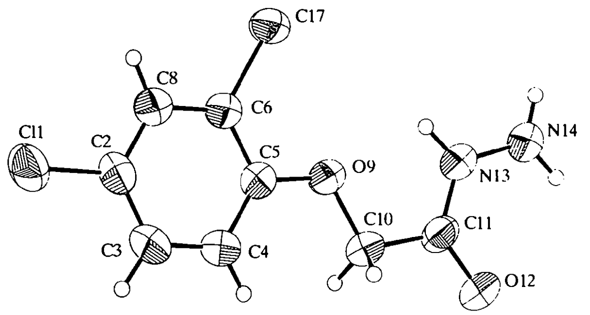

Fig. 1. Plot of the title molecule with 50% probability displacement ellipsoids for non-H atoms.

Experimental

Phenol on reacting with ethyl chloroacetate in dry acetone gave ethyl (2,4-dichlorophenoxy)acetate. Hydrolysis of this ester with hydrazine hydrate in absolute ethanol yielded compound (I). Single crystals were grown by slow evaporation of a solution of (I) in dimethylformamide.

Crystal data

$C_8H_8Cl_2N_2O_2$
$M_r = 235.06$
Triclinic
$P\bar{1}$
$a = 8.107\,(3)$ Å
$b = 8.530\,(3)$ Å
$c = 7.339\,(3)$ Å
$\alpha = 90.11\,(3)°$
$\beta = 98.44\,(3)°$
$\gamma = 94.859\,(3)°$
$V = 500.2\,(3)$ Å^3
$Z = 2$
$D_x = 1.561$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 16 reflections
$\theta = 6.8–9.2°$
$\mu = 0.623$ mm^{-1}
$T = 293\,(2)$ K
Prismatic
0.2 × 0.2 × 0.2 mm
Transparent

Data collection

Rigaku AFC-7*S* diffractometer
ω–2θ scans
Absorption correction: none
1436 measured reflections
1351 independent reflections
1046 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.041$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -8 \rightarrow 8$
3 standard reflections every 150 reflections intensity decay: −1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.154$
$S = 1.166$
1350 reflections
140 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.170$ e Å^{-3}
$\Delta\rho_{\min} = -0.198$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.10 (13)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *SHELXL*93.

The authors would like to express their thanks to DST, Government of India, for financial assistance under project SP/I2/FOO/93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1248). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 670–672

4-Methylspiro[4-azahomoadamantane-5,3'-[3'*H*]naphth[2,1-*b*][1,4]oxazine], a New Photochromic Spirooxazine

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(*Received 30 June 1997; accepted 21 November 1997*)

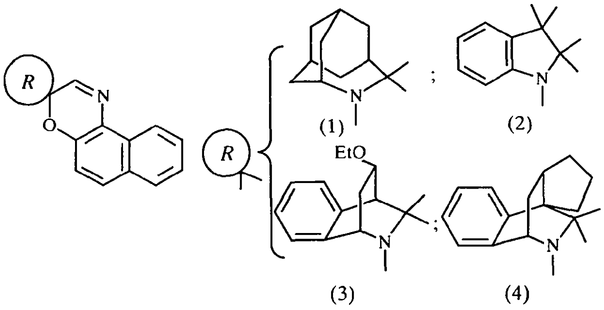
Abstract

Comparison of the molecular geometry of the title compound, $C_{22}H_{24}N_2O$, with that of other spirooxazines indicates that there is no correlation between the degree

of planarity of the oxazine ring and the photochromic properties. The C_{sp^3}—O bond at 1.4767 (7) Å is long, in keeping with its weakness.

Comment

Upon UV irradiation, spironaphthoxazines show a modification of their electronic absorption spectra due to the cleavage of the C_{spiro}—O bond. Ring closure may be induced either thermally or photochemically to give a reversible colour change referred to as photochromism (Chu, 1990). There has been renewed interest in spirooxazines in the past decade because of their industrial applications, such as in optical devices and as recording materials. Many structural variations have been investigated in attempts to extend the photochromic properties. In order to elucidate further the structure–property relationships, the molecular structure of the title compound, (1), has been determined for comparison with the previously known structures (2) (Millini *et al.*, 1991), (3) (Reboul *et al.*, 1995) and (4) (Pèpe *et al.*, 1995), particularly concerning the degree of planarity of the oxazine ring.



In compounds (3) and (4), the introduction of an azapolycycloalkane group on the sp^3-C atom of the oxazine ring leads to a hypsochromic shift (shorter wavelengths) in the visible absorption spectrum of the coloured form; unfortunately, this is accompanied by an increase in the rate of fading of the colour. In the title compound, which contains an azahomoadamantane group, a similar hypsochromic shift is obtained, and the photochromic behaviour as a whole is improved (Chamontin *et al.*, 1996). Indeed, the photochromic activity is better than that of any of the previous compounds (2)–(4).

Two geometric parameters seem to be important for the photochromic properties: the degree of planarity of the oxazine ring and the C_{sp^3}—O bond length. In compound (1), the r.m.s. deviation of the oxazine ring atoms from their mean plane is 0.010 Å. This ring is thus nearer to planarity than in compounds (2), (3) and (4), for which the corresponding r.m.s. deviations are 0.064, 0.171 and 0.189 Å, respectively, in contradiction of the usual assumption that good photochromic properties (particularly the absorbance) are correlated with deviations of the ring from planarity. The length of the C2—O1 bond is 1.4767 (7) Å, which is comparable to those in compounds (2), (3) and (4), which are 1.455 (3), 1.1467 (7) and 1.501 (3) Å, respectively. These are unusually long, indicating the relative weakness of the bond; a typical C—O bond length is 1.43 Å (Allen *et al.*, 1992).

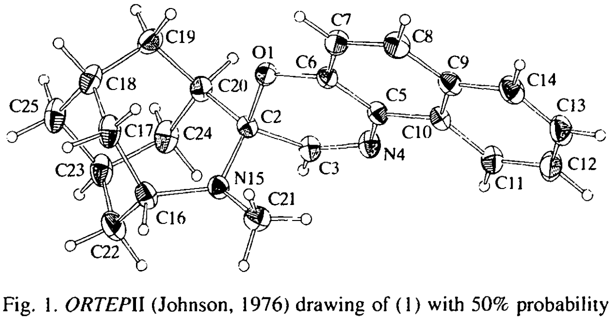


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (1) with 50% probability displacement ellipsoids.

Experimental

The naphthoxazine was prepared by reaction of 4,5-dimethyl-4-azahomoadamant-4-enium iodide (Sasaki *et al.*, 1978) and 1-amino-2-naphthol as previously described (Minkin *et al.*, 1994). Yellow rectangular platelet crystals were obtained by evaporation of a heptane solution.

Crystal data

$C_{22}H_{24}N_2O$
$M_r = 332.43$
Triclinic
$P\bar{1}$
$a = 6.704\ (1)$ Å
$b = 10.156\ (2)$ Å
$c = 13.321\ (2)$ Å
$\alpha = 91.09\ (2)°$
$\beta = 95.49\ (2)°$
$\gamma = 108.24\ (2)°$
$V = 856.3\ (2)$ Å^3
$Z = 2$
$D_x = 1.289$ Mg m^{-3}
$D_m = 1.27\ (2)$ Mg m^{-3}
D_m measured by flotation in benzene/chloroform

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 5–35°$
$\mu = 0.079$ mm^{-1}
$T = 293\ (2)$ K
Rectangular platelet
0.4 × 0.3 × 0.2 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3798 measured reflections
3798 independent reflections
3414 reflections with $I > 2\sigma(I)$

$\theta_{max} = 34.85°$
$h = -7 \rightarrow 7$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.089$
$S = 1.011$
3798 reflections
299 parameters
H atoms refined with U = 0.05 Å^2

$w = 1/[\sigma^2(F_o^2) + (0.0738P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.267$ e Å^{-3}
$\Delta\rho_{\min} = -0.261$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C6	1.3600 (8)	C2—C20	1.5412 (9)
O1—C2	1.4767 (7)	C3—N4	1.2744 (9)
C2—N15	1.4311 (8)	N4—C5	1.4070 (9)
C2—C3	1.5209 (9)		
C6—O1—C2	118.07 (5)	C3—C2—C20	108.93 (5)
N15—C2—O1	112.65 (5)	N4—C3—C2	126.58 (6)
N15—C2—C3	107.82 (5)	C3—N4—C5	116.64 (6)
O1—C2—C3	108.09 (5)	C6—C5—N4	120.91 (6)
N15—C2—C20	114.76 (5)	O1—C6—C5	121.56 (6)
O1—C2—C20	104.38 (5)		
C6—O1—C2—N15	87.45 (7)	C3—N4—C5—C6	−12.60 (9)
C6—O1—C2—C3	−31.57 (7)	C3—N4—C5—C10	167.62 (6)
C6—O1—C2—C20	−147.42 (5)	C2—O1—C6—C5	20.64 (8)
N15—C2—C3—N4	−97.57 (8)	C2—O1—C6—C7	−160.37 (6)
O1—C2—C3—N4	24.48 (9)	N4—C5—C6—O1	3.69 (9)
C20—C2—C3—N4	137.32 (7)	C10—C5—C6—O1	−176.54 (5)
C2—C3—N4—C5	−3.24 (10)	N4—C5—C6—C7	−175.26 (6)

The data set consists of the unique half of a parallelepiped rather than a sphere of reciprocal space; the extreme $\theta_{\max}$ is 34.5° and data are complete to θ = 23°.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *DATARED* (Pèpe, 1979). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

We thank Essilor International, Paris St Maur (France), and Transition Inc., St Petersbourg (USA), for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1201). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 672–674

4-Chloro-*N*-methyl-*N*-nitroaniline

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(*Received 25 September 1997; accepted 24 November 1997*)

Abstract

The molecular structure of (p-ClC_6H_4)(CH_3)NNO_2 (or $C_7H_7ClN_2O_2$) contains a planar NNO_2 nitroamino group which is twisted about the N—$C_{\rm phenyl}$ bond by *ca* 68° from the plane of the aromatic ring. The structural data are in agreement with the spectral results and indicate that there is no conjugation between the aromatic sextet and the nitroamino group. There are no specific intermolecular interactions.

Comment

Nitramines and related *N*-nitro compounds have attracted much attention during the last few decades. The crystal structures of *N*,*N*-dimethylnitramine and of some cyclic and open-chain aliphatic nitramines have been reported. Within the aromatic series, only tetryl (Cady, 1967) and its analogue (Holden & Dickinson, 1969) have been studied. An interesting feature of *N*-methyl-*N*-phenylnitramine and its derivatives is their ability to rearrange under the influence of acids or at increased temperature. The migration is entirely intramolecular, *i.e.* the *N*-nitro group shifts to an aromatic ring, three or five atoms from its original position, while remaining covalently bound to the aromatic residue (Shine, 1967). The molecular structures of secondary arylnitramines may provide a clue to the nature of the nitramine rearrangement. The title compound, (I), is the first member of the series to have been examined.