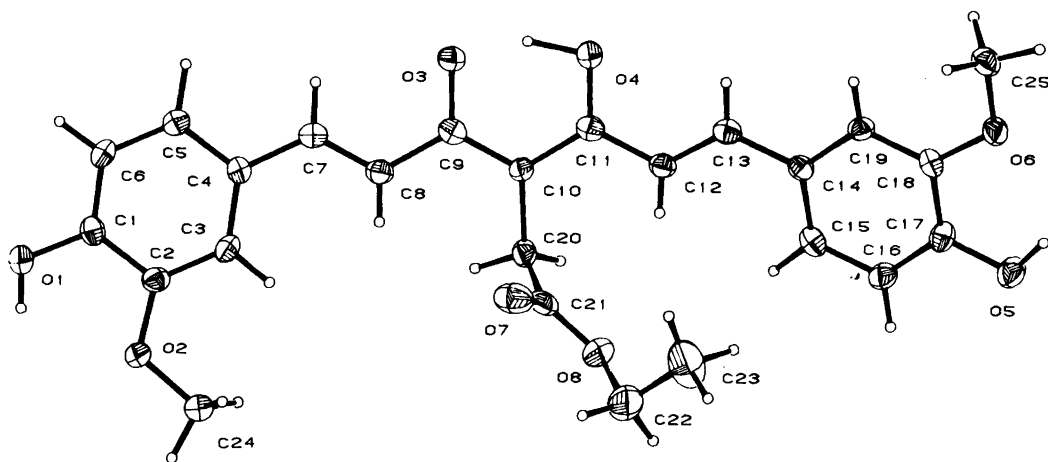
support the impression of more double bond character in C11–O4 and single bond character in C9–O3 in DDBHDD than in the respective bonds in DHMEDD. There seems to be no obvious explanation for the differences of the two enol rings. However, if the asymmetrical form of the enol ring is the preferred state, then the weaker intermolecular interactions between the DDBHDD molecules may explain the more expressed asymmetrical form in this structure. In the DHMEDD structure, an enol ring oxygen atom is also involved in intermolecular interactions and this may obscure the otherwise asymmetrical form. A review of structural studies of molecules containing enol rings is given by Semmingsen.[9]

Of the 5 phenyl rings included in the two structures, only 1 is without substituents, whereas 4 have hydroxy or methoxy substituents. The variation in bond length within the unsubstituted phenyl ring is observed to be small, only one bond (C21–C22: 1.392(2) Å) is found to be significantly longer than the shortest (C25–C26: 1.383(2) Å) by 4 e.s.d. On the other hand, bond lengths between carbon atoms in the substituted phenyl rings exhibit variations of more than 15 e.s.d. However, within each of the two structures, there are no significant differences between the respective phenyl ring bond lengths and thus the mean value may be considered. The mean bond length between the two oxygen substituted carbon atoms is found to be 1.415 Å in

Fig. 2. Drawing of the DHMEDD molecule with numbering indicated.

Table 5. Bond lengths and angles in the DHMEDD molecule with e.s.d. in parentheses; the C−H distances vary between 0.87 and 1.11 Å (mean 0.98 Å) with e.s.d. 0.03–0−04 Å

Distance	(Å)	Distance	(Å)
O3− O4	2.432(3)	O1− C1	1.368(3)
O2− C2	1.370(3)	O2−C24	1.435(4)
O3− C9	1.298(3)	O4−C11	1.308(3)
O5−C17	1.367(3)	O6−C18	1.380(3)
O6−C25	1.435(4)	O7−C21	1.207(4)
O8−C21	1.337(4)	O8−C22	1.467(4)
C1− C2	1.409(4)	C1− C6	1.375(4)
C2− C3	1.378(4)	C3− C4	1.397(4)
C4− C5	1.397(4)	C4− C7	1.457(4)
C5− C6	1.394(4)	C7− C8	1.338(4)
C8− C9	1.465(4)	C9−C10	1.407(4)
C10−C11	1.413(4)	C10−C20	1.512(4)
C11−C12	1.450(4)	C12−C13	1.329(4)
C13−C14	1.460(4)	C14−C15	1.399(4)
C14−C19	1.404(4)	C15−C16	1.386(4)
C16−C17	1.381(4)	C17−C18	1.399(4)
C18−C19	1.377(4)	C20−C21	1.514(4)
C22−C23	1.483(6)	O1−HO1	.86 (4)
O4−HO4	1.14 (4)	O5−HO5	.87 (4)

Angle	(°)	Angle	(°)
C2− O2−C24	116.8(2)	C18− O6−C25	117.6(2)
C21− O8−C22	117.4(3)	O1− C1− C2	120.7(3)
O1− C1− C6	119.6(3)	C2− C1− C6	119.7(3)
O2− C2− C1	114.1(3)	O2− C2− C3	126.3(3)
C1− C2− C3	119.6(3)	C2− C3− C4	121.1(3)
C3− C4− C5	118.8(3)	C3− C4− C7	122.8(3)
C5− C4− C7	118.5(3)	C4− C5− C6	120.3(3)
C1− C6− C5	120.5(3)	C4− C7− C8	126.8(3)
C7− C8− C9	123.0(3)	O3− C9− C8	117.1(3)
O3− C9−C10	120.7(3)	C8− C9−C10	122.2(3)
C9−C10−C11	119.0(3)	C9−C10−C20	122.1(3)
C11−C10−C20	118.9(3)	O4−C11−C10	120.3(3)
O4−C11−C12	117.5(3)	C10−C11−C12	122.2(3)
C11−C12−C13	124.3(3)	C12−C13−C14	126.5(3)
C13−C14−C15	122.0(3)	C13−C14−C19	119.6(3)
C15−C14−C19	118.4(3)	C14−C15−C16	121.0(3)
C15−C16−C17	119.8(3)	O5−C17−C16	118.9(3)
O5−C17−C18	121.0(3)	C16−C17−C18	120.0(3)
O6−C18−C17	113.7(3)	O6−C18−C19	126.1(3)
C17−C18−C19	120.2(3)	C14−C19−C18	120.5(3)
C10−C20−C21	112.7(3)	O7−C21− O8	124.9(3)
O7−C21−C20	124.4(3)	O8−C21−C20	110.7(3)
O8−C22−C23	109.1(3)	C1− O1−HO1	112 (3)
C9− O3−HO4	101 (2)	C11− O4−HO4	103 (2)
C17− O5−HO5	110 (3)		

Table 6. Some torsional angles in the DMHEDD molecule

| Dihedral angle	(°)
C24– O2– C2– C3	11.4(5)
C25– O6–C18–C19	11.8(4)
C21– O8–C22–C23	–88.0(5)
C22– O8–C21– O7	–1.8(5)
C22– O8–C21–C20	177.5(3)
O1– C1– C2– O2	.9(4)
C3– C4– C7– C8	–5.5(5)
C4– C7– C8– C9	–179.8(3)
C7– C8– C9– O3	12.0(4)
C7– C8– C9–C10	–168.9(3)
O3– C9–C10–C11	3.6(4)
C8– C9–C10–C11	–175.5(3)
C8– C9–C10–C20	3.6(4)
C9–C10–C11–C12	173.1(3)
C9–C10–C20–C21	–100.9(3)
C11–C10–C20–C21	78.2(4)
O4–C11–C12–C13	7.2(5)
C10–C11–C12–C13	–169.7(3)
C11–C12–C13–C14	174.4(3)
C12–C13–C14–C15	10.5(5)
C13–C14–C19–C18	176.8(3)
O5–C17–C18– O6	.4(4)
C10–C20–C21– O7	47.4(4)
C10–C20–C21– O8	–131.9(3)

DDBHDD and 1.404 Å in DHMEDD. In both cases this is significantly longer than the adjacent bonds, which, in turn, are significantly shorter than the next neighboring bonds.

The distances between the methoxy group oxygen atoms in DDBHDD are as short as 2.569 Å (O1–O2) and 2.584 Å (O5–O6) due to steric repulsion between the terminal methyl groups and the phenyl rings. With all angles fixed at 120° and unchanged bond lengths, the distances would be approximately 2.83 Å. Not taking the benzyl group into consideration, the molecule is very close to planar, as can be seen from the dihedral angles. The DDBHDD molecule is slightly twisted giving an angle of 25.8° between the phenyl groups, whereas the angle between the enol ring and ring C_1-C_6 and ring C_{14}-C_{19} is 20.5° and 7.0°, respectively.

Stereoscopic views of the molecular packings of the two structures are given in Figs. 4 and 5. There are no intermolecular hydrogen bonds in DDBHDD and the packing is thus governed by van der Waals' interactions only. It may be seen

from Fig. 4 that centrosymmetrically related molecules are connected through interactions between their respective phenyl groups (H231, H241) and the methoxy group atoms O5 and O6. Such centrosymmetric pairs are again linked through molecules at right angles to these groups by interaction between the ether oxygen atoms O1 and O2 and several atoms in the bay-shaped part in the molecules. Both interactions are illustrated in Fig. 6.

On the other hand, DHMEDD molecules are engaged in a hydrogen bond network in molecular layers parallel to the (101) plane. The geometry of the intermolecular interactions is given in Fig. 7. It may be noted that the hydrogen atoms in both cases are situated close to the oxygen atoms of the adjacent methoxy group. At the enol ring, a close intermolecular contact occurs with an O–H distance of 2.34 Å considerably below the sum of the van der Waals' radii. The interaction occurs between centrosymmetrically related molecules in different hydrogen-bonded layers. This may be looked upon as a C–H···O hydrogen bond[10]; electrostatic stabilisation more than outweighs van der Waals' repulsion making the contact attractive. As mentioned above, this may influence the geometry of the enol ring.
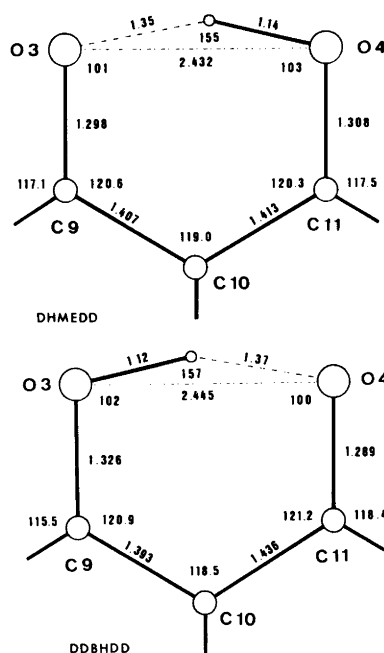
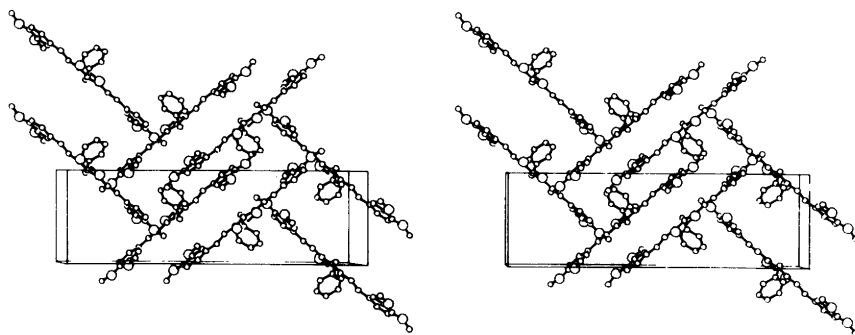*Fig. 3.* The geometry of the enol rings.

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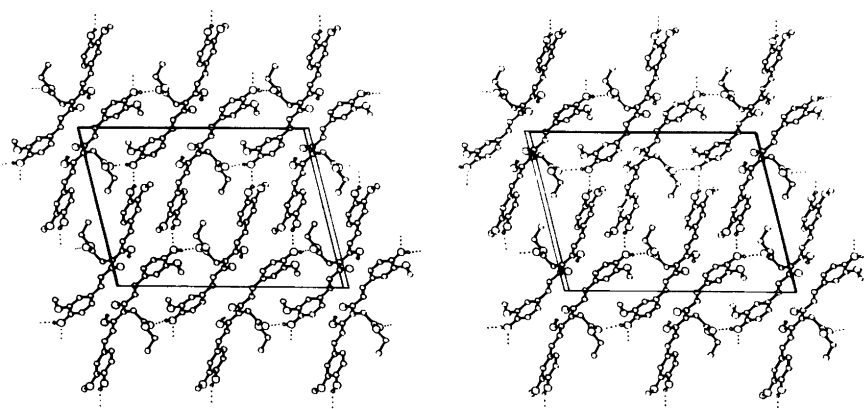Fig. 4. Molecular packing of DDBHDD in the crystal.

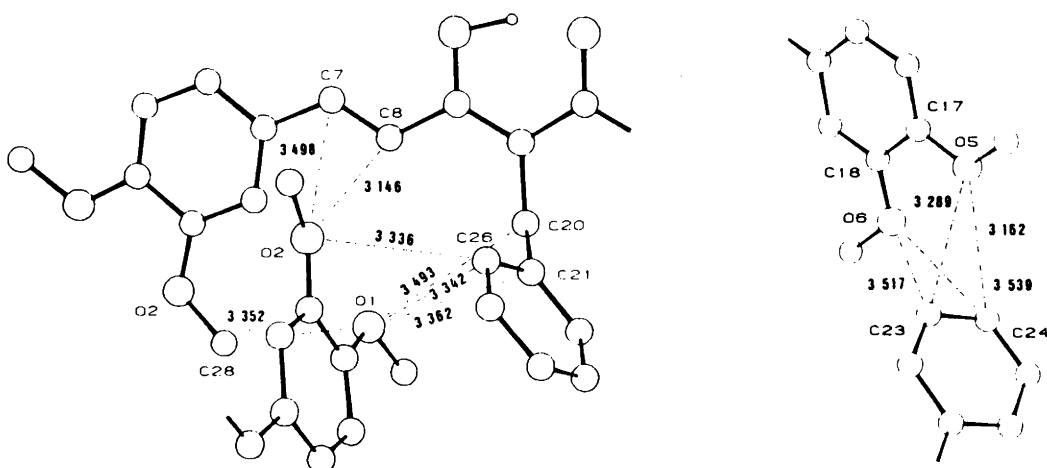Fig. 5. Molecular packing of DHMEDD molecules with hydrogen bonds indicated.

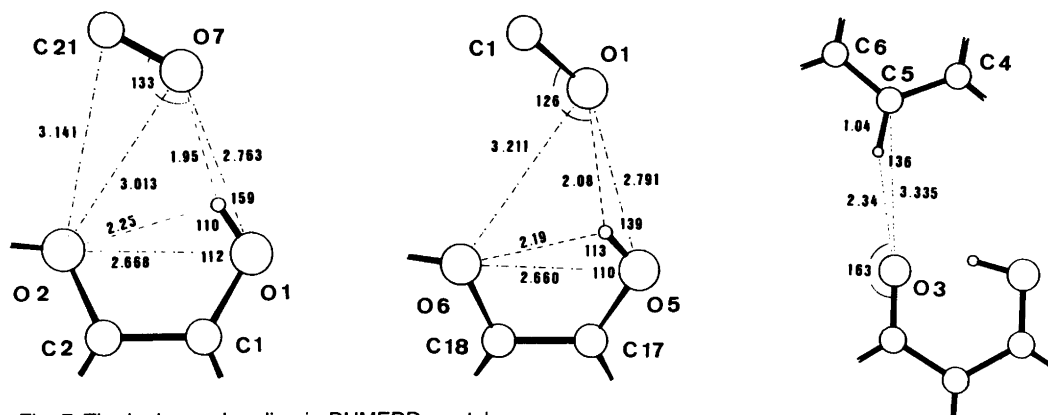Fig. 6. Close intermolecular contacts in the crystals of DDBHDD.

Fig. 7. The hydrogen bonding in DHMEDD crystals.

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