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Structure of 7-Chloro-4-ethyl-2,3,3a,4-tetrahydro-1*H*-pyrrolo[2,1-*c*][1,2,4]benzothiadiazine 5,5-Dioxide, $C_{12}H_{15}ClN_2O_2S$

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Abstract. $M_r = 286{\cdot}8$, triclinic, $P\bar{1}$, $a = 10{\cdot}162\,(4)$, $b = 8{\cdot}352\,(4)$, $c = 8{\cdot}258\,(18)$ Å, $\alpha = 90{\cdot}10\,(13)$, $\beta = 107{\cdot}62\,(6)$, $\gamma = 103{\cdot}54\,(4)°$, $V = 647\,(2)$ Å^3, $Z = 2$, $D_m = 1{\cdot}462$, $D_x = 1{\cdot}471$ Mg m^{-3}, graphite-monochromatized Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}443$ mm^{-1}, $F(000) = 300$, room temperature, final $R = 0{\cdot}0327$ for 1825 observed reflections. The N(2) atom is sp^2 hybridized. The C(2)—N(2) interatomic distance indicates some conjugation between N(2) and the benzene ring.

Introduction. The syntheses of a few series of 4-alkyl derivatives of 2,3,3a,4-tetrahydro-1*H*-pyrrolo[2,1-*c*][1,2,4]benzothiadiazine 5,5-dioxide substituted or unsubstituted in the benzene ring were described by Bernabei, Cameroni, Gamberini & Ferioli (1976) and by Cameroni, Bernabei, Forni & Baggio (1978). All the compounds were tested for cardiovascular effects in the anesthetized rat. They produced a marked increase in differential pressure which was often accompanied by a pronounced bradycardia (Cameroni *et al.*, 1978). The aim of the crystal structure determination was to obtain further information on the structure–activity relationships.

Experimental. Transparent elongated prism from 2-propanol, crystal $0{\cdot}51 \times 0{\cdot}34 \times 0{\cdot}25$ mm; D_m by flotation; Philips PW 1100 four-circle diffractometer; 25 reflections ($2 < \theta < 25°$) used for measuring lattice parameters with the Philips *LAT* routine; corrections for Lp and for absorption (spherical shape, $r = 0{\cdot}025$ cm); θ range 2–25°; three standard reflections monitored at intervals of 4 h with maximum intensity variation 2·1%; 2267 independent reflections measured, 442 $[I < 3\sigma(I)]$ considered unobserved; structure solved by direct methods (*MULTAN*, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); C(9), C(11) and C(12) located by ΔF synthesis; F magnitudes used in the least-squares refinement; coordinates of the H atoms calculated by geometrical considerations (*XANADU*, Roberts & Sheldrick, 1975) and confirmed with a ΔF synthesis; parameters refined: coordinates and anisotropic thermal parameters for non-hydrogen atoms, scale and secondary-extinction [final value $2{\cdot}04\,(7) \times 10^{-4}$ calculated anisotropic following Coppens & Hamilton (1970)] coefficients. Final $R_{\text{obs}} = 3{\cdot}27\%$, $R_{\text{all}} = 4{\cdot}26\%$; unit weights. Maximum least-squares shift/error in the last cycle of refinement 0·628; maximum and minimum heights in final difference Fourier map 0·30 and $-0{\cdot}28$ e Å^{-3}; atomic scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974); a locally modified version of *ORFLS* (Busing, Martin & Levy, 1962) and the program *PARST* (Nardelli, 1983) were used. Figures were drawn with the program *ORTEP*II (Johnson, 1976).

Discussion. Final atomic coordinates and equivalent isotropic temperature factors for the non-H atoms are listed in Table 1.* Bond distances and angles are given in Table 2. Fig. 1 shows a perspective view of the molecule with the atom numbering; the packing of the molecules is shown in Fig. 2.

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* Lists of structure factors, anisotropic thermal parameters of non-H atoms, coordinates of the H atoms, and equations of the least-squares planes with the deviations of the atoms from the planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38626 (21 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. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2) *for non-hydrogen atoms, with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j\beta_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Cl	13841 (1)	6747 (1)	2959 (1)	5·04 (2)
S	8526 (1)	6420 (1)	3249 (1)	2·81 (2)
O(1)	7693 (2)	4749 (2)	2942 (2)	3·74 (5)
O(2)	9235 (2)	7079 (2)	4979 (2)	3·96 (5)
N(1)	7467 (2)	7586 (2)	2277 (2)	2·72 (5)
N(2)	7939 (2)	7234 (2)	−400 (2)	3·10 (6)
C(1)	6847 (2)	7012 (3)	451 (3)	2·98 (6)
C(2)	9284 (2)	7072 (2)	375 (2)	2·51 (6)
C(3)	9758 (2)	6719 (2)	2107 (2)	2·53 (6)
C(4)	11141 (2)	6622 (3)	2907 (3)	2·80 (6)
C(5)	12085 (2)	6849 (3)	1986 (3)	3·00 (6)
C(6)	11653 (2)	7151 (3)	276 (3)	3·15 (7)
C(7)	10291 (2)	7267 (3)	−512 (3)	2·89 (6)
C(8)	5782 (3)	7913 (3)	−612 (3)	4·07 (8)
C(9)	5919 (3)	7771 (4)	−2366 (3)	5·06 (10)
C(10)	7478 (3)	7847 (3)	−2093 (3)	4·01 (8)
C(11)	8113 (3)	9390 (3)	2672 (3)	3·59 (7)
C(12)	7261 (3)	10203 (3)	3461 (4)	5·22 (10)

Table 2. *Bond distances* (Å) *and angles* (°) *for non-hydrogen atoms, with e.s.d.'s in parentheses*

Cl—C(5)	1·743 (3)	C(1)—C(8)	1·522 (4)
S—O(1)	1·430 (2)	C(2)—C(3)	1·420 (4)
S—O(2)	1·433 (3)	C(2)—C(7)	1·409 (4)
S—N(1)	1·650 (2)	C(3)—C(4)	1·382 (3)
S—C(3)	1·758 (3)	C(4)—C(5)	1·376 (4)
N(1)—C(1)	1·477 (4)	C(5)—C(6)	1·388 (4)
N(1)—C(11)	1·487 (3)	C(6)—C(7)	1·366 (3)
N(2)—C(1)	1·461 (4)	C(8)—C(9)	1·503 (5)
N(2)—C(2)	1·362 (3)	C(9)—C(10)	1·517 (4)
N(2)—C(10)	1·468 (4)	C(11)—C(12)	1·500 (5)
O(1)—S—O(2)	118·3 (3)	N(2)—C(2)—C(7)	121·2 (4)
N(1)—S—O(1)	107·1 (3)	C(3)—C(2)—C(7)	116·3 (3)
N(1)—S—O(2)	109·1 (3)	S—C(3)—C(2)	117·9 (3)
N(1)—S—C(3)	101·4 (3)	S—C(3)—C(4)	119·9 (3)
C(3)—S—O(1)	109·9 (3)	C(2)—C(3)—C(4)	122·3 (3)
C(3)—S—O(2)	109·7 (2)	C(3)—C(4)—C(5)	118·9 (4)
S—N(1)—C(1)	109·2 (3)	C(4)—C(5)—Cl	120·1 (3)
S—N(1)—C(11)	114·0 (3)	C(4)—C(5)—C(6)	120·6 (3)
C(1)—N(1)—C(11)	116·1 (4)	C(6)—C(5)—Cl	119·3 (3)
C(1)—N(2)—C(2)	123·4 (4)	C(5)—C(6)—C(7)	120·6 (4)
C(1)—N(2)—C(10)	112·3 (3)	C(2)—C(7)—C(6)	121·3 (4)
C(2)—N(2)—C(10)	123·9 (3)	C(1)—C(8)—C(9)	103·7 (3)
N(1)—C(1)—N(2)	111·7 (3)	C(8)—C(9)—C(10)	105·6 (3)
N(1)—C(1)—C(8)	115·7 (3)	N(2)—C(10)—C(9)	103·1 (3)
N(2)—C(1)—C(8)	103·7 (3)	N(1)—C(11)—C(12)	111·6 (4)
N(2)—C(2)—C(3)	122·5 (3)		

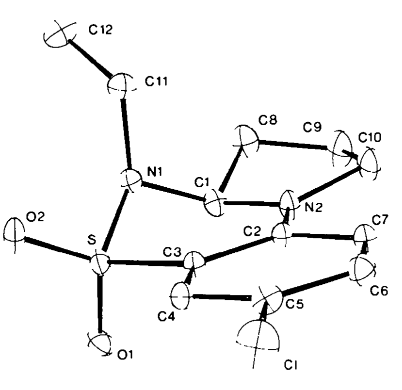

Fig. 1. Perspective view of the molecule.

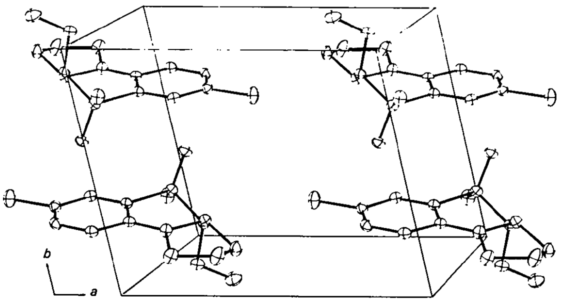

Fig. 2. Packing of the molecules.

The thiadiazine ring has a sofa conformation with a local pseudo-mirror through N(1) and C(2); the values of the ring-puckering coordinates calculated following Cremer & Pople (1975) are $Q = 0{\cdot}560\,(4)$ Å, $\varphi = -3{\cdot}7\,(6)^\circ$ and $\theta = 51{\cdot}7\,(5)^\circ$ [using the atom sequence N(1), C(1), N(2), C(2), C(3), S], with the last five atoms almost coplanar. N(1) is displaced 0·755 (4) Å from the mean plane passing through C(1), N(2), C(2), C(3) and S. C(11) is in an axial position, the N(1)—C(11) bond line forming an angle of 10·1 (2)° with the normal to this last mean plane.

The S atom is tetrahedrally coordinated, with the angle formed by the planes N(1),S,C(3) and O(1),-S,O(2) being 90·8 (2)°. The bond distances and angles involving the sulfone group are regular and agree perfectly with the values found for hydrochlorothiazide (6-chloro-3,4-dihydro-2*H*-1,2,4-benzothiadiazine-7-sulfonamide 1,1-dioxide) (Dupont & Dideberg, 1972); in particular, the value of the angle C(3)—S—N(1) [101·4 (3)°] shows the same deviation from 109·5° due to internal strain in the thiadiazine, already emphasized by the above authors.

The values of the bond angles at N(2) and the planarity of the system, *i.e.* the distance of this atom from the plane defined by C(1), C(2) and C(10) [0·053 (5) Å], show that N(2) is sp^2 hybridized. The C(2)—N(2) bond length [1·362 (3) Å] indicates that there is some conjugation between N(2) and the benzene ring. This could be important for the relationships between structure and activity.

The pyrrolidine ring shows a twist conformation [$Q = 0{\cdot}330\,(5)$ Å, $\varphi = 85{\cdot}5\,(8)^\circ$ for the sequence N(2), C(1), C(8), C(9), C(10)] with an approximate twofold axis passing through the C(8)—C(9) bond line and the N(2) atom.

The Cl substituent is displaced 0·032 (4) Å from the mean plane of the benzene and the value of the angle C(4)—C(5)—C(6) [120·6 (3)°] agrees well with the value of 121·4° predicted when a Cl substituent is present (Domenicano, Mazzeo & Vaciago, 1976).

The dihedral angles between the mean plane of the thiadiazine ring and those of the pyrrolidine and benzene rings are 6·9 (2) and 9·5 (1)° respectively.

All other distances and angles agree well with the expected values.

A crystallographic study on other products of this series has been undertaken in order to evaluate the structure modification by a 4-dialkylaminoalkyl substituent and to confirm the influence of the sp^2-hybridized N atom on the pharmacological activity.

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3′, 3″, 3‴-Phosphinetriyltripropionitrile, $C_9H_{12}N_3P$, at 100 K

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Abstract. $M_r = 193\cdot19$, monoclinic, $P2_1/m$, $a = 6\cdot597\,(2)$, $b = 12\cdot761\,(2)$, $c = 5\cdot9276\,(14)$ Å, $\beta = 90\cdot95\,(2)°$, $V = 498\cdot9\,(2)$ Å^3, $Z = 2$, $D_x = 1\cdot286\,(1)$, $D_m(298\text{ K}) = 1\cdot18\,(1)$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 0\cdot214$ mm^{-1}, $F(000) = 204$. Final $R = 0\cdot040$ for 2484 observed reflections. This low-temperature study shows that the bond lengths and angles in the two independent PCH_2CH_2CN groups are identical, although the C—P—C angles are different [96·79 (4) and 103·17 (4)°]. The result is at variance with recent data from a room-temperature structure determination.

Introduction. Generally, trialkylphosphines are very reactive compounds which oxidize easily and are strong nucleophiles towards carbon and transition metals. Cyanoalkylphosphines are exceptions, the lower members, $P(CH_2CN)_3$ and $P(CH_2CH_2CN)_3$, being air-stable, crystalline compounds with a low nucleophilic reactivity (Henderson & Buckler, 1960; Dahl, Henriksen & Trebbien, 1983). To elucidate the origins of this low reactivity a determination of the crystal structure of $P(CH_2CN)_3$ (Dahl & Larsen, 1979) and an examination of its charge density by theoretical (*ab initio* and CNDO/2) and experimental (X-ray diffraction, IR and photoelectron spectroscopy) methods was initiated (Borch, Dahl, Klæboe & Nielsen, 1981; Larsen, Rettrup & Dahl, 1981). To investigate if common features of the spatial arrangement of the molecules in the crystal can be related to the unusual properties (high melting points, inertness) of these compounds a structure determination was undertaken of $P(CH_2CH_2CN)_3$. After this work was completed another report of the crystal structure of $P(CH_2CH_2CN)_3$ appeared (Cotton, Darensbourg, Fredrich, Ilsley & Troup, 1981), but since our deter-

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