carbonate ion. The three remaining K–O(water) distances range from 2·827 to 3·065 Å. The variation in the K–O distances is typical.

The network of hydrogen bonds can be seen in Fig. 3. Each of the H atoms associated with the water molecules forms a single, strong hydrogen bond with an O atom of a neighboring carbonate group. The four unique O···O distances vary from 2·580 to 2·714 Å. The O–H···O angles are nearly linear: 166–174°.

A comparison of the powder-diffraction patterns indicates that the Ni salt, $K_2Ni(CO_3)_2(H_2O)_4$, is isomorphous with the Co salt presented here. This fact, coupled with the similarity of the infrared spectra, suggests that the two salts are isostructural.

The authors would like to thank the Robert A. Welch Foundation for support of this work (Grant F-017); the diffractometer was purchased with funds provided by the National Science Foundation (Grant GP-37028).

References

Blumentritt, J. E. (1967). M. S. Thesis, Texas Tech. Univ.
Butler, K. R. & Snow, M. R. (1975). *Acta Cryst.* **B31**, 354–358.
Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.
Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.
Elemans, J. B. A. A. & Verschoor, G. C. (1973). *J. Inorg. Nucl. Chem.* **35**, 3183–3189.
Freeman, H. C. & Robinson, G. (1965). *J. Chem. Soc.* pp. 3194–3200.
Gartland, G. L., Gatehouse, B. M. & Craven, B. M. (1975). *Acta Cryst.* **B31**, 203–211.
Geue, R. J. & Snow, M. R. (1971). *J. Chem. Soc* (*A*), pp. 2981–2987.
Harlow, R. L. & Simonsen, S. H. (1975). *Acta Cryst.* **B31**, 1313–1318.
Healy, P. C. & White, A. H. (1972). *J. Chem. Soc. Dalton*, pp. 1913–1917.
Kaas, K. & Sorensen, A. M. (1973). *Acta Cryst.* **B29**, 113–120.
Lynton, H. & Siew, P.-Y. (1973). *Canad. J. Chem.* **51**, 227–229.
Meyer, M. H., Singh, P., Hatfield, W. E. & Hodgson, D. J. (1972). *Acta Cryst.* **B28**, 1607–1613.
Ottersen, T., Warner, L. G. & Seff, K. (1974). *Acta Cryst.* **B30**, 1188–1191.
Prelesnik, B. V., Gabela, F., Ribár, B. & Krstanović, I. (1973). *Cryst. Struct. Commun.* **2**, 581–583.
Reynolds, W. C. (1898). *J. Chem. Soc. Trans.* **73**, 262–267.
Scott, D. R. (1967). *Electronic Spectra and Bonding of Transitional Metal Complexes*, Petroleum Research Fund Final Report.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1976). B32, 470

Conformational Studies on Oligomethylene Glycol Derivatives and Related Compounds. I. The Crystal and Molecular Structure of Ethylene Glycol Dibenzoate, $C_{16}H_{14}O_4$

By Serge Pérez and François Brisse

Département de Chimie, Université de Montréal, Montréal H3C 3V1, Canada

(*Received* 1 *April* 1975; *accepted* 18 *June* 1975)

The crystal structure of ethylene glycol dibenzoate, $C_{16}H_{14}O_4$, has been solved by direct methods from 1590 reflexions collected on a Picker diffractometer. The final R value is 0·040. The crystals, which have an orthorhombic unit cell of dimensions $a=7·558$ (5), $b=21·834$ (7) and $c=16·210$ (7) Å, belong to the space group *Pbca*. The molecule is in a quasi-*trans* conformation, only 0·15 Å short of the all-*trans* conformation. An interesting feature is the significant shortening of the ethylene part of the molecule where the CH_2–CH_2 distance is only 1·499 (2) Å. The implication of this observation may have important consequences for the structures of aliphatic and aromatic polyesters. The molecules are held in the crystal by van der Waals forces only.

Introduction

X-ray studies of various kinds of aliphatic polymers of the type $[O–(CH_2)_x–O–CO–(CH_2)_y–CO]_n$, especially of polyesters made of ethylene glycol ($x=2$), trimethylene glycol ($x=3$) and decamethylene glycol ($x=10$) were first investigated by Fuller & Erickson (1937), Fuller & Frosch (1939*a*, *b*), Fuller, Frosch & Pape (1942). For all the polyesters with $x=2$ and $y>4$, it was found that the length of the chemical repeat unit was always shorter, by about 0·5 Å, than the fully extended zigzag conformation.

Turner-Jones & Bunn (1962) determined the crystal structures of polyethylene adipate ($x=2$, $y=4$) and of polyethylene sebacate ($x=2$, $y=6$), and found a considerable deviation from the planar conformation in the glycol part of the chain.

Daubeny, Bunn & Brown (1954) were first to determine the structure of polyethylene terephthalate [O–CH_2–CH_2–O–CO–C_6H_4–CO]$_n$. Here again the fibre repeat was found to be 0·15 Å shorter than expected for an all-*trans* zigzag conformation. The departure from planarity was mostly localized in the glycol group. Later on Tomashpol'skii & Markova (1964) then Arnott & Wonacott (1966) reinvestigated the structure of polyethylene terephthalate. Their structures agree in general terms with that proposed earlier by Daubeny *et al.* (1954); however, there remain some puzzling discrepancies between the three structures.

Before a new refinement of the structure of polyethylene terephthalate can be proposed, more accurate information about the geometry of the oligomeric units must be provided.

This paper is the first of a series on the systematic study of dibenzoates and *para*-substituted dibenzoates of oligomethylene glycols (Pérez & Brisse, 1975*a*).

Experimental

Crystals of ethylene glycol dibenzoate, $C_{16}H_{14}O_4$, were obtained by slow evaporation of a methanol–acetone solution. Weissenberg and precession photographs indicated that the crystals were orthorhombic, space group *Pbca* (systematic absences: $0kl$, $k=2n+1$; $h0l$, $l=2n+1$; $hk0$, $h=2n+1$). The unit cell and the orientation of the crystal were obtained on a Picker FACS-I diffractometer by a least-squares fit to the settings of 12 well-centred reflexions. The unit-cell dimensions and other crystal data are presented in Table 1.

Table 1. *Crystal data*

$C_{16}H_{14}O_4$, F.W. 270·28, $F(000)=1136$
Orthorhombic, *Pbca*, $Z=8$, $d_{\text{obs}}=1·35$, $d_{\text{cal}}=1·342$ g cm^{-3}
$a=7·558$ (5), $b=21·834$ (7), $c=16·210$ (7) Å, $V=2675·12$ Å^3
$a=7·60$, $b=21·9$, $c=16·36$ Å (Bailey, 1949)
μ(Cu $K\bar{\alpha}$)$=6·02$ cm^{-1}, λ(Cu $K\alpha_1$)$=1·54056$ Å, $T=20$ (1)°C

Integrated intensities were collected on the diffractometer using Cu $K\bar{\alpha}$ graphite-monochromatized radiation for all the reflexions within one octant of the copper sphere limited by $2\theta \le 124°$. The θ–2θ scan technique was used with a scan rate of 1° (2θ)min^{-1} and a minimum scan width of 1·5° (2θ). Background counts of 20 s were taken at each end of the scan range. The intensities of three reference reflexions, measured after each group of 30 reflexions, decreased by about 15% of their initial values, over the duration of the data collection. The data reduction was performed in the usual manner with the programs of Ahmed, Hall, Pippy & Huber (1966). Of the 2123 measured reflexions, 1590 (74%) were considered observed. These reflexions have $I/\sigma(I) \ge 2·5$ where $\sigma(I)$ is the standard deviation estimated from counting statistics calculated by $\sigma(I)=[I_T+(t/40)^2B+(0·03I_N)^2]^{1/2}$ where I_T is the total count, B the total background, I_N the net count and t the scanning time over one reflexion. Because of the small dimensions of the crystal (0·17 × 0·18 × 0·26 mm) no absorption correction was applied. The X-ray scattering factors were obtained from Cromer & Waber (1965) for C and O and from Stewart, Davidson & Simpson (1965) for H.

Structure determination and refinement

A set of normalized structure factors $|E|$ was obtained after isotropic temperature factor correction. The statistical averages indicated a centrosymmetric distribution of the E's. The structure was solved by the multisolution method of Germain, Main & Woolfson (1970). 129 reflexions with $|E| \ge 1·9$, that is six reflexions per non-hydrogen atom to be found, were used to generate 858 $\sum_2$ relations. The phases of two reflexions were obtained from $\sum_1$ and four symbols were used. In Table 2 are listed the values of various parameters used as criteria for the choice of the best set of phases. The E map calculated with the set of phases having the best figure of merit revealed 12 strong peaks which were assigned to four O atoms and eight of the C atoms of the structure. It was surprising

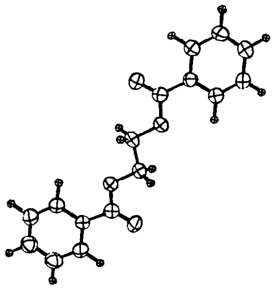

Fig. 1. View of a molecule of ethylene glycol dibenzoate parallel to the *bc* plane.

Table 2. *Figures of merit (FOM) of the best set of phases and extreme values*

	Absolute FOM	ψ_0^* (10^3)	Residual	Combined FOM
Best set of phases	1·017	0·186	25·1	2·98
Maximum value	1·017	0·269	41·2	
Minimum value	0·651	0·186	24·8	

* Test ψ_0, Cochran & Woolfson (1955).

Table 3. *Refinement summary*

Cycle	n	R^*	R_W^*	σ_F^*	Comments
1	81	0·221		23·72	Isotropic refinement
2—4	81	0·143		12·25	Isotropic refinement
5—7	183	0·098		7·84	Beginning of anisotropic refinement; 14 H atoms found
8–11	239	0·060		5·78	H refined isotropically
12–15	239		0·040	2·09	Weighting included

* $R=\sum\Delta F/\sum F_o$, $R_w=[\sum w\Delta F^2/\sum wF_o^2]^{1/2}$, $\sigma_F=[\sum w\Delta F^2/(m-n)]^{1/2}$, m=number of reflexions, n=number of refined parameters.

that only four of the 12 aromatic C atoms could be found. The remaining eight C atoms were easily located on a Fourier difference synthesis computed at this stage. The progress of the refinement is shown in Table 3.

Each reflexion was assigned a weight w inversely proportional to the variance derived from the value of $\sigma(I)$: $w = 1/\sigma^2(F)$. At the end of the refinement, the average shift to the coordinates ratio was less than 0·6σ. A final electron density map showed no significant residual density, the extreme fluctuations being 0·16 and $-0{\cdot}13$ e Å^{-3}.

In the last cycles of the refinement six strong reflexions, probably suffering from extinction, were removed.

Results and discussion

The positional and thermal parameters and their standard deviations are presented in Table 4.* A view of the ethylene glycol dibenzoate molecule and its thermal ellipsoids is shown in Fig. 1.

---

* The structure factor table has been deposited with British Library Lending Division as Supplementary Publication No. SUP 31221 (13 pp., 1 microfiche). Copies can be obtained from The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Fractional coordinates, thermal parameters and their e.s.d.'s*

The thermal parameters are the coefficients of the expression $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{12}a^*b^*hk + \ldots]$. The coordinates are in fractions of unit-cell edges $\times 10^5$ for O and C atoms and $\times 10^4$ for H. All thermal parameters are $\times 10^4$. The standard deviations refer to the least significant digit.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(11)	4059 (24)	27945 (6)	45696 (7)	1270 (14)	579 (9)	446 (8)	144 (10)	27 (9)	−61 (7)
O(21)	28450 (23)	−1284 (6)	40612 (7)	1267 (15)	578 (9)	451 (8)	98 (10)	66 (9)	−23 (7)
O(12)	12242 (19)	20197 (5)	37555 (7)	837 (11)	398 (6)	426 (7)	64 (7)	−16 (7)	55 (6)
O(22)	22110 (19)	6584 (5)	48876 (7)	872 (11)	416 (7)	434 (7)	48 (7)	−60 (7)	60 (6)
C(11)	1916 (26)	29167 (7)	31123 (10)	496 (13)	399 (10)	442 (10)	−12 (10)	3 (9)	−10 (9)
C(12)	3501 (29)	26349 (7)	23491 (11)	685 (15)	440 (11)	477 (12)	59 (11)	25 (11)	3 (9)
C(13)	−246 (30)	29558 (8)	16408 (11)	758 (16)	506 (12)	463 (11)	53 (13)	1 (11)	35 (10)
C(14)	−5333 (29)	35594 (9)	16840 (12)	633 (15)	577 (13)	585 (13)	73 (12)	−29 (12)	84 (11)
C(15)	−7010 (31)	38394 (8)	24408 (13)	705 (16)	459 (11)	686 (14)	119 (12)	14 (13)	70 (12)
C(16)	−3379 (29)	35212 (8)	31559 (12)	685 (15)	453 (11)	527 (12)	77 (12)	25 (11)	−17 (10)
C(17)	6082 (27)	25866 (8)	38846 (11)	632 (14)	431 (11)	482 (11)	−21 (11)	14 (10)	−6 (9)
C(18)	15638 (31)	16608 (8)	44852 (11)	877 (17)	437 (11)	441 (12)	−27 (12)	−101 (11)	55 (10)
C(21)	25622 (26)	−3080 (7)	54993 (10)	513 (13)	409 (10)	450 (10)	−0 (10)	−84 (10)	5 (9)
C(22)	21402 (28)	−632 (8)	62663 (10)	725 (16)	445 (11)	475 (11)	18 (12)	−71 (11)	−9 (10)
C(23)	21170 (33)	−4371 (8)	69543 (11)	941 (20)	568 (13)	415 (11)	61 (14)	−74 (12)	12 (10)
C(24)	25018 (35)	−10531 (8)	68816 (12)	928 (18)	536 (12)	514 (12)	42 (13)	−93 (13)	93 (11)
C(25)	29298 (32)	−12943 (8)	61167 (12)	911 (18)	432 (11)	629 (14)	116 (13)	−143 (13)	22 (11)
C(26)	29592 (29)	−9262 (8)	54280 (11)	698 (16)	453 (11)	506 (12)	72 (11)	−72 (11)	18 (10)
C(27)	25657 (27)	671 (8)	47421 (10)	617 (14)	414 (10)	498 (11)	3 (11)	−42 (11)	0 (10)
C(28)	20894 (30)	10423 (8)	41668 (11)	800 (17)	458 (12)	437 (11)	5 (12)	−33 (11)	96 (9)

	x	y	z	U		x	y	z	U
H(121)	747 (26)	2157 (7)	2322 (10)	632 (59)	H(241)	2456 (26)	−1343 (6)	7392 (10)	669 (60)
H(131)	90 (26)	2739 (7)	1069 (10)	693 (61)	H(251)	3244 (27)	−1753 (7)	6054 (11)	640 (65)
H(141)	−839 (25)	3814 (7)	1149 (10)	754 (66)	H(261)	3358 (26)	−1105 (7)	4812 (11)	768 (70)
H(151)	−1191 (26)	4306 (7)	2468 (11)	724 (61)	H(181)	2514 (25)	1844 (7)	4831 (10)	740 (60)
H(161)	−485 (25)	3744 (7)	3759 (11)	732 (63)	H(182)	411 (25)	1634 (8)	4840 (10)	730 (50)
H(221)	1845 (25)	427 (7)	6332 (10)	691 (62)	H(281)	3287 (26)	1054 (7)	3869 (11)	791 (66)
H(231)	1873 (27)	−252 (7)	7516 (11)	717 (60)	H(282)	1160 (23)	868 (7)	3765 (9)	621 (57)

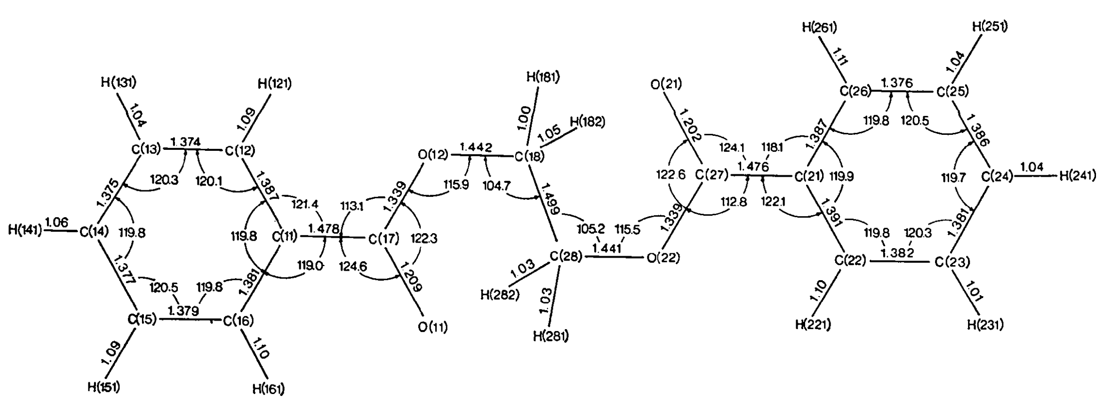

Fig. 2. Schematic diagram showing the bond distances and angles. These values have not been corrected for rigid-body motion.

Bond distances and angles

The interatomic bond distances and angles are schematically summarized in Fig. 2. The standard deviations of these quantities derived from the calculated e.s.d.'s of the fractional coordinates amount to 0·003 Å and 0·2° for non-hydrogen atoms bond distances and angles respectively, and amount to 0·02 Å for C–H distances.

Even though the molecule does not have any crystallographic symmetry elements, the X-ray data reveal a remarkable agreement between the chemically identical parts of the molecule.

The $C(sp^2)$–$C(sp^2)$ aromatic distances observed average 1·381 Å, very close to the mean bond length of 1·379 Å computed from 78 $C(sp^2)$–$C(sp^2)$ distances by Brisse & Sygusch (1974). The average $C(sp^2)$–H bond distance is $1{\cdot}06_8$ Å while individual values range from 1·01 to 1·11 Å. The average bond angle for each of the six-membered rings is 120°, and all the angles involving H atoms in the phenyl groups are consistent with sp^2 geometry.

The geometry of the carboxylic parts of this molecule is very similar to that of other benzoates. (Bailey, 1949; Ohrt & Parthasarathy, 1972; Apreda, Smith-Verdier & García-Blanco, 1973).

A more interesting feature shows up in the ethylene part of the molecule where the CH_2–CH_2 bond length is 1·499 (2) Å. This is considerably shorter than the expected $C(sp^3)$–$C(sp^3)$ distance of 1·537 (5) Å (Sutton, 1965). A similarly short CH_2–CH_2 distance was proposed by Daubeny *et al.* (1954) for the structure of polyethylene terephthalate although no clear justification was offered. Later, Tomashpol'skii & Markova (1964) then Arnott & Wonacott (1966), refining the same structure with intensities derived from a fibre diagram, chose 1·53 and 1·54 Å respectively for the CH_2–CH_2 distance. To confirm this very peculiar feature we have undertaken the determination of the structure of ethylene glycol di-*p*-chlorobenzoate. For this compound again the ethylene bond length is 1·493 (2) Å (Pérez & Brisse, 1975*b*). Note also that the two angles O(12)–C(18)–C(28) and O(22)–C(28)–C(18) involving the CH_2–CH_2 bond have values of 104·7 (2) and 105·2 (2)° respectively. These angles are also strikingly smaller than is usually accepted for a molecule with no apparent strain. The same observation can be made in the ethylene glycol di-*p*-chlorobenzoate molecule. Because of this remarkable short distance, all the bond distances and angles have been corrected for rigid-body motion by the method of Schomaker & Trueblood (1968). The root mean square error for the U_{ij}'s, $[\sum(\varDelta U_{ij})^2/(r-s)]^{1/2}$, where r is the number of U_{ij} and s the number of rigid-body parameters, was only 0·006 Å². This correction resulted in an average lengthening of the bonds by 0·003 Å. However, for the following bonds: C(11)–C(12), C(14)–C(15), C(18)–C(28), C(21)–C(22) and C(24)–C(25), the increases in distances were 0·007, 0·008, 0·006, 0·007 and 0·007 Å respectively. The corrected distance of 1·505 Å for the glycol bond remains significantly shorter than expected. The average distance of the H atoms bonded to C(18) and C(28) is 1·03 Å and the corresponding bond angles are consistent with sp^3 geometry.

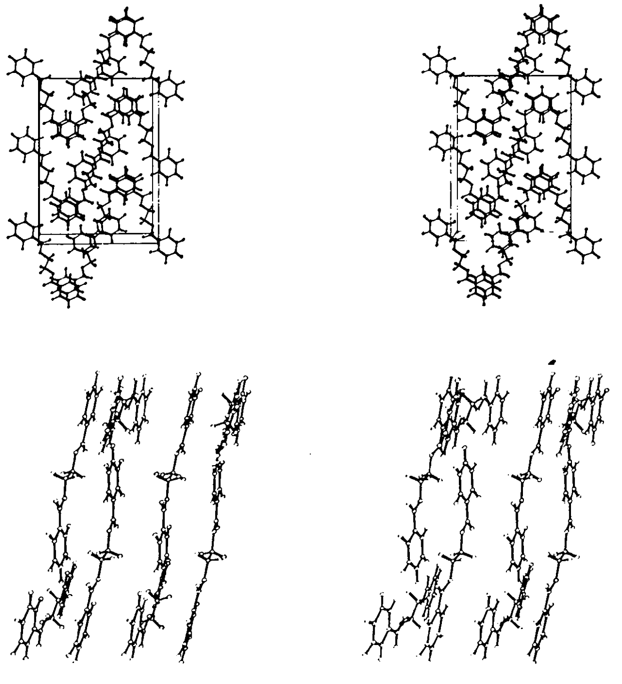

Fig. 3. Two views of the packing of the ethylene glycol dibenzoate molecules.

It is noteworthy that the length of the molecule, from C(11) to C(24) is 10·75 Å; this distance is identical with the fibre repeat *c* found by Daubeny *et al.* (1954) in polyethylene terephthalate.

Torsional angles and mean planes

The torsional angles listed in Table 5 do not differ very much from 0 or 180° so that the molecule has nearly the *trans* conformation. Here too there is a remarkable agreement between the chemically identical parts of the molecule. The departure from *trans*-planarity is spread all along the molecular chain. However the largest torsional angle of −172·8° lies in the CH_2–CH_2 region of the molecule.

The least-squares planes passing through the aromatic rings (planes *A* and *A'*) and through the carboxylic groups (planes *B* and *B'*) are presented in Table 6.

Table 5. *Torsional angles*

O(12)–C(18)–C(28)–O(22)	$\varphi_2 = -172{\cdot}8°$
C(17)–O(12)–C(18)–C(28)	$\varphi_1 = 175{\cdot}6$
C(27)–O(22)–C(28)–C(18)	$\varphi_1' = -176{\cdot}1$
C(18)–O(12)–C(17)–C(11)	$\omega = -176{\cdot}7$
C(28)–O(22)–C(27)–C(21)	$\omega' = 176{\cdot}4$
C(18)–O(12)–C(17)–O(11)	2·5
C(28)–O(22)–C(27)–O(21)	3·2

In both cases the carboxylic groups are tilted by about 3° with respect to the corresponding phenyl plane. As a result of the slight departure from the all-*trans* conformation, the two aromatic ring planes form an angle of 13° with each other.

Table 6. *Mean planes*

	Atoms	Deviation from plane		Atoms	Deviation from plane
Plane *A*	C(11)	0·001 (2) Å	Plane *A′*	C(21)	0·001 (2) Å
$\chi^2=13{\cdot}9$	C(12)	0·002 (2)	$\chi^2=3{\cdot}62$	C(22)	0·000 (2)
	C(13)	−0·006 (3)		C(23)	−0·003 (3)
	C(14)	0·006 (2)		C(24)	0·004 (3)
	C(15)	−0·002 (3)		C(25)	−0·002 (3)
	C(16)	−0·002 (2)		C(26)	−0·001 (2)
Plane *B*	O(11)	−0·001 (2)	Plane *B′*	O(21)	0·001 (2)
$\chi^2=5{\cdot}26$	O(12)	−0·001 (2)	$\chi^2=0{\cdot}98$	O(22)	0·000 (2)
	C(11)	−0·001 (2)		C(21)	0·001 (2)
	C(17)	0·005 (2)		C(27)	−0·002 (2)

Equations for the least-squares planes*

Plane *A*	$0{\cdot}956X+0{\cdot}290Y-0{\cdot}052Z-1{\cdot}722=0$
Plane *A′*	$-0{\cdot}966X-0{\cdot}199Y-0{\cdot}163Z+3{\cdot}194=0$
Plane *B*	$0{\cdot}933X+0{\cdot}359Y-0{\cdot}023Z-2{\cdot}305=0$
Plane *B′*	$-0{\cdot}976X-0{\cdot}179Y-0{\cdot}119Z+2{\cdot}838=0$

* The *X*, *Y* and *Z* axes are parallel to the **a**, **b** and **c** directions respectively.

Packing of the molecules

The non-bonded intermolecular distances shorter than 3·6 Å are presented in Table 7. None of the intermolecular contacts is less than 3·30 Å; therefore the molecules are held in the crystal by van der Waals forces only.

Table 7. *Intermolecular contacts shorter than* 3·6 Å

O(11)···C(26)	6		3·35 Å
O(11)···C(25)	6		3·44
O(11)···C(18)	2,	$-a+c$	3·49
O(12)···C(25)	5,	c	3·52
O(12)···C(13)	8		3·55
O(21)···C(14)	3,	$-b$	3·55
C(11)···C(14)	8		3·54
C(13)···C(17)	8,	$-a$	3·50

First symbol: equivalent position

1 (x,y,z)	3 $(-x,\frac{1}{2}+y,\frac{1}{2}-z)$
2 $(\frac{1}{2}+x,\frac{1}{2}-y,-z)$	4 $(\frac{1}{2}-x,-y,\frac{1}{2}+z)$

The positions 5 to 8 are centrosymmetrically related to the positions 1 to 4 respectively.

Second symbol: cell translations.

The packing of the ethylene glycol dibenzoate molecules is shown in Fig. 3. The molecules, approximately parallel to the *bc* plane, are packed in a herringbone manner. The packing diagrams reveal two different sequences in the packing. In one sequence phenyl groups are stacked side by side while in the second type phenyl groups and ethylene groups alternate.

We are grateful to Professor Marchessault of this department for bringing this problem to our attention. We would also like to thank Miss Beverly Leslie and Alain Faure for their assistance during the data collection and for the synthesis of the title compound. The financial support from the Ministère de l'Education du Québec is hereby gratefully acknowledged.

References

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. *World List of Crystallographic Computer Programs*, 2nd ed. Appendix, p. 52. Utrecht: Oosthoek.

APREDA, M. C., SMITH-VERDIER, P. & GARCÍA-BLANCO, S. (1973). *Acta Cryst.* **B29**, 2658–2664.

ARNOTT, S. & WONACOTT, A. J. (1966). *Polymer*, **7**, 157–166.

BAILEY, M. (1949). *Acta Cryst.* **2**, 120–126.

BRISSE, F. & SYGUSCH, J. (1974). *Acta Cryst.* **B30**, 480–486.

COCHRAN, W. & DOUGLAS, A. S. (1957). *Proc. Roy. Soc.* **A227**, 486–500.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

DAUBENY, R. P. DE, BUNN, C. W. & BROWN, C. J. (1954). *Proc. Roy. Soc.* **A226**, 531–542.

FULLER, C. S. & ERICKSON, C. L. (1937). *J. Amer. Chem. Soc.* **59**, 344–351.

FULLER, C. S. & FROSCH, C. J. (1939*a*). *J. Phys. Chem.* **43**, 323–334.

FULLER, C. S. & FROSCH, C. J. (1939*b*). *J. Amer. Chem. Soc.* **61**, 2575–2580.

FULLER, C. S., FROSCH, C. J. & PAPE, N. R. (1942). *J. Amer. Chem. Soc.* **64**, 154–160.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274–285.

OHRT, J. & PARTHASARATHY, R. (1972). *J. Cryst. Mol. Struct.* **2**, 213–233.

PÉREZ, S. & BRISSE, F. (1975*a*). *Acta Cryst.* **B31**, 2746–2747.

PÉREZ, S. & BRISSE, F. (1975*b*). *Canad. J. Chem.* To be published.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Supplement 1956–1959. London: The Chemical Society.

TOMASHPOL'SKII, Y. Y. & MARKOVA, G. S. (1964). *Polym. Sci. USSR.* **6**, 316–324.

TURNER-JONES, A. & BUNN, C. W. (1962). *Acta Cryst.* **15**, 105–113.