$\omega/2\theta$ scans
Absorption correction:
analytical (*PLATON*; Spek, 1990)
$T_{\min} = 0.227$, $T_{\max} = 0.508$
3079 measured reflections
2522 independent reflections

$R_{\rm int} = 0.044$
$\theta_{\max} = 71.94°$
$h = -10 \rightarrow 6$
$k = -11 \rightarrow 0$
$l = -38 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: 16.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.103$
$S = 1.077$
2522 reflections
130 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0601P)^2 + 1.0789P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.0001$

$\Delta\rho_{\max} = 0.442$ e Å^{-3}
$\Delta\rho_{\min} = -0.466$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0055 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Se1—C2	1.950 (3)	Se3—C4	1.960 (3)
Se1—C6	1.966 (3)	C4—C5	1.512 (4)
C2—Se3	1.966 (3)	C5—C6	1.511 (4)
C2—Se1—C6	100.64 (13)	C5—C4—Se3	113.6 (2)
Se1—C2—Se3	112.65 (13)	C6—C5—C4	116.1 (3)
C4—Se3—C2	99.91 (13)	C5—C6—Se1	113.1 (2)
C6—Se1—C2—Se3	53.42 (17)	Se3—C4—C5—C6	−71.2 (3)
Se1—C2—Se3—C4	−53.47 (17)	C4—C5—C6—Se1	70.4 (3)
C2—Se3—C4—C5	57.7 (2)	C2—Se1—C6—C5	−57.1 (3)

The non-H atoms were refined with anisotropic displacement parameters and the H atoms were subject to constrained refinement.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *HELENA* (Spek, 1997). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1184). Services for accessing these data are described at the back of the journal.

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Methylamine and Dimethylamine Salts of the Hydrogen Maleate Ion

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Abstract

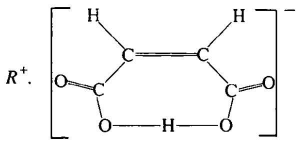
Methylammonium hydrogen maleate, $CH_6N^+.C_4H_3O_4^-$, crystallizes in space group *Pnam* with two independent anions in the asymmetric unit having crystallographic mirror planes bisecting the C═C bonds. Dimethylammonium hydrogen maleate, $C_2H_8N^+.C_4H_3O_4^-$, crystallizes in space group $P2_1/n$ without crystallographic symmetry constraints on the hydrogen maleate ion and this anion also possesses almost perfect mirror-plane symmetry. One of the anions in the methylammonium salt displays significant deviation from planarity [−12.00 (9)°]. The symmetry of the three anions and the difference in their conformations are rationalized from the hydrogen-bond interactions in the two salts.

Comment

Hydrogen maleate ions possess a short intramolecular hydrogen bond with corresponding O···O distances around 2.42 Å. One would expect that a short hydrogen bond like this would lead to a fairly rigid geometry. However, significant variations are observed with respect to both the symmetry of the short hydrogen bond and the planarity of the hydrogen maleate ion in salts of different cations. In a survey of neutron diffraction investigations of hydrogen maleate salts (Olovsson *et al.*, 1984), it was found that a symmetric hydrogen bond is frequently, but not necessarily, a consequence of the crystallographic symmetry and can also be observed in compounds without any symmetry constraints. The nature of the counter-ion was also found to influence the geometry of the hydrogen maleate ion. Popelier *et al.* (1989) compared the structures of hydrated hydrogen maleate salts of Li^+, Na^+, Ca^{2+}, Zn^{2+} and Mg^{2+}, and found that they displayed a great variation in their hydrogen-bond patterns, which are dominated by the interactions between the water molecules and the hydrogen maleate anions.

Using cations derived from simple organic amines, hydrogen bonds can be formed directly between cation and anion, and it may be the number of potential hydrogen-bond donors of the cation that influences the geometry and the crystal packing in the hydrogen maleate salts. Methylammonium and dimethylammonium are very similar cations which differ in their number of hydrogen-bond donors, the latter cation having one less than the former. To examine how the number of hydrogen-bond donors can influence the crystal packing of hydrogen maleates, and thereby the geometry of the anion, crystal structure determinations were undertaken for the hydrogen maleate salts with these two cations. Neither of the salts contain any solvent, which makes it easier to compare their hydrogen-bond interactions.

The symmetry of the diffraction pattern and the systematically absent reflections showed that methylammonium hydrogen maleate (MAHMA) belongs either to space group *Pnam* (a non-standard setting of *Pnma*, No. 62) or its non-centrosymmetric analogue $Pna2_1$.



MAHMA: $R^+ = CH_3NH_3^+$
DMAHMA: $R^+ = CH_3NH_2CH_3^+$

The subsequent structure determination revealed that all non-H atoms conform with the centrosymmetric space group, with the cation in a general position and two independent anions placed on crystallographic mirror planes bisecting their C═C bonds. The only atoms that could deviate from the centrosymmetric description are the two H atoms in the short intramolecular hydrogen bonds. Different models were employed in the two possible space groups during the refinements. Based on Hamilton's *R* ratio test (Hamilton, 1965), the best structural model for MAHMA is a centrosymmetric structure with two half-populated H atoms displaced 0.42 (2) and 0.34 (2) Å from the crystallographic mirror planes bisecting the short hydrogen bond. The entities of the crystal are shown in Fig. 1. The crystals of dimethylammonium hydrogen maleate (DMAHMA) are monoclinic (space group $P2_1/n$), with one independent molecule in the asymmetric unit (Fig. 2).

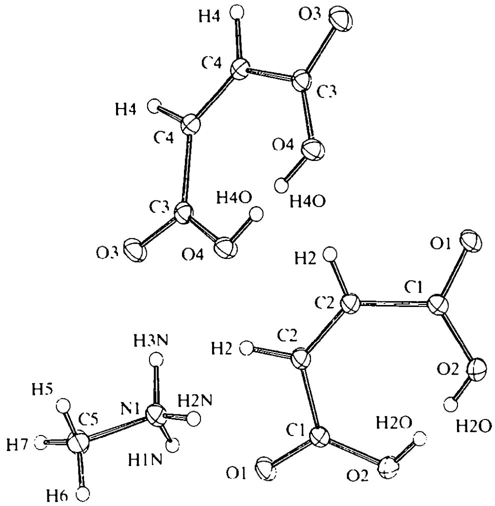


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of MAHMA showing the labelling scheme. Displacement ellipsoids enclose 50% probability.

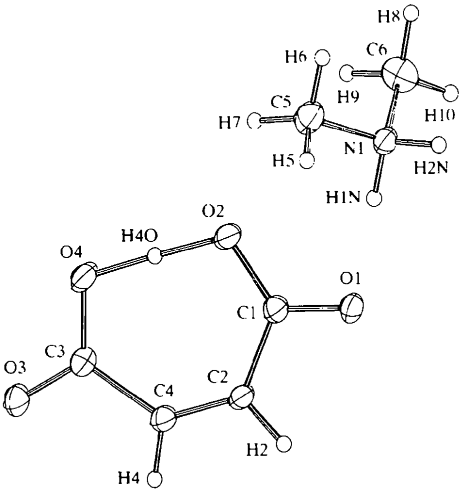


Fig. 2. *ORTEP*II (Johnson, 1976) drawing of DMAHMA showing the labelling scheme. Displacement ellipsoids enclose 50% probability.

The equivalent bond lengths and angles for the two cations listed in Table 5 are very similar. The hydrogen succinate salts of the same two cations have previously been investigated structurally (Kalsbeek & Larsen, 1991). In these salts, short O···O hydrogen bonds between the carboxylic acid and the carboxylate groups link the anions into infinite chains. Despite the difference between the hydrogen-bonding arrangements in the hydrogen succinate and hydrogen maleate salts, the cations have identical geometry within standard uncertainty. The stereochemistry of the cations is also the same, the cations adopting the low-energy staggered conformation in both types of salts.

The two title structures contain three independent hydrogen maleate ions. Crystallographic mirror-plane symmetry is imposed on the two anions in MAHMA, and within standard uncertainty, the anion in DMAHMA also possesses mirror-plane symmetry. The bond lengths and angles involving the non-H atoms listed in Table 6 conform well with the values found in other hydrogen maleate salts (Olovsson *et al.*, 1984; Popelier *et al.*, 1989; Sequira *et al.*, 1992), but the three anions show significant variations in their conformations. The anion in DMAHMA and the anion (C4, C3, O3, O4) in MAHMA can be considered as being almost planar, as illustrated by their torsion angles; O2—C1—C2—C4 −1.65 (11), C2—C4—C3—O4 −0.29 (11) and O4—C3—C4—C4′ −2.36 (10)°. The corresponding torsion angle (O2—C1—C2—C2′) in the other anion in MAHMA is −12.00 (9)°. Considering the mirror-plane symmetry, this anion adopts a bent conformation as shown in Fig. 1. Similar large variations from the planar conformation have only been observed previously in hydrogen maleate salts of fairly large organic cations (Larsen *et al.*, 1994). The deviation from a planar conformation does not influence the O···O distance in the short intramolecular hydrogen bond significantly; it is 2.4282 (9) Å in the bent anion, and 2.4240 (9) and 2.419 (1) Å in the two that are closer to planarity.

Variation in their hydrogen-bond interactions is the likely cause for these differences in the stereochemistry of the hydrogen maleate ions. The geometries of the hydrogen bonds observed in the two structures are shown in Tables 2 and 4. In both structures, the cation–anion interactions only involve the O atoms that do not take part in the short intramolecular hydrogen bond. The anion in DMAHMA contains two potential acceptor atoms (O1 and O3) which accept the two equivalent protons of the cation. Judging from their geometrical features, the two N—H···O hydrogen bonds appear to be identical. It is likely that it is the identical environment in the two carboxy groups that causes the intramolecular hydrogen bond to be symmetric, with two identical O—H distances [1.200 (13) and 1.219 (13) Å]. The dimethylammonium ions connect anions that are related by glide-plane symmetry into infinite chains (Fig. 3).

The methylammonium ion contains three H atoms that can take part in hydrogen bonds, with only two C=O groups to accept these protons. The way this is balanced in the crystal is to let one independent anion accept one proton and the other anion two. The three N—H···O hydrogen bonds that are formed in MAHMA are slightly longer than those in DMAHMA and show larger variations [2.8202 (10)–2.8973 (10) Å]. The most bent anion (O1, O2, C1, C2) is the one which accepts two protons. It is likely that it is in order to achieve the additional hydrogen-bond interaction that a bent conformation is imposed. The cation links three different anions, two with the bent conformation related by inversion symmetry and one with the planar conformation (Fig. 4).

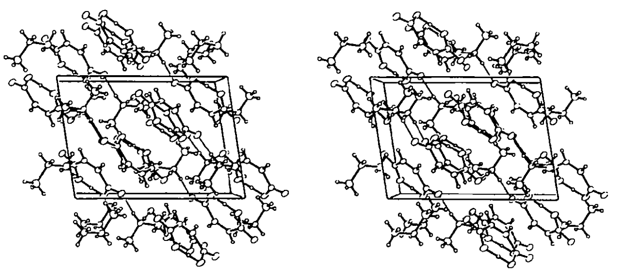


Fig. 3. View of the packing of DMAHMA in the crystal along the *a** axis. The *c** axis is vertical and the *b** axis is horizontal. Hydrogen bonds are indicated as thin lines.

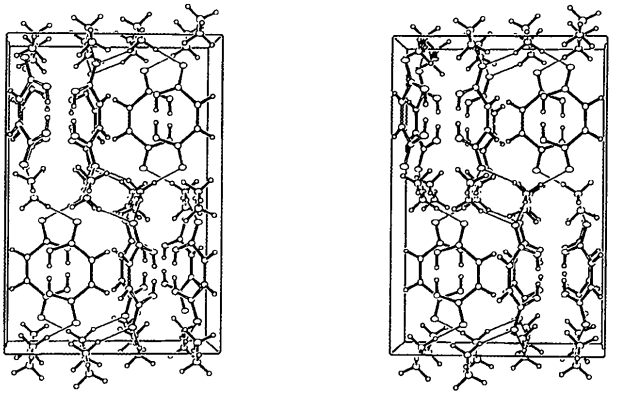


Fig. 4. View of the packing of MAHMA in the crystal along the *a* axis. The *c* axis is vertical and the *b* axis is horizontal. Hydrogen bonds are indicated as thin lines. The anion (C3, C4, O3, O4) is drawn with open bonds.

These crystal structure determinations have shown that the symmetry of the intramolecular hydrogen bond in hydrogen maleates depends exclusively on the symmetry of the crystalline environment and that in order to satisfy the hydrogen-bond interactions, the anion is able to accommodate significant deviations from planarity.

Experimental

MAHMA and DMAHMA were prepared by dissolving maleic acid in ethanol and subsequent slow addition of an equimolar amount of methylamine and dimethylamine, respectively. Slow evaporation of the solvent from the two solutions gave colourless crystals after several weeks.

MAHMA

Crystal data

$CH_6N^+.C_4H_3O_4^-$
$M_r = 147.13$
Orthorhombic
Pnam
$a = 6.4274\,(10)$ Å
$b = 11.826\,(2)$ Å
$c = 17.616\,(2)$ Å
$V = 1339.0\,(3)$ Å^3
$Z = 8$
$D_x = 1.460$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 17.45$–$20.02°$
$\mu = 0.127$ mm^{-1}
$T = 122.4\,(5)$ K
Rectangular
0.45 × 0.25 × 0.12 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
4435 measured reflections
4185 independent reflections
3157 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.011$
$\theta_{\rm max} = 39.76°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 31$
5 standard reflections
frequency: 167 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.075$
$S = 2.203$
4177 reflections
132 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\rm max} = -0.001$

$\Delta\rho_{\rm max} = 0.672$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.401$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0358 (12)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for MAHMA*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.15234 (9)	0.58567 (5)	0.08999 (3)	0.01770 (12)
O2	−0.00017 (9)	0.68412 (5)	0.18108 (3)	0.01810 (12)
C1	0.13828 (12)	0.61422 (6)	0.15780 (4)	0.01321 (13)
C2	0.28934 (12)	0.56289 (6)	0.21199 (4)	0.01394 (13)
O3	0.26685 (9)	0.16808 (5)	0.08860 (3)	0.01917 (12)
O4	0.26181 (9)	0.29462 (4)	0.18120 (3)	0.01739 (12)
C3	0.27091 (11)	0.19200 (6)	0.15716 (4)	0.01369 (13)
C4	0.28605 (11)	0.09630 (6)	0.21197 (4)	0.01355 (13)
N1	0.18257 (11)	0.37149 (6)	0.01090 (4)	0.01629 (13)
C5	0.36210 (14)	0.38554 (7)	−0.04100 (5)	0.01842 (15)

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2O···O2$^{\rm i}$	0.798 (18)	1.635 (18)	2.4282 (9)	172.1 (18)
O4—H4O···O4$^{\rm i}$	0.871 (18)	1.554 (18)	2.4240 (9)	176.7 (15)
N1—H1N···O1$^{\rm ii}$	0.901 (11)	1.961 (11)	2.8371 (10)	163.4 (9)
N1—H2N···O1	0.904 (11)	2.033 (11)	2.8973 (10)	159.6 (10)
N1—H3N···O3	0.942 (11)	1.889 (11)	2.8202 (10)	169.0 (9)

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

DMAHMA

Crystal data

$C_2H_8N^+.C_4H_3O_4^-$
$M_r = 161.16$
Monoclinic
$P2_1/n$
$a = 8.4738\,(8)$ Å
$b = 8.3444\,(13)$ Å
$c = 11.5727\,(10)$ Å
$\beta = 98.729\,(8)°$
$V = 808.8\,(2)$ Å^3
$Z = 4$
$D_x = 1.323$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 21.27$–$22.34°$
$\mu = 0.112$ mm^{-1}
$T = 122.4\,(5)$ K
Rectangular
0.40 × 0.30 × 0.25 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
6753 measured reflections
5630 independent reflections
4080 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.010$
$\theta_{\rm max} = 41.92°$
$h = 0 \rightarrow 15$
$k = -8 \rightarrow 15$
$l = -21 \rightarrow 21$
5 standard reflections
frequency: 167 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.076$
$S = 2.187$
5623 reflections
145 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\rm max} = 0.085$

$\Delta\rho_{\rm max} = 0.553$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.321$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0256 (18)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for DMAHMA*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.76068 (7)	0.15287 (8)	0.52278 (6)	0.01840 (12)
O1	0.85532 (6)	0.19880 (6)	0.45790 (4)	0.02361 (11)
O2	0.63296 (6)	0.23179 (6)	0.53448 (5)	0.02473 (11)
C2	0.79889 (7)	−0.00024 (8)	0.58744 (6)	0.01856 (12)
C4	0.72130 (8)	−0.07628 (8)	0.66347 (6)	0.01933 (12)
C3	0.57162 (8)	−0.03332 (8)	0.70950 (6)	0.01883 (12)
O3	0.52601 (6)	−0.12630 (6)	0.78100 (4)	0.02575 (12)
O4	0.49668 (6)	0.09666 (6)	0.67572 (5)	0.02666 (12)
N1	0.77447 (7)	0.50116 (7)	0.37508 (5)	0.01991 (11)
C5	0.75823 (9)	0.60659 (10)	0.47506 (7)	0.0268 (2)
C6	0.62586 (10)	0.49066 (10)	0.28980 (7)	0.0292 (2)

Table 4. *Hydrogen-bonding geometry (Å, °) for DMAHMA*

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4O···O2	1.200 (13)	1.219 (13)	2.419 (1)	177.6 (11)
N1—H1N···O1	0.944 (9)	1.805 (9)	2.7485 (9)	178.1 (8)
N1—H2N···O3$^{\rm i}$	0.929 (9)	1.819 (9)	2.7429 (9)	172.9 (9)

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

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'	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'	1.3399 (14)		
O1—C1—C2—C2'	167.57 (4)	O1—C1—C2—C4	178.87 (7)
O2—C1—C2—C2'	−12.00 (9)	O2—C1—C2—C4	−1.65 (11)
O3—C3—C4—C4'	177.39 (5)	C1—C2—C4—C3	−0.39 (13)
O4—C3—C4—C4'	−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: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976).

The authors wish to thank Mr Flemming Hansen for help with the data collections.

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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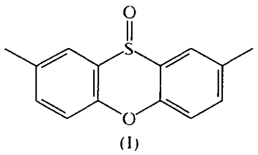
Abstract

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)