Model compounds for high modulus aromatic polyether-esters. X-ray structures and energy calculations of dimethyl 1,2-bis(phenoxy)ethane-4,4′-dicarboxylate and its chlorinated derivatives

Yukishige Kitano* and Akira Ishitani
Toray Research Center, Inc., 3-7 Sonoyama 3-Chome, Otsu, Shiga 520, Japan

and Toshihide Inoue
Plastics Research Laboratories, Toray Industries, Inc., 9-1, Ooe-cho, Minato-ku, Nagoya 455-91, Japan

and Tamaichi Ashida
Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan
(Received 6 May 1994; revised 24 May 1994)

The determination of the conformation of molecular chains and modes of packing of poly[ethylene-1,2-bis(phenoxy)ethane-4,4′-dicarboxylate] and its chlorinated derivatives is assisted by the X-ray crystallographic analysis and energy calculations of three model compounds. Molecules of dimethyl 1,2-bis(phenoxy)ethane-4,4′-dicarboxylate are packed in an orthorhombic crystal system, space group *Pbca*, with $a = 6.374(4)$ Å, $b = 35.094(6)$ Å, $c = 7.124(5)$ Å, and $z = 4$. The molecule has a crytallographic centre of symmetry at the centre of the CH_2-CH_2 bond and the two ether O atoms are oriented *anti* to each other. Molecules of dimethyl 1,2-bis(2-chlorophenoxy)ethane-4,4′-dicarboxylate are packed in a monoclinic crystal system, space group $C2/c$, with $a = 12.712(2)$ Å, $b = 7.594(1)$ Å, $c = 18.709(2)$ Å, $\beta = 100.06(1)°$, and $z = 4$. The molecule has a crystallographic two-fold axis at the centre of the CH_2-CH_2 bond and the O-CH_2-CH_2-O torsion angle of 69.9° makes the conformation of this part of the molecule *gauche*. Molecules of dimethyl 1,2-bis(2,6-dichlorophenoxy)ethane-4,4′-dicarboxylate are packed in a monoclinic crystal system, space group $P2_1/n$, with $a = 4.041(2)$ Å, $b = 12.799(1)$ Å, $c = 18.8528(9)$ Å, $\beta = 91.36(1)°$ and $z = 2$. The molecule has a crystallographic centre of symmetry at the centre of the CH_2-CH_2 bond and the two ether O atoms are oriented *anti* to each other. CH_2-CH_2 bond shortenings were observed in the three model compounds. The crystal structures were compared with energy-minimized molecular structures using the semi-empirical quantum-mechanical method MNDO, giving results in substantial agreement.

(Keywords: high modulus polyether-ester; model compound; crystal structure)

INTRODUCTION

A large number of studies on the conformation of polyethylenes, polyesters, polyamides and polypeptides have been carried out using the conformations of small molecules which are very close, in the solid-state, to those of the polymers. Moreover, a comparison between geometrical parameters resulting from single-crystal X-ray analysis of those small molecules or oligomers with those of related polymers, obtained by X-ray diffraction methods, leads to better understanding of the conformation and the relationships between the structure and the mechanical properties of polymers. In particular, in the case of liquid-crystalline polymers[1] and rigid-rod aromatic heterocyclic polymers[2], which have been well studied, the poor X-ray fibre patterns with only a small number of broad reflections make it practically impossible to perform precise structure analysis. In such a situation, model compounds may provide useful information on the structures of related polymers.

We have studied the crystal structures of model compounds and oligomers of polyesters[3-5] and polyamide[6] in order to clarify the conformational properties of the related polymers. In the present study, three monomer compounds have been selected which serve as models for high modulus aromatic polyether-esters. Dimethyl 1,2-bis(phenoxy)ethane-4,4′-dicarboxylate (**1**) and its chlorinated compound, dimethyl 1,2-bis(2-chlorophenoxy)ethane-4,4′-dicarboxylate (**2**) are model compounds of poly[ethylene-1,2-bis(phenoxy)ethane-4,4′-dicarboxylate](**4**) and its chlorinated derivative (**5**), belonging to the class of high modulus aromatic polyether-esters capable of being processed into fibres and films[7-9]. Dimethyl 1,2-bis(2,6-dichlorophenoxy)ethane-4,4′-dicarboxylate (**3**) is also a model compound of the corresponding chlorinated polymer (**6**) which exhibits high thermal stability in

*To whom correspondence should be addressed

0032-3861/94/24/5179-06

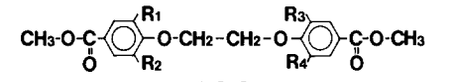
addition to self-extinguishing and flame retardant properties[10]. The structures of compounds **1–6** are shown in *Scheme 1*.

Compounds **1**, **2** and **3** do not show the full repeating unit of the corresponding polymers **4**, **5** and **6**, but extensive geometrical information of n-methylene dibenzoate compounds has been accumulated. In contrast, very few structural investigations have been carried out for phenyl alkyl ether compounds. Moreover, we have so far been unable to grow diffraction-quality single crystals of the corresponding ether-ester oligomers. This study is intended to provide a data base of accurate conformational and packing information and should help to establish criteria for predicting polyether-ester structures from small molecule data.

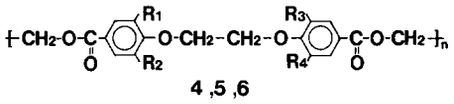
EXPERIMENTAL

Synthesis of dimethyl 1,2-bis(phenoxy)ethane-4,4'-dicarboxylate (1)

1 was obtained by heating sodium methyl *p*-oxybenzoate with 1,2-dichloroethane in methanol for 6 h at 150°C[11].



1,2,3



4,5,6

	R_1	R_2	R_3	R_4
1,4	H	H	H	H
2,5	Cl	H	H	Cl
3,6	Cl	Cl	Cl	Cl

Scheme 1

The white precipitate formed was filtered off and dried. Recrystallization from toluene gave analytically pure compound **1** (m.p. 154–157°C).

Synthesis of dimethyl 1,2-bis(2-chlorophenoxy)ethane-4,4'-dicarboxylate(2)

Into a vessel equipped with a reflux condenser charged with **1** (0.15 mol) in acetic acid, chlorine gas (0.33 mol) was introduced for 2 h at 95–105°C[12]. The reaction mixture was cooled to room temperature and the white precipitate formed was filtered off and dried and recrystallized from xylene to give analytically pure compound **2** (m.p. 204–206°C).

Synthesis of dimethyl 1,2-bis(2,6-dichlorophenoxy)ethane-4,4'-dicarboxylate(3)

Into a vessel equipped with a reflux condenser charged with **1** (0.15 mol) in 1,1,2,2-tetrachloroethylene, chlorine gas (0.66 mol) was introduced for 2 h at 95–105°C. The reaction mixture was cooled to room temperature and the white precipitate formed was filtered off and dried and recrystallized from xylene to give analytically pure compound **3** (m.p. 205–207°C).

The compounds were recrystallized for X-ray analysis from a mixture of tetrahydrofuran and dimethylformamide. Needle crystals were obtained.

X-ray structure determinations

Diffraction data were obtained with a Rigaku AFC-5R four-circle diffractometer equipped with graphite monochromated MoKα radiation for **1** and **2** and with graphite monochromated CuKα radiation for **3**, respectively. Crystal data and experimental details for the three crystals are summarized in *Table 1*. Three standard reflections, which were measured every 100 reflections, for the respective crystals remained constant throughout data collection indicating crystal and electronic stability.

Table 1 Crystal data and experimental conditions

	1	**2**	**3**
Formula	$C_{18}H_{18}O_6$	$C_{18}H_{16}Cl_2O_6$	$C_{18}H_{14}Cl_4O_6$
Formula weight	330.34	399.23	468.12
Crystal size (mm)	0.4 × 0.3 × 0.3	0.3 × 0.2 × 0.2	0.3 × 0.1 × 0.03
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbca*	*C2/c*	$P2_1/n$
a (Å)	6.374(4)	12.712(2)	4.041(2)
b (Å)	35.094(6)	7.594(1)	12.799(1)
c (Å)	7.124(5)	18.709(2)	18.8528(9)
β (deg)		100.06(1)	91.36(1)
V (Å^3)	1593(1)	1778.3(8)	974.7(5)
z	4	4	2
Crystal density (g cm^{-3})	1.377	1.491	1.595
λ (Å)	0.71069 (MoKα)	0.71069 (MoKα)	1.54178 (CuKα)
μ (cm^{-1})	0.97	3.95	59.49
F(000)	696	824	476
Scan method	*ω*	*ω*-2*θ*	*ω*-2*θ*
$2\theta_{max}$ (deg)	50.0	60.0	120.0
Scan speed (deg min^{-1})	8.0	2.0–20.0	16.0
Scan range (deg)	1.13 + 0.3 tan *θ*	0.70 + 0.35 tan *θ*	1.50 + 0.3 tan *θ*
No. of reflections			
Measured	1717	2868	1779
Observed [$I > 3\sigma(I)$]	995	1564	1126
$\Delta\rho_{max}$ (eÅ^{-3})	0.14	0.18	0.19
$\Delta\rho_{min}$ (eÅ^{-3})	−0.11	−0.26	−0.20
R	0.033	0.039	0.036
ωR	0.042	0.045	0.049
Symmetry in the molecule	i	2	i

Table 2 Fractional positional parameters and equivalent isotropic temperature factors for the non-hydrogen atoms of $C_{18}H_{18}O_6$ (**1**)

Atom	x	y	z	B_{eq} (Å^2)[a]
O(1)	0.2620(2)	0.47367(3)	0.4826(2)	3.7
O(2)	0.0144(2)	0.29872(4)	0.5626(2)	6.3
O(3)	−0.2743(2)	0.32441(3)	0.4415(2)	5.1
C(1)	0.4730(3)	0.48053(5)	0.5372(3)	3.7
C(2)	0.1869(3)	0.43714(4)	0.4963(2)	3.0
C(3)	−0.0109(3)	0.43152(5)	0.4227(2)	3.3
C(4)	−0.0998(3)	0.39580(4)	0.4236(2)	3.3
C(5)	0.0090(3)	0.36499(4)	0.4984(2)	3.3
C(6)	0.2064(3)	0.37120(5)	0.5718(3)	3.6
C(7)	0.2976(3)	0.40693(5)	0.5735(2)	3.5
C(8)	−0.0787(3)	0.32599(5)	0.5043(3)	3.9
C(9)	−0.3757(6)	0.28724(7)	0.4484(5)	6.2

[a] B_{eq} is the equivalent isotropic temperature factor calculated from the anisotropic temperature coefficients[15]

Table 3 Fractional positional parameters and equivalent isotropic temperature factors for the non-hydrogen atoms of $C_{18}H_{16}Cl_2O_6$ (**2**)

Atom	x	y	z	B_{eq} (Å^2)
Cl(1)	0.57243(5)	0.33552(8)	0.10101(3)	4.6
O(1)	0.4875(1)	0.0509(2)	0.17307(7)	3.8
O(2)	0.3246(1)	0.2545(2)	−0.15552(8)	5.1
O(3)	0.2083(1)	0.0432(2)	−0.14088(8)	4.4
C(1)	0.4618(2)	−0.0962(3)	0.2149(1)	3.9
C(2)	0.4342(2)	0.0665(3)	0.1040(1)	3.0
C(3)	0.4690(1)	0.1988(3)	0.0623(1)	3.1
C(4)	0.4227(2)	0.2226(3)	−0.0091(1)	3.2
C(5)	0.3383(1)	0.1169(3)	−0.0405(1)	2.9
C(6)	0.3009(2)	−0.0117(3)	0.0014(1)	3.3
C(7)	0.3484(2)	−0.0377(3)	0.0728(1)	3.4
C(8)	0.2916(2)	0.1480(4)	−0.1176(1)	3.4
C(9)	0.1568(3)	0.0688(5)	−0.2157(1)	5.4

Reflection data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied for **3** which resulted in transmission factors ranging from 0.75 to 1.00.

The structure for **1** was determined using direct phasing methods[13] and those for **2** and **3** using heavy atom methods. The structures were refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Refinements were continued until all shifts were smaller than one-third of the standard deviations of the parameters involved. Atomic scattering factors and anomalous dispersion terms were taken from the literature[14]. Hydrogen atoms were located from difference Fourier maps, and their parameters were isotropically refined. The function minimized was $\Sigma\omega(|F_o| - |F_c|)^2$ with $\omega = 4F_o^2/\sigma^2(F_o^2)$, where σ is the standard deviation based on counting statistics. Final difference Fourier maps showed no peaks of structural significance. All calculations were performed with VAX-based programs of the structure analysis package, TEXSAN (Molecular Structure Corporation, TX).

The final atomic parameters and equivalent thermal parameters for non-hydrogen atoms for **1**, **2** and **3** are given in *Tables 2*, *3* and *4*, respectively*.

*Tables of the positional parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, and observed and calculated structure factor amplitudes can be obtained from the authors upon request

Energy calculations

MNDO calculations were performed on a VAX 8650 computer using the MOPAC V5.0 semi-empirical molecular-orbital package (Quantum Chemistry Program Exchange No. 455, Department of Chemistry, Indiana University). The total energies were calculated as a function of the torsion angle ϕ, O(1)-C(1)-C(1′)-O(1′), in increments of 10° with other geometries being kept at crystallographic values for each molecule.

RESULTS AND DISCUSSION

Perspective views of the three molecules, with their atom numbering schemes, are presented in *Figure 1*[16]. The bond distances, angles and selected torsion angles of these molecules and deviation of atoms from the phenyl mean planes are summarized in *Tables 5* and *6*. Crystal packing diagrams are given in *Figures 2–4*.

Table 4 Fractional positional parameters and equivalent isotropic temperature factors for the non-hydrogen atoms of $C_{18}H_{14}Cl_4O_6$ (**3**)

Atom	x	y	z	B_{eq} (Å^2)
Cl(1)	0.3187(3)	0.14661(7)	0.16169(5)	4.5
Cl(2)	−0.1734(3)	−0.24178(7)	0.12865(5)	4.7
O(1)	0.1625(5)	−0.0469(2)	0.0837(1)	3.4
O(2)	−0.1449(9)	0.0214(2)	0.4098(1)	6.1
O(3)	−0.2902(8)	−0.1439(2)	0.3931(1)	5.0
C(1)	−0.081(1)	−0.0066(4)	0.0338(2)	4.3
C(2)	0.0665(8)	−0.0475(3)	0.1529(2)	2.9
C(3)	0.1335(8)	0.0366(3)	0.1968(2)	3.1
C(4)	0.057(1)	0.0348(3)	0.2680(2)	3.4
C(5)	−0.0954(8)	−0.0523(3)	0.2955(2)	3.1
C(6)	−0.1702(9)	−0.1374(4)	0.2520(2)	3.2
C(7)	−0.0879(8)	−0.1341(3)	0.1814(2)	3.1
C(8)	−0.175(1)	−0.0525(3)	0.3720(2)	3.7
C(9)	−0.380(1)	−0.1528(4)	0.4669(2)	5.8

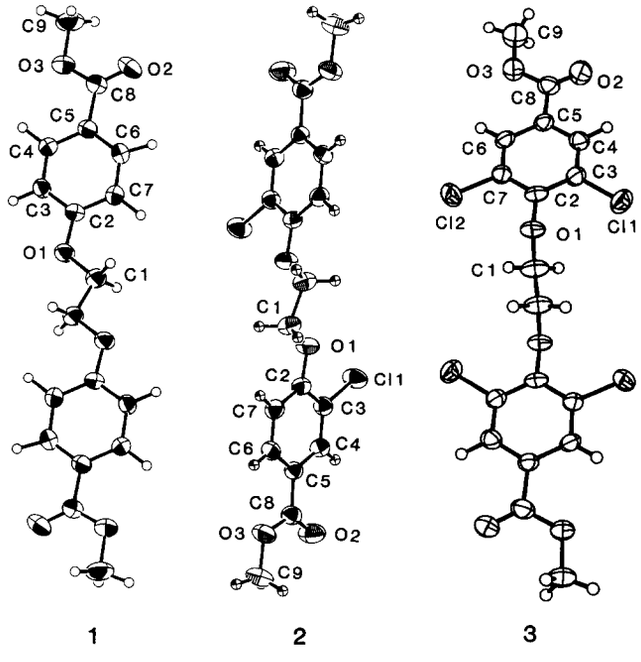


Figure 1 Perspective views of molecules **1**, **2** and **3**, with their atomic numbering schemes. Thermal ellipsoids are drawn at 50% probability level

Table 5 Bond lengths, angles and selected torsion angles

	1	2	3
Bond lengths (Å)			
O(1)-C(1)	1.421(2)	1.434(3)	1.440(4)
O(1)-C(2)	1.372(2)	1.355(2)	1.370(4)
O(2)-C(8)	1.200(2)	1.199(3)	1.190(4)
O(3)-C(8)	1.325(2)	1.335(2)	1.324(4)
O(3)-C(9)	1.456(2)	1.451(3)	1.451(4)
C(1)-C(1')	1.506(4)	1.489(4)	1.455(7)
C(2)-C(3)	1.380(2)	1.391(3)	1.381(4)
C(2)-C(7)	1.387(2)	1.391(3)	1.387(4)
C(3)-C(4)	1.376(2)	1.375(3)	1.385(5)
C(4)-C(5)	1.391(2)	1.385(3)	1.381(5)
C(5)-C(6)	1.380(3)	1.386(3)	1.392(5)
C(5)-C(8)	1.479(2)	1.480(3)	1.486(5)
C(6)-C(7)	1.382(2)	1.381(3)	1.379(5)
Cl(1)-C(3)		1.731(2)	1.733(3)
Cl(2)-C(7)			1.730(3)
Bond angles (deg)			
O(1)-C(1)-C(1')	105.9(2)	107.8(2)	107.5(4)
C(1)-O(1)-C(2)	118.0(1)	117.7(2)	114.8(2)
O(1)-C(2)-C(3)	115.2(1)	116.3(2)	120.8(3)
O(1)-C(2)-C(7)	124.4(2)	125.1(2)	120.9(3)
C(3)-C(2)-C(7)	120.4(2)	118.6(2)	118.3(3)
C(2)-C(3)-C(4)	120.3(2)	121.1(2)	121.6(3)
C(3)-C(4)-C(5)	120.3(2)	120.2(2)	119.2(3)
C(4)-C(5)-C(6)	118.5(2)	119.1(2)	120.3(3)
C(5)-C(6)-C(7)	122.0(2)	120.8(2)	119.3(3)
C(6)-C(7)-C(2)	118.4(2)	120.2(2)	121.3(3)
C(4)-C(5)-C(8)	122.8(2)	118.0(2)	118.3(3)
C(6)-C(5)-C(8)	118.7(2)	122.9(2)	121.4(3)
O(2)-C(8)-C(5)	124.1(2)	124.2(2)	124.0(3)
O(3)-C(8)-C(5)	112.6(2)	112.6(2)	112.3(3)
O(2)-C(8)-O(3)	123.3(2)	123.2(2)	123.7(3)
C(8)-O(3)-C(9)	116.3(2)	115.7(2)	117.1(3)
Cl(1)-C(3)-C(2)		119.4(1)	118.9(2)
Cl(1)-C(3)-C(4)		119.5(2)	119.5(3)
Cl(2)-C(7)-C(2)			119.9(2)
Cl(2)-C(7)-C(6)			118.7(3)
Torsion angles (deg)			
O(1)-C(1)-C(1')-O(1')	180	69.9(4)	180
C(1')-C(1)-O(1)-C(2)	−166.1(2)	174.0(4)	169.6(5)
C(1)-O(1)-C(2)-C(3)	−173.4(2)	−173.1(2)	−91.4(4)
C(1)-O(1)-C(2)-C(7)	5.2(2)	7.4(3)	91.3(4)
O(1)-C(2)-C(3)-C(4)	178.1(2)	178.0(2)	−175.8(3)
O(1)-C(2)-C(7)-C(6)	−177.5(2)	−179.1(2)	176.7(3)
O(2)-C(8)-C(5)-C(6)	−3.1(3)	−177.6(2)	−172.7(4)
O(2)-C(8)-C(5)-C(4)	177.5(2)	2.9(3)	7.5(6)
O(3)-C(8)-C(5)-C(6)	175.6(2)	2.0(3)	6.1(5)
O(3)-C(8)-C(5)-C(4)	−3.8(3)	−177.4(2)	−173.7(3)
O(2)-C(8)-O(3)-C(9)	0.8(3)	−1.6(3)	−0.5(6)
C(5)-C(8)-O(3)-C(9)	−177.9(2)	178.7(2)	−179.3(3)
Cl(1)-C(3)-C(2)-O(1)		−1.9(3)	4.0(4)
Cl(2)-C(7)-C(2)-O(1)			−2.1(4)

Prime atoms are related to the corresponding unprimed ones by inversion for **1** and **3** and by crystallographic two-fold axis for **2** through the molecular centres

Molecular and crystal structures of 1

Since there are four molecules per unit cell, the molecule has a crystallographic centre of symmetry at the centre of the CH_2-CH_2 bond, and the two ether O atoms are oriented *anti* to each other. The most interesting structural feature of the molecule is the geometry around the central ethylenic part where the CH_2-CH_2 bond length is 1.506(4) Å. This significant shortening of the C(sp^3)-C(sp^3) bond distance from the expected values of 1.537(5) Å[17] and 1.530 Å[18] was systematically found in other analogous derivatives: 1.499 Å in ethylene glycol dibenzoate[19], 1.493 Å in ethylene glycol di(*p*-chlorobenzoate)[20], 1.51 Å in dimethyl 4,4'-[ethylenebis-(oxycarbonyl)]dibenzoate [referred to as the linear dimer of poly(ethylene terephthalate) (PET)][3] and other n-methylene dibenzoate derivatives[21-23].

The bond angle, O(1)-C(1)-C(1'), 105.9(2)°, is much narrower than expected. Similar narrowings of the O(1)-C(1)-C(1') bond angle, which were generally accompanied by ethylenic bond shortening, were observed in the analogous derivatives. The deviation from planarity of the molecule is also mainly due to rotation around the methylene-O(1) bonds, and the torsion angle C(1')-C(1)-O(1)-C(2) is −166.1(2)°. This departure from a *trans* conformation is larger than that of ethylene glycol dibenzoate in which the corresponding torsion angle is 172.8° (ref. 19). The C(1) atom deviates significantly (0.198 Å) from the phenyl-ring plane. The torsion angle of C(1)-O(1)-C(2)-C(7) is 5.2(2)° and the dihedral angle

Table 6 Least-squares best planes of benzene rings and displacement (Å) of the atoms from the planes

	1	2	3
C(1)	0.198(2)	0.217(2)	1.428(3)
C(2)[a]	0.004(2)	0.013(2)	0.006(3)
C(3)[a]	−0.000(2)	−0.012(2)	0.003(3)
C(4)[a]	−0.003(2)	0.001(2)	0.004(4)
C(5)[a]	0.002(2)	0.009(2)	0.003(3)
C(6)[a]	0.003(2)	−0.011(2)	−0.005(3)
C(7)[a]	−0.006(2)	−0.003(2)	0.000(3)
C(8)	−0.008(2)	0.025(2)	0.014(3)
O(1)	0.047(2)	0.040(2)	0.079(3)
Cl(1)		−0.057(2)	−0.037(3)
Cl(2)			0.033(3)

[a]Atoms included in the calculation of the planes

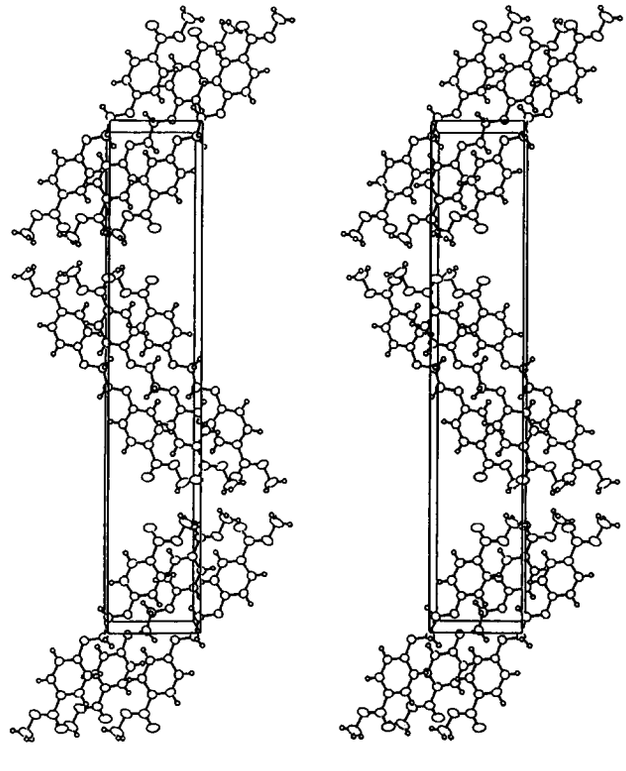


Figure 2 Stereoview for the mode of packing of the molecules of **1**. The *a*-axis is horizontal and the *b*-axis is vertical

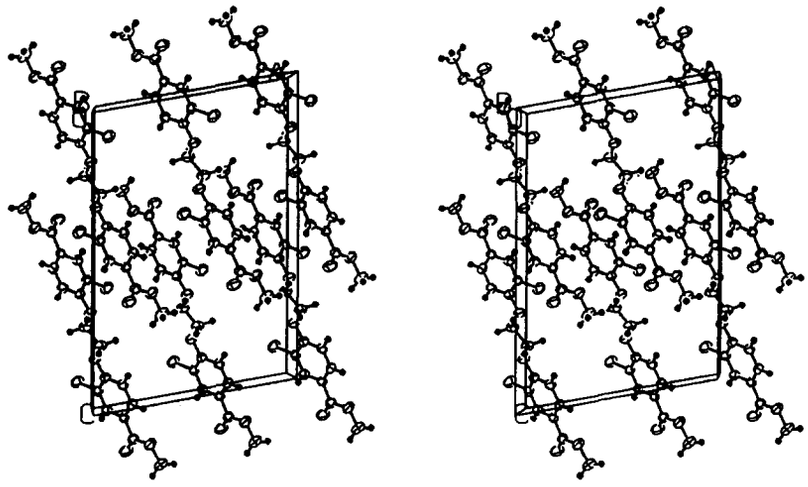


Figure 3 Stereoview for the mode of packing of the molecules of **2**. The *a*-axis is horizontal and the *c*-axis is vertical

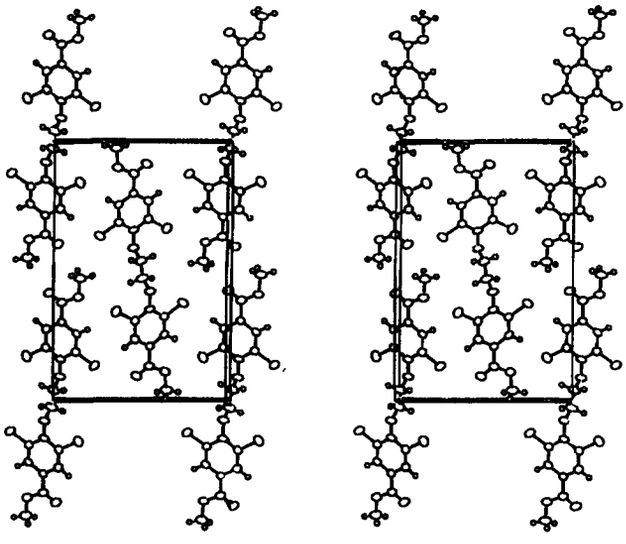


Figure 4 Stereoview for the mode of packing of the molecules of **3**. The *b*-axis is horizontal and the *c*-axis is vertical

between the phenyl-ring plane and the ethylene glycol plane is 14.1°.

The aromatic carbon C(2)-O bond length of 1.372(2) Å is within the values (1.357–1.378 Å) found in other aromatic ethers[24].

The plane of the carboxylic group is at an angle of 4.0° to the phenyl ring which is the same as the value in ethylene glycol dibenzoate[19] but smaller than the angle of 7.5° in ethylene glycol di(*p*-chlorobenzoate)[20] and 8.4° in the linear dimer of PET[3]. The distance between the terminal methyl carbons C(9)-C(9′) is 18.65 Å.

As shown in *Figure 2*, the molecules form a stacked herring-bone layer structure. The molecular chains are arranged in a layer with their long axes tilted to the *b*-axis by ~40° and packed side by side in such a way that the phenyl, ether or ester groups are arranged to the same height but with an opposite sense.

Molecular and crystal structures of 2

The molecules has a crystallographic two-fold axis on the centre of the CH_2-CH_2 bond, and the O(1)-C(1)-C(1′)-O(1′) torsion angle is 69.9° making the conformation of this part of the molecule *gauche*. The two phenyl-ring planes are nearly perpendicular to each other with the dihedral angle between the two planes being 81.2°. The CH_2-CH_2 bond length of 1.489(4) Å is much shorter than the value of **1**, but the O-CH_2-CH_2 angle of 107.8(2)° is a little open and the C(1′)-C(1)-O(1)-C(2) torsion angle is 174.0(4)°. The aromatic carbon C(2)-O bond length of 1.355(2) Å is the shortest of those found in the other aromatic ethers[24]. The C(1) atom which is *anti* to the C1(1) atom deviates greatly (0.217(2) Å) from the phenyl-ring plane with a C(1)-O(1)-C(2)-C(7) torsion angle of 7.4(3)°. The plane of the carboxylic group is nearly on the phenyl-ring plane with the dihedral angle between then being 2.8°. The distance between C(9)-C(9′) is 18.07 Å.

The molecular arrangement in the crystal viewed along the *b*-axis is illustrated in *Figure 3*. The molecules are stacked with their long axes tilted by ~23° from the *c*-axis.

Molecular and crystal structures of 3

Since the compound crystallizes in the monoclinic $P2_1/n$ space group with two molecules in the unit cell, there is an inversion centre in the middle of the ethylene carbon–carbon bond of the molecule and ether O atoms are oriented *anti* to each other.

The CH_2-CH_2 bond distance of the central ethylenic part is much shorter (1.455(7) Å) than that of **1** but the angle of O-C(1)-C(1′) is a little open (107.5(4)°). The O(1) atom deviates significantly (0.08 Å) from the phenyl-ring plane. The ethylene glycol plane is rotated ~90° to the phenyl-ring plane on account of the two chlorine atoms at the *ortho* position: the dihedral angle between the ethylene glycol plane and phenyl-ring plane is 79.6° with a C(1)-O(1)-C(2)-C(7) torsion angle of 91.3(4)°. The perpendicular distance between the two phenyl-ring planes is 2.75 Å. The dihedral angle between the carboxylic moiety and phenyl-ring plane is 6.5°. The distance between C(9)-C(9′) is 18.36 Å.

Molecular packing in the crystal is shown in *Figure 4*. The molecules are stacked with their long axes being inclined ~10° to the *c*-axis.

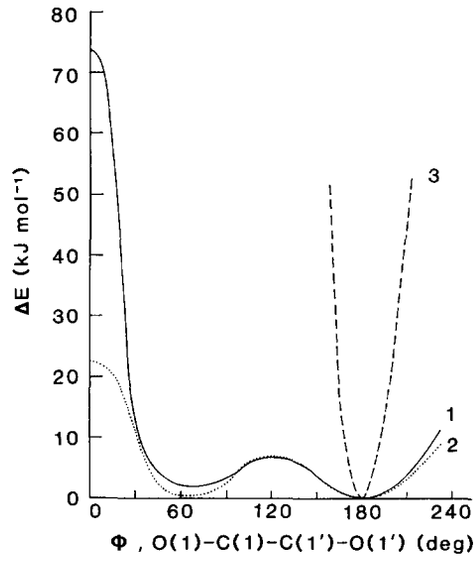


Figure 5 Variation of total energies with the torsion angle ϕ, (O(1)-C(1)-C(1')-O(1')) (deg) as calculated by MNDO for **1** (——), **2** (...) and **3** (– – –), respectively. In each case the energies are expressed relative to zero for energy minimum

Energy calculations

In order to assess the conformational features determined by X-ray analysis, theoretical calculations were performed using the MNDO semi-empirical quantum mechanics method. The results are shown in *Figure 5*. The calculations of total energies show that the torsion angle in the crystal structure for the compound **3** is energetically favoured since compound **3** has a deep potential minimum at 180° (*trans*) due to steric interference between the *ortho* chlorine atoms at the two phenyl rings. For compounds **1** and **2**, the total energy potential curves have two global minima, one at 180° (*trans*) and another at 60° (*gauche*). These two minima differed in energy by only 2.16 kJ mol^{-1} for **1** and 0.63 kJ mol^{-1} for **2** with the *trans* forms being lower in energy. The corresponding minima determined by X-ray analysis occur at 180° (*trans*) for **1** and at 69.9° (*gauche*) for **2**. In view of the rather low barriers (6.6–6.8 kJ mol^{-1}) between the two forms, it is expected that, at least at room temperature, *trans* and *gauche* preferences in the solid state could reflect contributions from crystal lattice forces. Thus, in this case, the quantum mechanical and the X-ray results are in substantial agreement.

Relevance to the corresponding polymers

From single crystal X-ray diffraction and energy calculations of the three oligomeric compounds it was found that the barrier between the *trans* and *gauche* conformation of the ether-linked methylene part is low enough to have both conformations in the solid-state for compounds **1** and **2**. Compound **3**, on the contrary, takes a *trans* conformation due to the steric interference between the *ortho* chlorine atoms at the two phenyl rings. Repeat units of the corresponding polymers were calculated using a combination of data from structures **1**, **2** and **3** for ether-linked aromatic rings and the data from the linear dimer of PET[3] for ester-linked aromatic parts. The values obtained were 19.7, 19.3 and 19.7 Å for polymers **4**, **5** and **6**, respectively. Polymer diffraction studies have indicated the crystallographic fibre repeat of the two crystalline modifications of polymer **4** to be 18.68 and 18.64 Å (ref. 25) and that of polymer **5** to be 18.4 Å (ref. 26). These values indicate that some kind of considerable distortion is required to account for the crystallographic repeats observed in these polymers. The crystal structure of polymer **5** will be reported in a separate paper[26].

REFERENCES

1 Tashiro, K., Hou, J., Kobayashi, M. and Inoue, T. *J. Am. Chem. Soc.* 1990, **112**, 8273
2 Wellman, M. W., Adams, W. W., Wolff, R. A., Dudis, D. S., Wiff, D. R. and Fratini, A. V. *Macromolecules* 1981, **14**, 935
3 Kitano, Y., Ishitani, A. and Inoue, T. *Acta Crystallogr.* 1991, **C47**, 363
4 Kitano, Y., Ishitani, A. and Ashida, T. *Polymer J.* 1991, **23**, 949
5 Kitano, Y. and Ashida, T. *Polymer J.* 1992, **24**, 1099
6 Kitano, Y., Ishitani, A. and Ashida, T. *Polymer J.* 1992, **24**, 783
7 Kobayashi, H. and Sasaguri, K. *US Pat. 3 816 368*, 1974
8 Komatu, H. *Jpn. Pat. 49-1795*, 1974
9 Abe, K., Kawakami, K., Yoshii, T. and Inoue, T. *US Pat. 4 539 260*, 1985; *Jpn. Pats H1-56656*, 1989 and *H1-56658*, 1989
10 Komatu, H., Yuguchi, S., Tanimura, M. and Matukawa, H. *US Pat. 3 705 130*, 1972
11 Inoue, T. and Komatu, H. *Jpn. Pat. 56-19339*, 1981
12 Inoue, T. and Komatu, H. *US Pat. 4 531 009*, 1985
13 Gilmore, C. J. 'MITHRIL, A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data', University of Glasgow, 1983
14 Ibers, J. A. and Hamilton, W. C. (Eds) 'International Tables for X-ray Crystallography', Vol. IV, Kynoch Press, Birmingham, 1974
15 Hamilton, W. C. *Acta Crystallogr.* 1959, **12**, 609
16 Johnson, C. K. 'ORTEP II,' Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976
17 Sutton, L. E. 'Tables of Interatomic Distances and Conformation in Molecules and Ions,' Suppl. 1956–1959, The Chemical Society, London, 1965
18 Allen, F. H., Kennard, O., Watson, D. G., Brammer, L. A., Orpen, G. and Taylor, R. *J. Chem. Soc., Perkin Trans.* 1987, **2**, S1–19
19 Perez, S. and Brisse, F. *Acta Crystallogr.* 1976, **B32**, 470
20 Perez, S. and Brisse, F. *Can. J. Chem.* 1975, **53**, 3551
21 Perez, S. and Brisse, F. *Acta Crystallogr.* 1977, **B33**, 3259
22 Perez, S. and Brisse, F. *Acta Crystallogr.* 1976, **B32**, 1518
23 Bocelli, G. and Grenier-Loustalot, M. F. *Acta Crystallogr.* 1982, **B38**, 2072
24 Haisa, M. and Kashino, S. *Acta Crystallogr.* 1977, **B33**, 485; and references cited therein
25 Shimizu, J., Okui, N., Imai, Y., Nishide, S. and Takaku, A. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 275
26 Kitano, Y. to be published