Data collection

Stoe IPDS diffractometer
Image plate scans
Absorption correction: none
10 929 measured reflections
4086 independent reflections (91% of theoretical)
3934 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0356$
$\theta_{\rm max} = 28.13°$
$h = -7 \rightarrow 7$
$k = -19 \rightarrow 20$
$l = -13 \rightarrow 13$
100 standard reflections
frequency: 4 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0316$
$wR(F^2) = 0.0801$
$S = 1.057$
4083 reflections
341 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 0.1319P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.117$
$\Delta\rho_{\rm max} = 0.140$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.196$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.04 (5)

Table 2. *Bond lengths (Å) for (II)*

Cl1—C16	1.791 (2)	C7—C8	1.525 (2)
O1—C2	1.208 (2)	C8—C14	1.533 (2)
O2—C2	1.324 (2)	C8—C9	1.551 (2)
O3—C4	1.209 (2)	C9—C20	1.531 (2)
O4—C15	1.434 (2)	C9—C11	1.541 (2)
C1—C2	1.503 (2)	C9—C10	1.563 (2)
C1—C10	1.551 (2)	C11—C12	1.536 (2)
C4—C18	1.502 (2)	C12—C13	1.541 (2)
C4—C5	1.539 (2)	C13—C17	1.526 (2)
C5—C6	1.543 (2)	C13—C14	1.546 (2)
C5—C19	1.553 (2)	C13—C15	1.549 (2)
C5—C10	1.563 (2)	C15—C16	1.521 (2)
C6—C7	1.522 (2)		

For both compounds, data collection: Stoe IPDS software package; cell refinement: Stoe IPDS software package; data reduction: Stoe IPDS software package; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP* (Zsolnai & Pritzkow, 1995) and *XPMA* (Zsolnai, 1996); software used to prepare material for publication: *SHELXL*93 and *ORTEP*.

This work has received partial support from JNICT (I&D n/226/94 and I&D n/316/94) and grant PRAXIS/2/2.1/QUI/17/94.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: HA1184). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 757–759

5-Methylthiophene-2-carboxaldehyde 4-Nitrophenylhydrazone–Water (1/1)

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(Received 26 September 1996; accepted 10 February 1997)

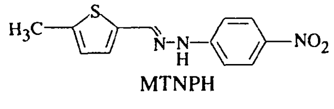
Abstract

The title compound, $C_{12}H_{11}N_3O_2S.H_2O$, is a practically planar organic hyperpolarizable molecule. The non-centrosymmetric packing of its monohydrate crystals and its relationships to non-linear optical properties are discussed.

Comment

Optimal second-order non-linear optical organic materials which contain stable molecules with large molecular hyperpolarizabilities in a non-centrosymmetric packing are of great interest for device applications (Bosshard, Sutter, Schlesser & Günter, 1993), but according to a statistical study, an overwhelming majority of achiral molecules crystallize centrosymmetrically (Jacques, Collet & Wilen, 1981).

In the course of our studies of materials exhibiting high second harmonic signals, the title compound, MTNPH, was synthesized. Due to its large hyperpolarizability and non-centrosymmetric packing, MTNPH is an organic non-linear optical molecule exhibiting a large second harmonic signal (Wong, Meier *et al.*, 1996).



MTNPH

The crystal structure of the monohydrate of MTNPH is presented as an example of the surprisingly high proportion of non-centrosymmetric crystals of similar achiral compounds formed by hydrazone derivatives of 4-nitrophenyl hydrazine and various electron-donating aromatic aldehydes (Wong, Bosshard, Pan & Günter, 1996). The X-ray structure analysis revealed an angle of 77 (1)° between the polar axis of the nitro group of the molecule and the polar crystallographic *b* axis. The hydrogen-bonding scheme of the packing is included in Fig. 1. Although the structure is otherwise different, the nearly coplanar arrangement of the MTNPH and water molecules is similar to that observed in *p*-nitrobenzaldehyde nicotinoylhydrazone monohydrate (Lu *et al.*, 1996), but with a much weaker hydrogen bond, which is in agreement with the low dehydration temperature at about 373 K, where the crystals of the title compound collapse. The crystal packing is characterized by a zigzag chain of water molecules, with the molecules of the title compound attached *via* weak hydrogen bonds (Fig. 1). Some details of the hydrogen-bonding scheme are given in Table 2.

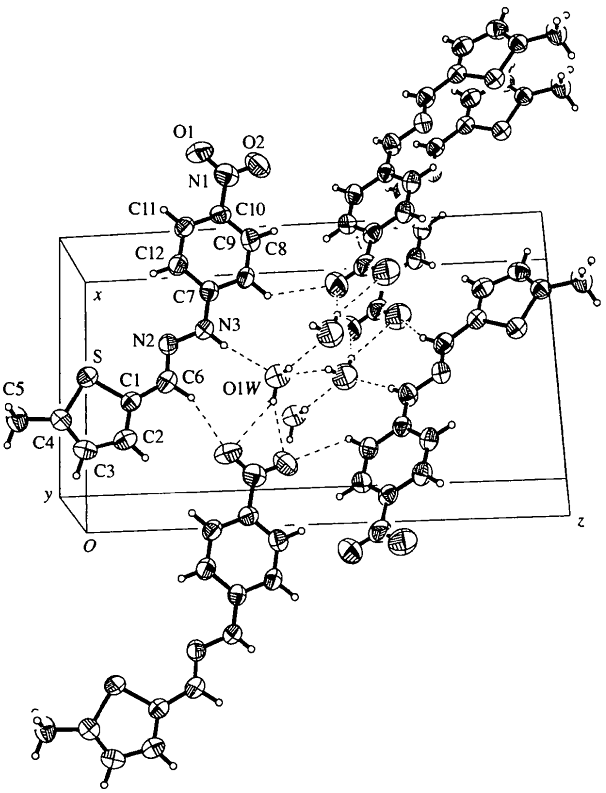


Fig. 1. The unit cell of MTNPH.H_2O with a displacement-ellipsoid plot (50% probability) of the title compound.

Experimental

MTNPH was synthesized according to Wong, Meier *et al.* (1996) and crystals were grown from a saturated acetonitrile solution by slow evaporation.

Crystal data

$C_{12}H_{11}N_3O_2S.H_2O$
$M_r = 279.31$
Monoclinic
$P2_1$
$a = 9.844\ (7)$ Å
$b = 3.901\ (3)$ Å
$c = 17.245\ (15)$ Å
$\beta = 93.17\ (6)°$
$V = 661.2\ (9)$ Å^3
$Z = 2$
$D_x = 1.403$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 10–12°$
$\mu = 0.252$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.25 × 0.25 × 0.20 mm
Red

Data collection

Syntex $P2_1$ four-circle diffractometer
ω scans
Absorption correction: none
3454 measured reflections
2594 independent reflections
1112 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0785$
$\theta_{\rm max} = 32°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 5$
$l = -25 \rightarrow 25$
2 standard reflections every 120 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0385$
$wR(F^2) = 0.0815$
$S = 0.674$
2594 reflections
193 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.203$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.251$ e Å^{-3}

Extinction correction: *SHELXL*93
Extinction coefficient: 0.005 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.03 (11)

Table 1. *Selected geometric parameters (Å, °)*

S—C1	1.728 (3)	N1—C10	1.441 (4)
S—C4	1.735 (3)	N2—C6	1.272 (4)
N1—O1	1.227 (3)	N2—N3	1.374 (3)
N1—O2	1.234 (3)	N3—C7	1.354 (4)
C1—S—C4	92.0 (2)	O2—N1—C10	118.6 (3)
O1—N1—O2	122.4 (3)	C6—N2—N3	116.1 (3)
O1—N1—C10	119.0 (3)	C7—N3—N2	120.7 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3N···O1*W*	0.86 (2)	2.19 (3)	3.041 (4)	171 (2)
O1*W*—H1*W*···O1^{i}	0.83 (4)	2.48 (4)	3.231 (5)	151 (4)
O1*W*—H1*W*···O2^{i}	0.83 (4)	2.42 (5)	3.183 (5)	154 (4)
O1*W*—H2*W*···O1*W*^{ii}	0.87 (4)	2.15 (3)	2.948 (6)	151 (4)
C6—H6···O1^{i}	1.00	2.49	3.390 (6)	155
C8—H8···O2^{iii}	1.00	2.55	3.273 (6)	132

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

H atoms on C atoms were calculated and treated with the conventional riding technique. H atoms on O and N atoms were located from difference maps and refined with isotropic displacement parameters.

Data collection: *P*3 *Users Manual* (Siemens, 1992). Cell refinement: *P*3 *Users Manual*. Data reduction: *SHELXTL-*

Plus (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*93.

The authors thank the Swiss National Science Foundation for financial support.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1423). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). **C53**, 759–761

Planar Chirality in 2,2-Diphenyl-1,3,6,9-tetraoxacycloundecane

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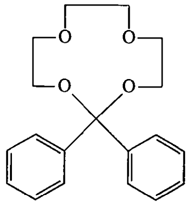
(*Received 6 November 1996; accepted 21 January 1997*)

Abstract

The crystal of benzophenone crown ether acetal, $C_{19}H_{22}O_4$, with an 11-membered ring has two crystallographically independent molecules in the unit cell. The bond lengths and angles in the ring moiety are similar to those of analogous crown ethers. The 11-membered rings are greatly twisted to adopt planar–chiral structures and the unit cell contains two sets of enantiomers.

Comment

A number of studies have been carried out on the crystal structures of a wide variety of crown ethers and their cation-binding complexes (Izatt & Christensen, 1978). However, X-ray crystal structure analyses of analogous crown ether acetals, which are characterized by the incorporation of an acetal functional group in the cyclic polyether linkage, have seldom been conducted. The structure of benzophenone crown ether acetal, (I), is reported and compared with those of unsubstituted crown ethers.



(I)

The molecular structure of the benzophenone crown ether acetal is shown in Fig. 1. The unit cell contains two crystallographically independent molecules (*A* and *B*).

The average values of C—C, C—O, C—O—C and C—C—O of the ring moiety are 1.496, 1.418 Å, 115.1 and 110.5° for molecule *A*, and 1.492, 1.419 Å, 115.3 and 110.8° for molecule *B*, respectively. These bond distances and angles are similar for both molecules and are also similar to those of 18-crown-6 (1.507, 1.411 Å, 113.5 and 109.8°; Dunitz & Seiler, 1974) and benzo-15-crown-5 (1.485, 1.419 Å, 115.7 and 110.0°; Hanson, 1978).

The torsion angles of the ring constituent C—C—O—C are |85.5 (3)|–|89.4 (3)|° and |125.4 (3)|–|157.5 (3)|°. The average value of 141.5° for the latter torsion angles is different from the average values of 168.3° in 18-crown-6 (|155.2|–|175.5|°) and 168.3° in benzo-15-crown-5 (|163|–|171|°). The O—C—C—O torsion angles are in the range |68.3 (3)|–|77.8 (3)|°. These values are comparable to those of the relatively rigid benzo-15-crown-5 (|66|–|72|°), while the more flexible 18-crown-6 has torsion angles of −67.6, 75.4 and 174.7°. The replacement of a dioxyethylene unit by an acetal functional group markedly decreases the flexibility of the macrocyclic ring. As a result, the 11-membered ring of the title compound is largely twisted to adopt a planar–chiral structure.

The O(acetal)—C(acetal)—C(aromatic)—C(aromatic *o*-position) torsion angles are in the range |11.6 (3)|–|18.2 (13)|° to reduce the steric repulsion between