the electrical conductivity σ at T_c, a strong increase as observed for MEM(TCNQ)$_2$ does not occur.

It has been shown in the preceding paper that the increase in conductivity in MEM(TCNQ)$_2$ between 290 and 320 K might be attributed to the increase of the disorder of the MEM molecules in this temperature interval. At the phase transition a further sharp increase of the MEM disorder has been observed by NMR measurements (Nechtschein, Oostra, Huizinga, van Bodegom, Sawatzky & Kommandeur, 1981) in agreement with the present structural study. As it seems unlikely that the increase in disorder alone explains the drastic increase of the conductivity at T_c, we tentatively assume that the larger regularity of the stacks also plays a role. It is clear, however, that more structure determinations and careful physical measurements on analogous TCNQ compounds above and below their phase transitions are required to reach definite conclusions.

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Conformational Characteristics of Anhydrous Sulfaguanidine: Computer Retrieval and Analysis of *N*-Substituted Arylsulfonamides

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Abstract

$C_7H_{10}N_4O_2S$, $M_r = 214{\cdot}25$, monoclinic, $P2_1/c$, $a = 9{\cdot}912\,(1)$, $b = 7{\cdot}530\,(1)$, $c = 24{\cdot}496\,(2)$ Å, $\beta = 95{\cdot}32\,(1)°$, $V = 1820{\cdot}4\,(6)$ Å^3, $D_c = 1{\cdot}563$ Mg m^{-3}, $Z = 8$ (two molecules in the asymmetric unit), $F(000) = 896$. The final $R = 0{\cdot}045$ for 3331 intensities. In both symmetry-independent molecules (SG) and (SG*) the coplanar guanidine moiety is fixed to the sulfone group *via* an intramolecular NH$\cdots$O(1) bond and assumes the tautomeric form $[H_2N{-}C_6H_4SO_2N{=}C(NH_2)_2]$ as shown, for example, by the short $S^{VI}{-}N(sp^2)$ distances of $1{\cdot}589\,(2)$ and $1{\cdot}594\,(2)$ Å. As revealed by a search of the Cambridge Crystallographic Data File for (121) compounds containing (aryl)SO_2NX,X' (X,X' = H,C,N,S,P) fragments, the conformations of these groups in SG and SG* about the $S^{VI}{-}N$ bond fall in the range determined by the majority of the molecular structures retrieved. The arylamino groups exhibit, however, significantly different rotations about $S^{VI}{-}$C(ring). One of them (SG*) resembles $[N(1){-}S^{VI}{-}C(1){-}C(6) = 94{\cdot}4°]$ the conformations found in $SG.H_2O$ and $Pd(SG)_2Cl_2$ and in the majority of compounds possessing (aryl)SO_2NX,X' groups. The

other assumes an unusual conformation [N(1)—S^{VI}—C(1)—C(6) = −12·5 °] which, however, does not affect the S^{VI}—C(1) length [1·767 (2) for SG and 1·763 (2) Å for SG*]. The distributions of the conformers about S^{VI}—C(ring) and S^{VI}—N bonds and their effect upon the bonds in the (aryl)SO_2N*X*,*X′* fragments are analyzed by use of the structures retrieved.

Introduction

X-ray diffractometry of the well shaped crystals obtained from an attempted cocrystallization of sulfaguanidine (SG) with a crown ether, bis(methyl 4,6-di-*O*-acetyl-α-D-glucopyranoside)-18-crown-6, revealed two SG molecules in the asymmetric unit. Accordingly, it was of interest to compare the conformations of the symmetry-independent molecules with each other and with those of SG.H_2O and $Pd(SG)_2Cl_2$ (Alléaume, Gulko, Herbstein, Kapon & Marsh, 1976). The unusual amount of rotation about S^{VI}—C(ring) in SG prompted us to retrieve and analyze structures possessing one or more (aryl)SO_2N*X*,*X′* moieties (*X*,*X′* = H,C,N,S,P) by use of the Cambridge Crystallographic Data Base adapted for an IBM 3031 computer in Budapest (National Affiliated Centre in Hungary).

Experimental

Intensities were collected on a CAD-4 diffractometer with graphite-monochromated Cu $K\bar{\alpha}$ radiation (λ = 1·5418 Å). Cell constants were determined by least squares from the setting angles of 25 reflexions; 3331 of the 3856 independent reflexions with $I > 3\sigma(I)$ were taken as observed. No absorption correction was applied. The phases for 190 reflexions having $E \geq 1{\cdot}82$ were obtained by *MULTAN* (Germain, Main & Woolfson, 1971). The *E* map revealed the positions of 24 of the 28 non-hydrogen atoms which were used to phase a Fourier synthesis (R = 0·23). Full-matrix least-squares refinement of positional and vibrational parameters reduced *R* to 0·068. At this stage H atoms, except those of phenyl groups, were located in a difference map. The coordinates of the eight phenyl H atoms were generated from assumed geometries. Anisotropic refinement of non-hydrogen atoms with fixed H coordinates improved *R* to 0·049. In further cycles H coordinates were also refined while vibrational

Table 2. *Fractional coordinates* ($\times 10^3$), *isotropic temperature parameters* (Å^2) *and bond distances* (Å) *for the* H *atoms of the symmetry-independent molecules SG and SG**

E.s.d.'s are given in parentheses.

	x	*y*	*z*	B_{iso}	*X*—H
H(2)	140 (2)	301 (3)	276 (1)	4·4	0·943 (22)
H(3)	−107 (3)	279 (4)	280 (1)	4·6	1·068 (24)
H(5)	−125 (3)	90 (3)	121 (1)	4·6	0·987 (25)
H(6)	116 (2)	132 (3)	118 (1)	4·4	1·009 (22)
H(21)	410 (3)	−86 (4)	218 (1)	5·6	0·970 (24)
H(22)	398 (3)	−244 (4)	174 (1)	5·6	0·883 (30)
H(31)	361 (3)	−201 (4)	85 (1)	5·0	0·918 (30)
H(32)	345 (2)	−7 (4)	60 (1)	5·0	0·912 (30)
H(41)	−301 (3)	132 (4)	234 (1)	5·6	0·944 (23)
H(42)	−309 (2)	78 (3)	177 (1)	4·8	0·888 (22)
H(2*)	110 (2)	143 (3)	360 (1)	4·4	0·978 (22)
H(3*)	−121 (2)	51 (3)	361 (1)	4·8	0·918 (22)
H(5*)	−132 (3)	222 (4)	517 (1)	4·6	1·010 (24)
H(6*)	97 (3)	322 (4)	515 (1)	4·8	0·963 (26)
H(21*)	351 (2)	116 (3)	347 (1)	4·3	0·885 (23)
H(22*)	382 (3)	−85 (3)	338 (1)	4·9	0·930 (22)
H(31*)	467 (3)	−180 (3)	468 (1)	4·9	0·859 (23)
H(32*)	477 (3)	−234 (4)	412 (1)	5·1	0·856 (27)
H(41*)	−295 (2)	25 (4)	472 (1)	5·1	0·886 (23)
H(42*)	−300 (3)	−25 (4)	410 (1)	4·9	0·906 (26)

Table 1. *Fractional coordinates* ($\times 10^5$) *for non-hydrogen atoms and* B_{eq} (Å^2) *of the symmetry-independent molecules SG and SG**

E.s.d.'s are in parentheses. B_{eq} values are given in the form: $4\,(b_{11}/\mathbf{a}^{*2}.b_{22}/\mathbf{b}^{*2}.b_{33}/\mathbf{c}^{*2})^{1/3}$.

	x	*y*	*z*	B_{eq}		*x*	*y*	*z*	B_{eq}
S(1)	32388 (5)	25106 (7)	19908 (2)	3·17 (2)	S(1*)	29433 (5)	29344 (7)	43850 (2)	2·96 (2)
O(1)	38548 (17)	17300 (28)	24921 (6)	4·21 (7)	O(1*)	31446 (15)	36052 (22)	38435 (6)	3·80 (6)
O(2)	34756 (16)	43857 (22)	19325 (7)	4·44 (7)	O(2*)	32681 (17)	41194 (23)	48342 (7)	4·34 (7)
N(1)	36707 (17)	16031 (24)	14481 (7)	3·23 (6)	N(1*)	37777 (17)	11613 (25)	45315 (6)	2·96 (6)
N(2)	38328 (23)	−13138 (29)	18155 (8)	4·62 (9)	N(2*)	37035 (20)	1008 (30)	36135 (7)	4·02 (8)
N(3)	36746 (20)	−8004 (27)	8911 (8)	3·85 (8)	N(3*)	43860 (21)	−16649 (28)	43405 (8)	4·18 (8)
N(4)	−27336 (18)	16204 (28)	19933 (8)	3·80 (8)	N(4*)	−27517 (18)	4937 (28)	43826 (8)	3·81 (7)
C(1)	14711 (21)	21880 (28)	19837 (8)	2·99 (7)	C(1*)	12190 (20)	23573 (28)	43805 (8)	2·89 (7)
C(2)	8451 (22)	26317 (32)	24484 (8)	3·39 (8)	C(2*)	5720 (21)	15714 (33)	39153 (8)	3·32 (8)
C(3)	−5382 (23)	24540 (34)	24546 (9)	3·64 (9)	C(3*)	−7451 (21)	9789 (32)	39182 (8)	3·40 (8)
C(4)	−13310 (21)	18243 (28)	19919 (8)	3·16 (7)	C(4*)	−14291 (20)	11322 (31)	43860 (9)	3·26 (7)
C(5)	−6901 (22)	14317 (32)	15221 (8)	3·57 (8)	C(5*)	−7962 (22)	19858 (36)	48427 (9)	3·85 (9)
C(6)	6928 (22)	16017 (33)	15184 (8)	3·48 (8)	C(6*)	5259 (23)	25862 (34)	48423 (9)	3·63 (9)
C(7)	37241 (19)	−1711 (32)	13965 (8)	3·21 (8)	C(7*)	39404 (19)	−840 (30)	41524 (8)	2·98 (7)

parameters were kept fixed (R = 0·046). Non-hydrogen parameters were then refined again, which resulted in a final $R = 0·045$ ($R_w = 0·069$) for observed reflexions ($R_{\rm tot}$ = 0·049).† Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). All calculations were performed on a PDP 11/34 minicomputer with the Enraf–Nonius SDP-34 system. The final coordinates for the non-hydrogen atoms are given in Table 1 and for the H atoms in Table 2.

Discussion

Bonding characteristics of sulfaguanidines

The corresponding bond lengths and angles (Table 3) of the symmetry-independent SG and SG* (Fig. 1) and those of SG.H_2O and Pd(SG)$_2$Cl$_2$ (Alléaume *et al.*, 1976) (apart from the C—N bond of the arylamino moiety of the latter, which is elongated by the complexation to Pd) agree within experimental error. In accord with the H positions located in difference syntheses, the strong S—N(1) multiple bonds together with the characteristic O(1)–S–N(1) $\gg$ O(2)–S–N(1) bond-angle inequalities (Kálmán, Párkányi & Kucsman, 1980) indicate two-coordinate (sp^2) N(1) atoms. For three-coordinate N atoms, in general, a significantly longer S$^{\rm VI}$—N length (1·62–1·69 Å) is accompanied by a considerably smaller O(1)–S–N angle which is nearer or even equal to O(2)–S–N (see below). Accordingly, though the coplanar guanidino groups are built up by three equally strong C—N multiple bonds, they assume the tautomeric form (I) observed in SG.H_2O and Pd(SG)$_2$Cl$_2$ (Alléaume *et al.*, 1976). [Note: the terms *amino* and *imino* forms are used by Alléaume *et al.* (1976) for the tautomers (I) and (II) of the guanidino moieties.]

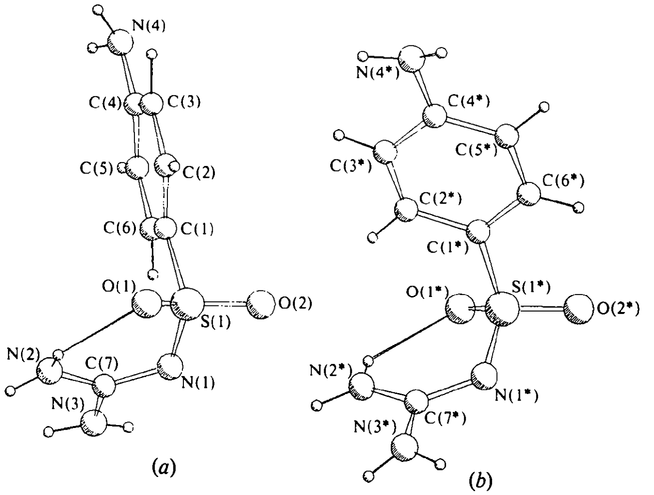

Fig. 1. Perspective views of the sulfaguanidine molecules. (*a*) SG and (*b*) SG*, showing the atom numbering. The intramolecular hydrogen bonds are also indicated.

	S–N(1)	O(1)–S–N(1)	O(2)–S–N(1)	Δ
SG	1·589 (2) Å	114·3 (2)°	106·2 (2)°	8·1°
SG*	1·594 (2)	112·6 (2)	105·9 (2)	6·7
SG.H_2O	1·586 (3)	114·3 (1)	105·1 (1)	9·2
Pd(SG)$_2$Cl$_2$	1·596 (3)	113·4 (1)	106·9 (1)	6·5

Similarly to the observations reported for SG.H_2O and Pd(SG)$_2$Cl$_2$ the characteristic synclinal position (Klyne & Prelog, 1960) of O(1) and C(7) (see below)

Table 3. *Bond distances* (Å) *and angles* (°)

	SG	SG*		SG	SG*
S(1)–O(1)	1·445 (2)	1·450 (1)	N(4)–C(4)	1·399 (3)	1·396 (3)
S(1)–O(2)	1·441 (2)	1·430 (2)	C(1)–C(2)	1·387 (3)	1·387 (3)
S(1)–N(1)	1·589 (2)	1·594 (2)	C(1)–C(6)	1·388 (3)	1·388 (3)
S(1)–C(1)	1·767 (2)	1·763 (2)	C(2)–C(3)	1·379 (3)	1·380 (3)
N(1)–C(7)	1·343 (3)	1·340 (3)	C(3)–C(4)	1·401 (3)	1·389 (3)
N(2)–C(7)	1·336 (3)	1·326 (2)	C(4)–C(5)	1·397 (3)	1·389 (3)
N(3)–C(7)	1·322 (3)	1·337 (3)	C(5)–C(6)	1·378 (3)	1·386 (3)
O(1)–S(1)–O(2)	115·0 (2)	116·5 (2)	C(1)–C(2)–C(3)	120·4 (3)	119·9 (3)
O(1)–S(1)–N(1)	114·3 (2)	112·6 (2)	C(2)–C(3)–C(4)	120·5 (3)	120·8 (3)
O(1)–S(1)–C(1)	107·0 (2)	107·2 (2)	N(4)–C(4)–C(3)	121·2 (3)	119·8 (3)
O(2)–S(1)–N(1)	106·2 (2)	105·9 (2)	N(4)–C(4)–C(5)	120·4 (3)	121·2 (3)
O(2)–S(1)–C(1)	107·7 (2)	107·9 (2)	C(3)–C(4)–C(5)	118·3 (3)	119·0 (3)
N(1)–S(1)–C(1)	106·0 (2)	106·1 (2)	C(4)–C(5)–C(6)	121·0 (3)	120·5 (4)
S(1)–N(1)–C(7)	121·5 (3)	121·6 (2)	C(1)–C(6)–C(5)	120·1 (3)	120·0 (4)
S(1)–C(1)–C(2)	118·5 (3)	119·0 (3)	N(1)–C(7)–N(2)	124·7 (3)	126·5 (3)
S(1)–C(1)–C(6)	121·8 (3)	121·2 (3)	N(1)–C(7)–N(3)	116·5 (3)	116·2 (3)
C(2)–C(1)–C(6)	119·6 (3)	119·8 (3)	N(2)–C(7)–N(3)	118·8 (3)	117·3 (3)

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35842 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Equations of planes in the form $AX + BY + CZ = D$ where X, Y and Z are orthogonal coordinates* (Å)

Deviations (Å $\times 10^3$) of relevant atoms from the planes are given in square brackets in the same order as the equations for SG and SG*.

Plane (1) for phenyl rings C(1)–C(6)

$$\text{SG} \quad -0{\cdot}0944X + 0{\cdot}9417Y - 0{\cdot}3229Z = -0{\cdot}0952$$
$$\text{SG*} \quad -0{\cdot}3115X + 0{\cdot}8891Y - 0{\cdot}3354Z = -2{\cdot}0559$$

[C(1) −11 (2), −16 (2); C(2) 7 (2), 6 (2); C(3) 5 (3), 13 (2); C(4) −13 (2), −22 (2); C(5) 9 (2), 12 (3); C(6) 3 (2), 7 (2); S(1) 47 (1), −165 (1); O(1) −948 (2), 627 (2); O(2) 1399 (2), 192 (2); N(1) −221 (2), −1719 (2); N(4) −27 (2), −39 (2)]

Plane (2) for guanidine moieties N(1), N(2), N(3), C(7)

$$\text{SG} \quad -0{\cdot}9983X - 0{\cdot}0481Y - 0{\cdot}0318Z = -3{\cdot}4735$$
$$\text{SG*} \quad 0{\cdot}9526X + 0{\cdot}3002Y - 0{\cdot}0497Z = 2{\cdot}3000$$

[N(1) −1 (2), 0 (2); N(2) −1 (2), 0 (2); N(3) −1 (2), 0 (2); C(7) 3 (2), 0 (2); S(1) 475 (1), −338 (1); O(1) −32 (2), 187 (2); H(21) −227 (30), 105 (20)]

Plane (3) defined by S(1), N(1), C(1)

$$\text{SG} \quad -0{\cdot}1148X + 0{\cdot}8624Y - 0{\cdot}4930Z = -1{\cdot}0800$$
$$\text{SG*} \quad 0{\cdot}0630X - 0{\cdot}2228Y - 0{\cdot}9728Z = -10{\cdot}7758$$

[O(1) −1167 (2), 1193 (1); O(2) 1259 (2), −1251 (2); C(2) −187 (2), 1202 (2); C(6) 255 (2), −1184 (2)· C(7) −1098 (2), 1124 (2)]

Angles between planes (e.s.d.'s 0·5–1·2°)

	SG	SG*
Planes (1) and (2)	86·6°	−89·2°
Planes (1) and (3)	10·8	83·8
Planes (2) and (3)	84·9	87·6

Table 5. *Hydrogen-bond-like interactions*

	H···*A*	∠*D*H···*A*
N(2)–H(21)···O(1)[x,y,z]	2·12 (3) Å	128·8 (1·7)°
N(3)–H(31)···N(4*)[$-x, y-\frac{1}{2}, \frac{1}{2}-z$]	2·12 (3)	158·7 (1·9)
N(3)–H(32)···O(2*)[$x, \frac{1}{2}-y, -\frac{1}{2}+z$]	2·00 (3)	160·7 (1·9)
N(4)–H(41)···O(2)[$-x, y-\frac{1}{2}, \frac{1}{2}-z$]	2·38 (3)	156·0 (2·0)
N(4)–H(42)···O(1*)[$-x, y-\frac{1}{2}, \frac{1}{2}-z$]	2·22 (3)	157·8 (1·9)
N(2*)–H(21*)···O(1*)[x,y,z]	2·10 (3)	131·0 (1·7)
N(2*)–H(22*)···N(4)[$-x, y-\frac{1}{2}, \frac{1}{2}-z$]	2·33 (3)	142·2 (1·7)
N(3*)–H(31*)···N(1*)[$1-x, -y, 1-z$]	2·40 (2)	151·9 (1·9)
N(3*)–H(32*)···N(1)[$1-x, y-\frac{1}{2}, \frac{1}{2}-z$]	2·32 (3)	160·7 (2·3)
N(4*)–H(41*)···N(1*)[$-x, -y, 1-z$]	2·33 (3)	162·1 (1·9)

determines the spatial arrangement of the coplanar guanidino group relative to the arylsulfonyl moieties [the angles (~90°) formed by the least-squares planes of the guanidino and phenyl groups are given in Table 4]. In both molecules this allows a puckered six-membered ring to close between O(1) and the terminal N(2) amino group *via* an intramolecular hydrogen bond (Table 5). The less puckered (Q = 0·28 Å, φ = 189°, θ = 121°, Cremer & Pople, 1975) ring in SG* assumes approximately an envelope form, while in SG it is of an intermediate screw-boat/envelope shape (Q = 0·35 Å, φ = 348°, θ = 70°).

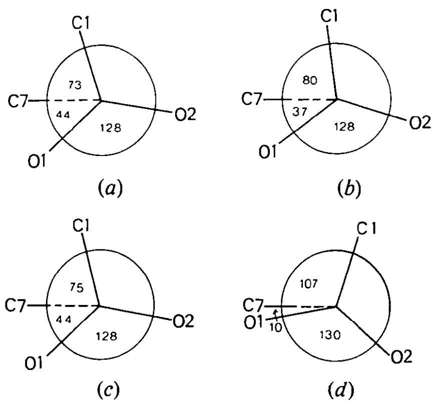

Fig. 2. Newman projections along S^{VI}–N(1). (*a*) SG; (*b*) SG* (present work); (*c*) SG.H_2O; (*d*) $Pd(SG)_2Cl_2$ (Alléaume, Gulko, Herbstein, Kapon & Marsh, 1976).

Hydrogen bonding

All O, N and H(N) atoms, except H(42*), participate in hydrogen bonds. Nevertheless, most of the NH···*A* bonds (Table 5) are weak. The intramolecular N(2)–H(21)···O(1) (for both SG and SG*) hydrogen bonds are among the strongest. The remaining eight reveal only minor differences between the involvement of SG and SG*. N(4) of the arylamino moiety in SG acts twice as donor with both of its H atoms, and once as acceptor in three weak hydrogen bonds. N(4*) is acceptor of a stronger and donor of a weaker hydrogen bond. N(1) as acceptor maintains one, while N(1*) participates in two weak hydrogen bonds. H(21*) is asymmetrically bifurcated.

Conformation of the [(*aryl*)SO_2N]C(7) *groups*

The Newman projections† along the S^{VI}–N bond in SG, SG* and SG.H_2O are alike (Fig. 2*a*,*b*,*c*) and conform, for example, to those of the quasi-similar *N*-sulfonylsulfilimines (*cf.* Table 5 of Kálmán, Párkányi & Kucsman, 1980). In $Pd(SG)_2Cl_2$ the (aryl)SO_2 moiety is turned clockwise by *ca* 30° about S^{VI}–N (Fig. 2*d*). A similar conformation occurs in bis(*p*-tolylsulfonyl)sulfur diimide (Gieren & Pertlik, 1974) and in some other compounds (Fig. 5). No direct connection between the complexation to Pd and this conformation could be revealed, however.

As shown by Fig. 1 and the relevant torsion angles (Table 6) the spatial arrangements of the arylamino groups are significantly different in SG and SG*. While the orientation of the phenyl ring in SG* is similar to that in $Pd(SG)_2Cl_2$ and not far from that of SG.H_2O, SG exhibits a peculiar phenyl position, *i.e.* the plane of the phenyl ring bisects the $O(1)S^{VI}O(2)$ angle. The

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† To eliminate ambiguity in the signs of the torsion angles discussed in this work, each structure is taken so that the torsion angle X–N–S–C(ring) (X = C, N, S, P) is always negative.

significant deviation from type II conjugation suggested by Koch & Moffitt (1951) in describing the interaction between the SO_2 moiety and the adjoining phenyl group and N atom [*cf.* Fig. 3 of Kálmán, Duffin & Kucsman (1971) given for *N*-sulfonylsulfilimines] does not affect, however, the length of the S^{VI}–C(ring) bond. In both structures they are alike: 1·767 (2) for SG and 1·763 (2) Å for SG*. To answer the question as to whether the length of S^{VI}–C(ring) is really independent of the amount of rotation about the same bond, compounds possessing (aryl)SO_2NX,X' fragments were retrieved by the *CONNSER* specifications shown in Table 7 from the Cambridge Crystallographic Data File containing 26 655 entries to January 1980. 11 out of 121 retrieved entries (marked with an asterisk in Table 8) were affected by error in FDAT entries (UNIMOL error-bit = 1 or NCOL = 0). They were subsequently saved by preparing additional connectivity cards (type 8) and transforming coordinates to a unique molecule. Mostly due to unpublished atomic coordinates, 17 entries could not be used; moreover, two irrelevant entries were deleted (Table 8). Along with the unpublished coordinates of PTOSSM (provided by Dr A. Gieren) the parameters of the title molecules (SG and SG*) and two related structures solved recently (Kálmán, Argay, Fischer & Teller, 1981; Kálmán, Párkányi, Kapovits & Kucsman, 1981) have also been taken into account. Thus, 120 independent fragments have been analyzed.

Table 6. *Relevant torsion angles* (°)

	SG	SG*
S(1)–N(1)–C(7)–N(2)	−21·0 (3)	14·4 (3)
O(1)–S(1)–N(1)–C(7)	44·3 (3)	−37·1 (3)
O(2)–S(1)–N(1)–C(7)	172·2 (3)	−165·5 (3)
C(1)–S(1)–N(1)–C(7)	−73·4 (3)	79·9 (3)
C(2)–C(1)–S(1)–N(1)	171·2 (3)	−82·1 (3)
C(6)–C(1)–S(1)–N(1)	−12·5 (3)	94·4 (3)
C(2)–C(1)–S(1)–O(1)	48·8 (3)	38·5 (3)
C(6)–C(1)–S(1)–O(1)	−134·9 (4)	−145·0 (3)
C(2)–C(1)–S(1)–O(2)	−75·4 (3)	164·8 (3)
C(6)–C(1)–S(1)–O(2)	100·9 (3)	−18·8 (3)

Table 7. *Retrieval of fragments with the required constitution*

```
Q (Ph)–SO2–N–X        Title
AT1   S       4
AT2   O       1
AT3   O       1
AT4   C       3
AT5   C       2
AT6   C       2   Type specifications
AT7   C       2
AT8   C       2
AT9   C       2
AT10  C       2
AT11  C,N,S,P 1
BO    1  2  2 A
BO    1  3  2 A
BO    1  4  1 A
BO    1 10  1 A
BO    4  5  5 C
BO    5  6  5 C   Connectivity specifications
BO    6  7  5 C
BO    7  8  5 C
BO    8  9  5 C
BO    9  4  5 C
BO   10 11 1,2

NOLN
END
```

Rotation about S^{VI}–C(*ring*)

The rotation of the phenyl rings about S^{VI}–C(ring) is represented by the ε_1 = N–S–C(1)–C(x) torsion

Table 8. *Reference codes of the structures possessing* (*aryl*)SO_2NX,X' *moieties*

Structures used			Not used
ABSBPP	IBAZUN	PSULAGO1*	ACPSTP
ACORBS10	IBSAZH	PSULTZ	BBSAZE
AIMTCX	IBSAZO	PSULTZ	BBSPRT
ASULDZ*	MANSAZ10	PTBZTS	BPSPOC
BCHXBS	MATOLS	PTSBZA	BSPROL
BCYTGA	MBECUR	PTSPIM	BSPRTL
BCYTGA	MBHGTS	PTSSIM	BTSITZ
BETCYH	MBZSAN10	PYCBSA	CBSPTL
BIMTIT	MCBESA	SACCAF	CYSPTL
BMPBSA10	MCXBAZ10	SAMPYM	KTTSIM
BOTSTZ	MINTSA	SAMPYM	MIEBSC
BOTSTZ	MORCXB	SAMPYMO1	MSPRTL
BPBSLF10	MPZTSA	SFDMOX	STHSAM
BPCBZS10	MTSAIN	SOGUAN20	SULTHE
BPHBZS10	MTSAIN	SULDAZ	THIRTS
BPTSTZ	MTSHCH	SULPMS*	THTHXN
BRBSMA10	MTSHCH	SULPDC10	TSITHZ
BSLTMO	MTSIMP	SULSUX	
BSPRTL10	MTSIMP	SUTHAZ*	
BSULFA	MTSISP	SUTHAZO1*	PTOSSM†
BSULFA	MTSITZ	SUTHAZO1*	PTOSSM†
BSUTDT	NABSUF	SUTHAZO2*	
BUNDHA10	NABSUF	SUTHAZO2*	SOGUANO1‡
BZSHPZ	NASOXH	TAIBYM	TPHPRO‡
CACTAZ*	NEBSMS	TBZPCM10	
CITSIB	NPSPAM	TOSDAZ	
CLPSAM	OAZBCH	TOSIMD	
CMANTS	PENTOS10	TOSIMS10	
CSAINC	PENTOS10	TOSTPP10	
CSBSMP	PHGBAN*	TPHPROO1	
CXMESX	PHGCAN*	TSAPNI	
DMCYAN	PHGFAN	TSBZQU*	
EBTHTP	PMBSAN10	TSCPIP	
EMXPSP	PMBSAN10	TSEMHP	
HMSPIO	PMTSZD	TSHOCZ	
HMTSIQ	PORTSH10	TSHOCZ	
HMTSIQ	PSAHPP	TSMPXZ	
HSLSTZ	PSULAG*	TSPOXZ	

* These structures could be used only after amendment of FDAT entries.

† Unpublished coordinates provided by Dr A. Gieren.

‡ Irrelevant entries (see SOGUAN20 and TPHPROO1, respectively).

angle where C(2) or C(6) is selected as C(x) so that ε_1 always falls between 0 and $-180°$ (Fig. 3). Each unit of the plotted ε_1 angles (0, 10, 20, 30°, *etc.*) refers to its neighborhood within $\pm 5°$. In the range -10 up to $-150°$ where SG represents the lower limit, the distribution of the number (N) of conformers is continuous and nearly Gaussian. The ε_1 values for SG*, SG.H_2O (SOGUAN20) and Pd(SG)$_2$Cl$_2$ (SULPDC10) fall in the range $-75 \pm 20°$ which possesses the highest population (58%). As expected, the scattergram of the S^{VI}–C(ring) lengths (limited to the values where the structure refinement resulted in $R < 0{\cdot}10$) plotted against ε_1 (Fig. 4) does not reveal any dependence of the widely different (140°) amounts of rotation. They are scattered within experimental error around 1·76 Å (the grand mean of the retrieved values is 1·761 Å) which agrees with that of 1·754 Å suggested by Kálmán (1973) for the S^{VI}–C(sp^2) single bond. Accordingly, we are now in a position to answer the question posed at the start: (*a*) apart from a narrow range of $\pm 10°$ in which no conformer was found, the rotation of the aryl moieties about S^{VI}–C(ring) is not hindered and (*b*) the S^{VI}–C(aryl) bonds, as suggested by Alléaume *et al.* (1976), hardly assume any double-bond character.

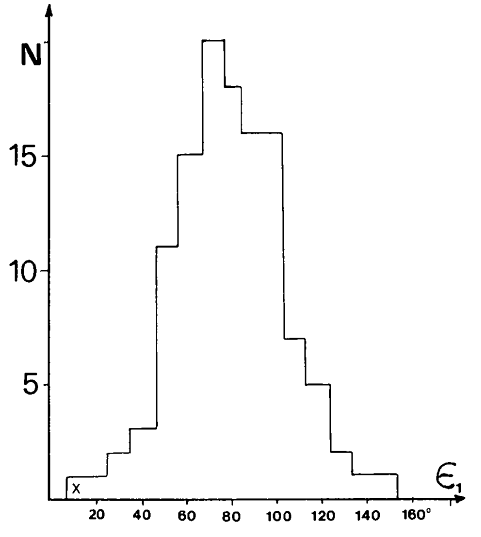

Fig. 3. The numerical distribution (N) of the amount of aryl-group rotation about S^{VI}–C(ring) plotted against the ε_1 = N–S–C(1)–C(x) torsion angle. C(x) is either C(2) or C(6) of the symmetrical six-membered ring. ε_1 values are grouped by 10° with a range of $\pm 5°$. X indicates the conformation of SG.

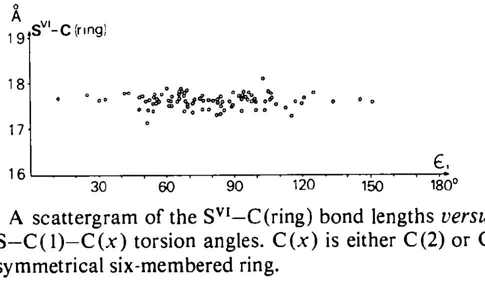

Fig. 4. A scattergram of the S^{VI}–C(ring) bond lengths *versus* ε_1 = N–S–C(1)–C(x) torsion angles. C(x) is either C(2) or C(6) of the symmetrical six-membered ring.

Rotation about S^{VI}–N

Prior to the analysis of the conformers, (aryl)SO_2NX,X' fragments have to be classified in terms of X and X':

$$\mathrm{SI}: X, X' = \mathrm{C, N, S\ or\ P}$$

$$\mathrm{SA}\begin{cases}\mathrm{SAH}: X = \mathrm{C, N\ or\ S};\ X' = \mathrm{H}\\ \mathrm{SAX'}: X = \mathrm{C, N\ or\ S};\ X' \neq \mathrm{H\ (C, N\ or\ S)}.\end{cases}$$

The conformers belonging to group SI can be described by one torsion angle, $\varepsilon_2 = X$–N–S–C. It is the same in group SAH, because the torsion angle H–N–S–C has little experimental significance. In group SAX′ the amount of rotation for an (aryl)SO_2 moiety can, however, be defined either to X or X' by ε_2 = X–N–S–C or $\varepsilon_2' = X'$–N–S–C. This ambiguity was eliminated by always taking the lower torsion angle (generally *sc*). A further source of ambiguity is the sign of the torsion angle ε_2. Apart from three structures (BRBSMA10, BUNDHA10 and PORTSH10) published with the absolute configuration, the relative configurations of the other 116 (aryl)SO_2NX,X' moieties are in unit cells, the majority (83%) of which have at least one mirror (*m*,*a*,*b*,*c*,*n*) or $\bar{1}$ symmetry. Thus the sign of ε_2 is arbitrary and does not give unambiguously the spatial arrangement of S^{VI}[O′,O,N,C] tetrahedra with respect to the other parts of the molecules. Thus the rotation about S^{VI}–N can be described only in terms of $|\varepsilon_2|$ limited to the range 0–180°. Nevertheless, the distribution of the rotamers (N), plotted against $|\varepsilon_2|$ ($<|\varepsilon_2'|$) in the same way as in Fig. 3, is rather characteristic (Fig. 5). An energy barrier is evident from the lack of points in the range 0–40°. This is in accord with the extended Hückel (EHMO) calculation of the energies for the rotamers of Me_2SNSO_2Me against the angle of rotation (α) about S^{VI}–N (Mezey & Kucsman, 1972). From 40° the population increases rapidly to a peak at $70 \pm 15°$. In this narrow range 61% of the rotamers (including SG, SG* and SG.H_2O) are located. This range corresponds to a local minimum at $\alpha = 0°$ in the Mezey & Kucsman (1972) diagram. Apart from Me_2SNSO_2Me (Kálmán, 1967; Kálmán, Párkányi & Kucsman, 1980) the related N-mesylamino moieties exhibit the same conformation about S^{VI}–N (Kálmán, Párkányi & Schawartz, 1977; Kálmán, Argay & Vassányi, 1977; Kálmán & Argay, 1978*a*,*b*). From the peak (N = 28) the population decreases even more rapidly to $N = 6$ at about $\varepsilon_2 = 100 \pm 15°$. Pd(SG)$_2Cl_2$ was found in this range. The population reaches a minimum in the neighborhood of 140° and then increases somewhat again at about 170°.

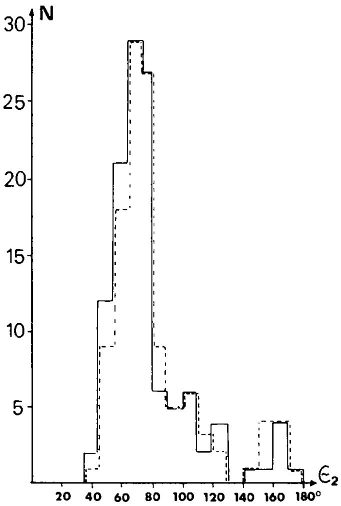

Fig. 5. The numerical distribution (N) of rotamers (full line) about S^{VI}–N plotted against $|\varepsilon_2| = X$–N–S–C(ring) torsion angles. The 32 structures of [(aryl)SO_2NX,X'] type are represented by $|\varepsilon_2|$ where $|\varepsilon_2|$ is always less than $|\varepsilon_2'| = X'$–N–S–C(ring). A second distribution (dashed line) in which the $32 |\varepsilon_2| < |\varepsilon_2'|$ values are plotted alternatively (following the alphabetical CODE list of the retrieved structure, Table 8) shows no significant difference from the distribution represented by the full line. $|\varepsilon_2|$ values are grouped by 10° with a range of ±5°.

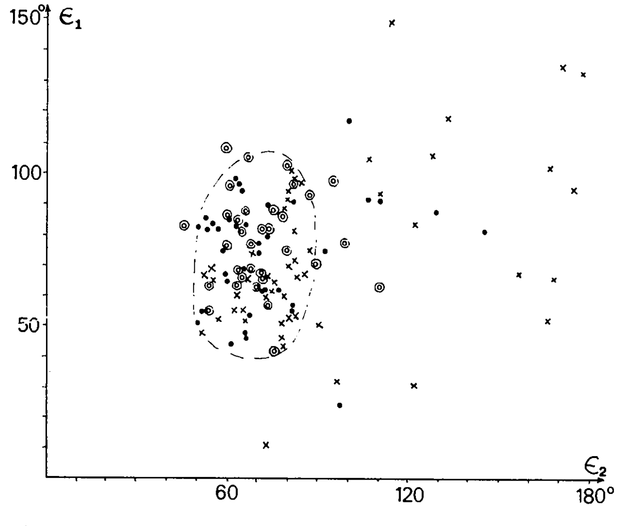

Fig. 6. A scattergram of ε_1 torsion angles plotted against ε_2 values showing a characteristic cluster of conformations about S^{VI}–C(ring) and S^{VI}–N bonds. The cluster is formed equally by SAH (full circle), SAX′ (double circle) and SI (cross) types of structures.

The scattergram of ε_1 values plotted *versus* the ε_2 torsion angles (Fig. 6) shows a characteristic distribution of the amounts of rotations about S^{VI}–C(ring) and S^{VI}–N. Some of the rotamers are scattered at random but the majority form a cluster in the range $\varepsilon_1 = (70\text{–}120°)$ and $\varepsilon_2 = (60\text{–}90°)$.

The marked directional preference of the rotations about S^{VI}–C(ring) and S^{VI}–N apparent in Figs. 3, 5 and 6 suggests that, though the fragments are in different environments from crystal to crystal, and represent three different types (SI, SAH and SAX′) of structures, in each there is some kind of common intramolecular effect at work.

The distribution of S^{VI}–N *distances versus* $NS^{VI}O'$ *angles*

Finally, a scattergram of S^{VI}–N distances plotted against the greater angle of the $NS^{VI}O$ pairs was prepared. The greater angle is always formed by the O′ atom which is synclinal (or synperiplanar) with X (Fig. 2). In Fig. 7 two distinct clusters can be recognized. One, at the lower right corner of the scattergram, is formed almost exclusively by the members of group SI. The other (in the middle of the diagram) is built up predominantly by those belonging to groups SAH and SAX′. This distribution seems to corroborate an empirical observation (Kálmán, Párkányi & Kucsman, 1980) which has been applied in the study of the title compound (see above). Accordingly, it is likely that a sulfonimido [(aryl)SO_2N=R(H)] rather than a sulfonamido [(aryl)SO_2NH–R] structure is formed whenever a pronounced difference between the NS^{VI}–O angles ($NS^{VI}O \ll NS^{VI}O' \geq 110°$) is accompanied by a strong S^{VI}–N bond (1·56–1·62 Å), while in a sulfonamido tautomer $NS^{VI}O'$ decreases to $NS^{VI}O$ (105–107°) and S^{VI}–N is lengthened (1·63–1·69 Å). There are few structures which violate this rule. For example, in the structures of SI type either a rather strong X=N double bond (*e.g.* PTOSSM) or complexation of N to a metal atom *via* its lone pair (*e.g.* CITSIB) may account for deviations. The effects upon the SA structures are less obvious. However, an analysis of these structures revealed that nine of the structures of SAX′ type (listed in Table 9 but omitted from Fig. 7) possessing markedly different $NS^{VI}O$ angles also exhibit markedly different orientations of the N[S^{VI},X,X'] trigonal pyramids relative to the S^{VI}[O′,O,N,C] tetrahedra from those 23 structures in which the $NS^{VI}O$ angles are similar. Two examples for each group are depicted in Fig. 8. From these Newman projections along S^{VI}–N the following can be seen:

(1) The conformations of the S^{VI}[O′,O,N,C] groups relative to X are the same (*i.e.* ε_2 is about 80 ± 15°) and resemble those depicted in Fig. 2.

(2) The additional X' substituents, however, occupy different orientations. (*a*) In 23 structures having equal (or similar) $NS^{VI}O$ angles by pairs, the X'–N–S–C torsion angles are synclinal (+*sc*). Thus, the orientation of the lone pair (lp) situated at the top of the pyramidal N(sp^3) lies in the bisecting plane of the $O'S^{VI}O$ angle (Fig. 8*a*,*b*). (*b*) The other nine structures, which possess different $NS^{VI}O$ angles by pairs, exhibit X'–N–S–C

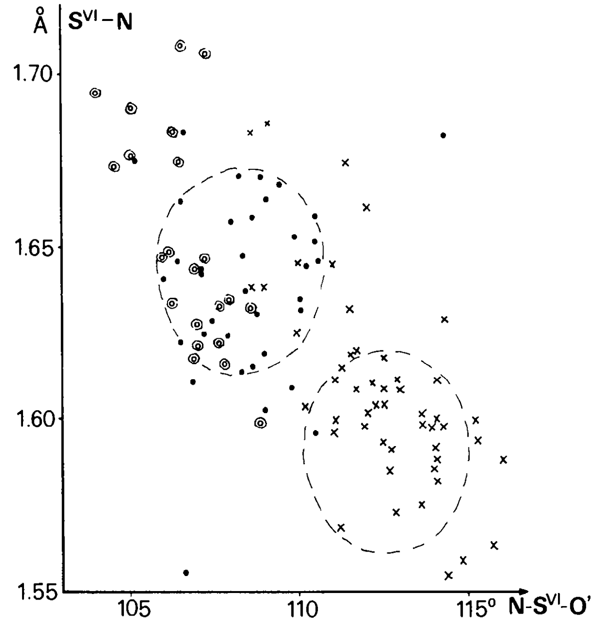

Fig. 7. A scattergram of S^{VI}–N distances *versus* the greater values of the $NS^{VI}O$ pairs. Apart from points scattered at random, two distinct clusters are apparent. One (at lower right corner) is formed almost exclusively by structures of SI type (cross). The other (in the middle of the plot) is formed predominantly by structures of SAH (full circle) and SAX′ (double circle) types.

Table 9. *Structures of SAX′* [*(aryl)* SO_2NX,X'] *type in which* $|\varepsilon_2'|(X'$–N–S–C) *is significantly greater than* $|\varepsilon_2|(X$–N–S–C) *together with* $110° < NS^{VI}O' \gg NS^{VI}O$ *pairs*

	ε_2	ε_2'	$NS^{VI}O'$	$NS^{VI}O$	Δ
BSLTMO	−75°	127°	112·2°	107·9°	4·3°
CXMESX	−74	146	111·0	106·5	4·5
IBAZUN	−87	−154	114·0	107·2	6·8
IBSAZH	−98	−163	114·9	107·7	7·2
MANSAZ10	−89	−155	111·0	106·9	4·1
MCBESA	−71	149	112·0	106·9	5·1
MORCXB	−72	158	111·7	106·2	5·5
OAZBCH	−98	−164	113·0	110·3	2·7
TSCPIP	−68	113	109·4	106·0	3·4

torsion angles at about ±150°. Consequently, in both subcases (Fig. 8*c*,*d*) the direction of the lone pair bisects the $OS^{VI}C$(ring) angle. The orientation of the lone pair in the majority of SI structures (Fig. 5) is the same. Moreover, in the SI structures in which the lp–N–S–C angle is synperiplanar (*i.e.* ε_2 is antiperiplanar, Table 10) $NS^{VI}O$ increases up to $NS^{VI}O' \geq 110°$. In summary, the orientation of the lone pair apparently plays an important role in the formation of the $NS^{VI}O$ angles. This fact, *mutatis mutandis*, may be applied in determining the predominant tautomeric form of a system

$$R^*SO_2NH\text{–}R \rightleftharpoons R^*SO_2N{=}R(H)$$

Table 10. *Structures of SI* [(aryl)$SO_2N{=}X$] *type in which* $|\varepsilon_2|(X$–N–S–C) *is antiperiplanar together with* $110° < NS^{VI}O' \sim NS^{VI}O$ *pairs*

	ε_2	$NS^{VI}O'$	$NS^{VI}O$	Δ
EBTHTP	168°	113·7°	113·7°	0·0°
HMTSIQ	178	110·6	110·0	0·6
MTSIMP	174	112·5	109·7	2·8
MTSISP	170	111·8	111·7	0·1

when difference maps do not reveal the location of the tautomeric H atoms.

Conclusion

The conformational characteristics [*e.g.* the unusual amount of rotation about S^{VI}–C(ring) in SG, *etc.*, see above] of the symmetry-independent molecules, SG and SG*, of the title compound in comparison with those of $SG.H_2O$ and $Pd(SG)_2Cl_2$ prompted us to carry out a computer retrieval of all *N*-substituted arylsulfonamides, the coordinates of which were found on CCD Files (Table 11). The study of 120 independent (aryl)SO_2NX,X' fractions suggests the following:

(1) The rotation about S^{VI}–C(ring) is not hindered (Fig. 3); moreover it has no influence upon the S^{VI}–C(ring) distances which are scattered around

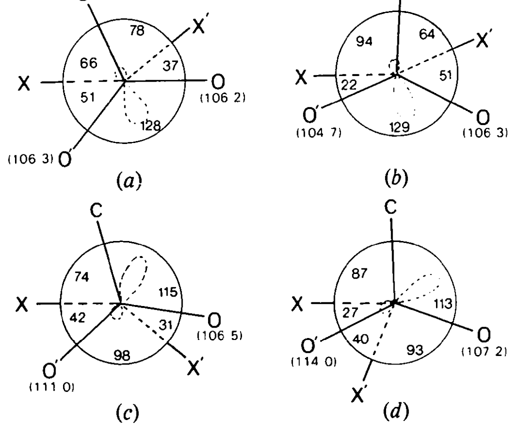

Fig. 8. Newman projections along S^{VI}–N for four selected structures of SAX′ = [(aryl)SO_2NX,X'] type. (*a*) BZSHPZ and (*b*) BETCYH are taken out of the 23 structures in which *X*′ lies in the bisecting plane of the $OS^{VI}C$ angle ($110° > NS^{VI}O' \sim NS^{VI}O$). Apart from the slight differences in $|\varepsilon_2|$ and $|\varepsilon_2'|$ *X* and *X*′ cannot be distinguished from each other. (*c*) CXMESX and (*d*) IBAZUN represents those nine structures (Table 9) in which *X*′–N–S–C(ring) is antiperiplanar (CXMESX: +*ap*, IBAZUN: −*ap*) while $NS^{VI}O'$ is greater than $NS^{VI}O$ and 110°, as well. The approximate orientations of the lone pairs, situated at the top of the pyramidal N(sp^3) atoms, are also indicated.

Table 11. *Bibliography*

The searches were carried out in August 1980 on the version of the BIB file which contained 25 655 entries. The 116 fragments in the SPSS system file are referenced by 121 independent publications to each of which is assigned a unit reference code (*e.g.* PTSPIM). This code, together with the shortened reference, uniquely defines each compound. The qualifications of these 121 entries are given in Table 8.

[illegible]	[illegible] BULL.SOC.CHIM.BELG. [illegible]
ACBPIS10	[illegible] MCLACHLAN- J.CHEM.SOC. [illegible]
ACPSIP	[illegible] ABEL- TETRAHEDRON LETT. [illegible]
AIMIC[illegible]	[illegible] ABEL- BULL.SOC.CHIM.BELG. [illegible]
ASUL[illegible]	[illegible] COOK- J.CHEM.SOC.,PERKIN [illegible]
BANAMP	[illegible] ENGLER- ACTA CRYSTALLOGR. [illegible]
[illegible]	[illegible] J.AM.CHEM.SOC. [illegible]
[illegible]	[illegible] IZV.JUG.CENT.KRIST.,SER.A 11,[illegible]
[illegible]	[illegible] J.ORG.CHEM. [illegible]
[illegible]	[illegible] BULL.CHEM.SOC.JPN. [illegible]
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[illegible]	[illegible] ABEL- J.CHEM.SOC.,CHEM.COMMUN. [illegible]
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[illegible]	[illegible] TAMURA- J.CHEM.SOC.C [illegible]
[illegible]	G.L.ABEL- BULL.SOC.CHIM.BELG. 87,[illegible] 1978.
[illegible]	[illegible] HAMODRAKAS- ACTA CRYSTALLOGR.,SECT.B 34,[illegible] 1978.
[illegible]	[illegible] CAMERON- CAN.J.CHEM. [illegible]
[illegible]	T.S.CAMERON- J.CHEM.SOC.,PERKIN 2 [illegible]
[illegible]	[illegible] BRENNAN- CHEM.PHARM.BULL. [illegible]
[illegible]	[illegible] ZACHARIS- J.HETEROCYCL.CHEM. [illegible]
[illegible]	[illegible] J.HETEROCYCL.CHEM. 2,[illegible] 1965.
[illegible]	H.M.ZACHARIS- J.HETEROCYCL.CHEM. [illegible]1301,1970
[illegible]	[illegible] ACTA CRYSTALLOGR.,SECT.A 31,[illegible]
[illegible]	[illegible] ASSOC.ITAL.CRIST.,ABSTR. [illegible]
[illegible]	M.BOLOGNESI- ACTA CRYSTALLOGR.,SECT.[illegible]
[illegible]	A.F.CAMERON- ACTA CRYSTALLOGR.,SECT.B [illegible]
MBECUP	[illegible] ACTA CRYSTALLOGR.,SECT.B [illegible]
MBHGTS	[illegible] J.CHEM.SOC.,PERKIN 1 [illegible] 1978.
[illegible]	[illegible] CRYST.STRUCT.COMMUN. 2,[illegible]
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1·76 Å within experimental error (Fig. 4). The distribution of the rotamers is not only continuous, but Gaussian, in the peak of which fall SG*, SG.H_2O and Pd$(SG)_2Cl_2$, while one of its ends is terminated by SG (labelled with X in Fig. 3).

(2) The free rotation of S^{VI}[O′,O,N,C] tetrahedra about S^{VI}—N is hindered in a wide range of $|\varepsilon_2|$ angles (0–40°) and there is also a less favorable range at about 140° (Fig. 5). In accord with the conclusion inferred from earlier studies of *N*-sulfonylsulfilimines (Kálmán, 1974) a sharp and high peak in the range 75 ± 15° represents 61% of the conformers (including those of SG, SG* and SG.H_2O). The rotamer of Pd$(SG)_2Cl_2$ falls in the lower part of the right slope of this maximum.

(3) The scattergram of the rotations about S^{VI}—C(ring) and S^{VI}—N (Fig. 6) shows that most conformers cluster around the range occupied by SG, SG.H_2O and Pd$(SG)_2Cl_2$. This suggests that some internal forces establish the same preferred conformation in these molecular fragments. This corresponds to the type II conjugation (Koch & Moffitt, 1951), at least in SI structures. This classification for structures of SAH and SAX′ types must be carried out with care.

(4) The plot of S^{VI}—N distances *versus* the greater values of the $NS^{VI}O$ pairs (Fig. 7) corroborated the observation (Kálmán, Párkányi & Kucsman, 1980) that the sulfonimido forms can, in general, be distinguished from the sulfonamido forms if short S^{VI}—N distances are accompanied by pronounced inequalities

in the $\mathrm{NS^{VI}O}$ pairs. All four sulfaguanidine structures exhibit such parameters (see above).

(5) The presence of 110° < $\mathrm{NS^{VI}O'}$ > $\mathrm{NS^{VI}O}$ inequalities in 9 of 32 structures of (aryl)$\mathrm{SO_2N}X,X'$ type helped to shed light on the role of the different spatial arrangement of the trigonal-pyramidal lp:N[$\mathrm{S^{VI}}$,X,X'] groups relative to the $\mathrm{S^{VI}}$[O′,O,N,C] tetrahedra from those found in the other 23 structures (Fig. 8). Of course, a deeper understanding of these phenomena is still ahead together with a study of any further correlations between the parameters of the retrieved *N*-substituted arylsulfonamides.

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Structure of 7-(Methyl 2-acetamido-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranosid-4-yl)theophylline Monohydrate

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Abstract

$\mathrm{C_{16}H_{21}N_5O_6.H_2O}$, $M_r = 397{\cdot}40$, crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 14·520 (5), b = 13·844 (6), c = 9·347 (3) Å, Z = 4, U = 1878·89 Å^3, D_c = 1·409 Mg m^{-3}, μ(Cu $K\alpha$) = 2·271 mm^{-1}. Final R = 0·059 for 1434 observed reflexions [$I > 2\sigma(I)$]. The interatomic distances and angles are in agreement with the given atom type and hybridization. The orientation of the base relative to the sugar ring, defined in terms of rotation about the C(4′)—N(7) glycosyl bond, is *anti* (75·5°). The theophylline conformation is defined by the mean torsion angles of 3·9 and 0·6° for the six-and five-membered rings, respectively. The sugar moiety exhibits a half-chair $^0H_5$ conformation. The packing is dominated by hydrogen bonds. Sugar–base interaction is realized through O(3′)···O(2), 2·730 (7) Å. The water molecule is hydrogen bonded to the sugar residue by O(W)···O(3′), 2·860 (8), and N(1′)···O(W), 2·951 (6) Å, as well as to the base moiety by O(W)···N(9), 3·046 (7) Å. There is no base stacking.

Experimental

The space group was deduced from Weissenberg photographs recorded with Cu $K\alpha$ radiation. The

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