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Double-helix pattern in a model compound of non-linear optical polymers[1]

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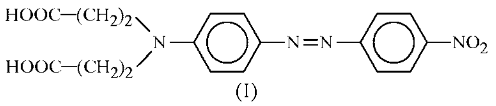
Molecules of the title compound, 3,3′-[4-(4-nitrophenyldiazenyl)phenylimino]dipropionic acid, $C_{18}H_{18}N_4O_6$, a model compound of second-order non-linear optically active polymers, form helicoidal rows *via* hydrogen bonding between carboxy groups. Pairs of helices are wrapped around the common axis in a double-helix arrangement unprecedented in dicarboxylic acids. The lateral packing of the helices shows an interdigitated antiparallel arrangement of the chromophore units.

Comment

Organic polymers containing push–pull chromophores covalently attached to the polymer chain as side groups are currently of interest in the field of second-order non-linear optics (NLO) (Prasad & Williams, 1991; Dalton *et al.*, 1999; Dalton, 2002). The non-centrosymmetry of the medium, a necessary condition for second-order NLO activity, is achieved in NLO organic polymers by applying a strong electric field above the glass transition temperature of the polymer (poling procedure). The poling procedure, both for the degree of polar order that can be achieved and for its time stability, is one of the most critical issues for the production of efficient NLO polymer materials (Dalton, 2002). Increasing the performance of poling procedures of NLO polymers would require a detailed preliminary knowledge of the local packing modes of the chromophore units. Although the crystal structures of several chromophores have been reported (Eaton *et al.*, 1987; Marder *et al.*, 1989, 1994; Coe *et al.*, 2000; Thallapally *et al.*, 2002), no structural determination of NLO polymeric systems has been reported to date.

Dicarboxylic acids have been studied as model compounds of stereoregular polyolefins (Corradini *et al.*, 1967) and main-chain liquid–crystalline polymers (Centore *et al.*, 1989; Centore & Tuzi, 1998) because of their possible ability to form, in the crystal phase, extended polymer-like rows *via* hydrogen bonds between carboxy groups. We report here the synthesis and crystal structure of the diacid, (I) (AZO33), which can be considered a realistic model for the packing of the relevant class of side-chain NLO polymers. It contains the same chromophore group as DR-1, which is one of the standard reference compounds in the field of organic NLO materials (Ricci *et al.*, 2000; Pliška *et al.*, 2000).



(I)

The molecular structure of (I) is shown in Fig. 1. The dihedral angle between the mean planes of the benzene rings is 21.17 (8)°; the geometry around atom N1 is substantially planar. These features are in accordance with the expected π-conjugation of the chromophore group.

In the crystal structure of (I), molecules form extended chains *via* hydrogen bonds between carboxy groups, thus simulating the covalent chains of a true polymer (Fig. 2). The hydrogen bonding is formed *via* the hydrogen-bonded dimer, which is typical for carboxylic acids (Leiserowitz, 1976; Steiner, 2002). The rows have geometric (though non-crystallographic) binary screw symmetry with pitch length 2*b*. In

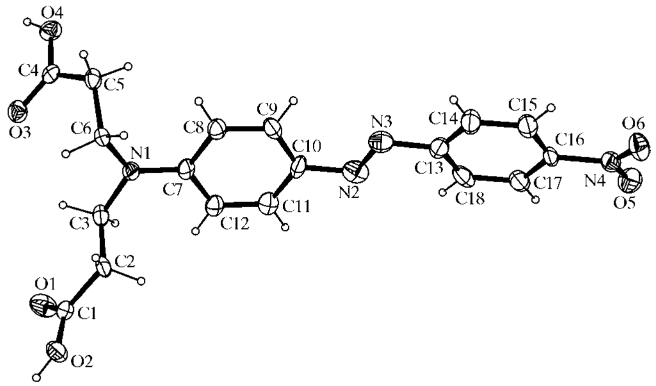


Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

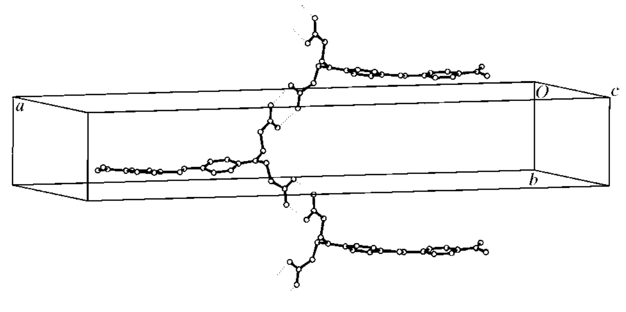


Figure 2
The row of hydrogen-bonded molecules of (I). H atoms have been omitted for clarity.

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[1] Dedicated to the memory of Professor Paolo Corradini.

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fact, each molecule is hydrogen bonded to two others obtained by C_2 rotation coupled with b or $-b$ translation. As can be seen from Fig. 2, consecutive chromophore units along the chain are arranged approximately perpendicular to the chain axis, on opposite sides. Pairs of helices translated by b with respect to each other are wrapped around the twofold crystallographic axes, giving rise to a double-helix pattern (Fig. 3). Within the helix topology, which is of current interest in crystal engineering (Desiraju, 2000; Vishweshwar *et al.*, 2002), the present report is a rare example of an all-organic solvent-free double helix formed by non-covalent aggregates of small molecules (Coupar *et al.*, 1997; Lavender *et al.*, 1999; Glidewell *et al.*, 2005; Mehta *et al.*, 2005).

A projection of the lateral packing is shown in Fig. 4. Owing to the crystallographic binary screw axes halfway between the binary axes along a, double helices identical to that of Fig. 3 and shifted by $b/2$ are generated. These are packed laterally along a in an interdigitated fashion, *i.e.* in such a way that each lateral group of a double helix fits well into the space between two consecutive chromophore groups of an adjacent double helix. The resulting packing of chromophore groups is rigorously antiparallel, with optimum mean distances of $b/2$ = 3.439 (1) Å. The double helix does not seem to be stabilized by specific interactions between the atoms of the two wrapped chains, but by the packing mode of the lateral chromophore units.

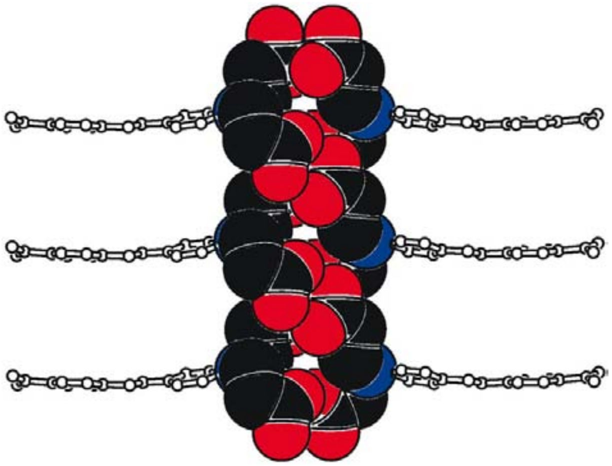

Figure 3
The double-helix pattern of (I).

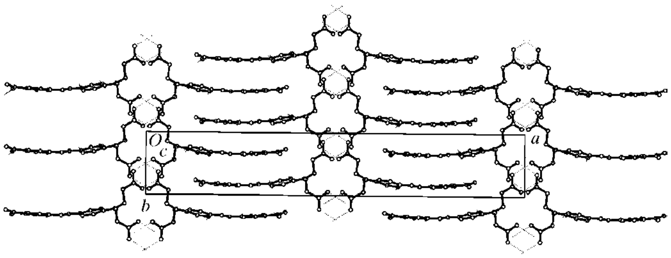

Figure 4
The lateral packing of (I) along *a*. H atoms have been omitted for clarity.

Some structural aspects found in model compound (I) may be viewed as general features of side-chain NLO polymers. In fact, the perpendicularity of the side chromophore groups with respect to the main chain, and the interdigitated antiparallel packing of Fig. 4, can also optimize excluded-volume effects and dipolar interactions in polymers.

Experimental

Compound (I) (AZO33) was prepared by diazotization of 4-nitroaniline followed by coupling with *N*,*N*-bis(2-carboxyethyl)aniline. *N*,*N*-Bis(2-carboxyethyl)aniline was obtained by alkylation of aniline with methyl 2-bromopropionate, followed by vacuum distillation of *N*,*N*-bis(2-methoxycarbonylethyl)aniline. Basic hydrolysis of this product gave *N*,*N*-bis(2-carboxyethyl)aniline. The synthesis of *N*,*N*-bis(2-carboxyethyl)aniline was carried out as follows. A mixture of aniline (10 g, 0,107 mol) and methyl 3-bromopropionate (44.6 g, 0.268 mol) was heated under reflux for 5 h. During this time, a 9% *w*/*w* aqueous NaOH solution (8.6 g, 0.215 mol) was added in portions. After 5 h, the reaction mixture was cooled to room temperature and the pH was adjusted to 7–8. The organic layer was extracted with chloroform, washed three times with water and dried over sodium sulfate; the solvent was then removed under reduced pressure. The crude product was purified by vacuum distillation. A dense yellow oil was obtained (yield 55%). ^{1}H NMR ($CDCl_3$): δ 2.563–2.656 (*t*, 4H, J = 9.4 Hz), 3.600–3.697 (*m*, 10H), 6.615–6.800 (*m*, 3H), 7.138–7.277 (*m*, 2H). The basic hydrolysis of *N*,*N*-bis(2-carboxyethyl)aniline was carried out as follows. To a boiling mixture of *N*,*N*-bis(2-methoxycarbonylethyl)aniline (3.0 g, 0.0126 mol) and ethanol (20 ml) was added a concentrated aqueous KOH solution (2.84 g, 0.0505 mol in 15 ml water) in portions. Boiling was continued for 1 h, adding water in order to keep the volume constant. After 1 h, the solution was cooled to room temperature and acidified with dilute HCl to pH 5. The resulting solution, containing *N*,*N*-bis(2-carboxyethyl)aniline, was used for the subsequent step of diazo-coupling. The procedure for the diazo-coupling is analogous to that which we have already described for the synthesis of similar diazo chromophores (Beltrani *et al.*, 2001). Purification of (I) was achieved by recrystallization from glacial acetic acid. The final yield for the diazotization/coupling step is 90% (m.p. 478 K, decomposition). Single crystals were obtained by slow evaporation from an ethanol solution. ^{1}H NMR (pyridine-d_5): δ 2.95 (*t*, 4H, J = 9 Hz), 4.11 (*t*, 4H, J = 9 Hz), 7.10 (*d*, 2H, J = 10 Hz), 8.05 (*d*, 2H, J = 10 Hz), 8.16 (*d*, 2H, J = 10 Hz), 8.35 (*d*, 2H, J = 10 Hz).

Crystal data

$C_{18}H_{18}N_4O_6$
M_r = 386.36
Monoclinic, $C2/c$
a = 43.062 (9) Å
b = 6.877 (2) Å
c = 11.979 (2) Å
β = 101.06 (2)°
V = 3481.5 (14) Å^3
Z = 8
D_x = 1.474 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 173 (2) K
Plate, red
0.59 × 0.13 × 0.02 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Thick-slice φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker–Nonius, 2002)
$T_{\min}$ = 0.936, $T_{\max}$ = 0.998
10530 measured reflections
3584 independent reflections
1587 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.094
$\theta_{\max}$ = 26.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.168$
$S = 1.00$
3584 reflections
253 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2 + 3.8477P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.254 (4)	N1—C3	1.463 (4)
O2—C1	1.278 (5)	N1—C6	1.464 (5)
O3—C4	1.273 (4)	N2—N3	1.248 (4)
O4—C4	1.275 (5)	N2—C10	1.442 (5)
N1—C7	1.370 (5)	N3—C13	1.454 (5)
C7—N1—C3	121.5 (3)	N2—N3—C13	112.9 (4)
C7—N1—C6	119.8 (3)	O1—C1—O2	123.4 (4)
C3—N1—C6	116.3 (3)	O3—C4—O4	123.2 (3)
N3—N2—C10	111.6 (4)		
C10—N2—N3—C13	177.2 (3)	O3—C4—C5—C6	14.0 (5)
O1—C1—C2—C3	14.2 (5)	C7—N1—C6—C5	82.8 (4)
C7—N1—C3—C2	76.7 (4)	C4—C5—C6—N1	74.9 (4)
C1—C2—C3—N1	168.9 (3)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1⋯O4^{i}	0.94	1.78	2.650 (4)	153
O2—H2⋯O3^{i}	0.85	1.82	2.665 (4)	169
O4—H3⋯O1^{ii}	0.93	1.75	2.650 (4)	163
O3—H4⋯O2^{ii}	0.98	1.69	2.665 (4)	177

Symmetry codes: (i) $-x, y-1, -z+\frac{1}{2}$; (ii) $-x, y+1, -z+\frac{1}{2}$.

H atoms of carboxy groups were located in a difference map. All other H atoms were generated stereochemically. All H atoms were refined using a riding model, with $U_{iso}(H) = U_{eq}$ of the carrier atom. Bond lengths in the carboxy groups clearly indicate that they are disordered, as is frequently observed in carboxylic acids (Leiserowitz, 1976). Coherently, H atoms bonded to both O atoms were assigned occupancies of 0.5 on the basis of peak heights.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DIRAX*/*LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3032). Services for accessing these data are described at the back of the journal.

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