

Fig. 2. A stereoscopic view of the unit cell. Hydrogen bonding in the dimers is shown by thin lines.

Bordner & Lombardino, 1985; Golic & Leban, 1987). The pyramidal coordination around the N is distorted due to intermolecular contact, with angles C—N—H 120 (3), S—N—C 117.2 (4) and S—N—H 110 (2)°. The H atom belonging to the NH group is located almost perpendicular to the heterocyclic ring; the C(1)—S(2)—N(3)—H(31) and C(10)—C(4)—N(3)—H(31) torsion angles are -85 (3) and 97 (3)°, respectively. The heterocyclic thiazine ring adopts a half-chair conformation.

Related literature. A search in the June 1990 edition of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) showed that no other 2,3-benzothiazines have been structurally characterized until now. However, 1,2-benzothiazines are relatively common.

This work has received partial support from CONICET and CICPBA, Argentina, and from

CNPq, Brazil, through a CONICET—CNPq exchange program. The utilization of National Cancer Institute, Frederick Cancer Research Facility, Advance Scientific Computing Laboratory (ASCL) facilities for the Cambridge Structural Database search are gratefully acknowledged.

References

- ALLEN, F. H., KENNARD, O. & TAYLOR, R. (1983). *Acc. Chem. Res.* **16**, 146–153.
- AUPERS, J., CARLISLE, C. H. & LINDLEY, P. F. (1974). *Acta Cryst.* **B30**, 1228–1233.
- CAMERMAN, N. & CAMERMAN, A. (1975). *Can. J. Chem.* **53**, 2194–2198.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- GOLIC, L. & LEBAN, I. (1987). *Acta Cryst.* **C43**, 280–282.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- KOJIĆ-PRODIĆ, B. & RUŽIĆ-TOROŠ, Ž. (1982). *Acta Cryst.* **B38**, 2948–2951.
- NORRIS, C. P., BERKE, H., BORDNER, J. & LOMBARDINO, A. C. (1985). *J. Heterocycl. Chem.* **22**, 837–840.
- O'CONNELL, A. M. & MASLEN, E. N. (1967). *Acta Cryst.* **22**, 134–145.
- ORAZI, O. O., CORRAL, R. A. & BRAVO, R. D. (1986). *J. Heterocycl. Chem.* **23**, 1701–1708.
- SHELDRICK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRICK, G. M. (1985). *SHELXS86*. In *Crystallographic Computing 3*, edited by G. M. ShelDRICK, C. KRUGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1991). **C47**, 2503–2505

4-Oxo-5-phenyl-2,3-dihydro-3a-azaphenalen-6-yl Benzenesulfonate

BY ERIC S. RAPER, JAMES R. CREIGHTON AND STEPHEN P. STANFORTH

Department of Chemical and Life Sciences, The Polytechnic, Newcastle-upon-Tyne, NE1 8ST, England

AND WILLIAM CLEGG

Department of Chemistry, The University, Newcastle-upon-Tyne, NE1 7RU, England

(Received 13 December 1990; accepted 14 May 1991)

Abstract. $C_{24}H_{19}NO_4S$, $M_r = 417.5$, monoclinic, $P2_1/n$, $a = 10.5374$ (4), $b = 12.9206$ (6), $c = 14.6462$ (6) Å, $\beta = 98.863$ (5)°, $V = 1970.3$ Å³, $Z = 4$, $D_x = 1.407$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 1.9$ cm⁻¹, $F(000) = 872$, $T = 295$ K, final $R = 0.0515$ for 2794 observed reflections with $F > 4\sigma_c(F)$ (σ_c from counting statistics only). The ring system is puckered, owing to the presence of the methylene-C

atoms, and has C—C distances ranging from 1.380 (4) to 1.518 (3) Å. The trigonal N atom forms two essentially equivalent C—N distances [mean 1.391 (3) Å], with a third to a neighbouring methylene-C atom at 1.488 (3) Å. The exocyclic ketonic carbonyl distance is 1.225 (2) Å and the sulfonate-S atom forms two essentially equivalent terminal S—O distances [mean 1.428 (2) Å], while

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

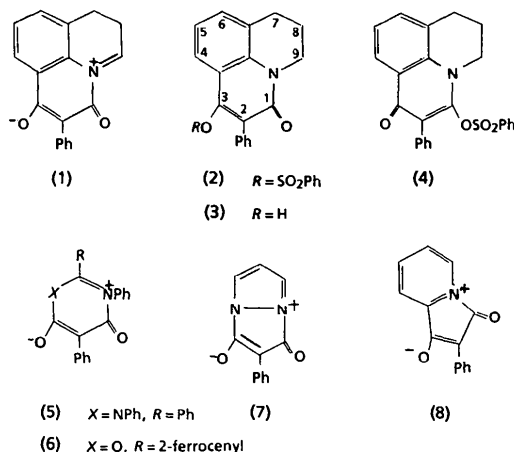
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(1)	4772 (2)	6866 (2)	1655 (1)	45 (1)
C(2)	5727 (2)	6137 (2)	2125 (1)	52 (1)
C(3)	4576 (2)	4737 (2)	1205 (2)	49 (1)
C(4)	6580 (2)	4387 (2)	2311 (2)	74 (1)
C(5)	6107 (3)	3328 (2)	2362 (2)	94 (2)
C(6)	5451 (3)	2908 (2)	1446 (2)	85 (1)
C(7)	4490 (2)	3688 (2)	974 (2)	61 (1)
C(8)	3485 (2)	3379 (2)	311 (2)	77 (1)
C(9)	2573 (2)	4056 (2)	-137 (2)	77 (1)
C(10)	2669 (2)	5092 (2)	97 (1)	60 (1)
C(11)	3667 (2)	5444 (2)	762 (1)	48 (1)
C(12)	3829 (2)	6506 (2)	1018 (1)	45 (1)
C(13)	4912 (2)	7974 (1)	1929 (1)	47 (1)
C(14)	4849 (2)	8281 (2)	2822 (2)	59 (1)
C(15)	4914 (2)	9313 (2)	3086 (2)	67 (1)
C(16)	5080 (2)	10048 (2)	2439 (2)	74 (1)
C(17)	5187 (2)	9761 (2)	1535 (2)	69 (1)
C(18)	5077 (2)	8734 (2)	1285 (1)	57 (1)
C(19)	1722 (2)	8861 (1)	840 (2)	48 (1)
C(20)	1847 (2)	9397 (2)	1663 (2)	57 (1)
C(21)	1862 (2)	10470 (2)	1632 (2)	72 (1)
C(22)	1775 (2)	10964 (2)	804 (2)	82 (1)
C(23)	1677 (2)	10410 (2)	-12 (2)	84 (1)
C(24)	1655 (2)	9352 (2)	-4 (1)	65 (1)
N	5564 (2)	5108 (1)	1873 (1)	54 (1)
S	1638 (1)	7508 (1)	876 (1)	55 (1)
O(1)	6620 (1)	6409 (1)	2713 (1)	73 (1)
O(2)	2953 (1)	7198 (1)	509 (1)	50 (1)
O(3)	1705 (1)	7147 (1)	1803 (1)	71 (1)
O(4)	626 (1)	7159 (1)	181 (1)	85 (1)

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

C(1)—C(2)	1.469 (3)	C(1)—C(12)	1.337 (3)
C(1)—C(13)	1.488 (3)	C(2)—N	1.383 (3)
C(2)—O(1)	1.225 (2)	C(3)—C(7)	1.396 (3)
C(3)—C(11)	1.408 (3)	C(3)—N	1.399 (3)
C(4)—C(5)	1.461 (4)	C(4)—N	1.488 (3)
C(5)—C(6)	1.512 (4)	C(5)—C(7)	1.518 (3)
C(6)—C(8)	1.381 (3)	C(8)—C(9)	1.387 (3)
C(9)—C(10)	1.380 (4)	C(10)—C(11)	1.395 (3)
C(11)—C(12)	1.426 (3)	C(12)—O(2)	1.413 (2)
S—O(2)	1.611 (2)	S—O(3)	1.427 (2)
S—O(4)	1.429 (2)	S—C(19)	1.751 (2)
C(2)—C(1)—C(12)	119.0 (2)	C(2)—C(1)—C(13)	117.3 (2)
C(12)—C(1)—C(13)	123.7 (2)	C(1)—C(2)—N	116.3 (2)
C(1)—C(2)—O(1)	122.8 (2)	N—C(2)—O(1)	120.9 (2)
C(7)—C(3)—C(11)	120.3 (2)	C(7)—C(3)—N	121.0 (2)
C(11)—C(3)—N	118.7 (2)	C(5)—C(4)—N	112.3 (2)
C(4)—C(5)—C(6)	113.8 (2)	C(5)—C(6)—C(7)	110.3 (2)
C(3)—C(7)—C(6)	121.4 (2)	C(3)—C(7)—C(8)	117.7 (2)
C(6)—C(7)—C(8)	120.9 (2)	C(7)—C(8)—C(9)	123.4 (2)
C(8)—C(9)—C(10)	118.4 (2)	C(9)—C(10)—C(11)	120.5 (2)
C(3)—C(11)—C(10)	119.8 (2)	C(3)—C(11)—C(12)	117.2 (2)
C(10)—C(11)—C(12)	123.0 (2)	C(1)—C(12)—C(11)	124.4 (2)
C(1)—C(12)—O(2)	120.2 (2)	C(11)—C(12)—O(2)	115.3 (2)
C(2)—N—C(3)	124.4 (2)	C(2)—N—C(4)	115.8 (2)
C(3)—N—C(4)	119.7 (2)	C(19)—S—O(2)	100.9 (1)
C(19)—S—O(3)	111.0 (1)	O(2)—S—O(3)	108.5 (1)
C(19)—S—O(4)	109.2 (1)	O(2)—S—O(4)	105.7 (1)
O(3)—S—O(4)	119.7 (1)	C(12)—O(2)—S	120.5 (1)

Table 2.* Fig. 1 contains a perspective view with the atoms labelled.

Related literature. Benzenesulfonation of 6-hydroxy-5-phenyl-2,3-dihydro-3a-azaphenalen-4-one (3) yields, in principle, either of the isomeric compounds (2) or (4) (Ollis, Ramsden & Stanforth, 1985) as part of the synthetic route to the novel cross-conjugated heterocyclic mesomeric betaine (1) (Ollis, Price & Stanforth, 1992). This crystal structure identifies the C-3 atom as the site of sulfonation and (2) as the only isomeric product of the above reaction.



* Lists of structure factors, anisotropic thermal parameters, full bond lengths and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54262 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the third S—O distance [1.611 (2) \AA] is linked to the substitution site.

Experimental. Colourless crystal, size 0.32 \times 0.44 \times 0.48 mm on glass fibre, Stoe-Siemens diffractometer, unit-cell parameters from 2θ values of 32 reflections (20–25 $^\circ$) measured at $\pm\omega$. Data collection in ω/θ -scan mode with on-line profile fitting (Clegg, 1981), $2\theta_{\text{max}} = 50^\circ$, index ranges $h - 12$ to 12 , $k 0$ to 15 , $l 0$ to 17 , together with some equivalents. No significant variation in intensities of three standard reflections, no absorption correction, 4212 reflections measured, 3481 unique, 2794 with $F > 4\sigma_c(F)$, $R_{\text{int}} = 0.026$. Solution by direct methods and difference syntheses, blocked-cascade least-squares refinement on F , weighting $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 9 - 83G + 152G^2 - 17H + 9H^2 + 93GH$, [$G = F_c/F_{\text{max}}$, $H = \sin\theta/\sin\theta_{\text{max}}$ (Wang & Robertson, 1985)], anisotropic thermal parameters for all non-H atoms, H atoms constrained with C—H = 0.96 \AA , H—C—H = 109.5 $^\circ$, aromatic H atom on ring angle external bisectors, $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, extinction parameter $x = 7.6(1) \times 10^{-6}$ [$F'_c = F_c/(1 + xF_c^2/\sin 2\theta)^{1/4}$]. $R = 0.0515$, $wR = 0.0173$, $S = 1.19$ for 272 parameters, mean $\Delta/\sigma = 0.018$, max. $\Delta/\sigma = 0.083$, $(\Delta\rho)_{\text{max}} = 0.044$, $(\Delta\rho)_{\text{min}} = -0.42 \text{ e \AA}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp 99, 149); *SHELXTL* (Sheldrick, 1985) and local computer programs.

Final atomic coordinates and U_{eq} 's are given in Table 1 with selected bond lengths and angles in

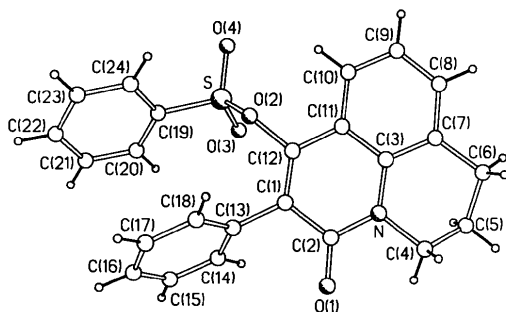


Fig. 1. A perspective view of (2) with atomic labelling.

The structures of the related cross-conjugated heterocyclic mesomeric betaines (5) (Kratky & Kappe, 1981) (6) (Debaerdemaeker & Friedrichsen, 1982) and (7) (Raston & White, 1984) and also of the pseudo cross-conjugated heterocyclic mesomeric betaine (8) (Potts, Murphy, DeLuca &

Kuehnlung, 1988), have all been confirmed by X-ray investigations.

References

- CLEGG, W. (1981). *Acta Cryst.* **A37**, 22–28.
 DEBAERDEMAEKER, T. & FRIEDRICHSEN, W. (1982). *Z. Naturforsch. Teil B*, **37**, 217–221.
 KRATKY, C. & KAPPE, T. (1981). *J. Heterocycl. Chem.* **18**, 881–884.
 OLLIS, W. D., PRICE, B. J. & STANFORTH, S. P. (1992). In preparation.
 OLLIS, W. D., RAMSDEN, C. A. & STANFORTH, S. P. (1985). *Tetrahedron*, **41**, 2239–2329.
 POTTS, K. T., MURPHY, P. M., DELUCCA, M. R. & KUEHNUNG, W. R. (1988). *J. Org. Chem.* **53**, 2898–2910.
 RASTON, C. L. & WHITE, A. H. (1984). *Aust. J. Chem.* **37**, 2577–2582.
 SHELDRICK, G. M. (1985). *SHELXTL Users Manual*. Revision 5.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.
 WANG, H. & ROBERTSON, R. E. (1985). *Structure and Statistics in Crystallography*, edited by A. J. C. WILSON, pp. 125–136. New York: Adenine Press.

Acta Cryst. (1991). **C47**, 2505–2506

Structure of 2-Azacycloheptanone Azine

BY R. W. H. SMALL

The Chemistry Department, The University, Lancaster LA1 4YA, England

(Received 15 May 1991; accepted 14 June 1991)

Abstract. $C_{12}H_{22}N_4$, $M_r = 222.34$, triclinic, $P\bar{1}$, $a = 10.80$ (1), $b = 6.00$ (1), $c = 5.410$ (5) Å, $\alpha = 113.16$ (6), $\beta = 77.21$ (5), $\gamma = 92.84$ (7)°, $V = 313.04$ Å³, $Z = 1$, $D_x = 1.175$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.685$ cm⁻¹, $F(000) = 122.0$, $T = 290$ K, $R = 0.039$ for 881 unique observed reflexions. The molecule lies on a centre of symmetry. The central N—N bond of the azine system is 1.419 (2) Å and the N—C bond to the ring is 1.297 (2) Å; the (N=CNC)₂ system is planar to within 0.02 Å, which together with the shortened distances indicates a weak π system. This results in a close intramolecular NH...N approach, H...N = 2.18 (2), N...N = 2.572 (2) Å.

Experimental. The compound was supplied by Dr S. W. Breuer. Crystals were readily deformable thin plates, tabular on (100), showing the forms {100}, {010}, {001}, {011}. Cell dimensions, initially from Weissenberg and precession photographs [$\lambda(\text{Cu } K\alpha) = 1.542$ Å], refined from setting angles of 20 reflexions in the range $10 < 2\theta < 40^\circ$ on Stadi-2 two-circle diffractometer (graphite-monochromatized Mo $K\alpha$).

This was also used for measurement of 1122 unique intensities, from a crystal of dimensions $0.3 \times 0.14 \times 0.07$ mm, for the layers $hk0$ to $hk6$, $h - 11$ to 12, $k - 7$ to 6, max. $\sin\theta/\lambda = 0.6$ Å⁻¹; variable ω scan, $2\theta'$ fixed, stationary background count, standard measured every 20 reflexions, intensity variation $< 5\%$ corrected for by linear interpolation. Lp corrections but not absorption corrections were applied, C- and N-atom positions were obtained by the use of the direct-methods program *EEES* of *SHELX76* (Sheldrick, 1976), which was used for all calculations. H-atom positions were obtained from ΔF maps. Full-matrix least-squares refinement of coordinates, U_{ij} of C and N atoms and U_{iso} of H atoms, using F values of 881 reflexions for which $I > 3\sigma(I)$ proceeded until Δ/σ was < 0.003 . At an intermediate stage of the refinement interlayer scale factors were refined. At the conclusion of the refinement of 123 parameters the largest features on the F map lay between -0.18 and 0.13 e Å⁻³, $R = 0.039$, $wR = 0.045$, $S = 1.514$, observation/parameter ratio $Q = 7.16$ and $w = 2.018/[\sigma^2(F) + 0.00098F^2]$. Atomic scattering factors from *International Tables for X-ray*