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Conformation of *N*-(*p*-Toluenesulfonyl)azacyclotridecane

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Abstract. $C_{19}H_{31}NO_2S$, $M_r = 337.56$, monoclinic, $P2_1/c$, $a = 21.284$ (2), $b = 5.541$ (1), $c = 15.992$ (2) Å, $\beta = 94.44$ (2)°, $V = 1880$ (1) Å³, $Z = 4$, $D_x = 1.19$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 1.55$ mm⁻¹, $F(000) = 736$, $T = 293$ K, $R = 0.043$ for 3112 independent observed reflections. The 13-membered ring adopts the [13333] conformation with C–C–C angles enlarged beyond tetrahedral, mean 114.3°. C(*sp*³)–C(*sp*³) bonds have a mean length of 1.523 Å. The sulfonamide N atom is distinctly pyramidal in character, with the N–S bond inclined at 28.5 (1)° to the C–N–C plane.

Introduction. The conformational properties of even-numbered medium-ring compounds (Dunitz, 1968; Anet, St. Jacques, Henrichs, Cheng, Krane & Wong, 1974) have been investigated to a greater extent than those of odd-numbered rings and only very limited information is available about the conformations of 13-membered rings (Dale, 1973; Anet & Rawdah, 1978). The unit cell of dimethyl 1-hydroxycyclotridecylphosphonate has two molecules in the asymmetric crystal unit, one with a well defined conformation and the other distinctly disordered (Samuel & Weiss, 1969); the ordered molecule has the [13333] conformation that Anet & Rawdah (1978) calculated to be the lowest-energy form of cyclotridecane. The predominant conformation of α,ω -bis(methyl dodeca-1,12-diylammonio)hexane dibromide, which displays some conformational disorder in the solid, is also the [13333] form (Rubin, Williamson, Takeshita, Menger, Anet, Bacon & Allinger, 1984). Hexacosamethylcyclotridecasilane (Me₂Si)₁₃ adopts a conformation that does not correspond to any of the conformations considered for cyclotridecane (Shafiee, Haller & West, 1986).

An X-ray study of the title compound was undertaken to provide conformational details of the azacyclotridecane ring.

Experimental. Colourless crystal, dimensions 0.20 × 0.20 × 0.40 mm. Enraf–Nonius CAD-4 diffractometer, Cu *K*α radiation. Cell dimensions from setting angles of 25 independent reflections with θ 18–25°. 4246 intensities surveyed in the range θ 2–72°; h –26–26, k 0–6, l 0–19; 3112 independent reflections with $I > 2.5\sigma(I)$, $R_{\text{int}} = 0.021$. Two reference reflections monitored periodically showed no significant variation in intensity. No absorption correction. Structure determined by direct phasing using *MITHRIL* (Gilmore, 1984). H atoms located in a difference Fourier synthesis. Full-matrix least-squares calculations on *F* with anisotropic thermal parameters for C, N and O atoms and isotropic for H atoms. Convergence at R 0.043, wR 0.056, S 2.72 for 332 parameters, $\Delta/\sigma < 0.35$ for C, N and O atoms, $w = 1/\sigma^2(|F_o|)$. Final $\Delta\rho$ max. 0.22, min. –0.46 e Å⁻³. Scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations on an SEL 32/27 computer with the *GX* system of programs (Mallinson & Muir, 1985).

Discussion. Atomic coordinates are listed in Table 1 and molecular dimensions in Table 2.* Fig. 1, drawn

* Lists of coordinates and bond lengths and angles for H atoms, structure factors, anisotropic thermal parameters and torsional angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43620 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

with *ORTEP* (Johnson, 1965), illustrates the molecular geometry; there is no indication of conformational disorder.

The torsional angles for the 13-membered ring are listed in Table 3 along with those calculated by molecular mechanics for the [13333] conformation of cyclotridecane (Anet & Rawdah, 1978). There is good agreement between the experimental and theoretical results, the differences ranging from 1 to 10° with a mean difference of only 4°.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²)

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	U_{eq}
C(1)	0.72369 (8)	0.37662 (36)	0.78299 (12)	0.047
C(2)	0.66452 (8)	0.22724 (36)	0.79032 (13)	0.050
C(3)	0.60564 (9)	0.34027 (46)	0.74668 (13)	0.061
C(4)	0.58269 (10)	0.56797 (44)	0.78963 (15)	0.063
C(5)	0.55101 (9)	0.52176 (43)	0.87013 (14)	0.061
C(6)	0.54180 (10)	0.74653 (48)	0.92370 (18)	0.072
C(7)	0.60209 (12)	0.83437 (43)	0.97206 (17)	0.069
C(8)	0.62482 (11)	0.67753 (46)	1.04570 (14)	0.064
C(9)	0.69114 (12)	0.73515 (59)	1.08381 (15)	0.074
C(10)	0.74309 (10)	0.71908 (42)	1.02369 (15)	0.061
C(11)	0.74173 (9)	0.48895 (36)	0.97258 (12)	0.052
C(12)	0.79281 (9)	0.48004 (36)	0.91122 (12)	0.050
C(13)	0.87058 (7)	0.32018 (30)	0.73624 (10)	0.042
C(14)	0.90796 (8)	0.51200 (37)	0.76590 (12)	0.053
C(15)	0.93749 (9)	0.65348 (38)	0.70970 (14)	0.059
C(16)	0.93041 (8)	0.61007 (35)	0.62443 (12)	0.054
C(17)	0.89273 (10)	0.42104 (42)	0.59615 (13)	0.063
C(18)	0.86270 (10)	0.27533 (40)	0.65105 (12)	0.057
C(19)	0.96247 (14)	0.76703 (61)	0.56307 (22)	0.079
S	0.83093 (2)	0.13987 (7)	0.80645 (3)	0.044
N	0.77636 (6)	0.30447 (26)	0.84372 (9)	0.043
O(1)	0.79897 (6)	-0.04753 (23)	0.75808 (8)	0.057
O(2)	0.87463 (6)	0.07751 (25)	0.87541 (8)	0.058

Table 2. *Interatomic distances* (Å) *and angles* (°)

C(1)–C(2)	1.519 (3)	C(1)–N	1.480 (3)
C(2)–C(3)	1.521 (3)	C(3)–C(4)	1.534 (4)
C(4)–C(5)	1.520 (4)	C(5)–C(6)	1.533 (4)
C(6)–C(7)	1.526 (4)	C(7)–C(8)	1.513 (4)
C(8)–C(9)	1.527 (4)	C(9)–C(10)	1.523 (4)
C(10)–C(11)	1.514 (4)	C(11)–C(12)	1.521 (3)
C(12)–N	1.475 (3)	C(13)–C(14)	1.389 (3)
C(13)–C(18)	1.382 (3)	C(13)–S	1.766 (2)
C(14)–C(15)	1.380 (3)	C(15)–C(16)	1.381 (3)
C(16)–C(17)	1.374 (3)	C(16)–C(19)	1.513 (4)
C(17)–C(18)	1.385 (4)	S–N	1.626 (2)
S–O(1)	1.435 (2)	S–O(2)	1.429 (2)
C(2)–C(1)–N	113.1 (2)	C(1)–C(2)–C(3)	113.5 (2)
C(2)–C(3)–C(4)	114.4 (2)	C(3)–C(4)–C(5)	114.7 (2)
C(4)–C(5)–C(6)	114.9 (2)	C(5)–C(6)–C(7)	113.8 (2)
C(6)–C(7)–C(8)	114.7 (3)	C(7)–C(8)–C(9)	114.9 (3)
C(8)–C(9)–C(10)	115.4 (2)	C(9)–C(10)–C(11)	113.9 (2)
C(10)–C(11)–C(12)	113.0 (2)	C(11)–C(12)–N	110.6 (2)
C(14)–C(13)–C(18)	119.8 (2)	C(14)–C(13)–S	120.3 (2)
C(18)–C(13)–S	119.8 (2)	C(13)–C(14)–C(15)	119.3 (2)
C(14)–C(15)–C(16)	121.6 (2)	C(15)–C(16)–C(17)	118.3 (2)
C(15)–C(16)–C(19)	121.3 (3)	C(17)–C(16)–C(19)	120.4 (3)
C(16)–C(17)–C(18)	121.5 (2)	C(13)–C(18)–C(17)	119.6 (2)
C(13)–S–N	107.8 (1)	C(13)–S–O(1)	107.3 (1)
C(13)–S–O(2)	108.2 (1)	N–S–O(1)	106.3 (1)
N–S–O(2)	107.1 (1)	O(1)–S–O(2)	119.6 (1)
C(1)–N–C(12)	115.3 (2)	C(1)–N–S	115.9 (2)
C(12)–N–S	120.2 (2)		

The C(*sp*³)–C(*sp*³) bond lengths are 1.513–1.534 Å, with a mean of 1.523 Å. There is undoubtedly some librational shortening, since the mean C(*sp*³)–C(*sp*³) bond lengths in cycloundecanone phenylsemicarbazone at 135 K and cycloundecylmethyl naphthylurethane at 120 K are 1.531 and 1.536 Å respectively (Freer, Gilmore, Russell, Sim & White, unpublished results). The C–C–C angles in the azacyclotridecane ring range from 113.0 to 115.4°, mean 114.3°. Though the H–C–H angles of 99.6–114.4° are subject to fairly large errors, the mean value of 106.9° is undoubtedly significantly smaller than tetrahedral. For comparison, mean C–C(*sp*³)–C and H–C(*sp*³)–H angles are 115.6 and 105.9° in cycloundecanone phenylsemicarbazone and 115.2 and 103.9° in cycloundecylmethyl naphthylurethane (Freer, Gilmore, Russell, Sim & White, unpublished results). In cyclodecane-1,6-diol the C–C–C angles are 113.4–120.1° and the H–C–H angles are 104.7–106.7° (Ermer, Dunitz & Bernal, 1973).

The N atom has pyramidal rather than planar geometry, the N–S bond being inclined at 28.5 (1)° to the C–N–C plane. The distinction between pyramidal arylsulfonamide and essentially planar amide N atoms is a general phenomenon, several other sulfonamides having similar pyramidal N atoms (Cox, McCabe, Milne & Sim, 1985). There is a notable conformational difference between *N,N'*-diacyl and *N,N'*-diarylsulfonyl derivatives of 3,7-diazabicyclo[3.3.1]nonan-

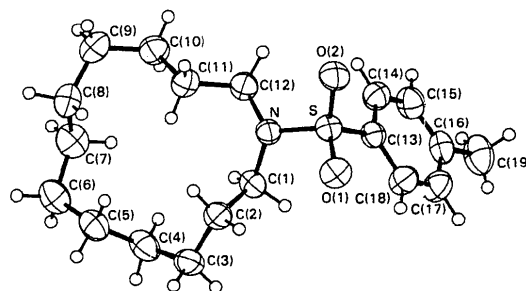


Fig. 1. Molecular structure and atomic numbering. The thermal ellipsoids of the C, N, O and S atoms are drawn at the 50% probability level and H atoms are represented by spheres of radius 0.1 Å.

Table 3. *Comparison of the torsional angles* (°) *in the 13-membered ring* (column A) *with molecular-mechanics results for cyclotridecane* (column B)

	A	B	A	B
N–1–2–3	164.0 (3)	160	7–8–9–10	-58.0 (3)
1–2–3–4	-70.2 (3)	-75	8–9–10–11	-48.7 (3)
2–3–4–5	-74.1 (3)	-77	9–10–11–12	178.3 (3)
3–4–5–6	166.5 (3)	170	10–11–12–N	-159.4 (3)
4–5–6–7	-75.7 (3)	-73	11–12–N–1	70.8 (2)
5–6–7–8	-72.7 (3)	-71	12–N–1–2	-110.2 (2)
6–7–8–9	168.7 (4)	168		-100

9-one, the former adopting the twin-chair and the latter the boat-chair conformation because of the different N...N lone-pair repulsions (McCabe, Milne & Sim, 1985).

The out-of-plane angle of the N-S bond in the title compound, 28.5°, is smaller than the N-C out-of-plane angle of 58.8° in cyclopropylamine (Rall, Harmony, Cassada & Staley, 1986) and 37.5° in aniline (Lister, Tyler, Høg & Larsen, 1974). The out-of-plane angle of the N-X bond in a molecule NX₃ with C_{3v} symmetry is related to the X-N-X angle by the equation

$$\varphi = \cos^{-1}[-\cos XNX/(\cos XNX/2)]^*$$

and in NH₃ where the H-N-H angle is 107.1° (Helminger, De Lucia & Gordy, 1971) the out-of-plane angle φ is 60.3°. In NMe₃ the C-N-C angle is ca 109° (Lide & Mann, 1958) and φ is therefore ca 56°. The shallower N pyramid in the arylsulfonamide is a consequence of some double-bond character in the N-S bond, 1.626 (2) Å.

I am grateful to the SERC for a grant towards the purchase of the diffractometer.

* For a molecule NX₂Y with C_s symmetry the appropriate expression for the angle between the N-Y bond and the X-N-X plane is

$$\varphi = \cos^{-1}[-\cos XNY/(\cos XNX/2)].$$

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Structure of N-Phenyl-5,6,7,8-tetrahydrobenzo[*a,i*]carbazole

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Abstract. C₂₆H₂₁N, *M_r* = 347.2, tetragonal, *P*4₁2₁2, *a* = 7.936 (1), *c* = 29.822 (3) Å, *V* = 1878.2 Å³, *Z* = 4, *D_x* = 1.229 Mg m⁻³, λ(Cu Kα) = 1.54178 Å, μ = 0.050 mm⁻¹, *F*(000) = 736, *T* = 298 K, final *R* = 0.041 for 976 observed reflections. The molecule has crystallographic twofold symmetry. The fused-ring system is non-planar, with the two halves inclined at an

angle of 30.3 (3)° along the twofold axis. The phenyl ring attached to the N atom is inclined at 112.1 (3)° to each half. The symmetry-equivalent tetrahydrobenzene rings have half-chair pucker.

Introduction. The title compound (I) was unexpectedly produced during the attempted synthesis of (III) from (II) by means of a carbene addition (Corey & Chaykovsky, 1962). A structural assignment was made

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