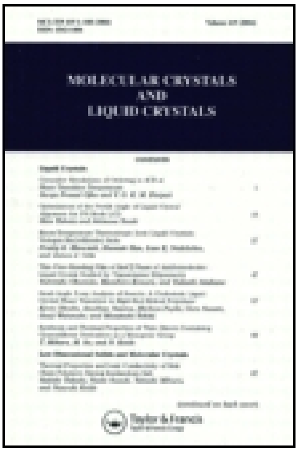

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Crystal Structure of Bis[4-(4′-Carboxy-Butanoyloxy)-Acetophenon Azine

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Crystal Structure of Bis[4-(4′-Carboxy-Butanoyloxy)-Acetophenon]Azine

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Bis[4-(4′-carboxy-butanoyloxy)-acetophenon]azine ($C_{26}H_{28}O_8N_2$) is a dicarboxylic acid that can be considered as a model for semiflexible mesogenic polyesters having formula [—COO—R—OOC—$(CH_2)_{2n}$-]$_x$ with R = -ϕ-C(CH_3)=N—N=C(CH_3)-ϕ- (-ϕ- = *p*-phenylene). It has been synthesized and its crystal structure has been determined by direct methods. Crystals are triclinic, space group P$\bar{1}$, a = 6.306(2), b = 7.738(2), c = 25.982(6) Å, α = 96.93(2)°, β = 93.16(4)°, γ = 93.93(3)° with two molecules in the unit cell. The structure was refined by full matrix least squares methods to R = 0.084 for 1962 observed reflections, having $I > 2.5\ \sigma(I)$. The structure is affected by positional disorder on one of the two terminal chains of the molecule. The conformation around the central =N—N= bond of the crystallographic independent molecule is not trans planar. The average planes of the phenyl rings belonging to the same molecule make a dihedral angle of 62.6°. Molecules are linked through hydrogen bonds between carboxylic groups and form parallel rows having linear symmetry *ti*.

Keywords: crystal structure, molecular structure, liquid crystal, model compounds, polymers

INTRODUCTION

In the last few years we have been investigating the phase behaviour and the crystal structure of some α,ω-dicarboxylic acids containing a mesogenic core as possible model compounds for the crystal packing of linear semiflexible polymers exhibiting mesogenic behaviour.[1–4]

In one of our reports,[2] we described the crystal structure of a dicarboxylic acid containing the mesogenic group R = -ϕ-C(CH_3)=N—N=C(CH_3)-ϕ- (-ϕ- = *p*-phenylene), and in that case, at variance with a previous result,[5] we found a non trans planar confrontation around the central N—N bond which was ascribed to crystal packing effects. In order to verify this hypothesis, we have undertaken the structural investigation of the title compound, having formula HOOC—$(CH_2)_3$—COO—R—OOC—$(CH_2)_3$—COOH, which is expected to exhibit a crystal packing similar to that of the compound of Reference 2. Futhermore, the title compound may be considered as a model for semiflexible polyesters having formula [—OOC—$(CH_2)_{2n}$—COO—R—]$_x$, which are the first thermotropic segmented chain liquid crystalline polymers described in the literature.[6]

EXPERIMENTAL PROCEDURE

Title compound was obtained by esterification of 4,4′-dihydroxy-α,α′-dimethylbenzalazine (prepared according to Reference 7) with glutaric anhydride, following a procedure already described by us.[4] Its purity was checked by ^{1}H NMR and DSC techniques. The compound undergoes a solid-solid phase transition at 152°C ($\Delta H = 3.0$ J/g). Melting occurs at 190°C to give an isotropic liquid; however, on melting, some chemical decomposition occurs in a similar was to what found by us for the analogous compound containing the biphenylene group.[3]

Single crystals, suitable for X-ray analysis, were obtained by slow evaporation of a methanol/water solution. Weissenberg and oscillation photographs suggested triclinic symmetry; furthermore the diffraction patterns did not extend to high sin θ/λ values.

Crystals belong to triclinic space group $P\bar{1}$ with $a = 6.306(2)$, $b = 7.738(2)$, $c = 25.982(6)$ Å, $\alpha = 96.93(2)°$, $\beta = 93.16(4)°$, $\gamma = 93.93(3)°$, $V = 1253(6)$ Å^3, $Z = 2$, $D_{\mathrm{cal}} = 1.316$ g cm^{-3}. A total of 4272 reflections were measured and collected on an Enraf Nonius CAD-4 automatic single crystal diffractometer with graphite monochromated CuKα radiation ($\lambda = 1.5418$ Å) using the ω-θ scanning mode. 2310 reflections having $I < 2.5\ \sigma(I)$ were considered unobserved.

During data collection, the intensity of two standard reflections, periodically measured, showed only random fluctuations. Lorentz and polarization corrections were applied but no correction for absorbtion and extinction was employed.

The structure was solved by direct methods with the program MULTAN82.[8] Final atomic parameters are given in Table I. The Fourier map calculated with the highest combined figure of merit showed all the molecule except one of the terminal chains. Successive Fourier maps showed two possible positions for this chain. The structure was refined with the program SHELX[9] imposing constraints on some bond lengths and bond angles of the terminal chain of the molecule that is affected by positional disorder. For such constraints standard values for C—C bond lengths and C—C—C bond angles were used (see Table II), while for the carboxyl group literature data were used.[10] The peaks of the Fourier maps corresponding to the two different positions of the disordered terminal had similar intensities, and subsequent refinement with occupancy factor of 0.5 gave quite acceptable *B*'s values for these atoms. Furthermore, it should be noted that, owing to the mode of hydrogen bonding between carboxylic groups (see discussion), the $P\bar{1}$ symmetry of the structure could be retained only with half occupancy of the two positions. Therefore the occupancy factor was not refined and taken equal to 0.5 for atoms affected by disorder. The coordinates and anisotropic thermal parameters of all non H atoms were refined on *F* (unit weights used throughout the refinement). All H atoms were geometrically positioned with the exception of those of the two methyl groups and of a carboxyl group, whose positions were defined on the basis of a difference Fourier map; the H atoms of the disordered carboxyl group were not considered in the structure analysis. To all H atoms isotropic thermal parameters equal to B_{eq} of the carrier atom were assigned. They were included in the structure factor calculations but not refined. The final *R* factors for 1962 observed reflections were $R = 0.084$, $Rw = 0.084$. The residual electronic density in the final difference

TABLE I

Refined positional parameters and equivalent temperature factors with e.s.d.'s in parentheses. ($B_{eq} = 4/3 \sum_i \sum_j b_{ij} \mathbf{a}_i\mathbf{a}_j$)

atom	x	y	z	B_{eq}
O1	1.249(1)	0.417(1)	1.0125(2)	8.3(2)
O2	1.412(1)	0.403(1)	0.9407(2)	8.3(2)
O3	0.830(1)	0.4056(8)	0.7861(2)	7.0(1)
O4	0.5675(8)	0.1943(7)	0.7846(2)	5.4(1)
O5	-0.0899(9)	0.2826(7)	0.2689(2)	6.3(1)
O6	0.037(2)	0.069(1)	0.2216(3)	14.5(1)
O7A	-0.640(2)	-0.010(2)	0.0314(4)	8.3(1)
O8A	-0.309(2)	0.093(2)	0.0213(4)	10.4(1)
O7B	-0.699(2)	0.079(2)	0.0703(4)	10.3(1)
O8B	-0.371(2)	0.192(2)	0.0629(5)	10.3(1)
N1	0.3351(9)	0.1964(8)	0.5442(2)	4.4(1)
N2	0.2321(9)	0.2007(8)	0.4954(2)	4.4(1)
C1	1.254(1)	0.372(1)	0.9640(3)	6.0(2)
C2	1.058(1)	0.275(1)	0.9366(3)	6.4(2)
C3	1.005(1)	0.338(1)	0.8842(3)	5.5(2)
C4	0.802(1)	0.239(1)	0.8586(3)	5.1(2)
C5	0.740(1)	0.295(1)	0.8060(3)	4.9(2)
C6	0.494(1)	0.221(1)	0.7340(3)	4.4(2)
C7	0.308(1)	0.298(1)	0.7286(3)	5.1(2)
C8	0.225(1)	0.3158(9)	0.6793(3)	4.3(2)
C9	0.326(1)	0.2528(9)	0.6353(3)	3.6(2)
C10	0.516(1)	0.1734(9)	0.6426(3)	4.0(2)
C11	0.601(1)	0.155(1)	0.6919(3)	4.5(2)
C12	0.234(1)	0.2644(9)	0.5824(2)	4.0(2)
C13	0.033(1)	0.365(1)	0.5755(3)	5.2(2)
C14	0.358(1)	0.2319(8)	0.4599(2)	3.7(2)
C15	0.592(1)	0.272(1)	0.4688(3)	5.2(2)
C16	0.253(1)	0.2336(9)	0.4070(2)	3.5(2)
C17	0.052(1)	0.1465(9)	0.3947(3)	4.0(2)
C18	-0.056(1)	0.1564(9)	0.3479(3)	4.2(2)
C19	0.035(1)	0.256(1)	0.3140(3)	4.6(2)
C20	0.232(1)	0.342(1)	0.3233(3)	4.9(2)
C21	0.342(1)	0.3285(9)	0.3710(3)	4.3(2)
C22	-0.085(2)	0.177(1)	0.2243(3)	8.5(3)
C23	-0.205(1)	0.236(1)	0.1826(3)	13.5(4)
C24A	-0.278(2)	0.103(1)	0.1364(4)	7.9(5)
C25A	-0.458(2)	0.162(2)	0.1030(3)	8.3(5)
C26A	-0.461(2)	0.080(2)	0.0476(3)	6.7(5)
C24B	-0.445(1)	0.220(2)	0.1839(3)	9.5(5)
C25B	-0.554(2)	0.289(2)	0.1377(4)	10.2(5)
C26B	-0.526(2)	0.177(2)	0.0876(3)	7.4(5)

Fourier map was less than 0.6 eÅ^{-3} and mainly localized near atoms of the disordered terminal.

Atomic scattering factors were taken from International Tables for X Ray Crystallography,[11] programs from Enraf Nonius Structure Determination Package.[12] All calculations were performed on a Digital Micro VMS V4.7 computer. Additional material to this paper (list of observed and calculated structure factors, coordinates and thermal parameters of hydrogen atoms) is available from the authors on request.

DISCUSSION

The model molecule is shown in Figure 1 along with lettering. Fractional atomic coordinates and thermal parameters of the crystallographic independent molecule

TABLE II

Selected bond lengths (Å), bond angles (°) and torsion angles (°) with e.s.d.'s in parentheses. Starred bond lengths and bond angles were fixed during refinement.

O1-C1	1.268(8)	C1-C2	1.50(1)
O2-C1	1.22(1)	C2-C3	1.528(9)
O3-C5	1.18(1)	C3-C4	1.52(1)
O4-C5	1.35(1)	C4-C5	1.521(9)
O4-C6	1.414(8)	C9-C12	1.477(8)
O5-C19	1.420(8)	C12-C13	1.51(1)
O5-C22	1.341(9)	C14-C15	1.49(1)
O6-C22	1.17(1)	C14-C16	1.495(7)
O7A-C26A	1.31(1)*	C22-C23	1.42(1)
O8A-C26A	1.21(1)*	C23-C24A	1.51(1)*
O7B-C26B	1.31(1)*	C23-C24B	1.51(1)*
O8B-C26B	1.21(1)*	C24A-C25A	1.52(2)*
N1-N2	1.397(6)	C24B-C25B	1.52(1)*
N1-C12	1.286(7)	C25A-C26A	1.50(1)*
N2-C14	1.283(7)	C25B-C26B	1.50(1)*

C5-O4-C6	117(1)	C15-C14-C16	119.9(9)
C19-O5-C22	121(1)	C14-C16-C17	119.4(9)
N2-N1-C12	114.2(9)	C14-C16-C21	121.7(9)
N1-N2-C14	114.2(9)	O5-C19-C20	119(1)
O1-C1-O2	122(1)	O5-C19-C18	117(1)
O1-C1-C2	117(1)	O5-C22-O6	119(1)
O2-C1-C2	121(1)	O5-C22-C23	112(1)
C1-C2-C3	112(1)	O6-C22-C23	128(1)
C2-C3-C4	110(1)	C22-C23-C24A	117(1)
C3-C4-C5	113(1)	C22-C23-C24B	117(1)
O3-C5-C4	126(1)	O7A-C26A-O8A	124(2)*
O4-C5-C4	109(1)	O7A-C26A-C25A	113(2)*
O4-C6-C7	118(1)	O8A-C26A-C25A	123(2)*
O4-C6-C11	119(1)	C23-C24A-C25A	113(1)*
C8-C9-C12	121(1)	C26A-C25A-C24A	112(1)*
C10-C9-C12	121(1)	C23-C24B-C25B	112(1)*
N1-C12-C9	117.0(9)	C24B-C25B-C26B	112(1)*
N1-C12-C13	123(1)	O7B-C26B-O8B	124(2)*
C9-C12-C13	119.6(9)	O7B-C26B-C25B	113(2)*
N2-C14-C15	125(1)	O8B-C26B-C25B	123(2)*
N2-C14-C16	115.4(9)		

C3-C2-C1-O1	138(1)	C17-C16-C14-C15	160(1)
C3-C2-C1-O2	-44(1)	C21-C16-C14-N2	154(1)
C3-C4-C5-O3	-2(1)	C21-C16-C14-C15	-24(1)
C3-C4-C5-O4	176(1)	C22-O5-C19-C20	93(1)
C4-C3-C2-C1	-178(1)	O6-C22-O5-C19	-6(1)
C5-C4-C3-C2	180(1)	C23-C22-O5-C19	-174(1)
C6-O4-C5-O3	2(1)	C26A-C25A-C24A-C23	153(2)
C6-O4-C5-C4	-177(1)	C24A-C23-C22-O5	-159(1)
C7-C6-O4-C5	-109(1)	C24A-C23-C22-O6	34(2)
C8-C9-C12-N1	-177(1)	C24A-C25A-C26A-O7A	121(2)
C9-C12-N1-N2	174(1)	C24A-C25A-C26A-O8A	-57(2)
C10-C9-C12-N1	1(1)	C24B-C23-C22-O5	-71(1)
C11-C6-O4-C5	77(1)	C24B-C23-C22-O6	122(1)
C13-C12-N1-N2	-6(1)	C24B-C25B-C26B-O7B	104(2)
C13-C12-C9-C8	4(1)	C24B-C25B-C26B-O8B	84(2)
C13-C12-C9-C10	-178(1)	C25B-C24B-C23-C22	179(2)
C14-N2-N1-C12	142(1)	C26B-C25B-C24B-C23	68(1)
C15-C14-N2-N1	-4(1)	C25A-C24A-C23-C22	162(2)
C16-C14-N2-N1	179(1)		
C17-C16-C14-N2	-22(1)		

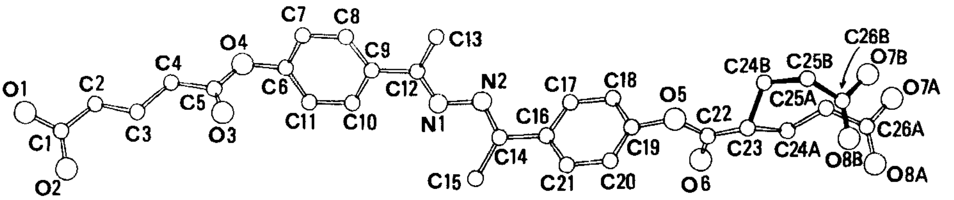

FIGURE 1 Molecular model with atomic numbering; the two alternative positions named A and B are shown.

are given in Table I. Selected bond lengths, bond angles and torsion angles are reported in Table II. Bond lengths and bond angles are in good agreement with values previously found for analogous compounds.[2,5] In particular, the structure of the central —R— group deviates from the planarity in the same way observed in bis[4-(5′-carboxypentyloxy)acetophenon]azine,[2] thus confirming the possibility of such a deviation in spite of the partial double-bond character of the =N—N= bond (see Table II). The planes of the phenyl rings are tilted one respect to the other by an angle of 62.6°, that is very close to the value 63.8° found in the compound of Reference 2. While this deviation from planarity might be due to crystal packing effects, it is interesting to note that a torsion around the central N—N bond is a very efficient way to increase the distance between the methyl group and the lone pair of the N atom three bonds apart, although the distance between methyl groups and N atoms remains unchanged (C15 . . . . . N1 = 2.70(1), C13 . . . . . N2 = 2.69(1) Å).

The terminal chain C1 . . . . . C5 of the molecule has a planar zig-zag conformation with exception for the torsion angle around bond C1—C2. For the terminal chain C22 . . . . . C26 a disorder occurs with two alternative positions, named A and B in the molecular model: one position corresponds to a nearly trans planar conformation (TTT) around the bonds —C22—C23—C24A—C25A—, and the other to a sequence of conformations G^+TG^- of the bonds —C22—C23—C24B—C25B—. The split atom positions have been considered as occupied in a 1:1 ratio (A:B).

The packing arrangement of Figure 2 shows molecules linked through hydrogen bonds between carboxylic groups that form parallel rows having linear symmetry *ti*. In fact, molecules are repeated along the rows only by inversion centers that arise in a statistical way from the 1:1 (A:B) ratio of the terminal C22 . . . . . C26. The statistical terminal (A, B) forms hydrogen bonds only if terminal A faces terminal B or vice versa; thus, O7A and O8A form hydrogen bonds with O8B$^{(ii)}$ and O7B$^{(ii)}$ (or O7B and O8B with O8A$^{(ii)}$ and O7A$^{(ii)}$). The terminal C1 . . . C4 of the molecule is faced by its centrosymmetric one so that O1 and O2 form hydrogen bonds with O2$^{(i)}$ and O1$^{(i)}$ repeated by the inversion centre. All the intermolecular distances between oxygen atoms bonded by hydrogen bonds, reported in Table III, are in good agreement with values reported in the literature.[10]

The crystal packing of the title compound is very similar to that of compound of Reference 2, showing a parallel packing of the rows of molecules with lateral correspondence of chemically homologous sections (aromatic-aromatic and aliphatic-aliphatic) and phenyl face to phenyl edge interactions in the lateral packing

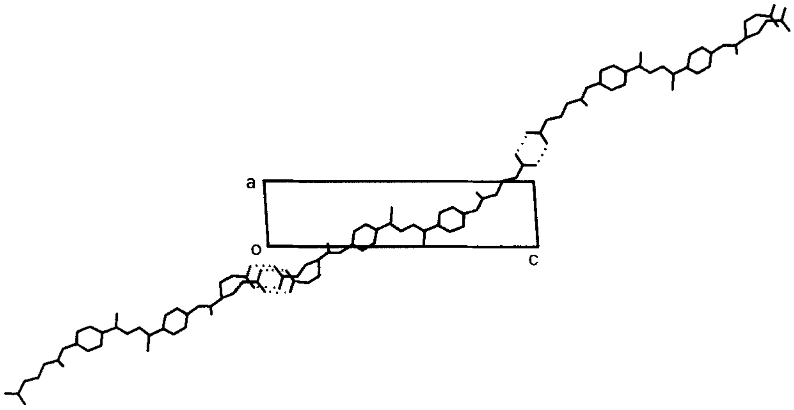

FIGURE 2 Molecular row viewed along the 010 direction.

TABLE III

Hydrogen bond distances

O1 ······· O2$^{(i)}$	2.624(9) Å
O7A ······ O8B$^{(ii)}$	2.68(2) Å
O8A ······ O7B$^{(ii)}$	2.59(2) Å

Symmetry code
(i) -x+3,-y,-z+2
(ii) -x+1,-y,-z

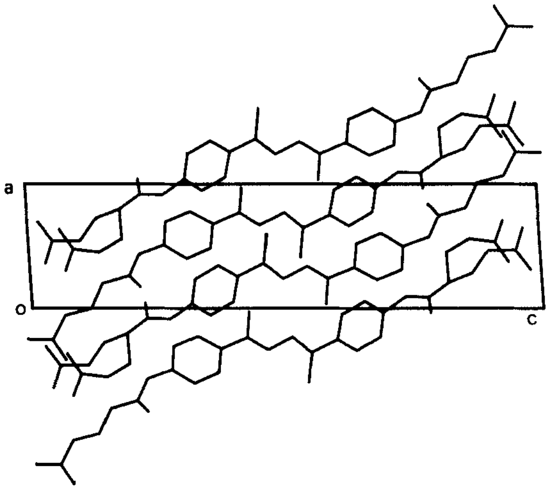

FIGURE 3 Crystal packing viewed along the 010 direction.

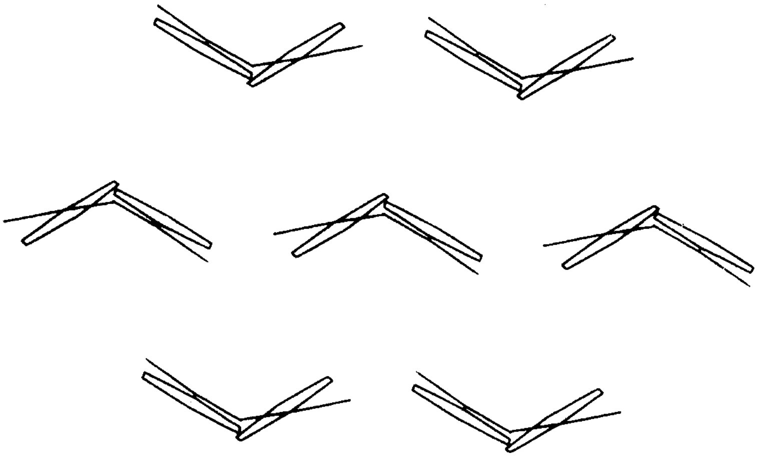

FIGURE 4 Projection of the mesogenic group —R— = -ϕ-C(CH_3)=N—N=C(CH_3)-ϕ-(-ϕ- = *p*-phenylene) along a direction parallel to the axis joining C6 and C19.

of the aromatic rings (Figure 3 and Figure 4). The crystal structure may be described as an assembly of molecular layers held together by hydrogen bonds and piled up along *c*. The long molecular axes are tilted with respect to the normal to the layers, thus simulating a smectic C type arrangement even if the title compound does not show any mesogenic behaviour.

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References

1. R. Centore, A. Roviello and A. Sirigu, *Liquid Crystals*, **6**, 175 (1989).
2. R. Centore, M. R. Ciajolo, A. Roviello, A. Sirigu and A. Tuzi, *Mol. Cryst. Liq. Cryst.*, **185**, 99 (1990).
3. R. Centore, M. R. Ciajolo, A. Roviello, A. Sirigu and A. Tuzi, *Mol. Cryst. Liq. Cryst.*, **214**, 105 (1992).
4. R. Centore, M. R. Ciajolo and A. Tuzi, *Acta Cryst.*, in press.
5. M. R. Ciajolo, A. Sirigu and A. Tuzi, *Acta Cryst.*, **C41**, 483 (1985).
6. A. Roviello and A. Sirigu, *J. Polymer Sci., Polym. Lett. Ed.*, **13**, 455 (1975).
7. G. Lock and K. Stack, *Chem. Ber.*, **79**, 295 (1946).
8. P. Main, Multan82. A system of computer programs for the automatic solution of crystal structures from X ray diffraction data. Department of physics, University of York, York, England (1982).
9. G. M. Sheldrick, SHELX86, Program for crystal structure determination, Univ. of Cambridge, England (1986).
10. L. Leiserowitz, *Acta Cryst.*, **B32**, 775 (1976).
11. International Tables for X-ray Crystallography, Vol. IV. Birmingham: Kynoch Press (1974) (Present distributor D. Reidel, Dordrecht, The Netherlands).
12. Enraf-Nonius, *Structure Determination Package*, Enraf-Nonius, Delft, The Netherlands (1985).