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Crystal and Molecular Structure of Diethyl Ether at 128°K

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Three-dimensional single-crystal X-ray diffraction data of the stable form of diethyl ether have been collected at 128°K. The unit cell is orthorhombic, $a = 11.81(2)$, $b = 8.07(2)$, $c = 10.85(3)$ Å, space group $P2_12_12_1$, $Z = 8$; there are two molecules in the asymmetric unit. The acentric structure has been solved by direct methods and refined to an R index of 0.052. Both molecules have approximately (C_{2v} *trans-trans*) symmetry and the rigid-body model is a good approximation to the thermal motion. For a planar molecule with five atoms, the normal equations matrix is singular and the molecular tensors have been found by a technique of regression on principal components. The packing is loose and this might explain the strong tendency of diethyl ether to give a vitreous form on cooling.

Solid diethyl ether [formula $(\text{CH}_3\text{CH}_2)_2\text{O}$] has been investigated by various techniques. This compound crystallizes in a metastable form (triple point 149.86°K) which, on further cooling, transforms into the stable form (triple point 156.92°K) (Counsell, Lee & Martin, 1971). A glassy state is obtained by depositing vapours or liquid on a surface held near liquid nitrogen temperature (Snyder & Zerbi, 1967; Grude, Haupt & Müller-Warmuth, 1966; Perchard, 1968). A preliminary report of crystallographic data on the stable form has been published (André, Fourme, Kahn & Renaud, 1971). We describe here the crystalline and molecular structure of this form.

Experimental

Merck spectroscopic quality grade diethyl ether kept over sodium was used. Single crystals were grown in sealed Lindemann glass capillaries (diameter 0.3 mm) directly on the goniometer head of Weissenberg and Buerger instruments. The attached cooling system gave a quasi-laminar flow of cold nitrogen which prevented

any frosting of the sample (Renaud & Fourme, 1967); the goniometer head was held near room temperature by means of a built-in furnace. The temperature of the gas was monitored and the overall long-range fluctuations were estimated to be at most $\pm 0.5^\circ\text{K}$. The calibration curve $T = f(mV)$ of the thermocouple was corrected by checking the melting point of several pure organic compounds sealed in capillaries.

Either by slow cooling of the liquid or by pouring liquid nitrogen on the sample, a glassy state was always obtained. At this point, a crystalline powder was induced through thermal shocks, using a small electrically heated manganine coil. From the powder, good single crystals were grown by a zone melting technique at 150°K (Renaud & Fourme, 1966); after a slow cooling down to 128°K, the crystals were grossly oriented between crossed 'Polaroids'.

Cell parameters and space group were determined from precession photographs (Zr-filtered Mo radiation $\lambda = 0.7107$ Å). Crystal data are: formula $(\text{CH}_3\text{CH}_2)_2\text{O}$, M.W. 74.12; orthorhombic, $a = 11.81(2)$, $b = 8.07(2)$, $c = 10.85(3)$ Å, $V = 1034$ Å³, space group $P2_12_12_1$;

$D_x=0.952 \text{ g.cm}^{-3}$; $F(000)=336$; $Z=8$ molecules per unit cell (two in the asymmetric unit); this result is in agreement with previous spectroscopic studies (Perchard, Monier & Dizabo, 1971).

The integrated reflexions $hk0 \rightarrow hk8$ of one single crystal were collected by the equi-inclination Weissenberg technique, using Ni-filtered Cu radiation. In addition, $h0l$ reflexions were recorded with a precession camera. The intensities were measured with a carefully scaled optical densitometer. Lorentz, polarization and spot-extension corrections were applied in the usual way. Absorption was neglected ($\mu R=0.11$ for Cu $K\alpha$). Among 1038 independent reflexions, 131 were too weak to be observed.

All subsequent calculations have been done using local versions of the X-ray 69 System of programs running on an IBM 360-91* then on a UNIVAC 1108 computer.† After data reduction and data scaling programs (*DATRDN* and *DATFIX*), starting values for level scale factors and an overall thermal parameter were obtained. Statistical tests on normalized structure factors confirmed an acentric space group (Table 1).

Table 1. *Statistics applied to E values*

	Experimental	Theoretical for centric	Theoretical for acentric
Average value of			
$ E $	0.901	0.798	0.886
E^2	1.000	1.000	1.000
$ E^2-1 $	0.673	0.968	0.736
Fraction greater than			
1	0.3619	0.3173	0.3679
2	0.0149	0.0455	0.0183
3	0.0000	0.0027	0.0001

Structure determination

The structure has been solved by direct methods, using the *PHASDT* program written by Zechmeister (1969). Further phases are determined and refined by applying the statistical triple-product relationship (Cochran, 1955) and the Sayre equation (Sayre, 1952) in a cyclic procedure to a set of initial phases. In $P2_12_1$, four initial reflexions are needed for origin specifications and enantiomorph selecting. Two two-dimensional and two three-dimensional reflexions were chosen;‡ this set was extended by three two-dimensional reflexions with phases permuted (in increments) in the usual way (Germain & Woolfson, 1968).

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† Computing Center of 'Université Paris Sud', 91, Orsay, France.

‡ For those reflexions, triple-products involving two-dimensional reflexions give a strong indication of phases near imaginary values.

Origin specifications and enantiomorph	Starting set		Phase (°)	
	h	k	(initial value)	(final value)
	11	0 4	2.49	0
	9	5 1	2.48	90
	9	7 0	2.09	90
	7	6 1	2.02	90
	6	8 0	2.91	0/180
	10	4 0	2.19	0/180
	0	8 2	2.44	0/180
				180

Using only E values greater than 1.4, about 100 phases were determined in 10 iteration cycles for each of the eight combinations. The two solutions with the highest correlation (q criterion) were recycled to determine 200 phases. One of the two corresponding E Fourier syntheses yielded the skeleton of the two independent molecules of diethyl ether.

Structure refinement

The coordinates of the oxygen and carbon atoms coming from the E map were taken as a starting point for full-matrix least-squares isotropic and anisotropic refinement (2+3 cycles). The scattering factors are from *International Tables for X-ray Crystallography* (1959); the quantity minimized is $w(|F_o|-|F_c|)^2$ with $w=1$ for measured reflexions and $w=0$ for reflexions too weak to be observed. At this stage, the reliability index R was 0.08 ($R=\sum(|F_o|-|F_c|)/\sum|F_o|$).

A final difference electron density map, calculated with the non-hydrogen atoms only contributing to the F_c 's, showed unequivocally all the 20 hydrogen atoms, including those of the methyl groups. The isotropic temperature factors of those atoms were fixed at 4.0 \AA^2 and all other parameters were varied for two anisotropic refinement cycles. The mean shift/error ratio was 0.08 for the last cycle, the largest one being 0.39 for one of the coordinates of a hydrogen atom; $R=0.051$ for measured reflexions.

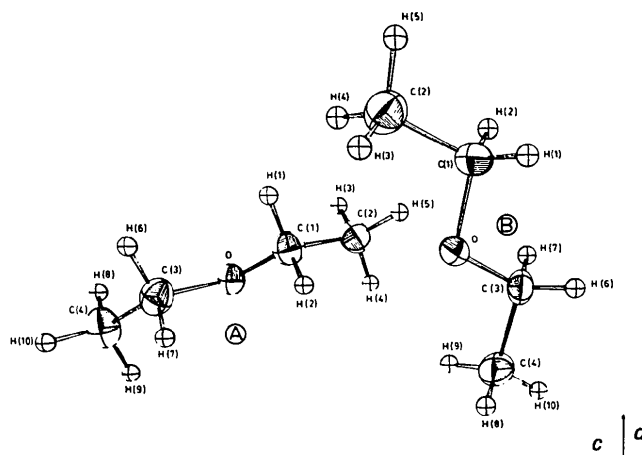


Fig. 1. Drawing of the asymmetric unit. Thermal ellipsoids are scaled to include 50% probability (Johnson, 1965).

Table 2. Atomic parameters

(a) Coordinates and thermal parameters of nonhydrogen atoms with e.s.d.'s in parentheses ($\times 10^5$)The thermal parameters are in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Molecule A	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	9595 (23)	49376 (33)	70947 (26)	469 (21)	693 (38)	397 (32)	-22 (26)	-16 (20)	6 (29)
C(1)	14435 (39)	41862 (57)	60279 (43)	511 (33)	1253 (72)	502 (48)	41 (45)	-5 (32)	-153 (51)
C(2)	15823 (41)	55001 (63)	50525 (48)	570 (36)	1496 (82)	566 (48)	-168 (51)	48 (33)	-14 (57)
C(3)	7745 (38)	37533 (53)	80567 (45)	615 (36)	890 (63)	588 (52)	-29 (41)	-101 (34)	142 (51)
C(4)	2668 (46)	46514 (62)	91552 (46)	826 (44)	1345 (84)	518 (50)	-85 (57)	36 (39)	35 (56)
Molecule B									
O	14438 (22)	16109 (35)	33776 (26)	303 (18)	928 (42)	368 (34)	54 (26)	24 (18)	36 (29)
C(1)	25903 (34)	11563 (57)	30930 (44)	325 (28)	1222 (72)	554 (55)	-20 (39)	12 (29)	-71 (54)
C(2)	31014 (39)	4214 (61)	42285 (46)	498 (34)	1252 (76)	598 (53)	150 (45)	-80 (31)	-56 (54)
C(3)	9124 (36)	24468 (53)	23830 (39)	491 (31)	1068 (63)	313 (45)	32 (42)	-24 (30)	1 (46)
C(4)	-2920 (37)	28038 (58)	27451 (46)	437 (32)	1316 (75)	644 (58)	192 (46)	-65 (32)	-7 (53)

Table 2 (cont.)

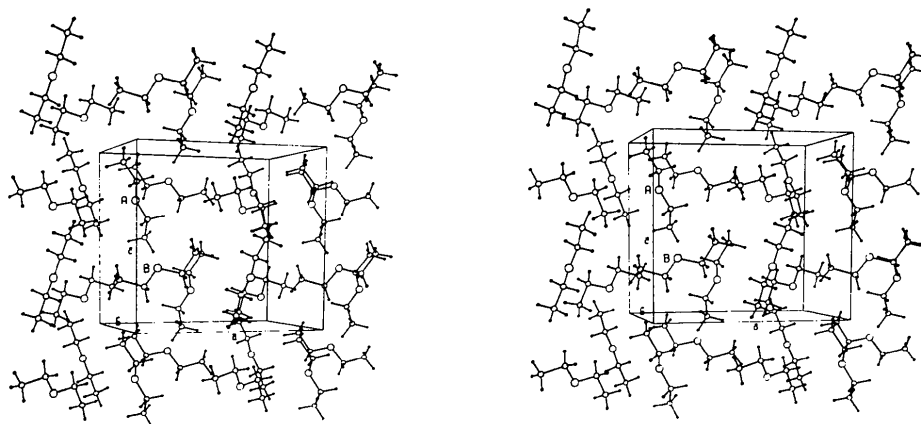
(b) Coordinates of hydrogen atoms ($\times 10^3$)(1) Assuming a C_{2v} symmetry and tetrahedral bond angles.(2) Found after the last cycle of full-matrix least squares refinement (e.s.d. are respectively 5,8,6 on the last digit of $x/a, y/b, z/c$).

Molecule A	(1)			(2)		
	x/a	y/b	z/c	x/a	y/b	z/c
H(1)	220	370	623	222	365	615
H(2)	94	329	571	89	311	566
H(3)	208	641	538	211	631	535
H(4)	82	595	484	92	602	487
H(5)	196	499	426	189	497	420
H(6)	151	325	831	153	310	854
H(7)	25	287	777	19	265	773
H(8)	76	556	944	71	575	942
H(9)	-50	513	891	-64	528	892
H(10)	12	385	983	13	393	982
Molecule B						
H(1)	260	33	241	271	24	240
H(2)	303	216	286	315	234	278
H(3)	265	-58	451	267	-62	451
H(4)	310	125	491	314	136	486
H(5)	388	4	407	393	6	400
H(6)	93	174	163	93	184	167
H(7)	132	351	221	134	358	220
H(8)	-68	176	296	-67	194	302
H(9)	-28	356	348	-34	344	360
H(10)	-70	335	205	-65	343	216

Besides this, the hydrogen atoms were *a priori* calculated assuming a (C_{2v} , *trans-trans*) molecular symmetry, with C-H bonds of 1.00 Å and tetrahedral bond-angles. Two new refinement cycles of all but hydrogen atom parameters gave a *R* index of 0.052. The final coordinates and thermal parameters of carbon and oxygen atoms remained practically unchanged [Table 2(a)]; the coordinates of 'free' and constrained hydrogen atoms are given in Table 2(b). Observed and calculated structure factors for the constrained solution are listed in Table 3.

Rigid body analysis of thermal motion

It could be expected that for a small molecule such as diethyl ether the rigid body model should apply. Moreover, it was of interest to compare the motions of the two independent molecules in the asymmetric unit. It should be noted that five coplanar atoms lie on a quadratic curve; this leads to a singularity in the least-squares normal-equations matrix (Schomaker & Trueblood, 1968). As pointed out by Johnson (1970), this singularity can be eliminated if the linear least-squares problem is solved by a statistical technique of regression on principal components. The program *JMTFAC* (Burns, Ferrier & MacMullan, 1967b) has

Fig. 2. Stereoscopic illustration of the contents of the unit cell (Johnson, 1965). a, b, c denote the cell axis translations.

soids was done according to size, shape and orientation (Table 6). The rigid body model gives a fairly good description of the thermal motion in both cases. The RMS amplitudes of libration and translation are also very similar.

Molecular structure

The asymmetric unit of the crystal structure is shown in Fig. 1. Bond lengths and bond angles are given in Table 7.

Table 4. Rigid-body tensors for diethyl ether

Schomaker–Trueblood analysis. Centre of mass coordinates.

	Molecule A			Molecule B		
	T. (\AA^2) $\times 10^4$	312	-9 269	-33 23 307	264	-3 215
R.M.S. amplitudes of translation (\AA)	0.16	0.19	0.17	0.15	0.18	0.16
L (deg ²)	13.8	3.7 9.3	2.38 -1.1 13.8	13.1	-2.8 6.9	-7.1 -3.4 12.3
R.M.S. amplitudes of libration (deg)	2.6	4.1	3.7	1.4	4.4	3.3
S. (\AA . rad) $\times 10^4$	-16 15 -27	-38 6 -8	7 -12 10	-35 7 -14	27 20 3	-3 1 15

Table 5. Comparison of observed and calculated U_{ij} ($\text{\AA}^2 \times 10^4$) (centre of mass coordinates)

Molecule A	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
	O	251	301	240	270	306	306	29	33	-33	-27	-16
C(1)	331	354	392	347	351	351	-1	-2	-37	-30	77	54
C(2)	323	298	522	543	389	389	56	55	14	7	7	14
C(3)	380	354	318	310	380	380	17	17	-61	-70	-90	-64
C(4)	319	298	470	473	547	547	62	61	59	-57	-22	-38
	R.m.s. deviation:32											
Molecule B	217	259	208	216	315	315	-12	-3	-8	-6	11	3
C(1)	291	291	316	275	357	357	-60	-47	-61	-54	16	21
C(2)	290	258	417	438	415	415	12	-2	0	-6	65	65
C(3)	310	292	237	256	339	339	56	39	-16	-25	56	58
C(4)	251	258	419	412	457	457	-10	0	4	9	47	49
	R.m.s. deviation:26											

Table 6. Size, shape and orientation parameters calculated on the basis of the Schomaker–Trueblood analysis

U^o and U^c denotes the sum of the eigenvalues of the observed and calculated ellipsoids; S and θ are the shape and orientation parameters according to Burns *et al.* (1967a).

	U^o ($\text{\AA}^2 \times 10^4$)	(ΔU^o) ($\text{\AA}^2 \times 10^4$)	$U^o - U^c$ ($\text{\AA}^2 \times 10^4$)	S	θ (deg)
Molecule A					
O	797	28	-80	38	34.8* (D)
C(1)	1074	44	22	38	16.4 (R)
C(2)	1234	47	5	16	10.9 (R)
C(3)	1079	45	35	9	12.5 (R)
C(4)	1336	51	18	7	6.0 (R)
Molecule B					
O	740	29	-50	42	28.2 (R)
C(1)	963	47	41	12	16.2 (R)
C(2)	1122	49	10	25	8.8 (R)
C(3)	886	42	-1	24	17.6 (R)
C(4)	1127	49	0	3	3.6 (R)

* The large value of the orientation parameter of the oxygen atom in molecule A is acceptable because of a nearly circular section of the thermal ellipsoid.

Table 7. Bond lengths and bond angles

Molecule A			
O—C(1)	1.426 (6) Å	O—C(1)—C(2)	108.33 (39)°
O—C(3)	1.432 (6)	O—C(3)—C(4)	108.29 (38)
C(1)—C(2)	1.507 (7)	C(1)—O—C(3)	111.65 (35)
C(3)—C(4)	1.518 (7)		
Molecule B			
O—C(1)	1.437 (5) Å	O—C(1)—C(2)	107.75 (37)°
O—C(3)	1.419 (5)	O—C(3)—C(4)	108.11 (35)
C(1)—C(2)	1.495 (7)	C(1)—O—C(3)	112.02 (32)
C(3)—C(4)	1.504 (7)		

'Means' molecule with C_{2v} symmetry
Bond lengths and bond angles are (a) uncorrected and
(b) corrected for rigid body motion.

	(a)	(b)
O—C(1)	1.428 Å	1.433 Å
C(1)—C(2)	1.506	1.512
C(1)—O—C(3)	111.83°	111.65°
O—C(1)—C(2)	108.12	107.54

Molecule A

The equation of the best plane for oxygen and carbon atoms is:

$$10.820X + 1.561Y + 3.812Z = 4.506$$

Distances of atoms from this plane:

O	0.009 Å
C(1)	0.008
C(2)	-0.008
C(3)	-0.009
C(4)	0.000

The skeleton does not depart significantly from planarity.

Molecule B

The equation of the best plane for oxygen and carbon atoms is:

$$3.605X + 7.210Y + 3.573Z = 2.907$$

Distances of atoms from this plane:

O	-0.018 Å
C(1)	-0.034
C(2)	0.026
C(3)	0.037
C(4)	-0.010

For this molecule, there is a small but significant departure from planarity.

The two independent molecules of the asymmetric unit, although in general position, have nearly perfect C_{2v} symmetry, with *trans-trans* configuration. This result is in agreement with previous conclusions from spectroscopic data (Snyder & Zerbi, 1967).

Average values for bond lengths and bond angles between oxygen and carbon atoms are also given.

Those values have been corrected for rigid-body libration (Schomaker & Trueblood, 1968).

Molecular packing

The most striking feature of the structure is a fairly loose packing (Fig. 2). All intermolecular distances between non-hydrogen atoms are larger than the sum of van der Waals radii by at least 0.2 Å; contacts are found only when hydrogen atoms are involved.

This fact explains why a vitreous form is usually obtained by cooling the liquid. The crystalline state is probably hardly energetically more favourable than the amorphous and, for the same reason, the existence of a metastable form is not surprising. Perchard *et al.*, (1971), from an analysis of spectroscopic data, concluded that the intermolecular forces in the stable phase are weak and that no association exists between the molecules of the asymmetric unit.

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