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The Crystal Structure of the Enol Tautomer of 1,3-Diphenyl-1,3-propanedione (Dibenzoylmethane) by Neutron Diffraction

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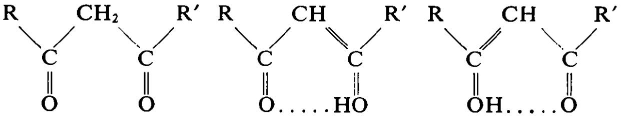
The crystal structure of the enol tautomer of 1,3-diphenyl-1,3-propanedione, $C_{15}H_{12}O_2$, has been determined from three-dimensional, neutron-diffraction data. The structure was refined by full-matrix, least-squares methods to an R value of 0·090 (0·042 for reflexions with $I \geq 2{\cdot}3\sigma_I$) and wR of 0·045 (0·038) using 1660 reflexions. The short, intramolecular O···O contact is 2·463 (4) Å. The enol H atom is asymmetrically placed with respect to the O atoms, the difference in O–H bond lengths being 0·199 (17) Å. Reasons for the asymmetry are discussed in terms of a unique enol tautomer and the disposition of near-neighbour atoms. The results are compared with two previous X-ray diffraction studies.

Introduction

Very short hydrogen bonds of the type –O···H···O–, where O···O is 2·4–2·6 Å, have attracted considerable attention. The main interest has been in the fields of carboxylic acids and their salts, phosphates and salt hydrates. Generally, the hydrogen bond is intermolecular, symmetrical (sometimes because of the symmetry restraints of the space group) and in an ionic environment. Accurate diffraction studies of systems, in which the bond is intramolecular, have also been undertaken. Recently, some work by Williams (1974) has revealed very short hydrogen bonds which are asymmetric. He concludes that the position of the H atom depends on its environment in the crystal.



(I) (II) (III)

(R, R′ = C_6H_5 for this study)

1,3-diketones (I) in the enol form (II),(III) form short, intramolecular hydrogen bonds. By placing different groups in the 1,3-positions, an asymmetric environment can be built into the molecule. These compounds do not have ionic character and tend to pack so that the minimum intermolecular distances are van der Waals contacts. Several of these compounds are being studied by neutron diffraction methods to obtain accurate location of the enol H atom and determine factors which influence the formation of symmetric and asymmetric hydrogen bonds.

Two X-ray diffraction studies have been made of dibenzoylmethane (Williams, 1966; Hollander, Templeton & Zalkin, 1973). The results of Williams indicate an asymmetric hydrogen bond, those of Hollander *et al.* a symmetric bond. This neutron-diffraction study was undertaken before the work of Hollander *et al.* was reported and resolves the ambiguity which has arisen.

Experimental

Dibenzoylmethane was purified by sublimation and recrystallized from cyclohexane/carbon tetrachloride solution. An approximate square prism of volume 47 mm^3 was cut from a large specimen and was used for the analysis. X-ray photographs of a small crystal from the same batch indicated that the cell dimensions and space group were as given in the X-ray structural analyses. The values used in this study are $a = 10{\cdot}853$, $b = 24{\cdot}441$ and $c = 8{\cdot}755$ Å; space group *Pbca* (Hollander *et al.*, 1973).

Data collection

The crystal was mounted so that the a^* axis was slightly offset from the φ axis of the goniostat. Neutron-diffraction data, at room temperature, were collected on the Australian Institute of Nuclear Science and Engineering four-circle diffractometer, 2TAN A, at the Australian Atomic Energy Commission's Research Reactor, HIFAR. Intensities were measured by a θ–2θ step-scan method (Elcombe, Cox, Pryor & Moore, 1971), each step being 0·01° in 2θ. The scan range was 2° in 2θ and the neutron wavelength was 0·983 Å. One quadrant of data was scanned, representing two equivalent sets, up to $2\theta = 65°$. Beyond this angle, the number of reflexions above the general background was small. The reflexion $0\bar{4}\bar{2}$ was measured after every 40 reflexions and showed no significant variation in intensity.

Each intensity was corrected for background and absorption. The absorption coefficient was 1·59 (6) cm^{-1} (measured by transmission through a crystal) and the variation in transmission coefficients was 0·606 to

0·671. For each reflexion, the variance was calculated from $\sigma_I^2=\sigma_C^2+\sigma_A^2+(0{\cdot}03I)^2$ where σ_C^2 is due to counting statistics, σ_A^2 is due to absorption (Elcombe *et al.*, 1971) and 0·03 is determined from the variation in the standard reflexion. The intensities of equivalent reflexions were averaged and, if the variance from the averaging procedure exceeded $\sigma_A^2+\sigma_C^2$, the former variance was substituted for this sum in determining σ_I^2. If the average intensity of a reflexion was negative, it was set to a small positive quantity but its variance was unchanged. The Lorentz factor was applied and the total number of unique reflexions was 1660.

Structure refinement

Structure factors were calculated with the carbon and oxygen positional parameters of Hollander *et al.* (1973). A Fourier synthesis revealed positions for all the H atoms. Refinement, by block-diagonal least squares, of positional and isotropic thermal parameters, gave an R value $(R=\sum||F_o|-k|F_c||/\sum|F_o|)$ of 0·16. All data were used (Moore, 1972), unit weight was assigned to each reflexion and the function minimized was $\sum w(|F_o|-k|F_c|)^2$. Further refinement with anisotropic temperature factors reduced R to 0·11. It was obvious that several reflexions were affected by extinction. Full-matrix, least-squares refinement, incorporating an isotropic extinction parameter (Coppens & Hamilton, 1970) and experimental weights, $w=\sigma_{F_o}^{-2}$, was carried out to convergence. The final R was 0·090 (0·042 for reflexions with $I\geq2{\cdot}3\sigma_I$) and wR $[wR=\sum(||F_o|-k|F_c||)^2/\sum|F_o|^2]$ was 0·045 (0·038). The extinction coefficient was 1·03 (5)×10^{-4} which corresponds to a mosaic spread of 5·7 seconds or a mean particle size of radius 1·01×10^{-3} mm. The reflexion with the most severe extinction was 200, the extinction factor being 0·34. The error-of-fit was 1·18. There was no dependence of $w\Delta^2$ on F_o or $(\sin\theta)/\lambda$. The final difference Fourier synthesis showed no unusual features. The coherent scattering amplitudes were as tabulated by Bacon (1972).

Results

Final atomic coordinates and thermal parameters are shown in Table 1. Interatomic distances and angles are in Table 2; the errors in this table include contributions from the variance–covariance matrix and the errors in the cell dimensions. The least-squares planes fitted to selected atomic groupings are in Table 3. A

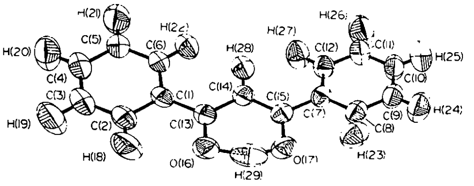


Fig. 1. A diagram of the molecule showing the atomic labelling. Atoms are represented as 50% probability thermal ellipsoids.

Table 1. *Final fractional coordinates and anisotropic thermal parameters* (Å²), × 10^4

The form of the temperature factor is $\exp[-2\pi^2(h^2a^{*2}U_{11}+\ldots+2hka^*b^*U_{12}+\ldots)]$. In this table and all subsequent tables, estimated standard deviations in the least significant digit(s) are shown in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	−569 (2)	−189 (1)	1882 (2)	488 (14)	550 (12)	442 (12)	−124 (11)	−11 (11)	16 (11)
C(2)	−1222 (3)	−516 (1)	856 (3)	541 (16)	683 (17)	546 (15)	−140 (14)	−12 (13)	−43 (13)
C(3)	−760 (3)	−1024 (1)	421 (3)	701 (19)	743 (18)	624 (17)	−193 (16)	−25 (15)	−155 (15)
C(4)	344 (3)	−1208 (1)	999 (3)	778 (19)	607 (17)	645 (17)	−120 (15)	0 (15)	−140 (14)
C(5)	1019 (3)	−882 (1)	1997 (3)	759 (20)	544 (15)	705 (17)	−5 (15)	−93 (16)	−70 (14)
C(6)	557 (2)	−375 (1)	2437 (3)	594 (15)	509 (13)	576 (14)	−37 (12)	−112 (12)	−50 (12)
C(7)	−338 (2)	1617 (1)	4702 (3)	557 (14)	459 (12)	516 (13)	37 (11)	111 (11)	12 (11)
C(8)	−1047 (3)	2054 (1)	5243 (3)	737 (19)	530 (15)	619 (15)	128 (14)	102 (15)	21 (13)
C(9)	−525 (3)	2431 (1)	6252 (3)	995 (24)	539 (16)	704 (18)	110 (16)	118 (18)	−27 (15)
C(10)	699 (3)	2386 (1)	6687 (4)	988 (23)	543 (16)	728 (19)	3 (16)	38 (18)	−108 (15)
C(11)	1404 (3)	1949 (1)	6151 (3)	760 (20)	609 (17)	756 (19)	−44 (15)	21 (17)	−146 (16)
C(12)	891 (2)	1566 (1)	5156 (3)	557 (16)	561 (15)	642 (15)	4 (13)	49 (13)	−69 (13)
C(13)	−1063 (2)	353 (1)	2298 (3)	498 (14)	535 (13)	508 (13)	−83 (11)	−13 (11)	51 (11)
C(14)	−448 (2)	706 (1)	3337 (3)	522 (15)	523 (14)	538 (14)	32 (12)	4 (13)	−9 (11)
C(15)	−919 (2)	1224 (1)	3648 (3)	523 (14)	523 (13)	521 (14)	30 (11)	64 (12)	71 (10)
O(16)	−2077 (3)	499 (1)	1691 (4)	514 (17)	716 (20)	802 (21)	−50 (15)	−136 (16)	32 (18)
O(17)	−1941 (3)	1388 (1)	2996 (4)	553 (19)	653 (18)	898 (24)	97 (16)	−44 (18)	51 (18)
H(18)	−2068 (6)	−368 (3)	392 (7)	758 (40)	1159 (48)	935 (41)	−104 (38)	−232 (34)	−208 (38)
H(19)	−1270 (7)	−1271 (3)	−383 (8)	1060 (48)	1139 (52)	1108 (50)	−133 (40)	−244 (42)	−437 (44)
H(20)	706 (7)	−1600 (3)	662 (8)	1141 (52)	802 (41)	1321 (58)	23 (39)	−33 (44)	−383 (41)
H(21)	1881 (7)	−1015 (2)	2447 (9)	1064 (49)	787 (36)	1358 (57)	167 (38)	−331 (46)	−282 (42)
H(22)	1088 (6)	−128 (2)	3215 (8)	909 (41)	748 (34)	1051 (43)	85 (30)	−405 (37)	−256 (34)
H(23)	−1987 (7)	2089 (3)	4905 (8)	915 (46)	893 (40)	1018 (43)	273 (37)	99 (39)	16 (35)
H(24)	−1077 (7)	2758 (3)	6674 (8)	1356 (56)	774 (37)	1135 (51)	294 (40)	116 (46)	−192 (39)
H(25)	1086 (8)	2675 (3)	7459 (9)	1521 (65)	876 (42)	1124 (49)	67 (42)	−108 (50)	−386 (45)
H(26)	2333 (7)	1911 (3)	6489 (9)	976 (50)	1038 (48)	1325 (58)	0 (41)	−143 (47)	−369 (44)
H(27)	1436 (5)	1233 (3)	4767 (7)	621 (31)	875 (40)	1088 (47)	84 (30)	18 (31)	−316 (37)
H(28)	382 (6)	581 (2)	3887 (7)	900 (41)	718 (32)	903 (39)	149 (31)	−297 (36)	−199 (30)
H(29)	−2222 (5)	1012 (3)	2267 (8)	628 (36)	1444 (67)	1005 (49)	65 (40)	−156 (33)	187 (49)

diagram of the molecule is shown in Fig. 1.* The thermal parameters of the non-hydrogen atoms were fitted to a rigid-body motion model (Schomaker & Trueblood, 1968). The results are in Table 4. Most differences between observed U_{ij} and those calculated from the model are of the order of 1-3σ. The major axes of translation and rotation of the rigid-body are nearly coincident. However, the H atoms have significant other motion. A 'riding motion' correction (Busing & Levy, 1964) was applied to bond lengths involving these atoms.

Discussion

Comparison with X-ray analyses

Comparison of our results, denoted J, with those of Williams (1966), denoted W, and Hollander *et al.* (1973), denoted H, show no gross differences. The co-

Table 2. *Interatomic distances* (Å) *and angles* (°)

Interatomic distances

C(1)—C(2)	1·397 (3)	1·400†
C(2)—C(3)	1·392 (4)	1·394
C(3)—C(4)	1·376 (4)	1·382
C(4)—C(5)	1·390 (4)	1·392
C(5)—C(6)	1·392 (3)	1·394
C(6)—C(1)	1·392 (3)	1·398
C(7)—C(8)	1·397 (3)	1·399
C(8)—C(9)	1·398 (4)	1·399
C(9)—C(10)	1·387 (4)	1·392
C(10)-C(11)	1·395 (4)	1·396
C(11)-C(12)	1·395 (4)	1·395
C(12)-C(7)	1·398 (3)	1·403
C(1)—C(13)	1·474 (3)	1·477
C(13)-C(14)	1·422 (3)	1·425
C(14)-C(15)	1·391 (3)	1·394
C(7)—C(15)	1·475 (3)	1·477
C(13)-O(16)	1·273 (4) 1·293*	1·279
C(15)-O(17)	1·311 (4) 1·332*	1·318
O(16)···O(17)	2·459 (4)	2·463

C(2)—H(18)	1·067 (7) 1·111*	1·069†
C(3)—H(19)	1·079 (7) 1·132*	1·083
C(4)—H(20)	1·078 (7) 1·133*	1·082
C(5)—H(21)	1·066 (8) 1·115*	1·073
C(6)—H(22)	1·077 (6) 1·121*	1·080
C(8)—H(23)	1·066 (8) 1·102*	1·072
C(9)—H(24)	1·065 (7) 1·110*	1·070
C(10)-H(25)	1·065 (8) 1·119*	1·065
C(11)-H(26)	1·054 (9) 1·104*	1·064
C(12)-H(27)	1·061 (6) 1·097*	1·064
C(14)-H(28)	1·066 (6) 1·104*	1·072
O(16)-H(29)	1·360 (9)	1·362
O(17)-H(29)	1·161 (9)	1·163

Interatomic angles

C(2)—C(1)—C(6)	118·9 (2)
C(2)—C(1)—C(13)	119·3 (2)
C(6)—C(1)—C(13)	121·8 (2)
C(1)—C(2)—C(3)	120·3 (2)
C(2)—C(3)—C(4)	120·2 (2)
C(3)—C(4)—C(5)	120·3 (2)
C(4)—C(5)—C(6)	119·6 (3)
C(5)—C(6)—C(1)	120·7 (2)
C(8)—C(7)—C(12)	119·9 (2)
C(8)—C(7)—C(15)	118·3 (2)
C(12)-C(7)—C(15)	121·8 (2)
C(7)—C(8)—C(9)	119·7 (3)
C(8)—C(9)—C(10)	120·6 (3)
C(9)—C(10)-C(11)	119·7 (3)
C(10)-C(11)-C(12)	120·3 (3)
C(11)-C(12)-C(7)	119·9 (2)
C(1)—C(13)-C(14)	122·2 (2)
C(1)—C(13)-O(16)	117·6 (2)
C(14)-C(13)-O(16)	120·1 (2)
C(13)-C(14)-C(15)	120·4 (2)
C(7)—C(15)-C(14)	124·0 (2)
C(7)—C(15)-O(17)	115·7 (2)
C(14)-C(15)-O(17)	120·3 (2)

C(1)—C(2)—H(18)	119·0 (4)
C(3)—C(2)—H(18)	120·6 (4)
C(2)—C(3)—H(19)	119·5 (5)
C(4)—C(3)—H(19)	120·3 (5)
C(3)—C(4)—H(20)	120·4 (4)
C(5)—C(4)—H(20)	119·3 (4)
C(4)—C(5)—H(21)	121·4 (4)
C(6)—C(5)—H(21)	119·0 (4)
C(5)—C(6)—H(22)	118·8 (4)
C(1)—C(6)—H(22)	120·5 (3)
C(7)—C(8)—H(23)	119·7 (4)
C(9)—C(8)—H(23)	120·6 (4)
C(8)—C(9)—H(24)	119·1 (5)
C(10)-C(9)—H(24)	120·3 (5)
C(9)—C(10)-H(25)	119·9 (5)
C(11)-C(10)-H(25)	120·4 (5)
C(10)-C(11)-H(26)	119·8 (4)
C(12)-C(11)-H(26)	119·9 (4)
C(11)-C(12)-H(27)	119·5 (4)
C(7)—C(12)-H(27)	120·6 (4)
C(13)-C(14)-H(28)	120·7 (3)
C(15)-C(14)-H(28)	118·9 (3)
C(13)-O(16)-H(29)	101·8 (3)
C(15)-O(17)-H(29)	102·6 (3)
O(16)-H(29)-O(17)	154·7 (5)

* Distance corrected for 'riding motion'.

† Distances in this column have been corrected for rigid-body motion.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31546 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Equations of planes through selected atomic groupings*

Planes are of the form $lX+mY+nZ+D=0$, where l, m and n are the direction cosines of the plane normal relative to orthogonal axes X, Y and Z, in Å, along a, b and c. D is the distance of the plane from the origin in Å. Deviations (Å), of relevant atoms, from the planes are shown in square brackets

Plane (1): C(13), C(14), C(15), O(16), O(17)

$$0{\cdot}5195X+0{\cdot}3776Y-0{\cdot}7665Z+1{\cdot}832=0$$

[C(13) 0·017, C(14) −0·008, C(15) −0·004, O(16) −0·013, O(17) 0·008, H(29) −0·008, H(28) 0·025, C(1) 0·074, C(7) −0·021]

Plane (2): C(1), C(2), C(3), C(4), C(5), C(6)

$$0{\cdot}4741X+0{\cdot}4281Y-0{\cdot}7694Z+1{\cdot}750=0$$

[C(1) −0·008, C(2) 0·005, C(3) 0·004, C(4) −0·009, C(5) 0·006, C(6) 0·003, H(18) 0·037, H(19) 0·025, H(20) −0·007, H(21) 0·007, H(22) 0·010]

Plane (3): C(7), C(8), C(9), C(10), C(11), C(12)

$$0{\cdot}2838X+0{\cdot}5566Y-0{\cdot}7808Z+1{\cdot}118=0$$

[C(7) 0·000, C(8) 0·005, C(9) −0·009, C(10) 0·008, C(11) −0·003, C(12) −0·001, H(23) −0·004, H(24) −0·023, H(25) −0·007, H(26) 0·000, H(27) −0·020]

Angles between planes (°)

(1)–(2)	(1)–(3)	(2)–(3)
3·9	17·0	13·2

Table 4. *Rigid-body tensors derived from the U_{ij} values of the non-hydrogen atoms*

T × 10⁴	454 (16)	27 (11)	25 (15)
(Å²)		505 (11)	50 (12)
			469 (17)
L × 10⁴	10 (1)	3 (2)	−1 (1)
(rad.²)		67 (6)	32 (4)
			35 (3)
S × 10⁴	−5 (4)	12 (2)	7 (2)
(rad. Å)	16 (6)	17 (7)	18 (5)
	−3 (4)	−16 (4)	−12*

R.m.s. amplitudes (Å) along principal axes of **T**

0·233 0·219 0·202

R.m.s. amplitudes (°) along principal axes of **L**

5·3 2·3 1·7

R.m.s. $\Delta U_{ij}=0{\cdot}0036\ (40)$

* Fixed at this value so that trace **S** = 0.

ordinates of the non-hydrogen atoms of J and H were subjected to a half-normal probability plot analysis (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972). This plot passes through the origin and has a slope of 2 which suggests the pooled estimated standard deviations of the coordinates are about one-half of the correct values. For individual values, differences of up to 5σ were observed, $\sigma^2=\sigma_J^2+\sigma_H^2$. If bond lengths are compared, there is reasonably good agreement between the uncorrected values of W and H and between the values of W, corrected for rigid-body motion, and similarly corrected values of J, but poor agreement between the values of H and the corrected distances of both J and W. Such variations surely suggest that comparison of coordinates, especially of coordinates derived from both X-ray and neutron methods, should only be undertaken after suitable correction for thermal motion.

The molecule is not planar. Dihedral angles between the various planar groups are the same as reported by W. Plane (2) is tilted upwards from plane (1) whereas plane (3) is twisted with respect to plane (1) and makes the larger dihedral angle with it.

The hydrogen bond O(16)···O(17) is 2·463 (4) Å, *cf.* the values of W, 2·468 (7), and H, 2·460 (2) Å. The hydrogen bond is asymmetric, consistent with the results of W but not H. The difference between O(16)–H(29) and O(17)–H(29) is 0·199 (17) Å. Short hydrogen bonds have often been discussed in terms of the thermal motion of the H atom after allowance for contributions from other atoms (Sequeira, Berkebile & Hamilton, 1967; Schlemper, Hamilton & La Placa, 1971; Finholt & Williams, 1973). In Table 5, the results of subtracting the thermal motion, calculated from the rigid-body parameters, from that derived from the least-squares refinement are shown for H(29). The root mean square amplitude of vibration along the O(16)···O(17) vector is 0·27 Å, a value larger than the above difference of 0·199 Å. However, the hydrogen bond can still be described as asymmetric. Whether this is a result of a unique enol tautomer or a large, shallow, asymmetric potential well caused by an asymmetric environment at the hydrogen bond (MacDonald & Speakman, 1972; Schlemper *et al.*, 1971) is uncertain.

Table 5. *R.m.s. component of thermal displacement along principal axes for* H(29) *after correction for rigid-body motion contributions*

	Displacement (Å)	Angle (°) made with O(16)···O(17)
Minimum	0·083	81
Intermediate	0·109	97
Maximum	0·275	11

Inspection of Fig. 4(*a*) of William's (1966) paper shows that the enol ring and a phenyl ring, with C atoms C(1)–C(6), pack such that both these rings are

Table 6. *Non-bonded contacts* (Å) *of* O(16) *and* O(17) *with other non-hydrogen atoms*

O(16)···	C(14)*	2·336	O(17)···	C(14)	2·344
	C(1)	2·352		C(7)	2·361
	C(2)	2·749		C(8)	2·730
	C(15)	2·766		C(13)	2·733
	C(6^{i})	3·427		C(3^{iii})	3·394
	C(4^{ii})	3·475		C(9^{iv})	3·608
	C(5^{ii})	3·553		C(12)	3·635
	C(6)	3·628		C(12^{i})	3·652
	C(6^{ii})	3·985†			

* Superscripts to the atomic labels denote the following transformations with respect to the coordinates in Table 1:

None	$x,\ y,\ z$	i	$-\tfrac{1}{2}+x,\ y,\ \tfrac{1}{2}-z$
ii	$-x,\ -y,\ -z$	iii	$-\tfrac{1}{2}-x,\ -y,\ \tfrac{1}{2}+z$
iv	$x,\ \tfrac{1}{2}-y,\ -\tfrac{1}{2}+z$		

† There are other contacts with O(16) between 3·628 and 3·985.

approximately parallel in adjacent molecules. The other phenyl ring has near-neighbour phenyl rings which are roughly perpendicular to it. Table 6 contains the shorter non-bonded contacts of O(16) and O(17). The outstanding feature is that O(16) has contacts with C(4), C(5) and C(6) of an adjacent molecule which are just greater than van der Waals contacts. Hence the environment in the vicinity of the hydrogen bond is asymmetric.

This 1,3-diketone is symmetrically substituted in the 1- and 3-positions. It might be expected that an equilibrium mixture of the two possible enol tautomers would result. The inequality in the bond lengths of the pairs C(13)–C(14), C(14)–C(15) and C(13)–O(16), C(15)–O(17) is not consistent with such a description. For a unique enol, the values of these bond lengths would be approximately 1·47, 1·33 and 1·2, 1·4 Å. If the final atomic positions obtained represented an average of the two enol tautomers, and any other combinations which might arise due to packing in the crystal, large thermal motion would be expected along the bond directions. This was not evident before or after correction for rigid-body motion. Our evidence, therefore, suggests a unique enol form which has been distorted by an asymmetric environment.

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References

ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* A**27**, 157–163.

BACON, G. E. (1972). *Acta Cryst.* A**28**, 357–358.

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

ELCOMBE, M. M., COX, G. W., PRYOR, A. W. & MOORE, F. H. (1971). *Programs for the Management and Processing of Neutron Diffraction Data.* Report AAEC/TM578, Australian Atomic Energy Commission.

FINHOLT, J. E. & WILLIAMS, J. M. (1973). *J. Chem. Phys.* **59**, 5114–5121.

HAMILTON, W. C. & ABRAHAMS, S. C. (1972). *Acta Cryst.* A**28**, 215–218.

HOLLANDER, F. J., TEMPLETON, D. H. & ZALKIN, A. (1973). *Acta Cryst.* B**29**, 1552–1553.

MACDONALD, A. L. & SPEAKMAN, J. C. (1972). *J. Chem. Soc. Perkin* II, pp. 825–832.

MOORE, F. H. (1972). *Acta Cryst.* A**28**, S256.

SCHLEMPER, E. O., HAMILTON, W. C. & LA PLACA, S. J. (1971). *J. Chem. Phys.* **54**, 3990–4000.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

SEQUEIRA, A., BERKEBILE, C. A. & HAMILTON, W. C. (1967). *J. Mol. Struct.* **1**, 283–294.

WILLIAMS, D. E. (1966). *Acta Cryst.* **21**, 340–349.

WILLIAMS, J. M. (1974). *Diffraction Studies of Real Atoms and Real Crystals.* Abstract I K-3, Int. Crystallogr. Conf., Melbourne.

Acta Cryst. (1976). B**32**, 1811

Structures of Uranyl-Decorated Lecithin and Lecithin–Cholesterol Bilayers

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Dipalmitoyl lecithin and dipalmitoyl lecithin–cholesterol bilayers are capable of binding about the same number of uranyl ions as lecithin molecules. Dispersions of the uranyl-decorated bilayers give very distinct continuous X-ray diffraction peaks up to the seventh order. Electron density projection onto the normal to the membrane is obtained with a resolution of about 6·5 Å. It gives two high peaks separated by 48 Å indicating that uranyl ions are bound at the surfaces of membranes in both lecithin and lecithin–cholesterol bilayers.

Introduction

Uranyl acetate has been widely used as a stain in electron microscopy to investigate the structure of biomembranes. Shah (1969) studied the interaction of uranyl ions with phospholipid monolayers, and concluded that uranyl acetate does not cause degradation of phospholipids and stabilizes the monolayer films. Recently we have shown that adding a very small amount of uranyl acetate to the dipalmitoyl lecithin–water system destroys the lamellar phase and results in dispersion of lecithin membranes (Inoko, Yamaguchi, Furuya & Mitsui, 1975). During the experiments we found that the dispersions of lecithin and lecithin–cholesterol membranes decorated by about equimolar

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