Crystal structure of 7-(*p*-toluenesulfonyl)-7-aza-1,4-dithiacyclononane (Ts[9]aneNS₂), C₁₃H₁₉NO₂S₃

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Abstract

C₁₃H₁₉NO₂S₃, monoclinic, *P*2₁ (No. 4), *a* = 11.7973(9) Å, *b* = 5.6054(3) Å, *c* = 11.9380(9) Å, β = 107.977(9)°, *V* = 750.9 Å³, *Z* = 2, *R*_{gt}(*F*) = 0.032, *wR*_{ref}(*F*²) = 0.083, *T* = 193 K.

Source of material

Ts[9]aneNS₂ was prepared as described by Craig et al. [1]. Diffraction quality crystals were obtained by cooling a warm saturated solution in toluene/hexane (2:1) to room temperature.

Experimental details

The structure was successfully refined in the chiral space group *P*2₁ with *Z* = 2. Thus a single conformational enantiomer is present in the crystal. The absolute structure parameter (Flack parameter) of the final model was ±0.00(8). The methylene carbon atom C6 was modeled as being disordered on two equally occupied positions. Describing C5 as positionally disordered has also

been tried but did not yield satisfactory results. The “splitting” into (equally positioned) C5A and C5B was introduced in order to properly calculate the positions of the hydrogen atoms which must be regarded disordered as a consequence of the disordering of C6.

Discussion

The overall conformation of the Ts[9]aneNS₂ molecule is very similar to the one found in the complex [(AuCl)₂(Ts[9]aneNS₂)]₂ in which each AuCl group is bonded to a thioether sulfur atom [2]. In particular, the mutual orientation of the nitrogen atom and the two sulfur atoms of the nine-membered ring is such that the molecule could act as a tridentate NS₂ ligand only after major conformational rearrangement. The bond angles at the nitrogen atom are ∠S3–N–C4 = 114.8(2)°, ∠S3–N–C5 = 116.9(2)°, and ∠C4–N–C5 = 116.8(3)° (sum: 348.5°). Hence the geometric arrangement at the N atom is that of a strongly flattened trigonal pyramid. The length of the S3–N bond (1.636(2) Å) lies between the values calculated for a S–N single bond (1.73 Å) and a S=N double bond (1.49 Å) [3]. Taken together the metrical data at the N atom indicate that the nitrogen lone pair is involved in π bonding to S3. The lengths of the bonds S3–N (1.636(2) Å), S3–O1 (1.433(2) Å), and S3–O2 (1.431(2) Å) fit very well with the average values of 1.642 Å (S–N) and 1.430 Å (S–O), respectively, which were determined from several sulfonamide structures [4]. *Gauche* conformation is observed at all ethylene C–C bonds. The corresponding torsion angles are ∠S1–C1–C2–S2 = –57.2(3)°, ∠S1–C6A–C5–N = 57.9(7)°, ∠S1–C6B–C5–N = –57.3(7)°, and ∠S2–C3–C4–N = –75.6(3)°. The transannular distances between the heteroatoms of the nine-membered ring are *d*(S1...S2) = 3.469 Å, *d*(S1...N) = 3.447 Å, and *d*(S2...N) = 3.412 Å. They cover a narrower range than in the above-mentioned gold complex where the S...S distance is 3.575 Å and the S...N distances are 3.306 Å and 3.386 Å. There are no unusual intermolecular contacts in the crystal structure of Ts[9]aneNS₂.

Table 1. Data collection and handling.

Crystal:	colorless tabular, size 0.21 × 0.38 × 0.63 mm
Wavelength:	Mo <i>K</i> _α radiation (0.71073 Å)
μ:	4.91 cm ^{–1}
Diffraction, scan mode:	Stoe IPDS, 194 exposures, Δφ = 1.6°
2θ _{max} :	51.88°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	9003, 2747
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 2570
<i>N</i> (<i>param</i>) _{refined} :	182
Programs:	SHELXS-97 [5], SHELXL-97 [6], DIAMOND [7]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1A)	2a		0.6878	−0.2702	0.6136	0.062
H(1B)	2a		0.6893	−0.1831	0.7413	0.062
H(2A)	2a		0.4963	−0.2743	0.6292	0.059
H(2B)	2a		0.5038	−0.0942	0.5283	0.059
H(3A)	2a		0.4216	0.0287	0.8534	0.045
H(3B)	2a		0.5137	−0.1632	0.8335	0.045
H(4A)	2a		0.5874	0.3112	0.9063	0.052
H(4B)	2a		0.5906	0.1062	1.0004	0.052
H(5A1)	2a	0.50	0.7389	0.3941	0.8620	0.078
H(5A2)	2a	0.50	0.8569	0.2842	0.9509	0.078
H(5B1)	2a	0.50	0.7842	0.3957	0.9251	0.078
H(5B2)	2a	0.50	0.8717	0.1930	0.9070	0.078

Table 2. Continued.

Atom	Site	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(6A1)	2a	0.50	0.8885	0.0696	0.8163	0.049
H(6A2)	2a	0.50	0.8775	0.3435	0.7825	0.049
H(6B1)	2a	0.50	0.8124	0.4321	0.7539	0.061
H(6B2)	2a	0.50	0.6771	0.3836	0.7409	0.061
H(8)	2a		0.6901	−0.0855	1.2134	0.041
H(9)	2a		0.7258	0.1597	1.3770	0.042
H(11)	2a		0.9973	0.4710	1.2939	0.054
H(12)	2a		0.9662	0.2222	1.1324	0.050
H(13A)	2a		0.9563	0.6040	1.4648	0.075
H(13B)	2a		0.8889	0.4210	1.5253	0.075
H(13C)	2a		0.8153	0.6242	1.4390	0.075

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
S(1)	2a		0.74474(7)	0.1257(2)	0.64078(6)	0.0463(4)	0.1113(8)	0.0332(3)	−0.0075(5)	0.0189(3)	0.0080(4)
S(2)	2a		0.46560(5)	0.1130(1)	0.68031(5)	0.0352(3)	0.0563(5)	0.0323(3)	0.0050(3)	0.0084(2)	0.0041(3)
S(3)	2a		0.78645(5)	−0.1174(1)	1.02358(5)	0.0304(3)	0.0366(4)	0.0315(3)	−0.0013(2)	0.0144(2)	−0.0054(2)
O(1)	2a		0.7020(2)	−0.2972(3)	1.0290(2)	0.048(1)	0.032(1)	0.0405(9)	−0.0059(8)	0.0192(8)	−0.0050(7)
O(2)	2a		0.8943(2)	−0.1854(4)	1.0010(2)	0.0379(9)	0.078(2)	0.052(1)	0.006(1)	0.0237(8)	−0.015(1)
N	2a		0.7155(2)	0.0639(4)	0.9178(2)	0.044(1)	0.039(1)	0.0275(9)	−0.0084(9)	0.0132(8)	−0.0040(8)
C(1)	2a		0.6641(3)	−0.1385(7)	0.6569(2)	0.059(2)	0.065(2)	0.037(1)	0.010(2)	0.020(1)	−0.011(1)
C(2)	2a		0.5297(2)	−0.1196(7)	0.6145(2)	0.056(2)	0.059(2)	0.035(1)	−0.006(2)	0.016(1)	−0.010(1)
C(3)	2a		0.4950(2)	0.0093(5)	0.8307(2)	0.035(1)	0.047(2)	0.035(1)	0.011(1)	0.017(1)	0.005(1)
C(4)	2a		0.5965(2)	0.1372(6)	0.9207(2)	0.057(2)	0.043(2)	0.031(1)	0.016(1)	0.013(1)	−0.006(1)
C(5A)	2a	0.50	0.7877(4)	0.2472(7)	0.8814(3)	0.099(3)	0.053(2)	0.045(2)	−0.043(2)	0.026(2)	−0.007(1)
C(5B)	2a	0.50	0.7877	0.2472	0.8814	0.099	0.053	0.045	−0.043	0.026	−0.007
C(6A)	2a	0.50	0.8304(5)	0.201(1)	0.7893(4)	0.040(3)	0.051(4)	0.032(2)	−0.002(2)	0.013(2)	0.005(2)
C(6B)	2a	0.50	0.7558(5)	0.305(1)	0.7589(5)	0.038(3)	0.051(4)	0.064(4)	−0.003(3)	0.016(3)	0.031(3)
C(7)	2a		0.8224(2)	0.0495(4)	1.1554(2)	0.026(1)	0.035(2)	0.027(1)	−0.0013(9)	0.0073(8)	−0.0006(9)
C(8)	2a		0.7523(2)	0.0292(5)	1.2295(2)	0.031(1)	0.042(2)	0.030(1)	−0.010(1)	0.0124(9)	−0.002(1)
C(9)	2a		0.7735(2)	0.1758(5)	1.3262(2)	0.033(1)	0.044(2)	0.029(1)	−0.003(1)	0.0109(9)	−0.001(1)
C(10)	2a		0.8633(2)	0.3477(5)	1.3513(2)	0.032(1)	0.041(2)	0.029(1)	−0.000(1)	0.0004(8)	0.000(1)
C(11)	2a		0.9341(2)	0.3585(6)	1.2772(2)	0.036(1)	0.055(2)	0.041(1)	−0.020(1)	0.007(1)	−0.002(1)
C(12)	2a		0.9158(2)	0.2122(6)	1.1808(2)	0.028(1)	0.061(2)	0.036(1)	−0.011(1)	0.011(1)	−0.004(1)
C(13)	2a		0.8826(3)	0.5136(6)	1.4540(2)	0.048(2)	0.055(2)	0.039(1)	−0.007(1)	0.001(1)	−0.009(1)

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