ORGANIC COMPOUNDS

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An Atypical Conformation of a Toluenesulfonamide

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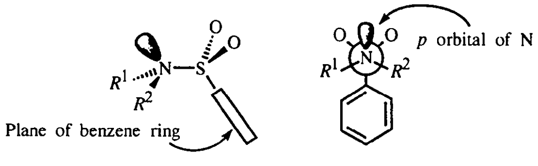
Abstract

An atypical conformation of a tosylamide was found in *cis*-1-(4-methylphenylsulfonyl)-2,5-bis(1-methylpyrrol-2-yl)pyrrolidine, $C_{21}H_{25}N_3O_2S$.

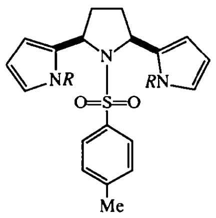
Comment

We were the first to recognize and draw attention to the characteristic conformation of arylsulfonamides (Beddoes *et al.*, 1986).



Side view Projection along N—S bond

Since our report, others (Crich, Bruncko, Natarajan, Teo & Tocher, 1995; Hökelek, Patir, Gülce & Okay, 1994; Chiaroni, Riche, Dekhane & Dodd, 1994; Menziani, Cocchi & De Benedetti, 1992) have rediscovered the typical conformation and several more examples have been reported (*e.g.* Beddoes, Kettle & Joule, 1994; Cobb, Demetropoulos, Korakas, Skoulika & Varvounis, 1996), including our own most recent example, *cis*-1-(4-methylphenylsulfonyl)-2,5-di(pyrrol-2-yl)pyrrolidine (*cis*-*N*-tosylpyrrole trimer), (1) (Zhao, Beddoes & Joule, 1997).



(1) *R*=H
(2) *R*=Me

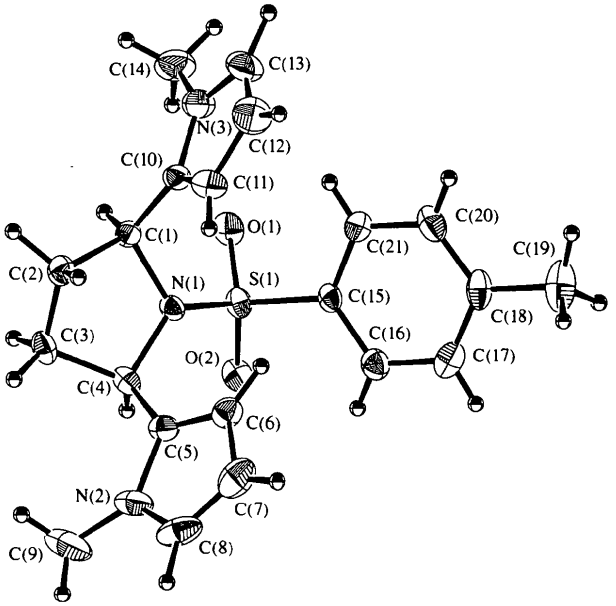
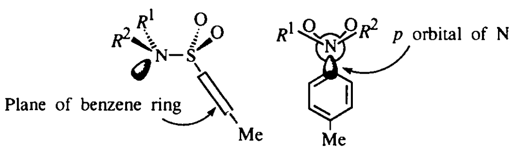


Fig. 1. View (*ORTEP*; Johnson, 1965) of one of the two molecules of (2) in the asymmetric unit, showing the atom-numbering scheme. Displacement ellipsoids represent 30% probability surfaces and H atoms are draw as circles of arbitrary radii.

In continuation of this last study, the *N*,*N*-dimethyl derivative, (2), was prepared. Anticipating little change in the three-dimensional structure established for (1) (Zhao, Beddoes & Joule, 1997), we carried out an X-ray study (Fig. 1) and were surprised to find that this compound adopts quite a different way of minimizing steric interactions between the toluenesulfonyl and the two pyrrole substituents, arranged as they are on three contiguous atoms of the central pyrrolidine ring.

In both (1) and (2) the two pyrrole residues are on one side of the pyrrolidine plane and the toluenesulfonyl group is on the other. In (1) the orientation of the sulfonamide unit is as shown in the scheme above, with the N atom essentially tetrahedral. However, in (2) the N atoms are considerably flattened: the angles sum to 354.8 and 354.9°, compared with 335.1° for (1), no doubt to help minimize non-bonded interactions. Of even greater interest is the conformation of the sulfonamide unit, which is as shown schematically below, with the O atoms and the nitrogen-substituent C atoms eclipsed. We are aware of no other examples of sulfonamides with this three-dimensional disposition of atoms.



Side view Projection along N—S bond

Experimental

cis-1-(4-Methylphenylsulfonyl)-2,5-bis(1-methylpyrrol-2-yl)-pyrrolidine was prepared by methylation of *cis*-1-(4-methylphenylsulfonyl)-2,5-di(pyrrol-2-yl)pyrrolidine (Zhao, Beddoes & Joule, 1997) using iodomethane with sodium hydride as base, and crystallized for X-ray analysis from dichloromethane/hexane, m.p. 447–449 K.

Crystal data

$C_{21}H_{25}N_3O_2S$
$M_r = 383.51$
Triclinic
$P\bar{1}$
$a = 15.240\,(2)$ Å
$b = 17.220\,(2)$ Å
$c = 7.8492\,(8)$ Å
$\alpha = 90.236\,(10)°$
$\beta = 104.33\,(1)°$
$\gamma = 79.41\,(1)°$
$V = 1960.0\,(4)$ Å^3
$Z = 4$
$D_x = 1.299$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 7.8–12.7°$
$\mu = 0.177$ mm^{-1}
$T = 296.2$ K
Tabular
0.40 × 0.20 × 0.10 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.981$, $T_{\max} = 1.000$
7242 measured reflections
6955 independent reflections

4275 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\max} = 25.05°$
$h = 0 \rightarrow 18$
$k = -20 \rightarrow 20$
$l = -9 \rightarrow 9$
3 standard reflections every 150 reflections intensity decay: −0.27%

Refinement

Refinement on F
$R = 0.048$
$wR = 0.034$
$S = 2.024$
4275 reflections
615 parameters
$w = 1/[\sigma^2(F_o)]$

$(\Delta/\sigma)_{\max} = <0.001$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S(1)—O(1)	1.432 (2)	S(2)—O(3)	1.431 (3)
S(1)—O(2)	1.429 (2)	S(2)—O(4)	1.429 (3)
S(1)—N(1)	1.618 (3)	S(2)—N(4)	1.618 (3)
S(1)—C(15)	1.758 (4)	S(2)—C(36)	1.759 (4)
N(1)—C(1)	1.503 (4)	N(4)—C(22)	1.502 (4)
N(1)—C(4)	1.483 (4)	N(4)—C(25)	1.483 (4)
O(1)—S(1)—O(2)	119.5 (2)	O(3)—S(2)—O(4)	119.2 (2)
O(1)—S(1)—N(1)	107.8 (1)	O(3)—S(2)—N(4)	108.2 (2)
O(1)—S(1)—C(15)	106.4 (2)	O(3)—S(2)—C(36)	106.8 (2)
O(2)—S(1)—N(1)	108.0 (1)	O(4)—S(2)—N(4)	108.0 (2)
O(2)—S(1)—C(15)	106.9 (2)	O(4)—S(2)—C(36)	106.8 (2)
N(1)—S(1)—C(15)	107.9 (2)	N(4)—S(2)—C(36)	107.4 (2)
S(1)—N(1)—C(1)	120.5 (2)	S(2)—N(4)—C(22)	121.0 (2)
S(1)—N(1)—C(4)	122.0 (2)	S(2)—N(4)—C(25)	121.5 (2)
C(1)—N(1)—C(4)	112.4 (3)	C(22)—N(4)—C(25)	112.3 (3)
O(1)—S(1)—N(1)—C(1)	−16.5 (3)		
O(1)—S(1)—N(1)—C(4)	136.3 (3)		
O(1)—S(1)—C(15)—C(16)	−144.2 (3)		
O(1)—S(1)—C(15)—C(21)	32.8 (3)		
O(2)—S(1)—N(1)—C(1)	−146.9 (2)		
O(2)—S(1)—N(1)—C(4)	5.9 (3)		
O(2)—S(1)—C(15)—C(16)	−15.5 (3)		
O(2)—S(1)—C(15)—C(21)	161.5 (3)		
N(1)—S(1)—C(15)—C(16)	100.4 (3)		
N(1)—S(1)—C(15)—C(21)	−82.6 (3)		
O(3)—S(2)—N(4)—C(22)	−16.7 (3)		
O(3)—S(2)—N(4)—C(25)	135.8 (3)		
O(3)—S(2)—C(36)—C(37)	37.0 (3)		
O(3)—S(2)—C(36)—C(42)	−141.6 (3)		
O(4)—S(2)—N(4)—C(22)	−147.0 (3)		
O(4)—S(2)—N(4)—C(25)	5.5 (3)		
O(4)—S(2)—C(36)—C(37)	165.6 (3)		
O(4)—S(2)—C(36)—C(42)	−13.0 (3)		
N(4)—S(2)—C(36)—C(37)	−78.8 (3)		
N(4)—S(2)—C(36)—C(42)	102.6 (3)		

There are two independent molecules in the asymmetric unit which are not significantly different from each other. The structure was solved by direct methods and expanded using Fourier techniques *DIRDIF*94 (Beurskens *et al.*, 1994). The pyrrolidine protons were found by difference Fourier techniques and were refined isotropically. All other H atoms were placed in calculated positions. The methyl protons were not refined, but their positions were recalculated after each round of least-squares refinement. Their isotropic displacement parameters were assigned values 1.2 times greater than the $B_{\rm eq}$ values of the atoms to which they were bonded. The remaining H atoms were refined isotropically.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR*92 (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1130). Services for accessing these data are described at the back of the journal.

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1,4,8,11-Tetrakis(diiodine)-1,4,8,11-tetrathiacyclotetradecane

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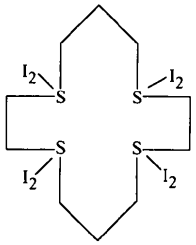
Abstract

The title compound, $C_{10}H_{20}S_4.4I_2$, [14]aneS$_4$.4I$_2$, possesses crystallographically imposed inversion symmetry and has all four S donor atoms coordinated to diiodine molecules. The principal geometric parameters for the two inequivalent pairs of interactions are S—I 2.803 (2) and 2.880 (2) Å, I—I 2.7894 (8) and 2.7571 (10) Å, and S—I—I 177.71 (5) and 172.50 (4)°. Molecules are linked by S···I and I···I intermolecular contacts to form an infinite three-dimensional lattice.

Comment

It is well known that sulfur-containing molecules such as acyclic (Rømming, 1960) and cyclic (Chao & McCullogh, 1960) thioethers react with I_2 to give stable charge-transfer complexes in which the sulfur binds the diiodine molecule to give an almost linear S—I—I grouping. Very recently, we and others have reported on the reaction of I_2 with a range of homoleptic thioether macrocycles (Blake, Gould, Radek & Schröder, 1993; Cristiani *et al.*, 1993; Blake *et al.*, 1997*a*,*b*; Baker, Harris, Durrant, Hughes & Richards, 1995). Although a number of stoichiometries have been observed in the solid state, 1:1 thioether–diiodine adducts appear to be the predominant species in solution regardless of either thioether ring size or the number of S donor atoms in the macrocycle (Blake *et al.*, 1997*a*).

In the present study, we have prepared a new 1:4 stoichiometry in the [14]aneS$_4$/I$_2$ system, namely $C_{10}H_{20}S_4.4I_2$, (1), in addition to the previously known 1:1 and 1:2 adducts (Blake *et al.*, 1997*a*). In the title compound, each of the four S donor atoms coordinates to a diiodine molecule and the resulting adduct exhibits crystallographically imposed inversion symmetry. As seen in related systems (Blake *et al.*, 1997*a*), the asymmetric unit contains geometrically inequivalent S—I—I units, characterized by the parameters: S1—I1 2.803 (2) and S4—I3 2.880 (2) Å, I1—I2 2.7894 (8) and I3—I4 2.7571 (10) Å, and S1—I1—I2 177.71 (5) and S4—I3—I4 172.50 (4)°. The FT–Raman spectrum of the solid adduct shows characteristic ν(I—I) peaks at 166 and 157 cm^{-1}, which correspond to the presence of two differently perturbed diiodine molecules (Deplano *et al.*, 1992), as indicated by the two different I—I distances. The pronounced negative correlation between the S—I and I—I distances has been remarked upon previously (Blake *et al.*, 1997*a*). The macrocyclic conformation differs from that seen in the free ligand [14]aneS$_4$ (DeSimone & Glick, 1976) and in [14]aneS$_4$.I$_2$, both of which have the same [3434] conformation (Dale, 1973), but also from that observed for [14]aneS$_4$.2I$_2$ (Blake *et al.*, 1997*a*). Although also having a [3434] conformation, the title compound is distinguished from the free ligand by having the S atoms lying along the edges rather than at the corners of the macrocycle (Fig. 1). Bond lengths and angles within the thioether ring correspond closely with literature values for other macrocyclic thioethers (Blake & Schröder, 1990).



(1)

Whereas adducts with 1:1 stoichiometry tend to have extended structures dominated by infinite one-dimensional chains comprising alternating macrocycle and I_2 molecules linked by S···I contacts, those with higher proportions of diiodine tend to adopt more complex three-dimensional motifs. Molecules of (1) are linked by both I···I and S···I intermolecular contacts to form an infinite three-dimensional lattice. The I···I

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