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References

Cochran, W. (1948). *Acta Cryst.* **1**, 54.
Cox, E. G., Gross, L. & Jeffrey, G. A. (1947). *Proc. Leeds Phil. Lit. Soc.* **5**, 1.
Goodwin, T. H. & Hardy, R. (1938). *Phil. Mag.* **25**, 1096.
Lipson, H. & Beevers, C. A. (1936). *Proc. Phys. Soc. Lond.* **48**, 772.
Robertson, J. M. (1936). *Phil. Mag.* **21**, 176.
Shaffer, P. A., Schomaker, V. & Pauling, L. (1946). *J. Chem. Phys.* **14**, 648.

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The Crystal Structure of Hexamethylenediamine and its Dihalides. Hexamethylenediamine Dihydrobromide

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Hexamethylenediamine dihydrobromide, $C_6H_{18}N_2Br_2$, is monoclinic, space group $P2_1/c$, with four molecules per unit cell. Only minute needle crystals were available, but the structure factors of the principal zone, (0*kl*), have been measured. A Patterson analysis determines the positions of the eight bromine atoms in this projection without ambiguity. This is followed by a two-dimensional Fourier synthesis from which the approximate positions of all the atoms can be estimated. The results are consistent with an extended chain structure of normal bond distances (1·4–1·6 A.), and with Br–N distances lying between 3·2 and 3·5 A. These results provide a basis for a more accurate determination of the structure of the isomorphous dihydrochloride.

Introduction

Very few detailed analyses of structures involving normal aliphatic carbon chains have yet been made. In the crystalline state such chains usually occur as fully extended zigzags of carbon atoms, and are generally assumed to be regular. Careful analyses have been made for certain long-chain paraffins (Müller, 1928), and very accurate values have been obtained for the average C–C distance along the chain, but the methods employed do not lead to the inspection of individual atoms or bonds within the molecule. Recent work on the normal aliphatic dicarboxylic acids, however, has indicated certain minor but apparently significant bond-length variations extending over chains of four and even eight methylene groups (MacGillavry, 1941; Morrison & Robertson, 1949). The investigation of such effects in normal aliphatic compounds of a different type is one reason for the present series of X-ray studies on hexamethylenediamine and its dihalides.

Recently, hexamethylenediamine has also attained considerable practical importance as one of the parent substances in the preparation of numerous polyamides of high molecular weight. These substances are prepared by the condensation of hexamethylenediamine with certain dibasic acids, such as adipic or sebacic acid, and the polymers so formed constitute some of the well-known 'nylon' fibres. X-ray structural analyses of some of these fibres have been made (Bunn & Garner, 1947), but the work is necessarily difficult because of the restricted amount of diffraction data available. The present single-crystal studies of one of the parent substances may be considered as a contribution to this field as well.

Hexamethylenediamine itself is a low-melting hygroscopic solid which demands a rather special technique for its preservation during X-ray experiments. The subject has therefore been approached by a preliminary study of the easily crystalline dihalides. The relatively heavy halogen atoms in these compounds also make it possible to elucidate the molecular structure in a very direct manner by means of Patterson series.

The structure of the dihydrobromide, which is described in the present paper, has been determined only approximately, because only minute crystals were available. It has been chosen as a starting-point, however, because the heavy bromine atoms make the analysis extremely direct. The approximate parameters obtained may then be utilized in a much more comprehensive analysis of the dihydrochloride, which appears to be isomorphous with the dihydrobromide. In the analysis of the dihydrochloride, which will be described in a subsequent paper, the finer details of the chain structure are established.

Crystal data

Hexamethylenediamine dihydrobromide, $C_6H_{18}N_2Br_2$; *M*, 278·0; m.p. 263° C.; *d*, calc. 1·656, found 1·667. Monoclinic prismatic, $a = 4{\cdot}68 \pm 0{\cdot}02$, $b = 14{\cdot}53 \pm 0{\cdot}04$,

$c=16\cdot21\pm0\cdot04$ A., $\beta=91°$ (approx.). Absent spectra, ($h0l$) when l is odd, ($0k0$) when k is odd. Space group, C^5_{2h}–$P2_1/c$. Four molecules per unit cell. No molecular symmetry. Volume of the unit cell $=1103$ A.^{3} Absorption coefficient for X-rays ($\lambda=1\cdot54$ A.), $\mu=91\cdot0$ cm.$^{-1}$. Total number of electrons per unit cell $=F(000)=552$.

The most suitable solvent proved to be glacial acetic acid, from which the dihydrobromide was obtained as very fine colourless needles, elongated in the direction of the a axis. Even after slow crystallization in a vacuum flask the cross-section of the needles did not exceed $0\cdot05\times0\cdot05$ mm. The X-ray measurements were therefore confined to rotation, oscillation and moving-film photographs taken about the a axis, and the β angle (91°) has been estimated only approximately.

Patterson analysis

From the data given above it is clear that two bromine atoms occupy general positions in the unit cell, and there should be a good chance of determining their co-ordinates by the Patterson method, the scattering power of bromine (atomic number 35) being five times greater than that of any other atom present. The structure amplitudes of the ($0kl$) reflexions were therefore evaluated (Table 2), and with the squares of these quantities as coefficients a double Fourier synthesis was performed, giving a projection of the interatomic vectors on the (100) plane. The resulting vector map, with contours drawn at unit intervals on an arbitrary scale, is shown in Fig. 1.

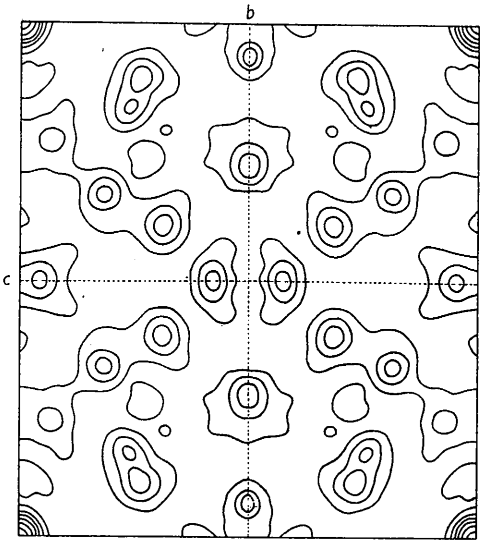

Fig. 1. Patterson projection on (100).

We note that the vector map (Fig. 1) shows twenty-four prominent peaks of equal height in the unit cell, apart from the peak at the origin. There are also at least four other peaks of somewhat less height, situated near the corners. Now, for a unit cell containing n atoms and a centre of symmetry, the number of distinct vectors, and hence the total number of peaks, should be $\frac{1}{2}n^2$. Of these, the number of peaks of double height, due to equal and parallel vectors, is $\frac{1}{2}n(n-2)$, and the number of peaks of normal height, due to single interactions across the centre of symmetry, is n.

In the present example $n=8$ (bromine atoms), and the number of peaks of double height should therefore be twenty-four, in agreement with the number observed. There should also be eight smaller peaks, due to single vectors. Of these, four can be determined accurately on the map, but the other four are only partially resolved. The vector map thus provides entirely independent evidence of the number of heavy atoms in the unit cell, and the result is in agreement with that deduced from the density, unit-cell volume and chemical formula.

With regard to the co-ordinates of the bromine atoms, it is observed that there are four vectors with y co-ordinate equal to $\frac{1}{2}b$ and four vectors with z co-ordinate equal to $\frac{1}{2}c$. These special positions arise from vectors between atoms related by the symmetry operations of the space group, as has been pointed out by Harker (1936). In the a-axis projection the equivalent points for the space group $P2_1/c$ are

$$(1)\ y,\ z;\qquad (2)\ -y,\ -z;$$
$$(3)\ \tfrac{1}{2}+y,\ \tfrac{1}{2}-z;\qquad (4)\ \tfrac{1}{2}-y,\ \tfrac{1}{2}+z;$$

and the following special vectors arise

$$(1)(3)\ \tfrac{1}{2},\ \tfrac{1}{2}-2z;\qquad (1)(4)\ \tfrac{1}{2}-2y,\ \tfrac{1}{2};$$
$$(2)(4)\ \tfrac{1}{2},\ \tfrac{1}{2}+2z;\qquad (2)(3)\ \tfrac{1}{2}+2y,\ \tfrac{1}{2}.$$

With two bromine atoms in the asymmetric unit there should be eight special vectors of this type, and this is the result shown by the Patterson map. Further analysis of this result provides four possible values for the y co-ordinate of each bromine atom, and four possible values for the z co-ordinate of each bromine atom, as follows:

$2\pi y/b$	14°	166°	81°	99°
$2\pi z/c$	78·5°	101·5°	40·5°	139·5°

The correct grouping of the co-ordinates may be found by an examination of the possible vectors given by the above values and comparison with the Patterson map. The final choice contains one co-ordinate from each pair of supplements, and any remaining ambiguity is easily eliminated by the calculation of a few structure factors. The result is as follows:

	Br (1)	Br (2)
$2\pi y/b$	81°	166°
$2\pi z/c$	78·5°	139·5°

This result may be verified in a simple and direct manner without recourse to structure-factor calculation by the construction of the theoretical vector map (Robertson, 1943). This is shown in Fig. 2, and it is clear that the correspondence with the experimental map in Fig. 1 is very exact.

Structure analysis and co-ordinates

With the co-ordinates of the bromine atoms determined, the structure analysis can proceed by successive approximations. The structure factors, with phase constants, were calculated for the bromine contributions alone, and a double Fourier synthesis was effected, giving a projection on the (100) plane. The electron-density map so obtained gave some resolution for all the atoms expected from the chemical structure, but with considerable distortions. The co-ordinates of the nitrogen and carbon atoms were now estimated from this result, and included in a revised set of structure-factor calculations. The co-ordinates were further refined by successive Fourier syntheses, and the final projection, over one-quarter of the unit cell, is shown by the electron-density map in Fig. 3. The positions assigned to the atoms are indicated in Fig. 4, and the co-ordinates are tabulated in Table 1. (The figures in brackets for the atoms N (1), C (1), C (6) and N (2) refer to the atoms required to complete the chain molecule; they are derived from the co-ordinates of the atoms in the quarter unit cell of Fig. 3 by the operations appropriate to the space group $P2_1/c$.)

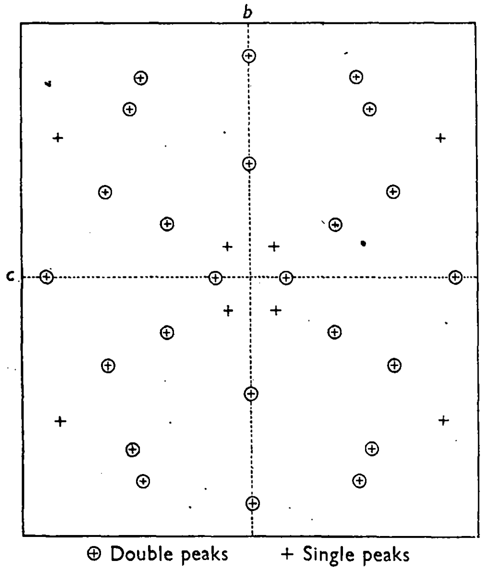

Fig. 2. Theoretical vector map, projected on (100).

It is clear from the appearance of the contour map that the lighter atoms are severely distorted by diffraction effects, and no great accuracy can be attached to the above co-ordinates. The Fourier series is also very incomplete, as weak reflexions could not be observed owing to the extremely small crystal specimens available. The chief value of the investigation is that it provides a reliable basis for the accurate determination of the isomorphous dihydrochloride structure which is described in a subsequent paper.

Table 1. *Co-ordinates referred to crystal axes*

(Origin at centre of symmetry)

Atom (cf. Fig. 4)	y (A.)	z (A.)	$2\pi y/b$ (°)	$2\pi z/c$ (°)
Br (1)	3·31	3·50	82·3	77·7
Br (2)	6·70	6·28	166·4	139·2
N (1)	5·57	4·03	138·5	89·3
	(−1·69	4·07	−41·5	90·7)
C (1)	6·54	2·96	162·7	65·7
	(−0·72	5·14	−17·3	114·3)
C (2)	0·23	5·62	5·8	124·8
C (3)	1·15	6·45	28·5	143·0
C (4)	2·22	7·18	55·2	159·4
C (5)	3·24	7·84	80·3	174·0
C (6)	3·08	0·18	76·6	4·0
	(4·18	8·28	103·4	184·0)
N (2)	1·60	0·85	39·6	18·9
	(5·66	8·95	140·4	198·9)

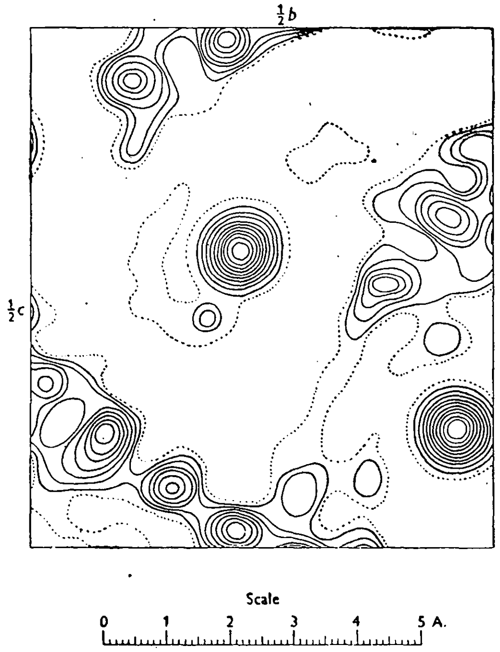

Fig. 3. Electron-density projection along a axis on (100), showing asymmetric unit. Contour intervals: one electron per A.^{2} except on bromine atoms where increment is 5 electrons per A.^{2} One-electron line dotted.

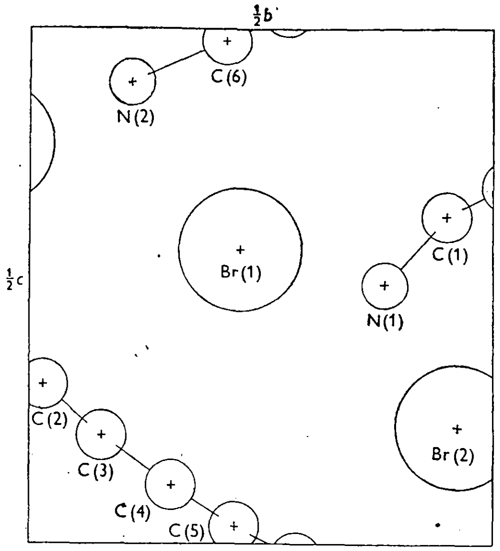

Fig. 4. Arrangement of atoms in the a-axis projection.

Owing to the absence of experimental data for the other zones no attempt has been made to evaluate the

Table 2. *Measured and calculated values of the structure factor*

hkl	$F_{\text{meas.}}$	$F_{\text{calc.}}$	*hkl*	$F_{\text{meas.}}$	$F_{\text{calc.}}$	*hkl*	$F_{\text{meas.}}$	$F_{\text{calc.}}$	*hkl*	$F_{\text{meas.}}$	$F_{\text{calc.}}$
040	151	+152	0,2,13	25	+ 33	059	67	+ 74	096	45	− 51
060	61	− 61	0,2,14	80	− 89	0,5,12	60	+ 69	097	74	− 76
0,10,0	53	− 51	0,2,15	36	− 37				0,9,11	25	− 36
0,12,0	60	− 65	0,2,16	25	+ 43	062	50	+ 54			
						063	159	+150	0,10,1	31	− 32
002	62	− 57	031	30	+ 35	064	48	− 53	0,10,3	64	+ 80
006	99	− 83	032	141	+120	065	62	− 70	0,10,4	50	+ 39
008	59	+ 64	034	45	− 36	067	63	− 57	0,10,5	33	− 41
0,0,10	81	+ 83	035	127	−108	0,6,10	32	− 29	0,10,7	42	− 46
0,0,12	79	− 67	037	47	+ 36	0,6,11	24	+ 13	0,10,10	35	− 29
0,0,18	43	+ 60	038	125	−119	0,6,15	69	− 71	0,10,15	28	− 56
			039	33	+ 24						
011	60	+ 72	0,3,10	73	+ 88	071	17	− 23	0,11,1	53	− 57
012	20	− 19	0,3,13	43	− 48	072	119	+103	0,11,3	58	+ 63
013	25	− 33				073	50	+ 38	0,11,6	25	− 28
014	112	+105	041	153	+138	075	43	− 47	0,11,7	36	+ 42
015	89	− 79	042	70	− 60	076	28	− 21	0,11,9	71	− 83
016	128	−121	043	26	+ 26	077	47	+ 51			
018	60	+ 65	046	16	− 8	078	62	− 75	0,12,1	49	+ 56
019	91	+ 87	047	56	− 48	079	46	− 55	0,12,3	35	− 28
0,1,10	41	− 49	048	38	+ 45	0,7,10	42	+ 55	0,12,6	25	+ 25
0,1,12	40	+ 47	0,4,10	68	+ 67	0,7,11	35	+ 45	0,12,7	25	− 17
0,1,13	48	− 44	0,4,11	72	+ 69				0,12,8	37	− 32
			0,4,12	54	− 57	081	129	+120			
021	12	+ 8	0,4,16	34	− 36	082	33	− 31	0,13,1	35	− 46
022	66	+ 80				084	49	+ 50	0,13,5	71	+ 82
023	24	+ 12	051	31	+ 34	087	62	− 57	0,13,7	35	− 43
024	240	−216	052	69	+ 57	088	23	− 11			
025	54	− 53	053	47	− 54	0,8,11	79	+ 89	0,14,1	35	− 53
026	21	− 21	054	108	+ 93				0,14,4	43	+ 46
027	56	− 47	055	17	+ 27	092	41	+ 45	0,14,10	20	− 11
028	61	+ 61	056	156	−138	094	30	+ 27			
029	18	+ 16	057	38	− 49	095	76	+ 90	0,15,3	33	+ 46

third co-ordinate of the atoms of the dihydrobromide structure directly. A reasonable model for the molecular structure may, however, be inferred from the information available. The projection (Figs. 3 and 4) shows parts of three molecules in which there is an almost linear arrangement of carbon atoms, with the two terminal nitrogen atoms inclined at a small angle to the carbon chain. We therefore infer that the plane of the carbon zigzag must lie almost at right angles to the projection plane, the view in elevation along the *b* axis being as shown in Fig. 5.

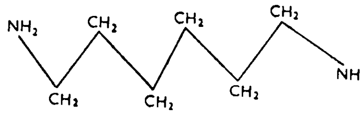

Fig. 5. Elevation view of hexamethylenediamine chain.

No attempt can be made to evaluate accurately the bond lengths in the chain, but the data are consistent with C–C and C–N distances of between 1·4 and 1·6 A. There is evidence that the terminal nitrogen atoms are somewhat deflected from the plane of the carbon chain, presumably by the influence of the ionic halogen lattice.

An extended view of the principal projection is shown in Fig. 6. If the remaining co-ordinates ($2\pi x/a$) of the bromine ions are assumed to be the same as the ($2\pi x/a$) co-ordinates of the chlorine ions in the dihydrochloride structure, then the Br–N distances lie between 3·2 and 3·5 A. These values are in good agreement with the sum of the bromine ionic radius (1·95 A.) and the ammonium ionic radius (1·40 A.) (Pauling, 1939).

Experimental

Hexamethylenediamine dihydrobromide was prepared by the slow addition of a concentrated solution of hydrobromic acid in acetic acid to a methanolic solution of hexamethylenediamine. Recrystallization from glacial acetic acid yielded extremely fine crystals.

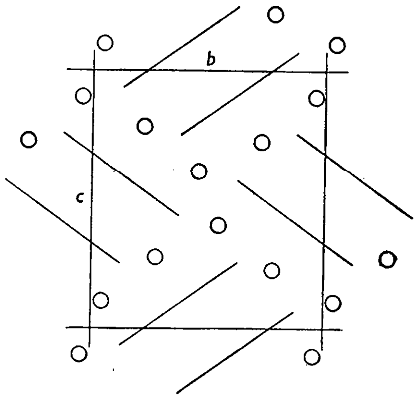

Fig. 6. Extended view of *a*-axis projection. The straight lines represent the hexamethylenediamine chains, the circles the bromine ions.

The X-ray work was carried out with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54$ A.). The crystal employed for the intensity work had a cross-section, normal to the rotation axis, of 0·05 × 0·05 mm. The ($0kl$) reflexions were recorded as the equatorial layer line of a moving-film photograph. The strong and weak reflexions were correlated by the multiple-film technique, and were estimated visually. Structure amplitudes, derived by the usual formulae for a mosaic crystal, are listed in Table 2.

In the Fourier synthesis the axial subdivisions were $\frac{1}{60}b = 0{\cdot}242$ A. and $\frac{1}{60}c = 0{\cdot}270$ A. The co-ordinates estimated for all the atoms were used in a recalculation of the structure factors, and the results are given in Table 2. The average discrepancy, referred to the measured structure factors, is 14 %. A systematic survey for all the reflexions possible with copper radiation was made, but to save space in the table only the structure factors actually measured are listed. These amount to only about 40 % of the possible number, owing to the small size of the crystal.

In the calculation of the structure factors the atomic scattering curves given in the *International Tables for the Determination of Crystal Structures* were employed, and were corrected for temperature according to the Debye-Waller formula, the constant B being given the value 2×10^{-16} A.^{2} The absolute scale was obtained by correlation with these calculated values.

In conclusion, one of us (W. P. B.) wishes to express his thanks to Messrs Imperial Chemical Industries Ltd., for a grant which enabled him to take part in this work.

References

Bunn, C. W. & Garner, E. V. (1947). *Proc. Roy. Soc.* A, **189**, 39.

Harker, D. (1936). *J. Chem. Phys.* **4**, 381.

MacGillavry, C. H. (1941). *Rec. Trav. Chim. Pays-Bas*, **60**, 605.

Morrison, J. D. & Robertson, J. M. (1949). *J. Chem. Soc.*

Müller, A. (1928). *Proc. Roy. Soc.* A, **120**, 437.

Pauling, L. (1939). *The Nature of the Chemical Bond.* Cornell: University Press.

Robertson, J. M. (1943). *Nature, Lond.*, **152**, 411.

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The Crystal Structure of Diethyl Terephthalate

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The crystal structure of diethyl terephthalate has been determined. The crystals are monoclinic, with cell dimensions $a = 9{\cdot}12$ A., $b = 15{\cdot}39$ A., $c = 4{\cdot}21$ A., $\beta = 93{\cdot}4°$. The space group is $P2_1/n$ with two centrosymmetrical molecules in the unit cell. The atomic co-ordinates were obtained from packing considerations and were refined by c-axis Fourier projections and line syntheses. The molecule is planar, with the exception of the terminal CH_3 groups, and the only intermolecular forces are of the van der Waals type, the shortest distance between adjacent molecules being 3·4 A.

Introduction

The structure of diethyl terephthalate is of particular interest since no previous detailed X-ray work on aromatic esters has been reported. It was hoped to obtain information concerning the molecular configuration, including the planarity of the molecule, interatomic distances and interbond angles, and also concerning the nature of the intermolecular contacts and binding forces in this type of compound.

Unit-cell and space-group measurements were made on some related esters (Table 1), and diethyl terephthalate was selected as the most suitable for a complete structure determination.

Experimental

Diethyl terephthalate crystallizes from most organic solvents in the form of c-axis needles with predominant {110} faces, terminated by the two {101} dome faces. There is also a good (101) cleavage. Pseudo-orthorhombic contact twins occur frequently by 180° rotation about the c axis, but these could be identified by their anomalous extinction effects between crossed nicols.

The unit-cell dimensions were obtained with an accuracy of ±0·015 A. from symmetrical oscillation photographs taken on a camera with calibrated knife-edges. Measurements were made from zero-layer-line reflexions for which θ approached 90°, and Cu $K\alpha_1$ and

Table 1

Compound	Formula	Space group	a (A.)	b (A.)	c (A.)	β (°)	No. of molecules
Diethyl terephthalate	$C_6H_4(COO.C_2H_5)_2$	$P2_1/n$	9·12	15·39	4·21	93·4	2
Dimethyl terephthalate	$C_6H_4(COO.CH_3)_2$	$Pbca$	22	7·1	5·7	—	4
Diethylol terephthalate	$C_6H_4(COO.C_2H_4OH)_2$	$P2_1/a$	25·9	5·48	8·58	99	4
Ethylene dibenzoate	$C_2H_4(OOC.C_6H_5)_2$	$Pbca$	21·9	16·36	7·60	—	8