

The Structure of *N*-(3-Bromo-1-methyl-2-piperidylidene)benzenesulfonamide

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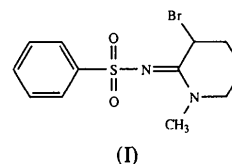
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Abstract. C₁₂H₁₅BrN₂O₂S, $M_r = 331.23$, orthorhombic, *Pbca*, $a = 15.978(2)$, $b = 19.391(4)$, $c = 8.783(1)$ Å, $V = 2721.2$ Å³, $Z = 8$, $D_m = 1.62$, $D_x = 1.62$ Mg m⁻³, $\lambda(\text{CuK}\alpha) = 1.5418$ Å, $\mu = 5.82$ mm⁻¹, $F(000) = 1344$, $T = 288\text{--}290$ K, $R = 0.050$ for 1746 unique reflections. The two C(2)–N bonds are of equivalent lengths [1.32(2) Å] and the four atoms of the N=C(–C)–N moiety are coplanar, indicating delocalization of the exocyclic double bond. The partial-double-bond character of the endocyclic C(2)–N(1) bond causes the piperidylidene ring to adopt a pseudo-half-chair conformation. The Br atom is in a pseudo-axial position on the chiral C atom of the piperidylidene ring.

Introduction. *N*-(3-Bromo-1-methyl-2-piperidylidene)benzenesulfonamide (US Patent No. 4468403) exhibits analgesic activity similar to that of the morphine alkaloids (Warren & Knaus, 1982). The activity can be blocked by Nalaxone[®] suggesting that it interacts with the same receptor as morphine and its derivatives. The title compound is also an intermediate in the synthesis of possible histamine H₂-receptor antagonists which, as effective inhibitors of gastric-acid secretion, are of clinical interest in the treatment of duodenal ulcers and related conditions (Ondrus, Pednekar & Knaus, 1985). Because further synthesis of the final antiulcer compound will involve substitution at the C atom to which Br is bonded, the present study was undertaken to determine the relative position of the Br atom, as well as to characterize the unique S–N=C–N linkage of the molecule.

Experimental. Colorless transparent crystals of the title compound (I) were obtained by slow evaporation of a 70/30 dichloromethane/diethyl ether solution. D_m determined by flotation in a bromobenzene/iodomethane mixture. Systematic absences from Weissenberg photographs uniquely defined the space group as *Pbca*. Intensity data collected from a single crystal (0.20 × 0.20 × 0.40 mm) on an Enraf–Nonius CAD-4

diffractometer with Ni-filtered CuK α radiation. Unit-cell parameters: least-squares refinement of 19 centered reflections in range $23.4 \leq 2\theta \leq 44.8^\circ$. Intensity measurements from an $\omega/2\theta$ scan of 1.0° at 6°min^{-1} . Five monitor reflections were measured periodically throughout the data collection. Absorption corrections (North, Phillips & Mathews, 1968); max. applied 1.841; min. 1.0. Max. $\sin\theta/\lambda$ 0.5588 \AA^{-1} . Ranges of hkl were $0 \leq h \leq 18$, $0 \leq k \leq 21$, $-9 \leq l \leq 9$. 4700 reflections measured, symmetry-equivalent reflections were averaged to 2303 ($R_{\text{int}} = 0.053$), 1746 unique, 320 systematically extinct, 237 reflections with $I < 2\sigma(I)$ were not used in the solution or refinement of the structure. $\sigma(I)^2 = I + c^2I^2 + (t_r/t_{\text{Bk}})^2(\sum \text{Bk} + c^2\sum \text{Bk}^2)$, where I = total intensity, Bk = total background count, t_r = time for the intensity measurement, t_{Bk} = time for the background measurement, c = instrument instability constant = 0.01.



The structure was solved by Patterson and heavy-atom Fourier methods. *ORFLS* full-matrix least-squares refinement on F with anisotropic thermal parameters for non-H atoms (Busing, Martin & Levy, 1962). Electron density corresponding to all H atoms observable from a difference Fourier synthesis. All H atoms were fitted by ideal geometry and assigned the isotropic thermal parameters of their covalently bonded C atoms. These H parameters were not further refined. Final $R = 0.050$, $wR = 0.059$, $S = 2.97$. Weights were obtained from counting statistics with $w^{1/2} = (2F_o/\sigma)$. Final $(\Delta/\sigma)_{\text{max}} = 0.011$. $(\Delta\rho)_{\text{max}} = 0.37$ and $(\Delta\rho)_{\text{min}} = -0.62 \text{ e \AA}^{-3}$; both are associated with the Br atom. Programs used were the *XRAY70* system (Stewart, Kundell & Baldwin, 1970). Scattering factors for C, N, O, S, Br from Cromer & Mann (1968), for H from Mason & Robertson (1966).

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Discussion. The refined atomic coordinates of the title compound are presented in Table 1.* The bond lengths and angles are given in Table 2. An ORTEP stereo drawing, illustrating the atomic numbering and molecular conformation, is shown in Fig. 1. The two structural features of particular interest are the delocalization of the exocyclic C(2)=N(2) bond between C(2) and N(1), and the position of the Br atom.

The C(2)—N(2) bond distance is 1.31 Å, whereas C(2)—N(1) is 1.33 Å. Both are longer than the 1.28 Å

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43492 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters (\AA^2) (e.s.d.'s in parentheses)

	x	y	z	B_{eq}^*
C(2)	2998 (4)	3933 (3)	2690 (1)	2.03 (2)
C(3)	3899 (4)	3750 (3)	2561 (8)	2.21 (2)
C(4)	4225 (4)	3704 (4)	933 (1)	3.12 (1)
C(5)	3947 (5)	4324 (4)	19 (8)	3.67 (2)
C(6)	2997 (5)	4361 (4)	-7 (6)	3.79 (2)
C(7)	1720 (4)	4366 (4)	1536 (9)	3.78 (2)
C(8)	1815 (4)	3222 (3)	6141 (7)	2.69 (1)
C(9)	1383 (4)	3716 (4)	6985 (8)	3.12 (2)
C(10)	609 (5)	3559 (4)	7539 (9)	3.68 (2)
C(11)	236 (5)	2916 (4)	7255 (9)	4.14 (3)
C(12)	671 (5)	2425 (4)	6388 (12)	5.53 (3)
C(13)	1462 (5)	2584 (4)	5824 (10)	4.41 (3)
N(1)	2619 (3)	4226 (3)	1495 (6)	2.47 (1)
N(2)	2528 (3)	3828 (3)	3897 (6)	2.53 (2)
O(1)	3249 (3)	2789 (3)	5080 (7)	4.86 (2)
O(2)	3197 (4)	3901 (3)	6477 (6)	5.33 (2)
S(1)	2814 (1)	3425 (1)	5406 (2)	2.81 (1)
Br(1)	4519 (1)	4489 (1)	3643 (1)	3.55 (2)

$$* B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2).$$

Table 2. Bond lengths (\AA) and angles ($^\circ$) (e.s.d.'s in parentheses)

C(2)—C(3)	1.50 (1)	C(3)—Br(1)	1.98 (1)
C(3)—C(4)	1.53 (1)	S(1)—O(1)	1.44 (1)
C(4)—C(5)	1.51 (1)	S(1)—O(2)	1.45 (1)
C(5)—C(6)	1.52 (1)	S(1)—C(8)	1.77 (1)
C(6)—N(1)	1.47 (1)	C(8)—C(9)	1.39 (1)
N(1)—C(7)	1.46 (1)	C(9)—C(10)	1.36 (1)
N(1)—C(2)	1.33 (1)	C(10)—C(11)	1.41 (1)
C(2)—N(2)	1.31 (1)	C(11)—C(12)	1.40 (2)
N(2)—S(1)	1.61 (1)	C(12)—C(13)	1.39 (1)
C(3)—C(2)—N(1)	118 (1)	C(13)—C(8)	1.39 (1)
C(3)—C(2)—N(2)	125 (1)	C(2)—N(2)—S(1)	126 (1)
N(1)—C(2)—N(2)	117 (1)	N(2)—S(1)—O(1)	113 (1)
C(4)—C(3)—C(2)	114 (1)	N(2)—S(1)—O(2)	110 (1)
Br(1)—C(3)—C(4)	109 (1)	O(1)—S(1)—C(8)	109 (1)
Br(1)—C(3)—C(2)	106 (1)	O(2)—S(1)—C(8)	107 (1)
C(3)—C(4)—C(5)	110 (1)	O(1)—S(1)—O(2)	118 (1)
C(4)—C(5)—C(6)	110 (1)	S(1)—C(8)—C(9)	119 (1)
C(5)—C(6)—N(1)	113 (1)	S(1)—C(8)—C(13)	119 (1)
C(6)—N(1)—C(7)	113 (1)	C(9)—C(8)—C(13)	121 (1)
C(6)—N(1)—C(2)	127 (1)	C(9)—C(10)—C(11)	121 (1)
C(7)—N(1)—C(2)	120 (1)	C(10)—C(11)—C(12)	119 (1)
		C(11)—C(12)—C(13)	119 (1)
		N(2)—S(1)—C(8)	99 (1)
		C(8)—C(9)—C(10)	119 (1)

bond distance of C=N found in oximes and imines (Levine, 1963), but shorter than the 1.35 Å C—N bond length found in *N,N*-dimethylformamide (Cobbedick & Small, 1973). Additionally, the C(6)—N(1)—C(2)—C(3) torsional angle has a value of 3.7(9) $^\circ$; least-squares-plane analysis indicates that the four atoms C(3), C(2), N(2) and N(1) lie in a plane ($\sigma = 0.001 \text{ \AA}$; $\chi^2 = 0.08$) and that the entire N(1), C(2), C(3), C(6), C(7), N(2) moiety adopts a relatively planar configuration ($\sigma = 0.025 \text{ \AA}$; $\chi^2 = 80.16$). These observations suggest that the formal C=N bond between C(2) and N(2) is resonance stabilized through the formation of a partial double bond between C(2) and N(1). Similar bond-delocalization effects have been observed in compounds related to the title compound. Ultraviolet and infrared spectral analysis have shown the presence of a tautomeric equilibrium between *N*-(1*H*-2-piperidylidene)cyanomethoxyformamide and *N*-(3,4,5,6-tetrahydro-2-pyridyl)cyanomethoxyformamide (Ondrus, Knaus & Giam, 1979). It may be noted that the S atom does not lie in the above mentioned N(1), C(2), N(2), C(6), C(7) plane [deviation = -0.17(3) Å]. The distances of C(4) and C(5) from this same plane are 0.28 (1) and -0.45 (1) Å respectively.

The pseudo-half-chair conformation of the piperidylidene ring is evident from Fig. 1. The Br atom lies in the unusual pseudo-axial position of this ring, probably to avoid steric-hindrance effects with the benzenesulfonamide substituent. Fig. 2 is a Newman projection looking down the C(2)—C(3) bond, with the conformational angles indicated. The Br atom lies 22 $^\circ$ closer to N(2) than to N(1), and is 19 $^\circ$ off the normal to the N(2), N(1), C(2), C(3) plane defined above.

This structure was determined as part of the requirements for a course in X-ray structure determination. We wish to thank Dr A. Sielecki, M. Fujinaga and Dr A. K. S. Muir for stimulating discussions and helpful advice and Dr M. Cowie for the use of Weissenberg cameras and generators. We are grateful to the Medical Research Council of Canada (Grant No. MT-4888) for financial support.

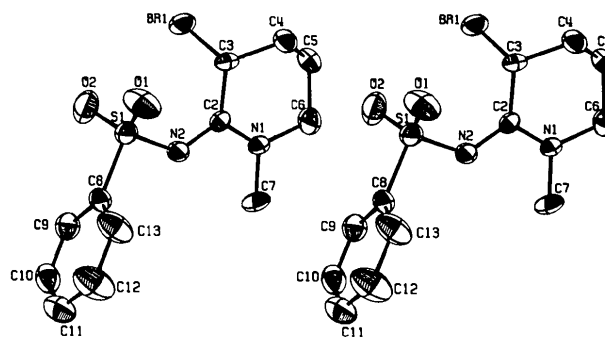


Fig. 1. ORTEP drawing (Johnson, 1976) of the title compound. The thermal ellipsoids enclose 50% probability.

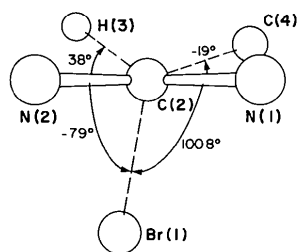


Fig. 2. Newman projection looking down the C(2)–C(3) bond.

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β -Propiolactam (1-Aza-2-cyclobutanone) at 170 K

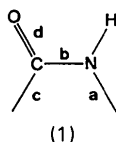
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Abstract. C_3H_5NO , $M_r = 71.08$, space group $P\bar{1}$, $a = 5.011$ (2), $b = 5.188$ (2), $c = 7.395$ (4) Å, $\alpha = 107.82$ (4), $\beta = 106.04$ (4), $\gamma = 99.23$ (3)°, $V = 169.48$ Å³ at 170 K, $Z = 2$, $D_x = 1.39$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu = 0.66$ cm⁻¹, $F(000) = 76$, $R = 0.037$ for 595 observed reflections. The four-membered ring is exactly planar (to within 0.001 Å), and the carbonyl O and amide H atoms also lie almost exactly in this plane [displacements -0.010 (1) and 0.005 (20) Å, respectively]. The molecules form centrosymmetric dimers linked by N–H...O hydrogen bonds.

Introduction. The recent synthesis of β -propiolactam by Pfaendler & Hoppe (1985) provides an opportunity to extend our knowledge about the structural details of the *cis* amide group (1) in the direction of small ring size.



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Experimental. A sample provided by Professor H. R. Pfaendler (University of Munich) was recrystallized from tetrachloromethane. Needles, crystal size $0.15 \times 0.25 \times 0.70$ mm, handled in dry atmosphere and enclosed in capillary; Enraf–Nonius CAD-4 diffractometer with cooling device; Mo radiation, graphite monochromator; ω – θ scan; unit-cell dimensions by least-squares fit to setting angles of 14 automatically centred reflections with $6 < \theta < 15^\circ$. No absorption correction. Max. $(\sin \theta)/\lambda$ in intensity measurements 0.64 Å⁻¹. Three data sets measured: at room temperature, 223 K and 170 K (see Table 1). All lead to similar results, and only the 170 K measurements and results are discussed here in detail as they are slightly more accurate than the others. Three standard reflections, ca 10% intensity loss during measurement period. 800 reflections measured, 741 unique, $R_{int} = 0.028$, 595 counted as observed [$I > 3\sigma(I)$], index range h

Table 1. Cell dimensions for β -propiolactam at three temperatures

T (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
170	5.011 (2)	5.188 (2)	7.395 (4)	107.82 (4)	106.04 (4)	99.23 (3)
223	5.038 (1)	5.199 (1)	7.402 (3)	106.77 (3)	106.53 (3)	99.37 (3)
293 (RT)	5.077 (1)	5.220 (2)	7.458 (2)	107.00 (3)	106.07 (3)	99.54 (3)