Table 5. *Selected geometric parameters (Å, °) for the title cations*

MAHMA		DMAHMA	
N1—C5	1.4816 (11)	N1—C5	1.4765 (9)
N1—H1N	0.901 (11)	N1—C6	1.4799 (9)
N1—H2N	0.903 (11)	N1—H1N	0.944 (9)
N1—H3N	0.943 (10)	N1—H2N	0.928 (9)
C5—N1	1.4815 (11)	C5—H5	0.953 (9)
C5—H5	0.930 (10)	C5—H6	0.971 (9)
C5—H6	0.939 (10)	C5—H7	0.984 (9)
C5—H7	0.987 (10)	C6—H8	0.990 (10)
		C6—H9	0.966 (9)
		C6—H10	0.960 (10)
C5—N1—H1N	108.7 (6)	C5—N1—C6	112.75 (6)
C5—N1—H2N	111.6 (7)	C5—N1—H1N	108.5 (5)
C5—N1—H3N	111.5 (6)	C5—N1—H2N	109.1 (5)
N1—C5—H5	106.8 (6)	N1—C5—H7	107.4 (5)
N1—C5—H6	109.3 (6)	N1—C6—H8	111.0 (5)
N1—C5—H7	108.7 (6)	N1—C6—H9	109.3 (5)
		N1—C6—H10	109.5 (6)

Table 6. *Selected geometric parameters (Å, °) for the maleate ions*

MAHMA		DAHMA	
C1—O1	1.2447 (8)	C1—O1	1.2396 (7)
C2—O1	1.2819 (9)	C1—O2	1.2915 (8)
C1—C2	1.4908 (10)	C1—C2	1.4911 (9)
C2—C2^{i}	1.3392 (14)	C2—C4	1.3359 (9)
C3—O3	1.2406 (9)	C4—C3	1.4920 (9)
C3—O4	1.2868 (9)	C3—O3	1.2381 (8)
C3—C4	1.4909 (10)	C3—O4	1.2874 (8)
C4—C4^{i}	1.3399 (14)		
O1—C1—C2—C2^{i}	167.57 (4)	O1—C1—C2—C4	178.87 (7)
O2—C1—C2—C2^{i}	−12.00 (9)	O2—C1—C2—C4	−1.65 (11)
O3—C3—C4—C4^{i}	177.39 (5)	C1—C2—C4—C3	−0.39 (13)
O4—C3—C4—C4^{i}	−2.36 (10)	C2—C4—C3—O3	−179.51 (7)
		C2—C4—C3—O4	−0.29 (11)

Symmetry code: (i) $x, y, \frac{1}{2} - z$.

For both compounds, data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *DREADD* (Blessing, 1987); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1534). Services for accessing these data are described at the back of the journal.

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2,8-Dimethylphenoxathiin 10-Oxide

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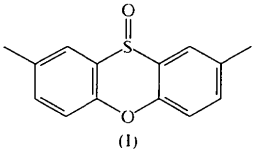
Abstract

An important precursor to biologically active compounds, 2,8-dimethylphenoxathiin 10-oxide ($C_{14}H_{12}O_2S$), is found to adopt a folded geometry. The dihedral angles between the aromatic rings are 11.8 (2) and 15.4 (2)° for the two independent molecules, with the S atoms lying out of the ring planes.

Comment

The synthesis of phenoxathiins is of current interest because they show a variety of biological activities. Some have antibacterial properties (Gavriliu *et al.*, 1996; Maior *et al.*, 1995), others have exhibited antitumor activity (Palmer *et al.*, 1988), and yet others can be used as antidepressants (Cooper *et al.*, 1992). These compounds may also be used as catalysts, for example, in chlorination reactions (Mais & Fiege, 1990) and in hydroformulation reactions (Kranenburg *et al.*, 1995).

The molecular structures of the two crystallographically independent conformations of the title compound, (I), are shown in Fig. 1. They are approximately related by a non-crystallographic inversion centre at (0.56,0.26,0.38). Both display a folded geometry with dihedral angles between the least-squares planes of the aromatic rings of 11.8 (2) and 15.4 (2)°. Thus, the molecule is flatter than the related unsubstituted



(I)

compound phenoxathiin 10-oxide (PTO), where the corresponding angle is 28° (Chen *et al.*, 1979). This is not, however, a simple fold about the S···O axis of the heterocyclic ring, for although the O atoms are coplanar with the aromatic rings the S atoms lie out of the plane. Examination of the geometric parameters (Table 1) reveals that the bond lengths are in good agreement with those in PTO, but that the internal bond angles of the heterocyclic ring are slightly larger in (I). This is consistent with a flattened geometry [C7—S1—C1 96.76 (16), C21—S2—C15 95.98 (16), C6—O2—C12 120.8 (3) and C20—O4—C26 120.3 (3)°, compared with 94.8 (3) and 118.8 (4)° in PTO]. The sulfoxide group lies nearly normal to the ring systems, as is shown by the torsion angles O1—S1—C1—C6 and O3—S2—C15—C16 [92.1 (3) and 86.5 (3)°, respectively; see also Table 1].

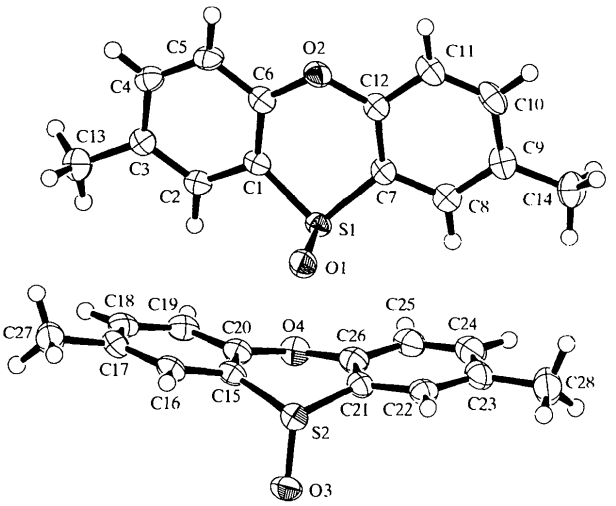


Fig. 1. The molecular structure of (I) with 50% probability ellipsoids and H atoms as small spheres of arbitrary size.

Experimental

2,8-Dimethylphenoxathiin (5.2 g, 22.8 mmol) was heated under reflux overnight in the presence of ethanol (125 ml) and hydrogen peroxide (15 ml, 27%). An additional amount of hydrogen peroxide (10 ml, 27%) was added and the solution heated for a further 3 h. The reaction mixture was cooled to room temperature, then the volume of solvent was reduced by half *in vacuo*. The white solid obtained was dissolved in toluene and purified by silica-gel column chromatography. The first fraction, assigned as 2,8-dimethylphenoxathiin 10,10-dioxide was obtained in 8% yield. Ethyl acetate was then used to elute (I) in 75% yield (m.p. 403–405 K). Solutions of (I) left in air were found to oxidize slowly back to 2,8-dimethylphenoxathiin 10,10-dioxide.

Crystal data

$C_{14}H_{12}O_2S$
M_r = 244.30
Monoclinic
$P2_1/c$
a = 13.274 (2) Å
b = 12.214 (4) Å
c = 15.044 (3) Å
β = 110.606 (14)°
V = 2282.9 (10) Å^3
Z = 8
D_x = 1.422 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 24 reflections
θ = 17.0–19.6°
μ = 0.268 mm^{-1}
T = 123 K
Cut needle
0.40 × 0.40 × 0.35 mm
Colourless

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4676 measured reflections
4481 independent reflections
2980 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 26.01°
h = 0 → 16
k = 0 → 15
l = −18 → 17
3 standard reflections
every 150 reflections
intensity decay: 4.85%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.170
S = 1.036
4481 reflections
311 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0831P)^2 + 1.7748P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.337 e Å^{-3}
$\Delta\rho_{min}$ = −0.659 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—O1	1.499 (2)	S2—C21	1.772 (3)
S1—C7	1.766 (3)	O2—C6	1.376 (4)
S1—C1	1.775 (4)	O2—C12	1.381 (4)
S2—O3	1.503 (3)	O4—C20	1.370 (4)
S2—C15	1.768 (4)	O4—C26	1.388 (4)
O1—S1—C7	107.38 (15)	O3—S2—C21	107.75 (15)
O1—S1—C1	107.46 (15)	C15—S2—C21	95.98 (16)
C7—S1—C1	96.76 (16)	C6—O2—C12	120.8 (3)
O3—S2—C15	106.70 (15)	C20—O4—C26	120.3 (3)
O1—S1—C1—C6	92.1 (3)	O3—S2—C15—C20	−84.9 (3)
O1—S1—C1—C2	−81.3 (3)	O3—S2—C15—C16	86.5 (3)
S1—C1—C6—O2	7.7 (5)	S2—C15—C20—O4	−11.4 (5)
O1—S1—C7—C12	−93.5 (3)	O3—S2—C21—C26	86.2 (3)
O1—S1—C7—C8	83.4 (3)	O3—S2—C21—C22	−86.9 (3)
S1—C7—C12—O2	−5.0 (5)	S2—C21—C26—O4	6.8 (5)

H atoms were refined as riding, including free torsion of the methyl groups. U_{iso} values for H atoms on aromatic C atoms were set to 1.2 times the U_{eq} values of the parent atoms and to 1.5 times the U_{eq} values for those in methyl groups.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SIR* (Burla *et al.*, 1989). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

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2-(Imidazol-1-yl)-1-(2-naphthyl)ethanone Oxime

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Abstract

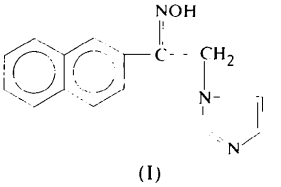
In the title compound, imidazol-1-ylmethyl 2-naphthyl ketone oxime, $C_{15}H_{13}N_3O$, the naphthalene and imidazole rings are essentially planar. The oxime group is twisted by 36.2 (1)° out of the naphthalene plane. The oxime configuration is *Z*. The structure is stabilized by intra- and intermolecular hydrogen bonds.

Comment

Oximes show geometric isomerism due to the double bond between the N and C atoms. The reaction of hydroxylamine hydrochloride with an unsymmetrical ketone may result in either a mixture of two isomeric oximes or only one of the isomers, depending on the structure of the ketone or the reaction conditions (Mixich & Thiele, 1979; Migrdichian, 1957). Because of the great differences in physical, chemical and biological properties of the geometric isomers, determination of the configuration of the isomers is important (Mathison *et al.*, 1989).

Oximes and oxime ethers have a broad pharmacological activity spectrum, encompassing antifungal, antibacterial, antidepressant and insecticidal activities, as well as activity as a nerve-gas antidote, depending on the pharmacophoric group of the molecule (Polak, 1982; Balsamo *et al.*, 1990; Holan *et al.*, 1984; Forman, 1964). An oximino group usually modifies the activity or sometimes is directly responsible for the activity.

In connection with our interest in the anticonvulsant compound nafimidone and antifungal–antibacterial agents with (arylalkyl)azole structures, we have prepared nafimidone oxime (Walker *et al.*, 1981). Since the structure of this oxime is important with respect to the activity and configuration of the O-ether derivatives of this compound that have been prepared in our laboratory, we studied its spectral properties and molecular geometry by UV, IR, ^{1}H NMR, mass spectroscopy, elemental analysis and X-ray crystallography. We report here the structure of nafimidone oxime, (I).



(I)

The naphthalene moiety is essentially planar, with bond lengths and angles in good agreement with those observed in other naphthalene derivatives (Elmalı *et al.*, 1995; Irngartinger *et al.*, 1993). The imidazole ring is also planar [$\Sigma(\Delta/\sigma)^2$ = 1.6]. The dihedral angle between these two planes is 96.98 (8)°. Some significant differences are observed for the bond distances in the imidazole ring compared with the averages derived from the Cambridge Structural Database quoted by Allen *et al.* (1987) [given in square brackets]: N1—C13 1.360 (3) [1.349 (18)], N1—C15 1.335 (2) [1.370 (10)], N2—C14 1.364 (3) [1.376 (11)], N2—C15 1.305 (3) [1.313 (11)] and C13—C14 1.344 (3) Å [1.360 (14) Å]. In two other imidazole oxime derivatives, all the C—N bond distances in the imidazole ring are intermediate between the expected single- and double-bond lengths (Grassi *et al.*, 1993; Bruno *et al.*, 1994). The exocyclic angles around the N1 atom show considerable asymmetry. However,