Another possibility of overlap exists between dopamine and a portion of the loxapine cation consisting of ring *C*, the hetero-atom bridge and N(15). Derivatives of clozapine, a closely related dibenzodiazepine featuring a 1,5-benzodiazepine portion, have been prepared and evaluated for neuroleptic activity (Ellefson, Woo, Miller & Kehr, 1978; Kukla, 1977). It was found, however, that the 1,5-benzodiazepine portion of the molecule (similar to the 1,5-benzoxazepine portion of loxapine) was not responsible for neuroleptic activity.

Data collection at Oak Ridge National Laboratory was sponsored by the Division of Basic Energy Sciences of the Department of Energy under contract with Union Carbide Corporation. This study was supported in part by postdoctoral fellowships from the National Institutes of Health (AM06237) and the Muscular Dystrophy Association (81-0360).

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Acta Cryst. (1982). B**38**, 3045–3049

4-Chloro-3-phenylfuroxan and 3-Chloro-4-phenylfuroxan*

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(*Received* 10 *May* 1982; *accepted* 28 *June* 1982)

Abstract

Of the two isomers [$C_8H_5ClN_2O_2$, M_r = 196·50, $F(000)$ = 800], 4-chloro-3-phenylfuroxan (isomer *A*) has the lower melting point (339–340 K). It is orthorhombic, space group *Pbca*, with a = 17·156 (4), b = 12·803 (3), c = 7·835 (2) Å, U = 1720·9 (7) Å^3, Z = 8, D_x = 1·52 Mg m^{-3}, μ(Cu $K\alpha$) = 3·68 mm^{-1}. The higher-melting isomer (347–348 K, isomer *B*), 3-chloro-4-phenylfuroxan, is monoclinic, space group $P2_1/c$, with a = 14·011 (4), b = 9·713 (2), c = 14·198 (4) Å, β = 119·66 (2)°, U = 1679·0 (8) Å^3,

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* Furoxan is furazan *N*-oxide.

0567-7408/82/123045-05$01.00

$Z = 8$, $D_x = 1{\cdot}56$ Mg m^{-3}, μ(Cu $K\alpha$) = 3·78 mm^{-1}. Both structures were solved and refined using diffractometer data (Cu $K\alpha$ radiation) and the final R values are 0·064 (for 985 reflections) and 0·048 (for 1949 reflections) respectively. In isomer B the asymmetric unit is formed by two independent molecules, which show some remarkable differences in the geometry of the furoxan ring; dipole–dipole interactions between the almost-facing bonds C—Cl and N→O and the different planarity of the chlorofuroxan groups can account for these differences, while the former effect can explain the tendency of this isomer to undergo isomerization to form A. The phenyl group is rotated with respect to the five-membered ring by 27·7 (1) and 25·4 (1)° in the two molecules; in isomer A this angle increases to 44·1 (1)°.

Introduction

Recently it has been shown (Calvino, Mortarini, Gasco, Sanfilippo & Ricciardi, 1980) that the two isomers of nitro(phenyl)furoxan and 4-phenyl-3-phenylsulfonylfuroxan have strong antimicrobic activity. The two title isomers were considered in order to correlate their expected reactivity in nucleophilic substitutions with possible antimicrobic activity. As part of this study we have performed the X-ray analysis of the chloro(phenyl)furoxan isomers, which have been prepared and characterized by Calvino, Gasco, Fruttero, Mortarini & Aime (1982). On the basis of the ^{13}C NMR spectra these authors assigned the lower-melting isomer as 4-chloro-3-phenylfuroxan (isomer A) and the higher-melting isomer as 3-chloro-4-phenylfuroxan (isomer B). They also observed that the latter compound is less stable and is easily converted by heating into its positional isomer.

The present investigation was undertaken, as part of a study of various disubstituted furoxans, in order to confirm the structural assignment and to see if the instability of form B can be explained by any geometrical or conformational effect.

Structure determination

Experimental results

Both isomers were recrystallized from petroleum ether (313–333 K) as colorless transparent elongated prisms, somewhat thinner for isomer B.

The unit-cell parameters were determined and refined using diffractometer data (Cu $K\alpha$ radiation). The intensities were collected with different techniques for the two compounds. For isomer A, 1275 independent reflections up to $2\theta = 120°$ were measured at room temperature on a Philips PW 1100 four-circle diffractometer (graphite-monochromatized Cu $K\alpha$ radiation, $\lambda = 1{\cdot}54178$ Å), using the θ–2θ step-scanning technique; 985 reflections with $I \geq 2\sigma(I)$ were used for the refinement. For isomer B, 2234 reflections up to $2\theta = 115°$ were collected at room temperature on a Nicolet $R3$ diffractometer (graphite-monochromatized Cu $K\alpha$ radiation); because of the relative instability of this isomer, the faster ω-scanning technique was employed with variable speed (from 3 to 29·3° min^{-1}); 1949 reflections with $I \geq 2\sigma(I)$ were used for the refinement. In both cases an experimental absorption correction based on the ψ-scan method (North, Phillips & Mathews, 1968) was applied. The data were corrected for background, Lorentz and polarization effects.

Structure solution and refinement

The computations were performed partly using the *SHELX* 76 program (Sheldrick, 1976) and partly with the *XTL* structure determination system supplied with the Nicolet diffractometer (Syntex, 1976). Isomer A was solved by Patterson and Fourier methods and the assignment 4-chloro-3-phenylfuroxan was confirmed. The refinement was carried out by full-matrix least squares and the positions of all H atoms were found on a difference Fourier map. In the final cycles the positional and anisotropic thermal parameters of all non-hydrogen atoms were refined. For the H atoms the positional parameters were varied with constraints on the C—H distances (1·01 ± 0·02 Å for the direct bond and 2·10 ± 0·04 Å for the distances from each H to the two adjacent C in the phenyl ring) and the isotropic thermal parameters were treated as a single variable [$U_{\rm H} = 0{\cdot}101$ (7) Å^2]. The weighting scheme was $w = 1/[\sigma^2(F_o) + qF_o^2]$, where $\sigma(F_o)$ is the estimated standard deviation of the observed amplitudes as derived from counting statistics and q is a parameter to be adjusted after each cycle; its final value was $q = 0{\cdot}005$. In the final stages of the refinement an empirical isotropic-extinction parameter [$F' = F(1 - 0{\cdot}0001 \times gF^2/\sin\theta)$, with the final $g = 0{\cdot}015$ (1)] was also varied in order to reduce some abnormal and systematic discrepancies found for the very large intensities. Convergence was achieved with $R = 0{\cdot}064$ (weighted $R = 0{\cdot}074$).*

For isomer B the solution was obtained by direct methods using 203 reflections with $|E| > 1{\cdot}7$ and three reflections in the starting set. The E map corresponding to the phase set with the best figures of merit revealed all 26 non-hydrogen atoms of the two independent molecules. The refinement was carried out as for isomer A. The positions of the H atoms were derived from geometrical considerations and were

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* Lists of structure factors and anisotropic thermal parameters for both isomers have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38050 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates* ($\times 10^4$) *and temperature factors* ($Å^2 \times 10^3$) *for isomer A*

For non-hydrogen atoms the equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U
Cl	473 (1)	4039 (1)	−3322 (1)	62 (1)
O(1)	−356 (1)	3614 (2)	1050 (4)	65 (1)
O(2)	628 (2)	3451 (2)	2995 (3)	68 (1)
N(1)	−416 (1)	3786 (2)	−677 (4)	60 (1)
N(2)	464 (1)	3589 (2)	1499 (3)	49 (1)
C(1)	299 (2)	3851 (2)	−1216 (5)	47 (1)
C(2)	871 (2)	3734 (2)	79 (3)	43 (1)
C(3)	1724 (2)	3741 (2)	40 (3)	46 (1)
C(4)	2139 (2)	3000 (3)	929 (5)	66 (2)
C(5)	2948 (2)	3007 (3)	883 (6)	80 (2)
C(6)	3333 (3)	3739 (3)	−44 (6)	81 (2)
C(7)	2924 (2)	4475 (3)	−913 (6)	81 (2)
C(8)	2110 (2)	4482 (3)	−897 (5)	65 (2)
H(4)	1851 (17)	2391 (25)	1464 (59)	101 (7)
H(5)	3236 (18)	2365 (24)	1339 (63)	101 (7)
H(6)	3910 (10)	3728 (25)	−133 (48)	101 (7)
H(7)	3219 (18)	5074 (24)	−1473 (52)	101 (7)
H(8)	1821 (18)	5102 (24)	−1395 (54)	101 (7)

Table 2. *Atom coordinates* ($\times 10^4$) *and temperature factors* ($Å^2 \times 10^3$) *for isomer B*

For non-hydrogen atoms the equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U
Cl	4686 (1)	1999 (1)	1521 (1)	74 (1)
O(1)	2107 (2)	4103 (2)	745 (2)	71 (1)
O(2)	3870 (2)	4941 (2)	1427 (2)	84 (1)
N(1)	1618 (2)	2833 (3)	507 (2)	64 (1)
N(2)	3273 (2)	3911 (2)	1158 (2)	62 (1)
C(1)	2400 (2)	1918 (3)	737 (2)	49 (1)
C(2)	3425 (2)	2593 (3)	1139 (2)	50 (1)
C(3)	2137 (2)	444 (3)	537 (2)	51 (1)
C(4)	1095 (2)	66 (3)	−268 (2)	61 (1)
C(5)	826 (2)	−1323 (3)	−440 (2)	71 (1)
C(6)	1573 (3)	−2310 (3)	156 (3)	75 (2)
C(7)	2602 (3)	−1939 (3)	941 (3)	73 (2)
C(8)	2887 (2)	−563 (3)	1142 (2)	62 (1)
Cl′	9669 (1)	226 (1)	3312 (1)	88 (1)
O(1′)	7192 (2)	2420 (2)	1453 (2)	72 (1)
O(2′)	8935 (2)	3186 (2)	2565 (2)	88 (1)
N(1′)	6676 (2)	1150 (2)	1172 (2)	65 (1)
N(2′)	8325 (2)	2185 (3)	2234 (2)	63 (1)
C(1′)	7410 (2)	212 (3)	1735 (2)	47 (1)
C(2′)	8438 (2)	846 (3)	2405 (2)	55 (1)
C(3′)	7105 (2)	−1249 (3)	1609 (2)	48 (1)
C(4′)	6011 (2)	−1610 (3)	1241 (2)	60 (1)
C(5′)	5700 (3)	−2963 (4)	1087 (3)	75 (2)
C(6′)	6447 (3)	−3980 (4)	1282 (3)	77 (2)
C(7′)	7529 (3)	−3656 (3)	1643 (3)	73 (2)
C(8′)	7867 (2)	−2287 (3)	1808 (2)	62 (1)
H(4)	566 (24)	777 (32)	−703 (24)	83 (3)
H(5)	119 (21)	−1439 (32)	−982 (22)	83 (3)
H(6)	1364 (24)	−3207 (26)	7 (23)	83 (3)
H(7)	3194 (23)	−2620 (34)	1335 (24)	83 (3)
H(8)	3559 (23)	−313 (34)	1668 (25)	83 (3)
H(4′)	5490 (24)	−914 (32)	1077 (25)	83 (3)
H(5′)	4961 (24)	−3177 (34)	831 (25)	83 (3)
H(6′)	6240 (27)	−4902 (30)	1128 (27)	83 (3)
H(7′)	7945 (25)	−4410 (33)	1683 (25)	83 (3)
H(8′)	8626 (21)	−2115 (31)	2035 (24)	83 (3)

refined with the same constraints; their single isotropic temperature factor converged to $U_H = 0{\cdot}083\,(3)\,Å^2$. The final value of the parameter q in the weighting scheme was 0·001 and no extinction parameter was considered. At convergence the R value was 0·048 (weighted $R = 0{\cdot}054$).

Refined coordinates and equivalent isotropic temperature factors (Hamilton, 1959) are given in Table 1 for isomer *A* and in Table 2 for isomer *B*.

Description and discussion of the structures

Figs. 1 and 2 show, for the two isomers, the projections of the molecules on the mean planes through the five-membered rings, together with the unconventional labelling of the atoms. Bond distances and angles are given in Tables 3 and 4.

In *A* both the furoxan and the phenyl groups are planar [Cl at 0·023 (1) Å from the furoxan plane] and the dihedral angle between the two planes is 44·1 (1)°. Table 2 shows that between the x coordinates of the two independent molecules of isomer *B* there is an almost constant translation of $\frac{1}{2}$. The furazan ring of molecule *B*(II), surprisingly enough, shows a significant deviation from planarity [$\chi^2 = 17{\cdot}29$, Cl′ at −0·040 (1) Å and O(2′) at 0·041 (3) Å from the least-squares plane] while the five-membered ring of molecule *B*(I) [Cl and O(1) at 0·056 (1) and −0·004 (3) Å from the plane] and both phenyl rings are planar. The dihedral angle between the phenyl and the furazan rings is 27·7 (1)° in molecule (I) and 25·4 (1)° in (II). The relative positions of the two molecules (Fig. 3) are such that the furazan group of one molecule faces the phenyl ring of the other and is almost parallel to it [dihedral angles: furazan(I)–phenyl(II) = 2·5 (1)°, furazan(II)–phenyl(I) = 6·4 (1)°]. The dihedral angles furazan(I)–furazan(II) and phenyl(I)–phenyl(II) are 23·6 (1) and 29·9 (1)°

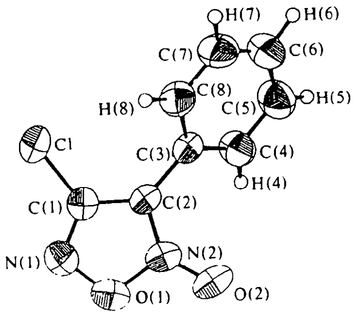

Fig. 1. Isomer *A*: an *ORTEP* II (Johnson, 1970) projection of the molecule on the plane through the five-membered ring. Thermal ellipsoids are drawn at the 50% probability level.

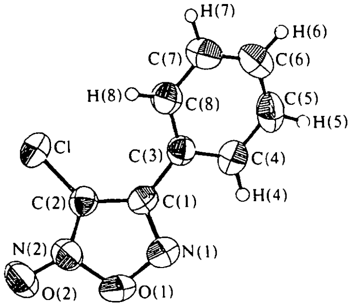

Fig. 2. An *ORTEP* II drawing of isomer *B* (as for Fig. 1).

Table 3. *Bond lengths* (Å) *and bond angles* (°) *for isomer A*

	Uncorrected	Corrected*		Uncorrected	Corrected*
Cl–C(1)	1·694 (4)	1·700	C(2)–C(3)	1·464 (5)	1·466
O(1)–N(1)	1·375 (5)	1·380	C(3)–C(4)	1·376 (5)	1·380
O(1)–N(2)	1·450 (3)	1·453	C(3)–C(8)	1·370 (4)	1·375
O(2)–N(2)	1·218 (4)	1·223	C(4)–C(5)	1·388 (5)	1·391
N(1)–C(1)	1·300 (4)	1·303	C(5)–C(6)	1·357 (6)	1·362
N(2)–C(2)	1·327 (4)	1·331	C(6)–C(7)	1·358 (6)	1·362
C(1)–C(2)	1·419 (4)	1·423	C(7)–C(8)	1·397 (5)	1·399

N(1)–O(1)–N(2)	108·4 (2)	N(2)–C(2)–C(1)	104·5 (3)
O(1)–N(1)–C(1)	105·0 (3)	C(2)–C(3)–C(4)	120·2 (3)
O(1)–N(2)–O(2)	117·4 (3)	C(2)–C(3)–C(8)	119·9 (3)
O(1)–N(2)–C(2)	107·7 (3)	C(4)–C(3)–C(8)	119·9 (3)
O(2)–N(2)–C(2)	134·9 (3)	C(3)–C(4)–C(5)	120·0 (3)
N(1)–C(1)–C(2)	114·4 (3)	C(4)–C(5)–C(6)	120·3 (4)
Cl–C(1)–N(1)	119·5 (3)	C(5)–C(6)–C(7)	119·7 (4)
Cl–C(1)–C(2)	126·1 (2)	C(6)–C(7)–C(8)	121·1 (4)
C(3)–C(2)–N(2)	123·0 (3)	C(3)–C(8)–C(7)	118·9 (4)
C(3)–C(2)–C(1)	132·5 (3)		

* Librational analysis of rigid-body motion was performed using the method of Schomaker & Trueblood (1968).

Table 4. *Bond lengths* (Å) *and bond angles* (°) *for isomer B*

	Uncorrected	Corrected*		Uncorrected	Corrected*
Cl–C(2)	1·674 (3)	1·674	Cl′–C(2′)	1·673 (2)	1·675
O(1)–N(1)	1·369 (3)	1·372	O(1′)–N(1′)	1·385 (3)	1·386
O(1)–N(2)	1·448 (3)	1·449	O(1′)–N(2′)	1·435 (3)	1·435
O(2)–N(2)	1·237 (3)	1·238	O(2′)–N(2′)	1·224 (3)	1·227
N(1)–C(1)	1·320 (4)	1·321	N(1′)–C(1′)	1·309 (3)	1·310
N(2)–C(2)	1·301 (4)	1·302	N(2′)–C(2′)	1·318 (4)	1·319
C(1)–C(2)	1·416 (4)	1·418	C(1′)–C(2′)	1·415 (3)	1·415
C(1)–C(3)	1·471 (4)	1·473	C(1′)–C(3′)	1·468 (4)	1·469
C(3)–C(4)	1·386 (3)	1·387	C(3′)–C(4′)	1·397 (4)	1·398
C(3)–C(8)	1·381 (4)	1·381	C(3′)–C(8′)	1·391 (4)	1·392
C(4)–C(5)	1·390 (4)	1·392	C(4′)–C(5′)	1·368 (5)	1·370
C(5)–C(6)	1·362 (4)	1·363	C(5′)–C(6′)	1·363 (6)	1·365
C(6)–C(7)	1·364 (4)	1·366	C(6′)–C(7′)	1·375 (6)	1·376
C(7)–C(8)	1·384 (4)	1·385	C(7′)–C(8′)	1·392 (4)	1·394

N(1)–O(1)–N(2)	108·1 (2)	N(1′)–O(1′)–N(2′)	107·5 (2)
O(1)–N(1)–C(1)	107·0 (2)	O(1′)–N(1′)–C(1′)	107·7 (2)
O(1)–N(2)–O(2)	118·4 (2)	O(1′)–N(2′)–O(2′)	117·8 (2)
O(1)–N(2)–C(2)	106·4 (2)	O(1′)–N(2′)–C(2′)	106·5 (2)
O(2)–N(2)–C(2)	135·2 (3)	O(2′)–N(2′)–C(2′)	135·7 (2)
N(1)–C(1)–C(2)	109·9 (2)	N(1′)–C(1′)–C(2′)	109·7 (2)
N(1)–C(1)–C(3)	120·6 (2)	N(1′)–C(1′)–C(3′)	120·3 (2)
C(2)–C(1)–C(3)	129·5 (2)	C(2′)–C(1′)–C(3′)	129·9 (2)
Cl–C(2)–N(2)	119·4 (2)	Cl′–C(2′)–N(2′)	118·7 (2)
Cl–C(2)–C(1)	131·9 (2)	Cl′–C(2′)–C(1′)	132·8 (2)
N(2)–C(2)–C(1)	108·7 (2)	N(2′)–C(2′)–C(1′)	108·5 (2)
C(1)–C(3)–C(4)	118·5 (2)	C(1′)–C(3′)–C(4′)	119·2 (2)
C(1)–C(3)–C(8)	121·9 (2)	C(1′)–C(3′)–C(8′)	121·8 (3)
C(4)–C(3)–C(8)	119·5 (2)	C(4′)–C(3′)–C(8′)	118·9 (2)
C(3)–C(4)–C(5)	119·0 (2)	C(3′)–C(4′)–C(5′)	120·3 (3)
C(4)–C(5)–C(6)	121·1 (2)	C(4′)–C(5′)–C(6′)	120·8 (4)
C(5)–C(6)–C(7)	119·9 (3)	C(5′)–C(6′)–C(7′)	120·2 (3)
C(6)–C(7)–C(8)	120·3 (3)	C(6′)–C(7′)–C(8′)	120·1 (3)
C(3)–C(8)–C(7)	120·2 (2)	C(3′)–C(8′)–C(7′)	119·7 (3)

* Librational analysis of rigid body motion was performed using the method of Schomaker & Trueblood (1968).

respectively. The distance between the centers of gravity of the rings in molecule *B*(I) and the centers of gravity of those in *B*(II) at $1-x, -y, -z$ is about 3·5 Å. The general trend of bond distances and angles in the furoxan groups follows that found in other disubstituted furoxan derivatives (Calleri, Chiari, Germain & Viterbo, 1973; Cameron & Freer, 1974; Chiesi Villa, Guastini, Calleri & Chiari, 1974; Calleri, Viterbo, Gaetani Manfredotti & Guastini, 1974; Calleri, Chiari, Chiesi Villa, Gaetani Manfredotti, Guastini & Viterbo, 1975, 1976, 1977; Calvino, Gasco, Serafino & Viterbo, 1981), but there are some interesting features of these chloro(phenyl)furoxans which are worth discussing. As can be seen in Table 4, the two independent molecules of *B* do not differ significantly in their bond distances, except for bonds O(1)–N(1) and O(1)–N(2). A common feature of most furoxan rings is the lengthening of O(1)–N(2) with respect to O(1)–N(1); the latter bond maintains an average value similar to that found in furazans (Viterbo & Serafino, 1978, and references therein) while the former is more or less stretched to a value longer than a single N–O bond. This is in agreement with the proposed isomerization reaction mechanism *via* the breaking of bond O(1)–N(2) and the formation of a dinitroso intermediate. The difference ΔNO between the two endocyclic N–O bonds ranges from 0·038 Å in isopropyl *N*-(4-methyl-3-furoxanyl)carbamate (Calleri, Chiari, Chiesi Villa, Gaetani Manfredotti, Guastini & Viterbo, 1977) to 0·112 Å in 3-methyl-4-nitrofuroxan (Cameron & Freer, 1974), but no systematic correlation can be found between the ΔNO values and the nature of the substituents. The significant difference in the value of ΔNO (0·079 and 0·050 Å for molecules I and II respectively) for the two identical molecules located in different crystal environments suggests that in this case packing forces have a considerable influence in determining the geometry of the N(1)–O(1)–N(2) moiety. Also, isopropyl *N*-(4-methyl-3-furoxanyl)carbamate crystallizes with two independent molecules in the asymmetric unit, but in that case no significant difference in bond distances and angles between the two molecules was found. The considerable effect of packing forces in isomer *B*, although rather disturbing, shows that when the molecules possess a large dipole moment the extrapolation of the molecular geometry in the crystal to that of the isolated molecule could be misleading. For 3-chloro-4-phenylfuroxan an important role is played by the repulsive dipole–dipole interaction between bonds C(2)–Cl and N(2)–O(2). The tension due to this interaction could be responsible for the easy

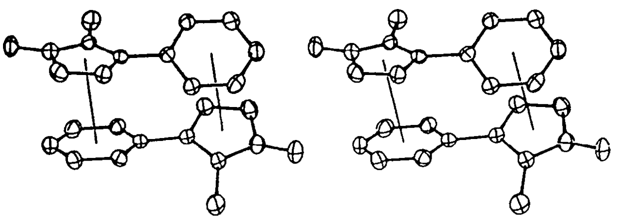

Fig. 3. Isomer *B*: an *ORTEP* II stereoview showing the relative disposition of the two independent molecules. Thermal ellipsoids are drawn at the 20% probability level.

isomerization to 4-chloro-3-phenylfuroxan and is partly released by out-of-plane distortions or by deformations of the ring. In molecule (I), where the deviation from planarity [torsion angle Cl—C(2)—N(2)—O(2)= −1·8 (5)°] is smaller than in (II) [torsion angle Cl′—C(2′)—N(2′)—O(2′) = 2·7 (5)°], the ring deformation is greater and ΔNO is larger. In isomer *A* the significant difference between angles N(1)—C(1)—C(2) and C(1)—C(2)—N(2) (9·9°) is larger than in isomer *B* and this is a feature common to all other disubstituted furoxans studied.

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Struktur von *trans*-1,2,4,5-Tetramethyl-3,6-diphenoxy-1,2,4,5-tetraaza-3,6-diphosphacyclohexan-3,6-disulfid

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(*Eingegangen am* 18. *März* 1982; *angenommen am* 5. *Juli* 1982)

Abstract

$C_{16}H_{22}N_4O_2P_2S_2$ is orthorhombic, $P2_12_12_1$, with a = 7·530 (2), b = 8·081 (2), c = 35·522 (2) Å, V = 2161·5 (5) Å^3, Z = 4, D_c = 1·316 Mg m^{-3}. The structure was solved by direct methods and refined to R = 0·047 (R_w = 0·052) for 1776 contributing reflections. The heterocycle has a twist conformation; the PNN angles range from 111·9 (5) to 116·4 (5)°, and the NPN angles are 99·3 (3) and 101·0 (3)°. Mean bond distances: P—N 1·648 (6), N—N 1·40 (1), P—S 1·910 (3), P—O 1·597 (5), O—C 1·384 (8) Å.

Einleitung

Über die Struktur des *cis*-Isomeren der Titelverbindung (1) wurde von Engelhardt & Viertel (1982) berichtet. Es zeigte sich, dass der zugrundeliegende Phosphor-Stickstoff-Sechsring in Twistform vorliegt. Hier soll

0567-7408/82/123049-04$01.00