0·05 and 0·02 Å in molecules *A* and *B* respectively. This slight aplanarity is brought about by a distortion due to the fused ring structure as seen in the C(1)—C(10)—C(5)—C(4) torsion angles, −8·8 (4)° in molecule *A* and −5·0 (4)° in molecule *B*. The puckered central six-membered ring has a chair conformation, and the average endocyclic torsion angles, 56·7° in molecule *A* and 57·6° in *B*, are similar to those of photosantonin (Sheldon, Shaefer, Gulbis, Ruble, Burgstahler & Lee, 1982) and 14-chlorosantonin (Takayanagi, Ogura & Iitaka, 1978). As seen in Fig. 1, the dienone rings of the independent molecules lie close to each other with an interplanar angle of 28°. The molecules are nearly stacked parallel along the *b* axis in the crystal as shown in Fig. 2. Short intermolecular contacts less than 3·6 Å are seen involving the O atoms: C(1)···O(1) = 3·236 (3) Å and C(2)···O(1) = 3·388 (3) Å between molecules *A* at *x*, *y*, *z* and $\frac{1}{2}-x$, $1-y$, $-\frac{1}{2}+z$; O(1)···C(3′) = 3·466 (3) Å and O(1)···C(4′) = 3·556 (3) Å between molecules *A* and *B* in the same unit; O(3)···C(11′) = 3·536 (4) Å between molecules *A* at *x*, *y*, *z* and *B* at $1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$. The carbonyl oxygen O(1) is in close contact with the —C(1)H=C(2)H— moiety in the dienone ring of the symmetry-related molecule. These short intermolecular contacts surrounding the dienone ring offer strong crystal fields permitting only restricted movements of atoms during photochemical reactions in the solid state.

References

Asher, J. D. M. & Sim, G. A. (1965). *J. Chem. Soc.* pp. 6041–6055.

Cocker, W. & McMurry, T. B. H. (1960). *Tetrahedron*, **8**, 181–204.

Cohen, M. D. & Schmidt, G. M. J. (1964). *J. Chem. Soc.* pp. 1966–2000.

Inayama, S., Shimizu, N., Hori, H., Ohsaka, T., Hirose, T., Shibata, T. & Iitaka, Y. (1982). *Chem. Pharm. Bull.* **30**, 3856–3859.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

Kropp, P. J. (1967). In *Organic Photochemistry*, Vol. 1, edited by D. L. Chapman. New York: Marcel Dekker.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Matsuura, T., Sata, Y., Ogura, K. & Mori, M. (1968). *Tetrahedron Lett.* pp. 4627–4630.

Nakazaki, M. & Arakawa, H. (1962). *Proc. Chem. Soc. London*, p. 151.

Sheldon, R. I., Shaefer, C. G., Gulbis, J., Ruble, J. R., Burgstahler, A. W. & Lee, B. (1982). *Acta Cryst.* B**38**, 649–651.

Takayanagi, H., Ogura, H. & Iitaka, Y. (1978). *Chem. Pharm. Bull.* **26**, 2729–2733.

White, D. N. J. & Sim, G. A. (1975). *J. Chem. Soc. Perkin Trans.* 2, pp. 1826–1831.

Acta Cryst. (1985). C**41**, 1781–1783

Structure of 1,4,9-Triazaphenoxathiin at 163 K

By S. B. Larson and S. H. Simonsen

Department of Chemistry, University of Texas at Austin, Austin, TX 78712, *USA*

G. E. Martin

Department of Medicinal Chemistry and Pharmacognosy, College of Pharmacy, The University of Houston, Houston, Texas 77004, *USA*

and K. Smith

*Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA*2 8*PP, Wales*

(*Received* 31 *May* 1985; *accepted* 12 *August* 1985)

Abstract. $C_9H_5N_3OS$, $M_r = 203{\cdot}22$, orthorhombic, *Pbca*, $a = 14{\cdot}892\ (5)$, $b = 15{\cdot}778\ (4)$, $c = 7{\cdot}1688\ (15)$ Å, $V = 1684{\cdot}4\ (8)$ Å^3, $Z = 8$, $D_x = 1{\cdot}603$, $D_m(295\ \text{K}) = 1{\cdot}597\ (1)$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 3{\cdot}43$ cm^{-1}, $F(000) = 832$, $R = 0{\cdot}0451$ for 1842 observed reflections. The molecule is composed of a planar pyridine ring and a planar pyrazine ring. The dihedral angle between the rings is 172·47 (8)°; 172·15 (5)° is obtained when S and O are included in the calculation of each plane. Both N atoms in the pyrazine ring have unsymmetrical bond lengths as do S and O in the central ring.

0108-2701/85/121781-03$01.50

Introduction. Previously we have reported the synthesis and a comprehensive two-dimensional ^{1}H NMR study of the title compound (Martin, Gampe, Ford, Willcott, Morgan, Ternay, Okafor & Smith, 1983) and more recently, the dihedral angle as part of another study (Kimura, Simonsen, Puig-Torres & Martin, 1985) on the effects of annular substitution on the dihedral angle of the phenoxathiin system. We now present the details of the determination of the structure of 1,4,9-triazaphenoxathiin (I) at 163 K.

Experimental. A summary of data collection and structural refinement is given in Table 1. Crystals were colorless, transparent prisms. Density measured by flotation in aqueous $ZnCl_2$. Structure solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by full-matrix least-squares method [$\sum w(F_o - F_c)^2$ minimized, $w = \sigma_F^{-2}$]. Scattering factors and anomalous-dispersion corrections for S, O, N and C from *International Tables for X-ray Crystallography* (1974); H scattering factors from Stewart, Davidson & Simpson (1965). All atomic positional parameters refined as well as anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms. H atoms located in an electron density difference map as peaks of 0·71–0·84 e Å^{-3}. Atomic parameters are found in Table 2.* Least-squares planes calculated with a program supplied by Cordes (1983). Principal computer programs given by Gadol & Davis (1982).

Discussion. Atom labeling, bond lengths and bond angles are shown in Fig. 1. The structural features are very similar to those of phenoxathiin (II) (Kimura *et al.*, 1985), 3-azaphenoxathiin (III) (Caldwell, Martin, Simonsen, Inners & Willcott, 1981), and 1,3-diazaphenoxathiin (IV) (Puig-Torres, Martin, Smith, Larson & Simonsen, 1984). The pyrazine ring exhibits bond lengths that are alternately longer and shorter than the 1·3330 (7) Å for C—N and 1·3875 (9) Å for C—C found in pyrazine itself (de With, Harkema & Feil, 1976). The major effect of annular substitution with N on the structure of phenoxathiin is seen in the central six-membered ring. Within each structure neither the C—S bond lengths nor the C—O bond lengths are equal. The C—S distances through the series are: 1·761 (2), 1·767 (2) Å for (II); 1·749 (1), 1·764 (1) Å for (III); 1·750 (3), 1·764 (3) Å for (IV) and 1·751 (2), 1·762 (2) Å for (I). The C—O distances through the series are: 1·384 (3), 1·391 (3) Å for (II);

Table 1. *Summary of data collection and refinement for 1,4,9-triazaphenoxathiin*

(*A*) Data collection (163 K)^{i,ii}	
Radiation	Mo $K\alpha$
Mode	ω scan
Scan range	Symmetrically over 1·0° about $K\alpha_{1,2}$ maximum
Background	Offset 1·0 and −1·0° in ω from $K\alpha_{1,2}$ maximum
Scan rate (° min^{-1})	2·0–6·0
Exposure time (h)	48·4
Stability analysis^{ii}	
Computed *a*	0·0007 (4)
b	−0·000021 (8)
Correction range (on *I*)	0·993–1·013
2θ range (°)	4·0–60·0
Range in *hkl*, min.	0, 0, 0
max.	20,22,10
Total reflections measured	2813
Crystal dimensions (mm)	0·41 × 0·35 × 0·34
Crystal volume (mm^3)	0·028
Crystal faces	$\bar{2}\bar{1}1, 21\bar{1}, \bar{2}11, 2\bar{1}\bar{1}, 100, \bar{1}0\bar{1}, \bar{1}0\bar{2}, 211, 2\bar{1}1, 001, 010, 0\bar{1}0$
Absorption correction, transmission-factor range	0·911–0·920
(*B*) Structure refinement	
Instability factor p^{ii}	0·04
Reflections used ($F \geq 5\sigma_F$)	1842
No. of variables	147
Goodness of fit, *S*	1·882
R, *wR*	0·0451, 0·0563
R for all data	0·0637
Max. shift/e.s.d.	0·014
Max. peak in difference map (e Å^{-3})	0·48 [between S(10) and C(10A)]
Min. density in difference map (e Å^{-3})	−0·49

Notes: (i) Unit-cell parameters were obtained by least-squares refinement of the setting angles of 45 reflections with $23{\cdot}3 < 2\theta < 29{\cdot}1°$. (ii) Syntex $P2_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system. Data reduction was carried out as described by Riley & Davis (1976). Crystal and instrument stability were monitored by re-measurement of four check reflections after every 96 reflections. As detailed by Henslee & Davis (1975), these data are analyzed to relate intensity variation as a function of exposure time by the equation $y = 1{\cdot}0 + ax + bx^2$ where x is exposure time, y is the intensity-variation fraction and a and b are coefficients determined by least-squares fit.

Table 2. *Atomic positions in fractional coordinates and* U_{iso} (H *atoms*) *or* U_{eq} *for all atoms in* 1,4,9-*triazaphenoxathiin*

	x	y	z	U_{eq}*/U_{iso}(Å^2)
S(10)	0·19257 (4)	0·43016 (3)	0·51125 (7)	0·02294 (15)
C(10A)	0·21066 (13)	0·53629 (13)	0·4507 (3)	0·0183 (5)
N(1)	0·28698 (13)	0·56906 (12)	0·5117 (2)	0·0238 (5)
C(2)	0·3031 (2)	0·6512 (2)	0·4707 (3)	0·0272 (6)
C(3)	0·2421 (2)	0·69887 (14)	0·3722 (3)	0·0264 (6)
N(4)	0·16391 (13)	0·66619 (12)	0·3115 (3)	0·0240 (5)
C(4A)	0·14875 (14)	0·58617 (13)	0·3500 (3)	0·0193 (5)
O(5)	0·06749 (10)	0·55744 (10)	0·2854 (2)	0·0246 (5)
C(5A)	0·04449 (13)	0·47258 (14)	0·2939 (3)	0·0200 (5)
C(6)	−0·0333 (2)	0·4494 (2)	0·2009 (3)	0·0260 (7)
C(7)	−0·0595 (2)	0·3651 (2)	0·2054 (3)	0·0311 (7)
C(8)	−0·0077 (2)	0·3070 (2)	0·3033 (4)	0·0316 (7)
N(9)	0·06743 (12)	0·32920 (12)	0·3937 (3)	0·0256 (5)
C(9A)	0·09231 (14)	0·41025 (13)	0·3882 (3)	0·0197 (5)
H(2)	0·358 (2)	0·678 (2)	0·515 (4)	0·037 (8)
H(3)	0·253 (2)	0·757 (2)	0·342 (4)	0·034 (7)
H(6)	−0·063 (2)	0·492 (2)	0·138 (4)	0·029 (7)
H(7)	−0·112 (2)	0·346 (2)	0·140 (4)	0·053 (9)
H(8)	−0·024 (2)	0·245 (2)	0·301 (4)	0·032 (7)

* For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{A}_{ij}$ where $\mathbf{A}_{ij}$ is the dot product of the *i*th and *j*th direct-space unit-cell vectors.

---

* Tables of anisotropic thermal parameters, bond lengths and angles involving H, torsion angles, least-squares planes and structure-factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42431 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1·377 (2), 1·385 (2) Å for (III); 1·376 (3), 1·392 (3) Å for (IV); and 1·373 (3), 1·383 (3) Å for (I). For the N-containing structures, the shorter distance in the pairs corresponds to the bonds of S or O to the ring having the most N-substitution. The CCS [averages: (II), 120·6 (1); (III), 123·16 (6); (IV), 123·2 (1); (I), 123·8 (1)°] and CCO [averages: (II), 122·1 (1); (III), 124·28 (7); (IV), 124·2 (1); (I), 124·9 (1)°] angles are larger in the aza analogs than in the parent compound. The CSC angle (range: 99·9–100·3°) remains fairly constant for the three aza compounds, but is more than 2° greater than the CSC angle in phenoxathiin [97·8 (1)°]. The COC angles (range: 120·2–121·5°) in the aza analogs are likewise greater by 3–4° than the COC angle in the parent [117·4 (2)°].

The pyrazine and pyridine rings are both planar; no atom of either deviates by more than 0·006 Å. S(10) is −0·0359 (5) Å from the plane of the pyrazine ring and 0·0142 (5) Å from the plane of the pyridine ring. O(5) deviates from these planes by −0·018 (2) and −0·006 (2) Å respectively. The dihedral angle between these planes is 172·47 (8)°. Including S and O in the least-squares planes (for each planar portion) results in a dihedral angle of 172·15 (5)°.

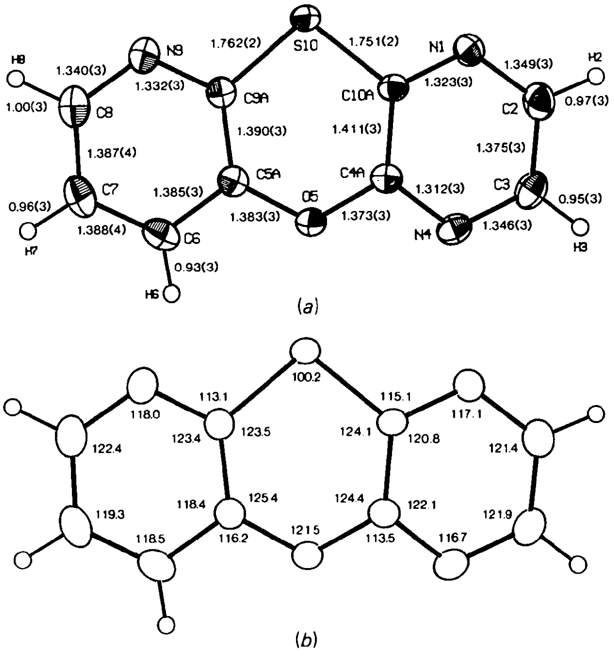

Fig. 1. (*a*) View of title compound illustrating atom labeling and bond lengths (Å) with e.s.d.'s. Thermal ellipsoids scaled to 50% probability. (*b*) View giving bond angles (°); e.s.d.'s are in the range 0·1 to 0·2°.

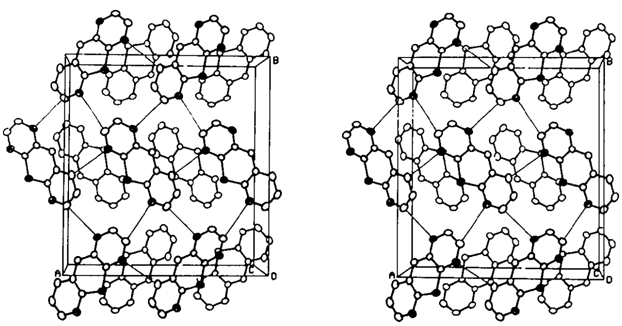

Fig. 2. Stereoview of molecular packing as viewed down the *c* axis. S and N atoms have been darkened for identification. Closest contacts have been indicated by thin lines.

Fig. 2 illustrates the packing of the molecules which occurs in undulating sheets stacked in the **c** direction (two such sheets are differentiated by degree of darkness). In the **a** direction the closest contact is N(1)···H(6), 2·76 (2) Å; in the **b** direction they are N(4)···H(8), 2·56 (3) Å and N(9)···H(2), 2·77 (3) Å. In the **c** direction S(10)···N(4), 3·393 (2) Å, is the closest contact.

This work was supported by the Robert A. Welch Foundation through grants No. F-017 to SHS and No. E-792 to GEM and by the North Atlantic Treaty Organization through grant No. 019.81 to GEM and KS.

References

CALDWELL, S. R., MARTIN, G. E., SIMONSEN, S. H., INNERS, R. R. & WILLCOTT, M. R. III (1981). *J. Heterocycl. Chem.* **18**, 479–484.

CORDES, A. W. (1983). Personal communication.

GADOL, S. M. & DAVIS, R. E. (1982). *Organometallics*, **1**, 1607–1613.

HENSLEE, W. H. & DAVIS, R. E. (1975). *Acta Cryst.* B**31**, 1511–1519.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

KIMURA, M., SIMONSEN, S. H., PUIG-TORRES, S. & MARTIN, G. E. (1985). In preparation.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MARTIN, G. E., GAMPE, R. T. JR, FORD, J. J., WILLCOTT, M. R. III, MORGAN, M., TERNAY, A. L. JR, OKAFOR, G. O. & SMITH, K. (1983). *J. Heterocycl. Chem.* **20**, 1063–1975.

PUIG-TORRES, S., MARTIN, G. E., SMITH, K., LARSON, S. B. & SIMONSEN, S. H. (1984). *J. Heterocycl. Chem.* **21**, 995–1000.

RILEY, P. E. & DAVIS, R. E. (1976). *Acta Cryst.* B**32**, 381–386.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

WITH, G. DE, HARKEMA, S. & FEIL, D. (1976). *Acta Cryst.* B**32**, 3178–3184.