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Structure of 2-(*p*-Toluenesulfonyl)-1,2,3,4-tetrahydro-1-isoquinolinecarbonitrile

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Abstract. $C_{17}H_{16}N_2O_2S$, $M_r = 312.4$, monoclinic, $P2_1$, $a = 10.278$ (1), $b = 6.467$ (1), $c = 11.972$ (1) Å, $\beta = 95.46$ (1)°, $V = 792.1$ (2) Å³, $Z = 2$, $D_x = 1.31$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 17.74$ cm⁻¹, $F(000) = 328$, room temperature, $R = 0.054$ for 1088 observed reflexions. The heterocyclic fragment of the molecule exhibits a conformation intermediate between half-chair and sofa. The N atom shows considerable pyramidalization [sum of valency angles = 353 (1)°].

Introduction. This work is a continuation of our studies of the structures of Reissert compounds (Reissert, 1905). It is of interest to determine the effects of substituents on the molecular conformation in such a group of compounds. Our aim is to compare the arrangement of the side fragments relative to the central N(2) atom depending on the character and dimensions of those fragments. So far we have investigated the structure of 2-benzoyl-1,2,3,4-tetrahydro-1-isoquinolinecarbonitrile (I) (Plywaczyk, Tykarska, Jaskólski & Kosturkiewicz, 1984), ethyl 1-cyano-1,2,3,4-tetrahydro-2-isoquinolinecarboxylate (II) (Gzella, Jaskólski, Rychlewska & Kosturkiewicz, 1984) and 2-(*p*-toluenesulfonyl)-1,2,3,4-tetrahydro-isoquinoline (III) (Urbaniak, Jaskólski, Rozwadowska & Kosturkiewicz, 1986), which is the product of reductive decyanation of the present Reissert compound.

Experimental. Crystals obtained from methanol, colorless plates. Space group from Weissenberg photographs and the lack of a symmetry center from statistics. Crystal $0.03 \times 0.15 \times 0.5$ mm. Syntex $P2_1$ diffractometer, θ - 2θ scan. Cell parameters from least-squares treatment of setting angles of 15 reflexions with $16 \leq 2\theta \leq 26^\circ$. An empirical absorption

correction was applied, using ψ scans (North, Phillips & Mathews, 1968) (correction factors were in the range 0.77–0.99). 1175 reflexions with $2\theta \leq 115^\circ$, measured in the range $h: -11 \rightarrow 11$, $k: 0 \rightarrow 7$, $l: 0 \rightarrow 13$. No significant intensity variation ($\pm 2.7\%$) for two standard reflexions (0 $\bar{1}$ 1, 200) recorded every hour. Peak profile analysis according to Lehmann & Larsen (1974), 1091 observed reflexions with $I \geq 2\sigma(I)$. Structure solved by heavy-atom method using *SHELX76* program (Sheldrick, 1976). Full-matrix least-squares refinement (function minimized: $\sum w(F_o - F_c)^2$) of anisotropic non-H atoms. H atoms from molecular geometry, included with fixed isotropic thermal parameters in F_c calculation. $R = 0.054$, $wR = 0.070$, $S = 4.2$, $w = 1/[\sigma^2(F_o) + 0.0001F_o^2]$. $\Delta/\sigma \leq 0.2$, $\Delta\rho_{\max} = 0.22$, $\Delta\rho_{\min} = -0.17$ e Å⁻³.

Computer programs: *SHELX76* (Sheldrick, 1976) and local programs (Jaskólski, 1982). Scattering factors those stored in *SHELX76*. Molecular illustrations drawn using *PLUTO* (Motherwell & Clegg, 1978) and *ORTEP* (Johnson, 1976).

Discussion. Atomic parameters are given in Table 1, bond lengths and angles in Table 2.† The labeling sequence and a view of the molecule are presented in Fig. 1. The molecule consists of an aromatic ring condensed with a heterocyclic hydrogenated ring containing a cyano group and linked through the ring N atom to a toluenesulfonyl group. Bond lengths and angles in the aromatic rings do not deviate significantly from standard values, and the planes of these rings form an angle of 43.4 (1)°. The C9—C1—N2 angle is tetrahedral [110.4 (4)°] in

† 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 52131 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Final fractional coordinates and equivalent isotropic thermal parameters

$$U_{eq} = (U_1 U_2 U_3)^{1/3}$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
S(11)	-0.2130 (2)	0.0	-0.2181 (1)	0.0676 (6)
O(12)	-0.2903 (5)	0.111 (1)	-0.1455 (4)	0.088 (2)
O(13)	-0.2340 (5)	-0.2200 (9)	-0.2374 (4)	0.079 (2)
N(2)	-0.2409 (5)	0.1091 (9)	-0.3406 (4)	0.059 (2)
C(1)	-0.1965 (5)	0.011 (1)	-0.4401 (4)	0.053 (2)
C(3)	-0.2441 (6)	0.338 (1)	-0.3500 (6)	0.063 (3)
C(4)	-0.3499 (7)	0.394 (1)	-0.4430 (6)	0.072 (3)
C(10)	-0.3517 (6)	0.260 (1)	-0.5450 (6)	0.063 (2)
C(5)	-0.4309 (6)	0.312 (2)	-0.6418 (6)	0.079 (3)
C(6)	-0.4407 (8)	0.187 (2)	-0.7357 (7)	0.091 (4)
C(7)	-0.3703 (7)	0.005 (2)	-0.7327 (6)	0.088 (3)
C(8)	-0.2911 (7)	-0.052 (1)	-0.6388 (6)	0.074 (3)
C(9)	-0.2818 (6)	0.076 (1)	-0.5439 (5)	0.058 (2)
C(11)	-0.0564 (7)	0.055 (1)	-0.4531 (5)	0.062 (3)
N(12)	0.0499 (6)	0.089 (1)	-0.4637 (5)	0.079 (3)
C(14)	-0.0478 (6)	0.034 (1)	-0.1694 (5)	0.065 (2)
C(15)	0.0396 (7)	-0.129 (2)	-0.1778 (6)	0.081 (3)
C(16)	0.1684 (8)	-0.105 (2)	-0.1331 (8)	0.090 (3)
C(17)	0.2110 (7)	0.080 (2)	-0.0818 (6)	0.078 (3)
C(18)	0.1242 (8)	0.240 (2)	-0.0792 (6)	0.083 (3)
C(19)	-0.0047 (7)	0.220 (1)	-0.1210 (6)	0.074 (3)
C(20)	0.3514 (9)	0.097 (2)	-0.0296 (8)	0.109 (4)

The y coordinate of atom S(11) defines the origin.

Table 2. Bond lengths (\AA) and selected angles ($^\circ$)

C(1)—N(2)	1.461 (8)	C(9)—C(10)	1.393 (10)
C(1)—C(9)	1.511 (8)	C(11)—N(12)	1.134 (9)
C(1)—C(11)	1.491 (9)	S(11)—O(12)	1.425 (6)
N(2)—C(3)	1.487 (9)	S(11)—O(13)	1.454 (6)
N(2)—S(11)	1.627 (6)	S(11)—C(14)	1.756 (7)
C(3)—C(4)	1.524 (10)	C(14)—C(15)	1.395 (12)
C(4)—C(10)	1.497 (11)	C(15)—C(16)	1.388 (11)
C(5)—C(6)	1.380 (13)	C(16)—C(17)	1.395 (15)
C(5)—C(10)	1.393 (10)	C(17)—C(18)	1.372 (14)
C(6)—C(7)	1.383 (16)	C(17)—C(20)	1.521 (12)
C(7)—C(8)	1.374 (11)	C(18)—C(19)	1.376 (11)
C(8)—C(9)	1.400 (10)	C(19)—C(14)	1.390 (12)
N(2)—C(1)—C(9)	110.4 (4)	N(2)—S(11)—O(12)	105.8 (3)
N(2)—C(1)—C(11)	112.3 (5)	N(2)—S(11)—O(13)	105.7 (3)
C(9)—C(1)—C(11)	110.6 (4)	O(12)—S(11)—C(14)	108.2 (3)
C(1)—N(2)—C(3)	112.2 (5)	C(1)—C(9)—C(10)	120.3 (5)
C(1)—N(2)—S(11)	120.3 (4)	C(1)—C(11)—N(12)	179.6 (6)
C(3)—N(2)—S(11)	120.1 (4)	S(11)—C(14)—C(15)	119.3 (5)
N(2)—C(3)—C(4)	107.6 (5)	S(11)—C(14)—C(19)	120.5 (5)
C(3)—C(4)—C(10)	114.3 (6)	C(16)—C(17)—C(20)	119.4 (8)
C(4)—C(10)—C(9)	121.5 (6)	C(18)—C(17)—C(20)	121.9 (8)
O(13)—S(11)—C(14)	107.5 (4)		

contrast to the value of $114.4(2)^\circ$ found in (I) (Plywaczyk *et al.*, 1984), but in agreement with the value found in (III) [$109.7(5)^\circ$] (Urbaniak *et al.*, 1986), which is rather unexpected, since (III) has no cyano group on C(1). The sum of valence angles around N(2) is $352.6(15)^\circ$ showing its considerable pyramidalization. The average of the absolute values of torsion angles around the heterocyclic ring is 34.2° . The C1—C9—C10—C4 angle is $-2.9(7)^\circ$ and the remaining torsion angles determine the configuration to be intermediate between sofa and half-chair. The corresponding asymmetry parameters (Duax & Norton, 1975) are $C_2^{2,3} = 12.5$ and $C_3^2 = 13.6$. The configuration is, thus, intermediate

between that of (I) and (II). The nitrile C—N bond distance $1.134(9) \text{\AA}$ is equal to that in (I) (Plywaczyk *et al.*, 1984). The geometry around C(1) is almost the same as in (III), which lacks a nitrile group. The sulfonyl S—O bond lengths [$1.425(6)$ and $1.454(6) \text{\AA}$] are comparable with those in (III) [$1.437(6)$ and $1.445(6) \text{\AA}$]. The C—S distance [$1.756(7) \text{\AA}$] is shorter than in (III) [$1.778(8) \text{\AA}$] but similar to that in *p*-toluenesulfonic acid [$1.753(2) \text{\AA}$] reported by Arora & Sundaralingam (1971). The S—N bond length [$1.627(6) \text{\AA}$] is shorter than in (III) [$1.666(6) \text{\AA}$]. The O—S—O angle in the present structure, $120.3(3)^\circ$, is similar to that in (III). It appears that there are no significant geometrical differences from previously determined Reissert compounds.

The inspection of intramolecular nonbonding contacts shows one short contact C(1)—H(1)⋯O(13) [C(1)⋯O(13) = $2.906(8) \text{\AA}$, \angle C(1)—H(1)⋯O(13) = $108.2(5)^\circ$] which can be considered as a weak hydrogen bond. Molecular packing in the unit cell is

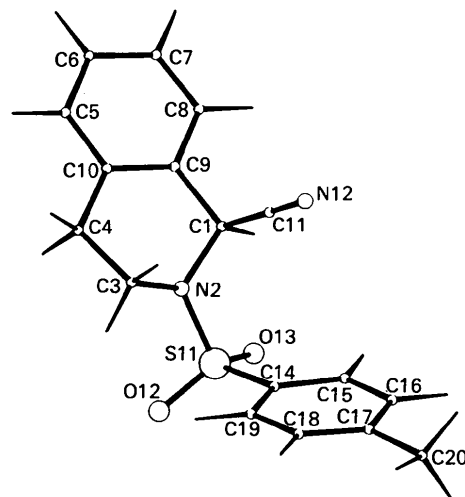


Fig. 1. The view of the molecule with atom numbering.

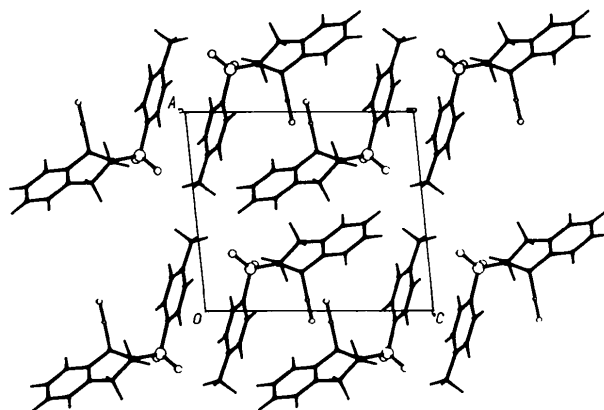


Fig. 2. Projection of the structure down b.

shown in Fig. 2. There are no unusual intermolecular contacts in the structure.

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Structure of Bis(1,3-di-*o*-anisyl-2-thioxo-1,3,2λ⁵-diazaphosphorinan-2-yl) Oxide*

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Abstract. C₃₄H₄₀N₄O₅P₂S₂, *M_r* = 710·80, monoclinic, *P*2₁/*c*, *a* = 12·122 (4), *b* = 18·844 (4), *c* = 7·738 (3) Å, β = 106·99 (2)°, *V* = 1690·5 (9) Å³, *Z* = 2, *D_x* = 1·40 g cm⁻³, λ(Mo Kα) = 0·71069 Å, μ = 3·01 cm⁻¹, *F*(000) = 748, *T* = 291 K, *R* = 0·032 for 2067 observed reflections. The centrosymmetric molecule possesses a linear P—O—P linkage with a P—O bond length of 1·593 (1) Å. The diazaphosphorinane ring adopts a chair conformation with the thiophosphoryl sulfur atom in the equatorial position and the bridging oxygen atom in the axial position. The aromatic substituent at N(3) is axially oriented whereas the substituent at N(1) is rather equatorial. Both nitrogen atoms are pyramidally coordinated.

Introduction. As part of our studies on macrocyclic phosphoramidate derivatives (Dutasta & Simon, 1987), we have investigated the synthesis of rigidified molecules containing the 1,3,2-diazaphosphorinane ring

* *P,P'*-Oxybis(1,3-di-*o*-methoxyphenyl-1,3,2λ⁵-diazaphosphorinane 2-sulfide).

as the binding subunit. The present structure determination was undertaken to identify the main compound (1) formed in the reaction between hexamethylphosphorus triamide (HMPT) and *N,N'*-di-*o*-anisyl-1,3-propanediamine. The unexpected dimeric structure of (1) containing two 1,3,2-diazaphosphorinane rings was first suggested from the NMR and mass spectroscopy data. Knowledge of structures of 1,3,2-diazaphosphorinanes is still rather limited and detailed structural data previously available mainly concern compounds (2) [*R* = OC₂H₅, *R'* = *t*-C₄H₉, *X* = S, *Y* = CH₃; Belov *et al.*, 1981; *R* = Si(C₆H₅)₃, *R'* = *t*-C₄H₉, *X* = lone pair, *Y* = H; Nifant'ev, Sorokina, Vorob'eva, Borisenko & Nevskii, 1985].

The determination of the molecular structure of the title compound is of particular interest as, to our knowledge, no thiopyrophosphoramidic structures have been reported so far. Only the X-ray structures of the acyclic octamethylpyrophosphoramidate (4) in metal complexes have been described (Hussain, Joesten & Lenhart, 1970; Kepert, Patrick & White,