

The Crystal Structure of [1,2,5]Thiadiazolo[3,4-g]benzofurazan 1-Oxide, C₆H₂N₄O₂S

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The structure of [1,2,5]thiadiazolo[3,4-g]benzofurazan 1-oxide was solved by direct methods, and refined by full-matrix least squares, from diffractometer intensities (Mo $K\alpha$ radiation). The compound (m.p. 160°C) crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 4.655$ (5), $b = 15.769$ (8), $c = 9.723$ (4) Å, $\beta = 93.42$ (6)°, $Z = 4$ ($R = 3.5\%$). The H atoms, located on a difference synthesis, were refined isotropically. The molecule, excluding the extranuclear atoms, is approximately planar; the thiadiazolo moiety shows extended π delocalization.

Introduction

The title compound was prepared by A. J. Boulton and co-workers (personal communication) to investigate the effect of fusion of the thiadiazolo ring on the tautomerization rate of benzofuroxan. The effect was marked since the free energy of activation, ΔG^* , increased to ~ 21 kcal mol⁻¹ from ~ 14 kcal mol⁻¹, the characteristic value for benzofuroxan derivatives (e.g. Boulton, Katritzky, Sewell & Wallis, 1967; Altaf-ur-Rahman, Boulton, Clifford & Tiddy, 1968). The present thiadiazolobenzofuroxan may show two positional isomers: the 1-oxide and the 3-oxide. NMR investigations carried out at the University of East Anglia (A. J. Boulton, personal communication) showed that, at room temperature and in polar or non-polar solvents, both isomers were in evidence, the ratio being 1:1:1 in favour of the 3-oxide; this ratio stays fairly constant over a range of $\sim 50^\circ\text{C}$, until the spectrum begins to coalesce.

Structure determination

Experimental results

The compound prepared by Boulton and co-workers was recrystallized from benzene and toluene, in which it is very soluble; squat yellowish prisms, elongated along x , suitable for the X-ray analysis were obtained from toluene. The crystals began to soften at $\sim 152^\circ\text{C}$, well below the melting point. This may indicate a phase change in the solid state; at any rate, only one phase seemed to be present in the crystallization products; this turned out to be the 1-oxide isomer.

The space group and approximate values of the cell parameters were determined by Weissenberg photographs; the latter were then refined by least

squares from diffractometer observations (Mo $K\alpha$ radiation).

Crystal data

C₆H₂N₄O₂S, $M_r = 194.18$, m.p. 160°C, monoclinic, $a = 4.655$ (5), $b = 15.769$ (8), $c = 9.723$ (4) Å, $\beta = 93.42$ (6)°, $U = 712.4$ (9) Å³, space group $P2_1/c$; $F(000) = 392$, $D_c = 1.81$ g cm⁻³, $Z = 4$.

The intensities of 1250 independent reflexions were measured at room temperature on a Philips four-circle diffractometer (Mo $K\alpha$, graphite-monochromatized radiation) by the θ - 2θ step-scanning technique; 1080 reflexions had $I \geq 2.5\sigma(I)$ and were used in the analysis. The scattering factors were those of Cromer & Mann (1968) for neutral S, O, N and C, and those of Stewart, Davidson & Simpson (1965) for H.

Structure solution and refinement

The solution was found with the *MULTAN* suite of programs (Declercq, Germain, Main & Woolfson,

Table 1. Atomic coordinates

Standard deviations are in parentheses.

	x	y	z
S	0.5334 (2)	0.9262 (1)	0.2793 (1)
O(1)	0.9484 (4)	0.5890 (1)	0.0972 (2)
O(2)	0.6139 (4)	0.6150 (1)	0.2588 (2)
N(1)	1.1103 (5)	0.6383 (2)	0.0132 (3)
N(2)	0.7765 (5)	0.6468 (1)	0.1778 (2)
N(3)	0.5641 (5)	0.8231 (1)	0.2798 (2)
N(4)	0.7501 (5)	0.9498 (1)	0.1591 (2)
C(1)	1.0482 (6)	0.7176 (2)	0.0386 (3)
C(2)	0.8453 (5)	0.7240 (2)	0.1410 (3)
C(3)	0.7460 (5)	0.8047 (2)	0.1835 (3)
C(4)	0.8539 (5)	0.8764 (2)	0.1151 (3)
C(5)	1.0615 (6)	0.8685 (2)	0.0091 (3)
C(6)	1.1575 (6)	0.7919 (2)	-0.0259 (3)
H(5)	1.112 (6)	0.925 (2)	-0.037 (3)
H(6)	1.265 (7)	0.781 (2)	-0.094 (3)

1973). With 212 E 's ($E_{\min} = 1.4$) and 2000 Σ_2 relationships, eight sets of phases were generated. The E map from the most consistent set showed all 13 non-hydrogen atoms. The H atoms were located on a difference map. The refinement was by full-matrix anisotropic least squares with unit weights; there was no evidence of secondary extinction. The H atoms were refined isotropically. The results are shown in Table 1. At convergence R was 0.035 (or 0.032 on the exclusion of 53 reflexions which were progressively given zero weight because of poor agreement).^{*} The overall thermal vibration is comparatively small and an analysis of the thermal ellipsoids showed no unusual trend.

^{*} Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32759 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

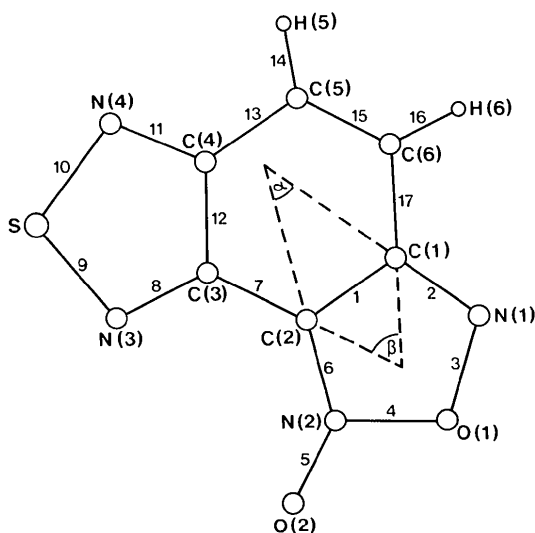


Fig. 1. Projection of the molecule onto the furazan-ring plane, showing the adopted numbering scheme.

Table 2. Bond distances (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

1	1.417 (4)	2	1.311 (4)	3	1.383 (3)	4	1.470 (3)
5	1.232 (3)	6	1.314 (3)	7	1.424 (4)	8	1.332 (3)
9	1.633 (2)	10	1.632 (3)	11	1.334 (3)	12	1.420 (4)
13	1.460 (4)	14	1.02 (3)	15	1.340 (4)	16	0.87 (3)
17	1.436 (4)						
1, 2	111.4 (2)	2, 3	106.9 (2)	3, 4	107.4 (2)		
4, 5	117.6 (2)	4, 6	106.3 (2)	5, 6	136.2 (2)		
6, 1	108.0 (2)	6, 7	131.4 (2)	7, 1	120.6 (2)		
7, 8	129.0 (2)	7, 12	116.5 (2)	8, 9	105.9 (2)		
8, 12	114.4 (2)	9, 10	99.8 (1)	10, 11	106.5 (2)		
11, 12	113.2 (2)	11, 13	124.7 (2)	12, 13	122.0 (2)		
13, 14	114 (2)	13, 15	120.1 (3)	14, 15	125 (2)		
15, 16	126 (2)	15, 17	119.5 (3)	16, 17	114 (2)		
17, 1	121.2 (2)	17, 2	127.5 (3)				

Fig. 1 is the projection of the molecule onto the furazan-ring plane, showing the unconventional numbering scheme already adopted in preceding articles (e.g. Calleri, Chiari, Villa, Manfredotti, Guastini & Viterbo, 1975, 1976). Table 2 presents the intramolecular bonds and angles with reference to Fig. 1.

Description and discussion

Even though, on the basis of statistical tests, the molecule as a whole cannot be considered rigorously planar, none of the endocyclic atoms is more than 0.04 \AA from the mean plane and the angles between the three rings are between 177 and 179 $^\circ$. The molecule, therefore, is approximately planar; the details are in Table 3. The furazan ring is planar with O(2) at -0.016\AA , and its dimensions compare well with the average values for the disubstituted furoxans. The difference between bonds 4 and 3, 0.087 \AA , is among the largest noted so far; most fused-ring furoxans, however, are characterized by $\Delta(4-3)$ values larger than those of the disubstituted derivatives whose mean Δ value is $\sim 0.06 \text{\AA}$ (Calleri *et al.*, 1975, 1976; Calleri, Viterbo, Villa & Guastini, 1975). The dimen-

Table 3. Least-squares mean planes, in fractional coordinates and referred to the unit-cell axes, with the distances, $\delta(\text{\AA})$, of the atoms from the planes

The distances of the atoms not included in the plane equations are given in parentheses; $\chi^2 = \Sigma (\delta/\sigma)^2$.

Plane 1: molecular skeleton	$3.3137x + 0.6927y + 6.3899z = 4.1917$			
	$\chi^2 = 233.6$			
Plane 2: thiadiazolo ring	$3.3498x + 1.0522y + 6.2905z = 4.5165$			
	$\chi^2 = 10.1; \angle_{2,1} = 178^\circ$			
Plane 3: six-membered ring	$3.2994x + 0.9339y + 6.4109z = 4.3786$			
	$\chi^2 = 15.4; \angle_{3,1} = 179^\circ, \angle_{3,2} = 179^\circ$			
Plane 4: furazan ring	$3.2496x + 0.3878y + 6.5401z = 3.9423$			
	$\chi^2 = 3.3; \angle_{4,3} = 178^\circ, \angle_{4,2} = 177^\circ, \angle_{4,1} = 179^\circ$			

Deviations of atoms from planes (\AA)

	Plane 1	Plane 2	Plane 3	Plane 4
S	0.003	0.003		
O(1)	-0.002			0.003
O(2)	(-0.077)			(-0.016)
N(1)	0.015		(-0.033)	0.001
N(2)	-0.034		(-0.073)	-0.005
N(3)	0.035	-0.001	(0.044)	
N(4)	-0.034	-0.006	(0.001)	
C(1)	0.027		-0.001	-0.004
C(2)	0.011		-0.011	0.006
C(3)	0.013		0.014	
C(4)	-0.020	-0.010	-0.005	
C(5)	0.015	0.010	-0.007	
C(6)	0.024		0.011	

sions of the thiadiazolo ring are similar to those of thiadiazole itself (Dobyns & Pierce, 1963; Momany & Bonham, 1964) and are comparable with those of fused-ring and disubstituted thiadiazoles (e.g. Shefter, Evans & Taylor, 1971; Mellini & Merlino, 1976). The lengths of the thiadiazolo-ring bonds are all intermediate between the expected ideal values for the single and double bonds, or even slightly closer to the double-bond values (Pauling, 1960; Gillespie, 1972). The average π -bond order is then considerable ($> 30\%$) and, in conclusion, the thiadiazolo moiety shows an extended π delocalization which implies appreciable $d\pi$ bonding from S (e.g. Saegebarth & Cox, 1965; Mellini & Merlino, 1976).

The X-ray investigation has shown that the compound prepared by Boulton and co-workers (who found that the 3-oxide slightly predominates in solution) crystallizes from benzene and toluene as the 1-oxide. We find a useful reference point with the furoxano- and furazano-fused benzofuroxans (Boulton, Gripper Gray & Katritzky, 1965). These compounds, in fact, show a slightly more stable 3-oxide form ($\Delta G \leq 150 \text{ cal mol}^{-1}$), one form only in the solid state (not yet investigated) and an activation energy ($\Delta G^* \approx 22 \text{ kcal mol}^{-1}$) comparable with that of the present furoxan. The fact that ΔG^* for the furoxan-fused benzofuroxans is intermediate between that of the benzofuroxan derivatives ($\sim 14 \text{ kcal mol}^{-1}$) and that of the aryl-alkyl furoxans ($\sim 33 \text{ kcal mol}^{-1}$) can be accounted for by considering the different stability of the *o*-dinitroso derivatives which are the intermediates of the isomerization reaction (Mallory, Manatt & Wood, 1965; Boulton *et al.*, 1965; Altaf-ur-Rahman *et al.*, 1968). The benzene ring in *o*-dinitrosobenzene possesses the full benzene resonance stabilization whilst the benzo-fused ring in *o*-dinitrosobenzofuroxans clearly has less resonance energy, and, finally, the disubstituted furoxans rearrange *via* dinitroso olefins which are even less stable. In the present compound also, the condensation with the thiadiazolo ring produces effects similar to those observed in the furoxano-fused benzofuroxans. It is then sensible that the ΔG^* for the equilibration of the two forms is here close to that of the named furoxans.

A different approach to this problem was suggested by Boulton & Middleton (1974) who found that the ΔG^* for the isomerization of thieno[2,3-*c*]furoxan is even smaller ($12\text{--}13 \text{ kcal mol}^{-1}$) than that for the benzofuroxans, despite the fact that the aromaticity of thiophene cannot be greater than that of benzene. These authors took into consideration ring strains. The angle between bonds 2 and 6 (α in Fig. 1) is $38 (\pm 2)^\circ$ for the unfused furoxans and furazans (Calleri *et al.*, 1975; Manfredotti, Guastini, Calleri & Viterbo, 1976) which is close to the ideal value (36°) for the angle between non-adjacent sides of a regular pentagon. The corresponding angle is 72° in the thienol[2,3-*c*]furoxans and this corresponds to an angular defor-

Table 4. *Relevant intermolecular contacts*

N(4) ⁱ ...H(5)	2.42 (3) Å
N(4) ⁱ ...C(5)	3.439 (4)
N(3) ⁱⁱ ...H(6)	2.52 (3)
N(3) ⁱⁱ ...C(6)	3.297 (4)
S ⁱⁱⁱ ...N(1)	3.259 (3)
S ⁱⁱⁱ ...O(2)	3.072 (2)
N(4) ⁱ ...H(5)–C(5)	175 (2)°
N(3) ⁱⁱ ...H(6)–C(6)	149 (3)

Symmetry code: (i) $2 - x, 2 - y, z$; (ii) $1 + x, \frac{3}{2} - y, z - \frac{1}{2}$;
(iii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

mation of $72 - 38 = 34^\circ$ with respect to the unfused furoxans. The greater the strain, the smaller should be ΔG^* and *vice versa*. The angle in question is in fact 39.8° for 5-methylbenzofurazan 1-oxide (Britton & Noland, 1972) which implies a deformation of only $60 - 39.8 = 20.2^\circ$ for the fusion to benzene. In the present compound α is $42.3(3)^\circ$ and therefore the deformation for the fusion to benzene is here 17.7° . This value does not seem to be sufficiently smaller than that for methylbenzofuroxan to justify the raising of ΔG^* to $\sim 21 \text{ kcal mol}^{-1}$. There is, however, another source of strain to be considered: this concerns the angle between bonds 7 and 17 (β in Fig. 1), which is $80 (\pm 4)^\circ$ for the unfused furoxans and furazans, and 74° in 3,4-diphenyl-1,2,5-thiadiazole (Mellini & Merlino, 1976). The fusion of the furoxan to the thiophene ring reduces this angle to $44\text{--}47^\circ$ (Boulton & Middleton, 1974; Calleri, Viterbo, Villa & Guastini, 1975). The fusion to a six-membered ring causes a much smaller contraction: the angle β (Fig. 1) is $62.8(3)^\circ$ in methylbenzofuroxan (Britton & Noland, 1972). In the present compound β is $61.9(2)^\circ$ and, therefore, the ΔG^* increase of $\sim 7 \text{ kcal mol}^{-1}$ is to be related to the different resonance stabilization of the corresponding dinitroso derivatives, rather than to ring strains. At any rate, considering that the benzofuroxans also show one form only in the solid state, we may tentatively consider $\Delta G^* \approx 22 \text{ kcal mol}^{-1}$ as the critical value below which it is difficult to crystallize both the positional isomers. It is worth noting that here the angle between bonds 8 and 11 is $47.6(3)^\circ$, identical to that shown by 1,2,5-thiadiazole itself (Dobyns & Pierce, 1963).

The important contacts are given in Table 4, and are clearly of limited extent; we may also add that there is no interaction between N(3) and O(2) [N(3)...O(2) 3.297(3) Å]. The packing offers no clue to the explanation of why the equilibrium should be displaced towards the 1-oxide isomer on crystallization. The effect is probably related to the thermodynamics of crystallization of the two forms.

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The Molecular Structure of μ -Cyclopentadienyl- μ -bromobis(triisopropylphosphine)dipalladium

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The crystal and molecular structure of the novel complex μ -(C₅H₅)- μ -Br-Pd₂[P(CH(CH₃)₂)₃]₂ has been determined by three-dimensional X-ray analysis. The monoclinic unit cell (space group $P2_1/c$) contains four molecules, and has the lattice parameters: $a = 13.002$ (2), $b = 15.551$ (2), $c = 15.733$ (2) Å, $\beta = 116.7$ (1)°. The Pd and P atoms lie almost on a straight line, with the two Pd atoms bonded together and bridged by the Br atom and by the cyclopentadienyl ring. This ring can be considered as formed by an alkene group plus an allyl group.

Introduction

In the course of investigations being carried out at this Institute to study transition-metal complexes (Felkin & Turner, 1977), a dimeric Pd complex was isolated, corresponding to the formula μ -(Cp)- μ -Br-Pd₂[P(iPr)₃]₂ (I).^{*} Two other compounds with similar bridging groups had already been described by X-ray

structural analysis: μ -(Cp)- μ -(C₄H₇)-Pd₂[P(Bz)₃]₂ (II) (Werner, Tune, Parker, Kruger & Brauer, 1975) and μ -(C₃H₅)- μ -I-Pd₂[P(Bz)₃]₂ (III) (Kobayashi, Iitaka & Yamasaki, 1972). In structures II and III, the Pd atoms are bonded to each other, and, furthermore, are bridged on opposite sides of the Pd–Pd bond: in complex II by a cyclopentadienyl ring and a methylallyl group, and in complex III by an allyl group and an I atom. In both structures the cyclopentadienyl or allyl groups are disordered, whereas, in complex I the absence of

^{*} Cp: cyclopentadiene; iPr: isopropyl; Bz: benzene.