$N \cdots O(1) = 2.63$ Å. The molecules are linked together by intermolecular hydrogen bonds parallel to y and z (Fig. 2), and these sheets are in turn linked by other hydrogen bonds parallel to x (Table 3). This three-dimensional network results in hard crystals (as shown by the relatively small values of B for the N and O atoms).

The C atom skeleton is similar to that of tricholomic acid and the unusual amino acid reported by Baldwin, Hoskins & Kruse (1976) and it is possible that these compounds are related biogenetically.

Details of the isolation and chemical properties will be published separately by Dr Vermeulen and Mr Potgieter.

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Trimethylene Glycol Dibenzoate*

BY SERGE PÉREZ AND FRANÇOIS BRISSE

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Abstract. $C_{17}H_{16}O_4$, $M_r = 284.3$, *Pbcn*, $Z = 4$, $a = 11.224$ (4), $b = 8.961$ (3), $c = 14.692$ (4) Å, $F(000) = 600$, $d_c = 1.278$, $d_o = 1.29$ g cm^{-3}. The structure was solved by direct methods. The anisotropic block-diagonal least-squares weighted refinement was concluded with the final values $R = 0.064$ and $R_w = 0.047$ for the 543 observed reflexions. The molecule lies on a twofold axis of rotation. The torsion angles within the 'trimethylene' part of the molecule correspond to a *gauche–gauche* conformation. The aromatic ring plane is tilted by 6° from the carboxylic plane.

Introduction. In our previous work on the crystal structures of small molecules related to the poly(oligomethylene terephthalates) it was found that the conformations of ethylene glycol dibenzoate and hexamethylene glycol dibenzoate were closely related to those of poly(ethylene terephthalate) and poly(hexamethylene terephthalate) respectively (Pérez & Brisse, 1976a, 1977). In order to arrive at a possible conformation for poly(trimethylene terephthalate), we determined the crystal structure of trimethylene glycol di-*p*-chlorobenzoate (Pérez & Brisse, 1976b). However,

since the comparison of the crystal structures of ethylene glycol dibenzoate and ethylene glycol di-*p*-chlorobenzoate (Pérez & Brisse, 1975) revealed that these molecules, differing only by Cl substitution on the terminal phenyl rings, adopted completely different conformations, we decided to undertake the crystal structure determination of trimethylene glycol dibenzoate.

Trimethylene glycol dibenzoate was synthesized according to the procedure described by Vogel (1962). The crystals, m.p. 59°C, were obtained by slow evaporation from a methanol solution. A preliminary photographic investigation indicated that the crystals were orthorhombic, space group *Pbcn* (systematic absences: $hk0$, $h + k \neq 2n$; $h0l$, $l \neq 2n$; $0kl$, $k \neq 2n$). The unit-cell dimensions were obtained by a least-squares fit to the settings of 12 reflexions centred on an automatic diffractometer.

Integrated intensities were collected on a Picker FACS-I diffractometer using Mo $K\alpha$ ($\lambda K\alpha_1 = 0.70926$ Å) graphite-monochromatized radiation for all the reflexions within one octant of the sphere limited by $2\theta \leq 47.5°$. The θ–2θ scan technique was used with a scan rate of 1° (2θ) min^{-1} and a minimum peak width of 1.75° (2θ). Background counts of 20 s were taken at each end of the scan range.

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* Conformational Studies of Oligomethylene Glycol Derivatives and Related Compounds. VII.

The intensities of three reference reflexions, measured every 30 reflexions, decreased by about 5% of their initial values over the duration of the data collection. The data reduction was performed in the usual way using the program of Ahmed, Hall, Pippy & Huber (1966). 1018 reflexions were collected. Of these, only 543 (53%) had a net intensity greater than $2 \cdot 5\sigma(I)$, where $\sigma(I)$ is calculated by the relation given by Pérez & Brisse (1975). Because of the smallness of the crystal ($0 \cdot 22 \times 0 \cdot 25 \times 0 \cdot 30$ mm) and the very low value of the absorption coefficient, μ(Mo $K\alpha$) = $0 \cdot 77$ cm^{-1}, no absorption correction was applied. The X-ray scattering factors for O and C were obtained from Cromer & Waber (1965) and from Stewart, Davidson & Simpson (1965) for H.

A set of normalized structure factors was calculated with the assumption that the *group* of atoms was in random position and orientation. This computation was performed using the molecular geometry obtained from the structure of trimethylene glycol di-*p*-chloro-benzoate (Pérez & Brisse, 1976b). The structure was solved with the *MULTAN* program (Main, Woolfson, Lessinger, Germain & Declercq, 1974) using all E's ≥ $1 \cdot 70$. Three of the 16 different solutions provided by this computation converged to the same solution. The resulting E map revealed all the nonhydrogen atoms. At this stage the R value, $R = \Sigma \Delta F / \Sigma F_o$, was $0 \cdot 23$. The atomic coordinates and individual isotropic temperature parameters were refined with unit weights by full-matrix least squares. The refinement converged to an R value of $0 \cdot 13$. The refinement was continued with anisotropic thermal parameters. All the H atoms, located on a difference Fourier synthesis, were included in the refinement with individual isotropic temperature factors, and each reflexion was assigned a weight w defined by $1/\sigma^2 F_o$. The final agreement indices (for the observed reflexions only and for all the reflexions, respectively) were:* $R = 0 \cdot 064$, $0 \cdot 105$; $R_w = (\Sigma w\Delta F^2/\Sigma wF_o^2)^{1/2} = 0 \cdot 047$, $0 \cdot 054$; and $\sigma_F = [\Sigma w\Delta F^2/(m - n)]^{1/2} = 2 \cdot 02$, $1 \cdot 47$, where m is the number of reflexions and n is the number of variables refined. The average parameter shift was less than $0 \cdot 3\sigma$. A final difference Fourier map showed no significant residual electron density. The extreme fluctuations were in the range $-0 \cdot 18$ to $0 \cdot 15$ e Å^{-3}.

Discussion. Since the unit cell contains only four molecules, they have to be located on the crystallographic twofold axes of rotation. The positional parameters with their standard deviations are presented in Table 1. The stereoscopic pair showing the structure of trimethylene glycol dibenzoate and its thermal ellipsoids is presented in Fig. 1. The bond distances and

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32783 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional coordinates and their e.s.d.'s* ($\times 10^4$ *for* O *and* C, $\times 10^3$ *for* H)

	x	y	z
O(11)	2613 (4)	1892 (5)	3423 (3)
O(12)	869 (3)	3062 (5)	3573 (3)
C(11)	1484 (6)	1522 (6)	4788 (4)
C(12)	503 (5)	1980 (7)	5284 (5)
C(13)	329 (7)	1356 (8)	6145 (4)
C(14)	1118 (7)	309 (9)	6454 (5)
C(15)	2094 (6)	−158 (8)	5960 (5)
C(16)	2265 (6)	486 (8)	5112 (5)
C(17)	1730 (6)	2157 (7)	3854 (4)
C(18)	1080 (7)	3843 (8)	2722 (5)
C(38)	0	4718 (12)	2500
H(121)	−14 (4)	275 (5)	511 (3)
H(131)	−40 (4)	172 (6)	643 (3)
H(141)	99 (4)	−12 (5)	695 (3)
H(151)	262 (5)	−107 (6)	620 (3)
H(161)	300 (4)	14 (6)	473 (4)
H(181)	183 (4)	447 (5)	276 (3)
H(182)	120 (4)	311 (5)	228 (3)
H(381)	−13 (5)	545 (6)	301 (3)

Table 2. *Mean planes and deviations from them* (Å)

The planes are expressed by $lX + mY + nZ - p = 0$, with x,y,z and p in Å.

Plane A ($\chi^2 = 1 \cdot 85$)		Plane B ($\chi^2 = 1 \cdot 18$)	
C(11)	−0·001 (6)	O(11)	−0·001 (4)
C(12)	0·004 (6)	O(12)	−0·001 (4)
C(13)	−0·006 (7)	C(11)	−0·001 (6)
C(14)	0·004 (8)	C(17)	0·006 (6)
C(15)	0·004 (7)		
C(16)	−0·004 (7)		
O(11)*	−0·107 (7)		
O(12)*	0·117 (7)		
C(17)*	0·003 (6)		
C(18)*	−0·004 (7)		

Plane A: $0 \cdot 549X + 0 \cdot 726Y + 0 \cdot 414Z - 4 \cdot 817 = 0$
Plane B: $0 \cdot 465X + 0 \cdot 778Y + 0 \cdot 424Z - 4 \cdot 805 = 0$

* Not included in the mean-plane calculation.

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angles are shown on a schematic diagram of the molecule with the same numbering that was used for trimethylene glycol di-*p*-chlorobenzoate (Fig. 2). The standard deviations of the interatomic bond distances and angles for the nonhydrogen atoms are $0 \cdot 007$ Å and $0 \cdot 4°$ respectively, and $0 \cdot 03$ Å for bond distances involving H atoms.

The $C(sp^2)-C(sp^2)$ aromatic distances average $1 \cdot 380$ Å and the average value of the bond angles within the six-membered ring is $120 \cdot 1°$. The C—H distances are normal (mean $1 \cdot 00$ Å, range $0 \cdot 84$ to $1 \cdot 08$ Å), as are the C—C—H bond angles. The bond distances and angles within the 'trimethylene' part of the molecule compare extremely well with those found
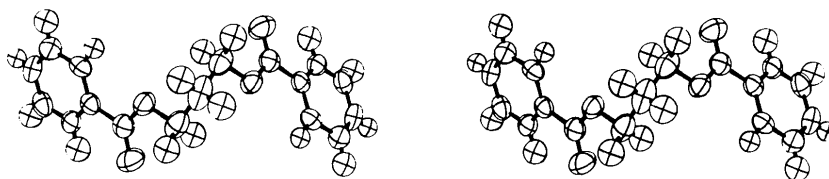
Fig. 1. A stereoscopic view of the molecule of trimethylene glycol dibenzoate with its twofold axis of rotation vertical.
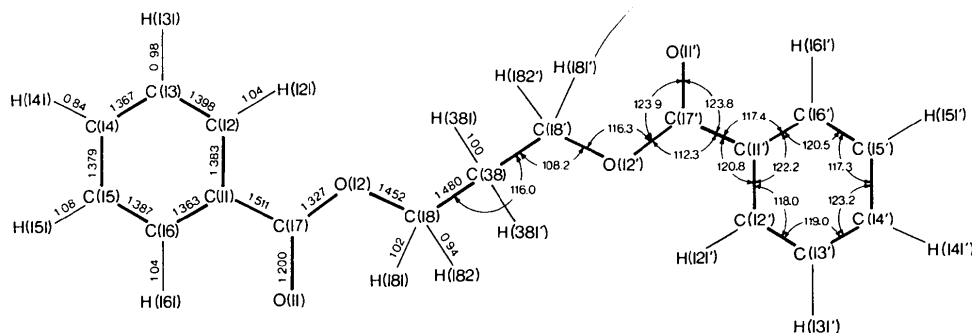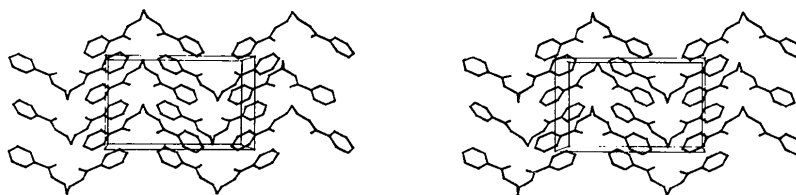

Fig. 2. Bond distances (Å) and angles (°).

Fig. 3. Molecular packing of trimethylene glycol dibenzoate.

Table 3. Comparison of torsion angles (°)

The primed atom is related by a twofold axis of rotation to the unprimed atom having the same number.

	This work	Trimethylene glycol di-p-chlorobenzoate (Pérez & Brisse, 1976b)
C(17)—O(12)—C(18)—C(38)	$\varphi_1 = 176\cdot8$	$-176\cdot7$
O(12)—C(18)—C(38)—C(18')	$\varphi_2 = -66\cdot8$	$-66\cdot3$
C(18)—O(12)—C(17)—C(11)	$\omega = 174\cdot1$	$179\cdot1$
C(18)—O(12)—C(17)—O(11)	$-4\cdot8$	$-1\cdot3$

in trimethylene glycol di-p-chlorobenzoate. In the series of the n-methylene glycol dibenzoates previously studied (Pérez & Brisse, 1976a), the —CH$_2$—CH$_2$— bonds show a significant shortening. This feature is also observed for trimethylene glycol dibenzoate where the two equivalent bond distances [—C(18)H$_2$—C(38)H$_2$—] are 1·480 (7) Å. This is the most severe shortening so far observed. The geometry of the carboxylic group is very similar to that of other benzoates (Brisse & Pérez, 1976). The deviations from

the phenyl mean plane (plane A) and from the carboxylic plane (plane B) are given with the least-squares equations of the mean planes in Table 2. Plane A is tilted by 6° from plane B. The torsion angles which characterize the conformation of this molecule are compared in Table 3 with those of the p-chloro-substituted analogue. Contrary to what was observed for ethylene glycol dibenzoate and di-p-chloro-benzoate, the conformations of trimethylene glycol dibenzoate and its di-p-chloro-substituted derivative are very similar. The only significant differences between these two molecules are localized at the torsion angles φ_1, around the C(18)—O(12) bond, and ω, which is the angle between the aromatic and carboxylic moieties. The distance between the centres of the aromatic cycles in trimethylene glycol dibenzoate is 9·62 Å and compares very well with half the fibre repeat, 19·1 Å (Poulin-Dandurand, Pérez & Brisse, 1977), of the parent polymer poly(trimethylene terephthalate). There is only one intermolecular distance shorter than 3·40 Å: C(18)[x,y,z]—O(11)[x—½, ½+y, ½—z] = 3·267 Å. The packing of the molecules within a unit cell is shown in Fig. 3.

We wish to thank the National Research Council of Canada for financial assistance. Figs. 1 and 3 were drawn with the program *ORTEP* (Johnson, 1965) on the CYBER 74 computer at the Université de Montréal.

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trans-6a, 11b-Dihydro-5-methylbenzo[*b*]thieno[2,3-*c*]quinolin-6-one (I) and *cis*-6a,11b-Dihydrobenzo[*b*]thieno[2,3-*c*]quinolin-6-one 7,7-Dioxide (II)

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Abstract. (I): $C_{16}H_{13}NSO$, monoclinic, $P2_1/a$, $a = 10.258$ (6), $b = 14.518$ (9), $c = 8.898$ (5) Å, $\beta = 104.9$ (2)°, $Z = 4$, $d_x = 1.39$ g cm^{-3}, $\mu R_{max} = 5.7$. The structure was solved by the symbolic addition procedure. The tetracyclic ring system is *trans*. (II): $C_{15}H_{11}NSO_3$, triclinic, $P\bar{1}$, $a = 8.300$ (4), $b = 10.768$ (8), $c = 7.957$ (4) Å, $\alpha = 110.2$ (1), $\beta = 73.7$ (1), $\gamma = 100.8$ (1)°, $Z = 2$, $d_x = 1.49$ g cm^{-3}, $\mu R_{max} = 8.2$. The structure was solved by the heavy-atom method. The tetracyclic ring system is *cis*.

Introduction. Heterocyclic analides, such as benzo[*b*]thiophene, undergo photocyclization in the presence of dissolved oxygen to yield heterocyclic condensed quinolines (Kanaoka, Itoh, Hatanaka, Flippen, Karle & Witkop, 1975). X-ray analyses were performed on two of these quinolines to determine the stereoconfiguration of the ring fusion.

Both crystals were obtained through B. Witkop of NIAMD. Data for both compounds were collected on an automatic computer-controlled diffractometer (Cu $K\alpha$, $\lambda = 1.54178$ Å, Ni filter) using the θ–2θ scan technique. The crystal of (I) ($\sim$0.55 × 0.58 × 0.19 mm) gave 2074 independent reflections out to a $2\theta_{max}$ of 126.5° and the crystal of (II) ($\sim$0.13 × 0.38 × 0.68 mm) yielded 1574 reflections.

The structure of (I) was solved by the symbolic addition procedure for centrosymmetric molecules (Karle & Karle, 1966). For molecule II, the S atom was located in a Patterson map and the remaining atoms were found in two cycles of difference Fourier maps. Full-matrix least-squares refinement (Busing *et al.*, 1971) was carried out on both molecules. The atomic scattering factors used were those listed in *International Tables for X-ray Crystallography* (1962). The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where the weights w (derived from estimated standard deviations of observed intensity) were calculated

(I)   (II)