

N(6)] à leur plan moyen sont toujours inférieures à 0,005 (3) Å avec un χ^2 de 12, ce qui peut être comparé à celles des atomes du cycle aromatique [C(23), C(24), C(25), C(26), C(27) et C(28)] où la déviation maximum est de 0,007 (4) Å avec un χ^2 de 6.

La molécule adopte donc une géométrie en forme d'escalier, les plans des cycles étant presque parallèles entre eux (angle dièdre de 6,6° seulement), le barycentre d'un cycle étant à 1,088 (4) Å du plan moyen défini par l'autre cycle. Le plan défini par la chaîne éthyle forme respectivement des angles dièdres de 85,4 et 88,4° avec les plans des cycles thiadiaziniques et benzénique. Le groupement sulfone est symétrique, les deux distances S—O étant identiques à 0,5% près, alors que les deux distances S—N sont différentes l'une de l'autre de 7,2% avec un certain caractère de double liaison pour la liaison S(1)—N(6). L'atome d'azote N(2) est hybridé en sp^2 ; la somme des valeurs des trois angles de liaison le concernant est égale à 360°. On remarquera également que la liaison simple C(4)—C(5) est à peine plus longue que les liaisons du cycle benzénique, ce qui dénote une large conjugaison entre les atomes N(2), C(3), C(4), C(5) et N(6).

On trouvera dans le Tableau 1 les paramètres de position des atomes autre que les hydrogènes et dans le Tableau 2 les longueurs de liaisons et les angles de liaison de la molécule d'où découlent les remarques qui viennent d'être faites.

La possibilité de contact intermoléculaire pouvant expliquer une contrainte qui serait propre à imposer la planéité à l'hétérocycle thiadiazinique.

En conclusion, on retiendra que l'originalité du composé étudié tient essentiellement à sa planéité qui devrait permettre d'enrichir les relations de structure-activité dans la série examinée.

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Structure of Bis(4-methoxyphenyl) Glutarate

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Abstract. $C_{19}H_{20}O_6$, $M_r = 344.4$, orthorhombic, $Pbca$, $a = 43.46$ (2), $b = 10.378$ (6), $c = 7.780$ (5) Å, $V = 3509.0$ Å³, $Z = 8$, $D_x = 1.304$ g cm⁻³, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu = 7.19$ cm⁻¹, $F(000) = 1456$, $T = 293$ K. The structure was refined to $R = 0.052$ for 1978 reflections with $I > 3\sigma(I)$. The molecules are approximately linear with the phenyl rings *cis* to one another. They pack in a parallel manner in the crystal with the

principal interactions being between polar methoxy groups and adjacent phenyl rings.

Introduction. Thermotropic smectic and nematic liquid-crystalline behaviour has been investigated for a wide range of polymers containing mesogenic units based on biphenyl groups (Ober, Jin & Lenz, 1984; Shibaev & Plate, 1984). In polymers with these mesogenic groups in side chains, a spacer unit between the biphenyl group and the main chain is often required in order to produce liquid-crystalline ordering. Interestingly, poly(*p*-

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Table 1. Non-H atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters

	$B_{eq} = \frac{1}{3}\pi^2(\sum U_{ij})$			
	x	y	z	$B_{eq}(\text{\AA}^2)$
C(1)	79 (1)	2917 (4)	8348 (5)	8.2 (3)
O(1)	9951.3 (5)	1690 (2)	8714 (3)	6.9 (1)
C(2)	9650 (1)	1481 (3)	8281 (4)	5.3 (2)
C(3)	9475 (1)	2309 (3)	7283 (4)	5.7 (2)
C(4)	9171 (1)	2020 (3)	6916 (4)	5.7 (2)
C(5)	9047 (1)	904 (2)	7554 (4)	5.2 (1)
C(6)	9219 (1)	54 (2)	8520 (3)	5.4 (2)
C(7)	9521 (1)	346 (3)	8886 (3)	5.5 (2)
O(2)	8748.2 (4)	534 (2)	7081 (3)	6.4 (1)
C(8)	8504 (1)	1198 (3)	7716 (4)	5.4 (2)
O(3)	8529.2 (4)	2064 (2)	8737 (3)	6.5 (1)
C(9)	8219 (1)	640 (3)	6987 (4)	6.5 (2)
C(10)	7926 (1)	1369 (3)	7375 (4)	6.1 (2)
C(11)	7656 (1)	745 (3)	6432 (5)	7.0 (2)
C(12)	7351 (1)	1263 (3)	6910 (4)	6.1 (2)
O(4)	7295.9 (5)	2080 (2)	7948 (4)	9.1 (2)
O(5)	7127.3 (4)	644 (2)	6017 (3)	6.2 (1)
C(13)	6819 (1)	931 (2)	6389 (4)	5.1 (1)
C(14)	6688 (1)	2066 (2)	5827 (4)	5.8 (2)
C(15)	6381 (1)	2286 (2)	6200 (4)	5.8 (2)
C(16)	6209 (1)	1378 (2)	7076 (3)	5.0 (1)
C(17)	6340 (1)	234 (2)	7596 (3)	5.4 (2)
C(18)	6650 (1)	20 (2)	7245 (3)	5.4 (2)
O(6)	5905.8 (4)	1703 (2)	7368 (3)	6.3 (1)
C(19)	5728 (1)	856 (4)	8386 (5)	7.7 (3)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

C(1)—O(1)	1.419 (5)	C(10)—C(11)	1.528 (6)
O(1)—C(2)	1.368 (4)	C(11)—C(12)	1.478 (6)
C(2)—C(3)	1.386 (5)	C(12)—O(4)	1.195 (4)
C(2)—C(7)	1.387 (5)	C(12)—O(5)	1.358 (4)
C(3)—C(4)	1.384 (6)	O(5)—C(13)	1.402 (4)
C(4)—C(5)	1.371 (4)	C(13)—C(14)	1.379 (4)
C(5)—C(6)	1.379 (4)	C(13)—C(15)	1.370 (4)
C(5)—O(2)	1.404 (4)	C(14)—C(15)	1.384 (6)
C(6)—C(7)	1.377 (6)	C(15)—C(16)	1.383 (4)
O(2)—C(8)	1.358 (4)	C(16)—C(17)	1.377 (4)
C(8)—O(3)	1.204 (4)	C(16)—O(6)	1.378 (4)
C(8)—C(9)	1.480 (6)	C(17)—C(18)	1.393 (6)
C(9)—C(10)	1.512 (6)	O(6)—C(19)	1.414 (5)
C(1)—O(1)—C(2)	117.9 (3)	C(10)—C(11)—C(12)	114.4 (3)
O(1)—C(2)—C(3)	124.4 (3)	C(11)—C(12)—O(4)	127.4 (3)
O(1)—C(2)—C(7)	116.0 (3)	C(11)—C(12)—O(5)	110.0 (3)
C(3)—C(2)—C(7)	119.7 (4)	O(4)—C(12)—O(5)	122.6 (3)
C(2)—C(3)—C(4)	120.3 (3)	C(12)—O(5)—C(13)	118.6 (2)
C(3)—C(4)—C(5)	118.9 (3)	O(5)—C(13)—C(14)	120.7 (3)
C(4)—C(5)—C(6)	121.7 (4)	O(5)—C(13)—C(18)	117.8 (3)
C(4)—C(5)—O(2)	120.0 (3)	C(14)—C(13)—C(18)	121.5 (4)
C(6)—C(5)—O(2)	118.0 (3)	C(13)—C(14)—C(15)	118.2 (3)
C(5)—C(6)—C(7)	119.3 (3)	C(14)—C(15)—C(16)	120.8 (3)
C(2)—C(7)—C(6)	120.1 (3)	C(15)—C(16)—C(17)	120.6 (4)
C(5)—C(7)—C(8)	119.3 (2)	C(15)—C(16)—O(6)	115.5 (3)
O(2)—C(8)—O(3)	123.2 (3)	C(17)—C(16)—O(6)	129.3 (3)
O(2)—C(8)—C(9)	108.4 (3)	C(16)—C(17)—C(18)	118.7 (3)
O(3)—C(8)—C(9)	128.3 (3)	C(13)—C(18)—C(17)	120.3 (3)
C(8)—C(9)—C(10)	115.6 (3)	C(16)—O(6)—C(19)	117.6 (2)
C(9)—C(10)—C(11)	109.8 (3)		

Principal intermolecular contact distances

C(2)—C(3 ⁱⁱ)	3.446 (5)	C(15)—C(16 ⁱⁱ)	3.568 (4)
C(1)—C(7 ⁱⁱⁱ)	3.533 (3)	C(7)—C(3 ⁱ)	3.598 (4)

Symmetry operation applied to second atom: (i) $x, 0.5-y, 0.5+z$; (ii) $0, 0.5-y, 1.5-y$; (iii) $0, y-0.5, 1.5-z$.

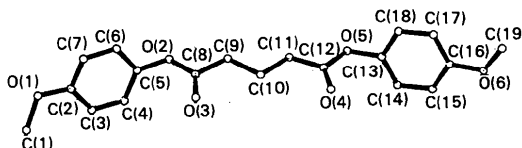


Fig. 1. ORTEP (Johnson, 1965) drawing of the molecule with atom numbering.

biphenyl acrylate) with direct attachment of biphenyl groups to the main chain displays smectic liquid-crystalline order, though the *p*-biphenyl acrylate monomer is not mesogenic (Blumstein, 1978).

In order to understand the steric and interactive requirements for the ordering of side groups in this polymer, we have been investigating low-molar-mass analogues of segments of the chain such as esters of glutaric acid containing substituted phenyl and biphenyl groups. Here, we report a study of the structure of bis(4-methoxyphenyl) glutarate.

Experimental. Preparation by the method of Patai, Bentov & Reichmann (1952); colourless acicular crystals grown from ethanol, crystal $0.5 \times 0.5 \times 0.1$ mm mounted about *c*, Stoe Stadi-2 two-circle diffractometer, $(\sin\theta)/\lambda < 0.6 \text{ \AA}^{-1}$; lattice parameters from maximum fit of axial row reflections ($15 < 2\theta < 80^\circ$); 3132 unique reflections measured of which 1978 had $I > 3\sigma(I)$; $h 0 \rightarrow 50$, $k 0 \rightarrow 11$, $l 0 \rightarrow 6$; standard reflection on each layer measured every 25 reflections, no significant change; no correction for absorption and extinction; structure solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971) and refined by full-matrix least squares on F to $R = 0.052$, $wR = 0.059$, non-H atoms anisotropic, H atoms in calculated positions and not refined; in the final refinement cycles $w = 2.5289/[\sigma^2(F) + 0.000447F^2]$; max. $\Delta/\sigma = 0.05$, $\Delta\rho$ excursions = $\pm 0.1 \text{ e \AA}^{-3}$ (no structural significance). Scattering factors from *International Tables for X-ray Crystallography* (1974); structure refinement using *SHELX76* (Sheldrick, 1976)

and geometry calculations using *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Discussion. The final atomic coordinates are listed in Table 1* and bond lengths and angles and principal intermolecular contacts in Table 2. The molecular structure and atom numbering are shown in Fig. 1.

The molecule is basically linear with the terminal phenyl rings *cis* to one another. The two terminal methoxy groups lie in the planes of the rings and point

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51474 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

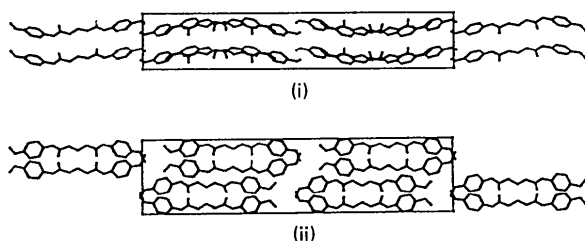


Fig. 2. ORTEP (Johnson, 1965) projections down (i) *b* and (ii) *c*.

in opposite directions. This is the conformation reported for the methoxy groups in 1,4-dimethoxybenzene (Goodwin, Przybylska & Robertson, 1950). The ester groupings form planes normal to the adjacent phenyl ring.

Krigbaum, Watanabe & Ishikawa (1983) have studied the liquid-crystal behaviour of poly(esters) based on 4,4'-dihydroxybiphenyl. The molecules take up extended forms with the ester groups *cis* for an odd number and *trans* for even number of methylene units. This is compatible with the present structure as shown in the figures, where the unit-cell contents are shown in Fig. 2 in projections down *b* and *c*. The approximately linear molecules pack in a parallel manner confirming the potential for liquid-crystal behaviour when acting as side groups on polymer chains. Several short intermolecular contacts have been observed (Table 2), particularly one of 3.533 (3) Å between the methyl

group, C(1), and the phenyl ring at C(7), and one of 3.446 (5) Å between C(2) and C(3) in adjacent phenyl rings. These intermolecular contacts indicate that interactions between the phenyl rings and the polar groups on neighbouring rings are of prime importance in determining the packing geometry.

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Ammonium Hydrogen Oxalate Hemihydrate: X-ray and Neutron Diffraction Studies

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Abstract. $\text{NH}_4^+\cdot\text{HC}_2\text{O}_4^- \cdot 1/2\text{H}_2\text{O}$, $M_r = 116.1$, orthorhombic, *Pnma*, $a = 11.237$ (1), $b = 12.341$ (2), $c = 6.901$ (1) Å, $V = 957.00$ (2) Å³, $Z = 8$, $D_m = 1.614$, $D_x = 1.612$ Mg m⁻³, $F(000) = 488$, $T = 295$ K; (1) X-ray data, Mo *K*α, $\lambda = 0.71069$ Å, $\mu(\text{calc.}) = 0.1509$ mm⁻¹, 1781 unique reflections, $R = 0.0331$; (2) neutron data, $\lambda = 1.210$ Å, $\mu(\text{obs.}) = 0.2316$ mm⁻¹, 2093 reflections measured, $R = 0.0397$. The hydrogen oxalate ions form infinite chains *via* an asymmetric hydrogen bond, with an O...O distance of 2.562 (1) Å. Ammonium ions are disordered. The H-atom sites in the ammonium ions have similar possibilities for

hydrogen bonding. The shortest separation between the disordered sites is 0.22 (5) Å and the largest is 0.90 (1) Å. Both data sets were corrected for thermal diffuse scattering.

Introduction. The present work is part of a project involving studies of the influence of the environment on the electron and proton distribution in acid salt compounds containing hydrogencarbonate or hydrogen carboxylate groups (Fernandes, Tellgren & Olovsson, 1988).

The X-ray structure of $\text{NH}_4\text{HC}_2\text{O}_4 \cdot 1/2\text{H}_2\text{O}$ has been investigated by Küppers (1973). Some physical properties of this compound have been measured by Küppers and co-workers, *e.g.* density (Küppers, 1973),

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