123·3 kJ mol^{-1}, but *A* converged on a slightly different minimum at 127·9 kJ mol^{-1}. Using *MMI-CARB*, all three molecules converged on the same minimum at 117·7 kJ mol^{-1}. A slightly better least-squares molecular fit was also obtained with the modified program, giving a mean difference of 0·04 Å, *versus* 0·05 Å for the *MMI* program.

The agreement between the mean observed and the calculated dimensions is given in Table 4 for comparison with the observed differences between the three molecules shown in Fig. 1. With the exception of the bond lengths C(6)—O(1) and C(5)—O(5), the *MMI-CARB* program reproduced the dimensions of the molecule to within 3σ for an individual molecule. The C(6)—O(1) and C(5)—O(5) bonds are the external bonds in a C—O—C—O—C sequence and have been observed to be longer than normal both in other 1,6-anhydro sugars (*cf.* Table 3 in Noordik & Jeffrey, 1977) and in the linkage bonds between residues in oligosaccharides (*cf.* Table 5 in Jeffrey, Pople & Radom, 1974). Although this is also believed to be a consequence of the 'anomeric effect', it was not parameterized as such in *MMI-CARB*, as were the better-understood C(1)—O bond lengths and torsion potentials.

The orientations of the three hydroxyl groups given in Table 3 depend on the intermolecular hydrogen bonding, which is not modelled by the molecular-mechanics calculations which refer to isolated molecules. The large discrepancies shown in Table 3 between the observed and calculated values of these torsion angles are therefore neither unexpected nor significant.

A further calculation was carried out with the three C—C—O—H torsion angles fixed at their observed value for the three molecules. This gave minimum energies of 147·6, 136·3 and 130·4 kJ mol^{-1} for molecules *A*, *B* and *C* respectively, significantly greater than those of the unrestricted molecules. There were also small differences in the optimized bond lengths and valence angles which were less than the experimental standard deviations. The mean values for the three molecules are shown in Table 4.

References

ALLINGER, N. L. (1976). *Adv. Phys. Org. Chem.* **13**, 1–82.

ALLINGER, N. L. & CHUNG, D. Y. (1976). *J. Am. Chem. Soc.* **98**, 6798–6803.

CHOONG, W. (1979). *Cryst. Struct. Commun.* **8**, 27–32.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

JEFFREY, G. A. & PARK, Y. J. (1979). *Carbohydr. Res.* **74**, 1–5.

JEFFREY, G. A., POPLE, J. A. & RADOM, L. (1974). *Carbohydr. Res.* **38**, 81–95.

JEFFREY, G. A. & TAYLOR, R. (1980). *J. Comput. Chem.* In the press.

JEFFREY, G. A. & YATES, J. H. (1979). *Carbohydr. Res.* **74**, 319–322.

NEWTON, M. D., JEFFREY, G. A. & TAKAGI, S. (1979). *J. Am. Chem. Soc.* **101**, 1997–2002.

NOORDIK, J. H. & JEFFREY, G. A. (1977). *Acta Cryst.* B**33**, 403–408.

NYBURG, S. C. (1974). *Acta Cryst.* B**30**, 251–253.

POPPLETON, B. J., JEFFREY, G. A. & WILLIAMS, G. J. B. (1975). *Acta Cryst.* B**31**, 2400–2404.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TAKAGI, S. & JEFFREY, G. A. (1978). *Acta Cryst.* B**34**, 2551–2555.

Acta Cryst. (1980). B**36**, 865–869

Crystal and Molecular Structures of Diazapolycyclic Compounds. VI. 1*H*,4*H*- and 3*H*,4*H*-2,3-Dimethylpyridazino[1,2-*b*]benzo[*g*]phthalazine-6,13-dione

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Abstract

The crystal structures of 1*H*,4*H*- and 3*H*,4*H*-2,3-dimethylpyridazino[1,2-*b*]benzo[*g*]phthalazine-6,13-dione have been solved by direct methods. The molecules have been compared by half-normal probability plots. The rings to which the methyl groups are bonded present different conformations. The hybridization of the N atoms is almost sp^2. [Crystal data: $C_{18}H_{16}N_2O_2$, M_r = 292·34. Isomer 1*H*,4*H*: triclinic, $P\bar{1}$, *a* = 13·1795 (9), *b* = 8·0356 (5), *c* = 7·8197 (5) Å,

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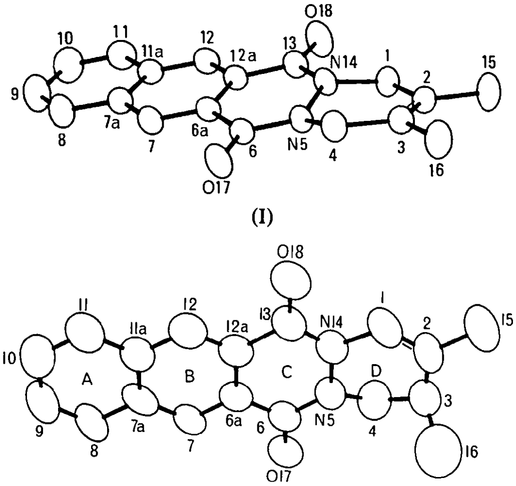
α = 119·55 (1), β = 101·72 (1), γ = 82·37 (1)°, Z = 2, D_x = 1·38 Mg m^{-3}. Isomer 3*H*,4*H*: monoclinic, $C2/c$, a = 14·5110 (9), b = 10·4883 (6), c = 19·9077 (23) Å, β = 102·45 (1)°, Z = 8, D_x = 1·31 Mg m^{-3}.]

Introduction

Following the project for obtaining analogues of tetracyclines with biological activity (López, Lora-Tamayo, Navarro & Soto, 1974; Gómez-Contreras, Lora-Tamayo, Navarro & Pardo, 1978), a new ring has been added to some tricyclic compounds (Foces-Foces, Cano & García-Blanco, 1977; Apreda, Foces-Foces, Cano & García-Blanco, 1978) and the study of the isomers 1*H*,4*H*- and 3*H*,4*H*-2,3-dimethylpyridazino-[1,2-*b*]benzo[*g*]phthalazine-6,13-dione (hereafter compounds I and II) was undertaken.

Experimental and refinement methods

The crystal and experimental data and structure-refinement parameters are given in Table 1. The structures were solved with *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). For (I), the *E* map showed a chicken-wire pattern. A hypothesis was set with the highest peaks of the map centring the molecular rings. This hypothesis was refined successfully by the tangent formula and all the heavy atoms were obtained. The solution of (II) presented no difficulty. After refinement final difference syntheses for the structures showed no electron densities >0·18 and 0·48 e Å^{-3}, respectively.



(I)

(II)

Fig. 1. *ORTEP* drawing (Johnson, 1965) of (I) and (II) showing the atom numbering.

Table 1. *Crystal and experimental data and structure-refinement parameters*

	(I)	(II)
	$C_{18}H_{16}N_2O_2$	$C_{18}H_{16}N_2O_2$
System	Triclinic	Monoclinic
a (Å)	13·1795 (9)	14·5110 (9)
b (Å)	8·0356 (5)	10·4883 (6)
c (Å)	7·8197 (5)	19·9077 (23)
α (°)	119·55 (1)	
β (°)	101·72 (1)	102·45 (1)
γ (°)	82·37 (1)	
V (Å^3)	704·89 (8)	2958·6 (4)
M_r	292·34	292·34
D_x (Mg m^{-3})	1·38	1·31
Space group	$P\bar{1}$	$C2/c$
Z	2	8
Crystal size (mm)	0·35 × 0·32 × 0·14	0·48 × 0·32 × 0·27
Stability	No significant variation	
Technique and geometry	Four-circle diffractometer (Philips PW 1100) with graphite-monochromated radiation; $\omega/2\theta$ scan mode	
Radiation	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0·0851	0·0811
Total measurement, up to θ (°)	28	28
Number of independent reflexions	2562	2672
Criterion for observed reflexions	$I > 2\sigma(I)$	$I > 3·5\sigma(I)$
Number of observed reflexions	1657	1174
Atomic scattering factors	*International Tables for X-ray Crystallography* (1974)	
Computer programs	XRAY 70 system (Stewart, Kundell & Baldwin, 1970)	
Solution	*MULTAN* 77 system	
Refinement method	Block-diagonal on observed *F*'s	
H atoms	From difference synthesis	
Parameters refined*		
Non-hydrogen atoms	(coordinates and anisotropic temperature factors)	
	198	198
Hydrogen atoms	(coordinates and isotropic temperature factors)	
	64	45
Extinction correction	Not applied	
Number of reflexions per parameter	6·3	4·5
Weighting scheme	Empirical so as to give no trends in $\langle w\Delta^2\rangle$	
R (obs.)	0·051	0·103
R_w (obs.)	0·055	0·115

* H(3) was fixed. Refinement only on *U*'s of H(4*b*), H(15*a*), H(16*a*), H(16*b*) and H(16*c*) (II).

The atomic coordinates are listed in Tables 2 and 3. Table 4 gives bond distances and angles. Some torsion angles are displayed in Table 5.*

Discussion

The molecules, with the atomic numbering, are shown in Fig. 1. They have been compared by half-normal

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* Lists of structure factors and anisotropic thermal parameters for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34990 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final positional parameters* (× 10^4) *with their e.s.d.'s for the heavy atoms*

		(I)				(II)	
	x	*y*	*z*		*x*	*y*	*z*
C(1)	1906 (2)	−591 (4)	2314 (4)	C(1)	3709 (9)	3683 (10)	4284 (4)
C(2)	2517 (2)	1082 (4)	3890 (4)	C(2)	4436 (7)	3336 (9)	4041 (4)
C(3)	2076 (2)	2693 (4)	5115 (4)	C(3)	5161 (7)	2489 (11)	4443 (4)
C(4)	930 (2)	2944 (3)	5043 (4)	C(4)	4808 (8)	1788 (12)	5001 (5)
N(5)	357 (1)	1166 (3)	3794 (3)	N(5)	4321 (4)	2726 (6)	5388 (3)
C(6)	−678 (2)	1321 (3)	3884 (3)	C(6)	4334 (5)	2467 (6)	6064 (3)
C(6a)	−1326 (2)	−225 (3)	2269 (3)	C(6a)	3627 (4)	3077 (6)	6373 (3)
C(7)	−2367 (2)	−148 (3)	2303 (4)	C(7)	3623 (5)	2887 (7)	7051 (3)
C(7a)	−3007 (2)	−1613 (4)	778 (4)	C(7a)	2931 (5)	3408 (6)	7355 (3)
C(8)	−4089 (2)	−1578 (4)	759 (4)	C(8)	2909 (6)	3191 (7)	8058 (3)
C(9)	−4681 (2)	−3041 (5)	−709 (5)	C(9)	2220 (7)	3733 (8)	8325 (4)
C(10)	−4224 (2)	−4602 (4)	−2250 (5)	C(10)	1512 (7)	4477 (8)	7937 (4)
C(11)	−3198 (2)	−4689 (4)	−2287 (4)	C(11)	1528 (7)	4739 (8)	7262 (4)
C(11a)	−2550 (2)	−3201 (3)	−775 (4)	C(11a)	2224 (5)	4186 (6)	6964 (3)
C(12)	−1485 (2)	−3228 (3)	−784 (4)	C(12)	2254 (6)	4399 (7)	6260 (4)
C(12a)	−884 (2)	−1759 (3)	687 (3)	C(12a)	2912 (5)	3839 (6)	5966 (3)
C(13)	221 (2)	−1797 (3)	619 (3)	C(13)	2892 (6)	4004 (7)	5212 (3)
N(14)	775 (1)	−277 (3)	2107 (3)	N(14)	3589 (4)	3441 (6)	4973 (3)
C(15)	3669 (2)	714 (6)	3854 (6)	C(15)	4443 (12)	3701 (18)	3299 (5)
C(16)	2644 (2)	4463 (5)	6696 (5)	C(16)	6089 (14)	3093 (19)	4751 (9)
O(17)	−1032 (1)	2704 (2)	5269 (2)	O(17)	4937 (3)	1736 (5)	6387 (2)
O(18)	655 (1)	−3089 (2)	−697 (3)	O(18)	2266 (4)	4624 (6)	4841 (3)

Table 3. *Final positional parameters* (× 10^3) *with their e.s.d.'s and bond distances* (Å) *for the hydrogen atoms*

		(I)					(II)		
	x	*y*	*z*	C–H		*x*	*y*	*z*	C–H
H(1*a*)	205 (2)	−170 (3)	257 (3)	0·99 (3)	H(1)	329 (8)	400 (10)	411 (6)	0·71 (11)
H(1*b*)	206 (2)	−85 (4)	106 (4)	0·96 (3)	H(3)	564 (15)	189 (19)	424 (8)	1·09 (21)
H(4*a*)	65 (2)	382 (3)	448 (3)	1·00 (3)	H(4*a*)	532 (8)	122 (11)	533 (6)	1·05 (11)
H(4*b*)	81 (2)	334 (3)	635 (3)	0·95 (3)	H(4*b*)	420 (15)	130 (19)	483 (8)	1·01 (11)
H(7)	−262 (2)	86 (3)	333 (4)	0·89 (2)	H(7)	411 (6)	256 (7)	724 (4)	0·80 (8)
H(8)	−439 (2)	−47 (4)	177 (4)	0·96 (2)	H(8)	345 (7)	252 (9)	826 (5)	1·06 (9)
H(9)	−540 (2)	−295 (4)	−71 (4)	0·94 (3)	H(9)	213 (6)	358 (9)	872 (5)	0·85 (11)
H(10)	−468 (2)	−563 (4)	−328 (4)	0·99 (2)	H(10)	99 (7)	485 (10)	811 (5)	0·98 (11)
H(11)	−288 (2)	−571 (4)	−332 (4)	0·95 (2)	H(11)	96 (7)	522 (9)	702 (5)	1·00 (9)
H(12)	−118 (2)	−419 (3)	−174 (3)	0·89 (2)	H(12)	173 (7)	482 (9)	601 (5)	0·92 (9)
H(15*a*)	387 (3)	83 (6)	288 (6)	0·90 (6)	H(15*a*)	388 (15)	346 (19)	297 (8)	0·97 (11)
H(15*b*)	384 (3)	−53 (6)	369 (6)	0·94 (5)	H(15*b*)	522 (14)	385 (19)	338 (8)	1·12 (21)
H(15*c*)	409 (3)	149 (5)	505 (6)	0·94 (3)	H(15*c*)	470 (15)	424 (16)	340 (8)	0·69 (18)
H(16*a*)	235 (3)	553 (6)	657 (6)	0·93 (5)	H(16*a*)	614 (15)	330 (19)	425 (8)	1·03 (21)
H(16*b*)	334 (3)	446 (5)	663 (5)	0·93 (4)	H(16*b*)	671 (15)	274 (19)	495 (8)	0·98 (11)
H(16*c*)	264 (3)	475 (6)	790 (7)	0·86 (6)	H(16*c*)	600 (15)	379 (19)	505 (8)	0·97 (11)

probability plots for interatomic distances up to 4·0 Å (Abrahams & Keve, 1971) (Fig. 2). The main differences result for those points in which C(1), C(2), C(3) and C(4) are involved.

From the torsion angles in the *D* rings we have calculated the distortion parameters for the amide groups (Winkler & Dunitz, 1971). The deformations are greater at N than at C, as is usual (Table 6). The average angle around the N atoms is within the range 118·2–119·8°, as is usual for sp^2 hybridization. The conformations for the pyridazine rings have been described according to a model for flexible six-membered rings (Cano, Foces-Foces & García-Blanco, 1977) and the resulting parameters are listed in Table 6. For (I) the ring has a half-chair conformation at the C(2)–C(3) bond, while for (II) the ring adopts a conformation between monoplanar at N(14)–C(1) and monoplanar at C(1)–C(2).

The diazaquinone rings are planar. The attached O atoms have deviations from their respective rings of 0·088 (2) and −0·072 (2) Å for O(17) and O(18) respectively in (I). Similarly, for (II) the O atoms deviate 0·123 (5) and 0·054 (6) Å.

The C–C lengths in the aromatic moiety range from

Table 4. *Bond lengths* (Å) *and angles* (°)

	(I)	(II)		(I)	(II)		(I)	(II)
C(1)–C(2)	1·492 (3)	1·303 (17)	C(6)–C(6a)	1·470 (3)	1·454 (10)	C(9)–C(10)	1·411 (4)	1·385 (12)
C(1)–N(14)	1·467 (3)	1·443 (11)	C(6)–O(17)	1·228 (2)	1·234 (8)	C(10)–C(11)	1·350 (4)	1·377 (12)
C(2)–C(3)	1·317 (3)	1·475 (13)	C(6a)–C(7)	1·371 (4)	1·366 (9)	C(11)–C(11a)	1·422 (3)	1·403 (12)
C(2)–C(15)	1·511 (4)	1·527 (15)	C(6a)–C(12a)	1·409 (3)	1·418 (8)	C(11a)–C(12)	1·402 (4)	1·428 (10)
C(3)–C(4)	1·491 (3)	1·510 (15)	C(7)–C(7a)	1·411 (3)	1·390 (11)	C(12)–C(12a)	1·372 (3)	1·357 (12)
C(3)–C(16)	1·511 (4)	1·495 (21)	C(7a)–C(8)	1·420 (4)	1·426 (9)	C(12a)–C(13)	1·464 (4)	1·505 (10)
C(4)–N(5)	1·475 (3)	1·516 (13)	C(7a)–C(11a)	1·425 (3)	1·407 (9)	C(13)–N(14)	1·367 (3)	1·343 (11)
N(5)–C(6)	1·366 (3)	1·369 (9)	C(8)–C(9)	1·362 (4)	1·355 (13)	C(13)–O(18)	1·222 (3)	1·226 (9)
N(5)–N(14)	1·417 (2)	1·411 (8)						
N(14)–C(1)–C(2)	115·6 (2)	125·2 (9)	C(6a)–C(6)–O(17)	122·7 (2)	122·5 (6)	C(12)–C(11a)–C(7a)	119·1 (2)	117·4 (7)
C(1)–C(2)–C(3)	122·4 (2)	120·4 (8)	C(6)–C(6a)–C(12a)	120·4 (2)	120·2 (6)	C(11)–C(11a)–C(12)	122·3 (2)	121·8 (6)
C(1)–C(2)–C(15)	112·3 (2)	117·7 (10)	C(7)–C(6a)–C(12a)	120·2 (2)	119·2 (6)	C(11a)–C(12)–C(12a)	120·8 (2)	121·9 (7)
C(3)–C(2)–C(15)	125·3 (3)	121·5 (10)	C(6)–C(6a)–C(7)	119·3 (2)	120·6 (6)	C(12)–C(12a)–C(6a)	120·2 (2)	119·6 (6)
C(2)–C(3)–C(4)	121·9 (2)	112·2 (9)	C(6a)–C(7)–C(7a)	120·6 (2)	122·0 (6)	C(13)–C(12a)–C(6a)	120·0 (2)	119·3 (7)
C(2)–C(3)–C(16)	125·3 (2)	116·3 (11)	C(7)–C(7a)–C(11a)	119·0 (2)	119·7 (6)	C(12)–C(12a)–C(13)	119·8 (2)	121·2 (6)
C(4)–C(3)–C(16)	112·8 (2)	108·8 (9)	C(8)–C(7a)–C(11a)	118·8 (2)	117·9 (7)	C(12a)–C(13)–N(14)	117·1 (2)	116·6 (6)
C(3)–C(4)–N(5)	114·8 (2)	109·1 (9)	C(7)–C(7a)–C(8)	122·2 (2)	122·4 (6)	C(12a)–C(13)–O(18)	123·4 (2)	120·9 (7)
C(4)–N(5)–N(14)	117·3 (2)	115·0 (6)	C(7a)–C(8)–C(9)	120·7 (2)	119·6 (7)	N(14)–C(13)–O(18)	119·5 (2)	122·5 (7)
C(6)–N(5)–N(14)	121·9 (2)	122·0 (6)	C(8)–C(9)–C(10)	120·2 (3)	122·6 (8)	C(13)–N(14)–N(5)	122·7 (2)	123·8 (6)
C(4)–N(5)–C(6)	115·9 (2)	117·4 (6)	C(9)–C(10)–C(11)	121·0 (2)	119·4 (9)	C(1)–N(14)–N(5)	117·6 (2)	114·8 (7)
N(5)–C(6)–C(6a)	117·1 (2)	117·8 (6)	C(10)–C(11)–C(11a)	120·8 (2)	119·7 (8)	C(13)–N(14)–C(1)	115·3 (2)	120·9 (7)
N(5)–C(6)–O(17)	120·2 (2)	119·7 (7)	C(11)–C(11a)–C(7a)	118·6 (2)	120·8 (6)			

Table 5. *Main torsion angles* (°)

	(I)	(II)		(I)	(II)
N(14)–C(1)–C(2)–C(3)	4·7 (4)	8·4 (15)	C(12a)–C(13)–N(14)–N(5)	8·1 (3)	−0·2 (10)
C(1)–C(2)–C(3)–C(4)	1·4 (4)	18·4 (13)	C(13)–N(14)–N(5)–C(6)	−11·7 (3)	5·2 (10)
C(2)–C(3)–C(4)–N(5)	11·5 (4)	−47·2 (11)	N(14)–N(5)–C(6)–C(6a)	7·9 (3)	−7·1 (9)
C(3)–C(4)–N(5)–N(14)	−31·5 (3)	54·7 (10)	N(5)–C(6)–C(6a)–C(12a)	−1·6 (4)	4·4 (9)
C(4)–N(5)–N(14)–C(1)	38·8 (3)	−30·1 (9)	C(6)–C(6a)–C(12a)–C(13)	−1·5 (4)	0·3 (9)
N(5)–N(14)–C(1)–C(2)	−24·9 (3)	−2·6 (13)	C(6a)–C(12a)–C(13)–N(14)	−1·6 (4)	−2·4 (10)
O(18)–C(13)–N(14)–C(1)	−17·1 (3)	8·5 (12)	O(17)–C(6)–N(5)–C(4)	−17·6 (3)	20·6 (10)
C(12a)–C(13)–N(14)–N(5)	8·1 (3)	−0·2 (10)	C(6a)–C(6)–N(5)–N(14)	7·9 (3)	−7·1 (9)
O(18)–C(13)–N(14)–N(5)	−172·9 (2)	179·7 (6)	O(17)–C(6)–N(5)–N(14)	−172·1 (2)	173·0 (6)
C(12a)–C(13)–N(14)–C(1)	163·8 (2)	−171·5 (7)	C(6a)–C(6)–N(5)–C(4)	162·4 (2)	−159·5 (6)

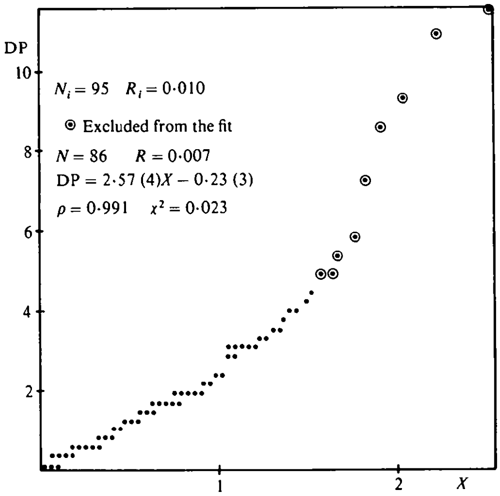

Fig. 2. Half-normal probability plot.

Table 6. *Conformational parameters* (°)

E.s.d.'s are about 0·6°.

(*a*) Distortion parameters for N(14) and N(5)

	N(14)		N(5)	
	(I)	(II)	(I)	(II)
χ_N	24·2	−8·8	25·5	−27·6
χ_C	0·9	0·0	0·0	−0·1
τ	175·5	−175·9	175·2	−173·3

(*b*) Parameters for the pyridazine ring [φ_0 is the torsion angle around N(5)–N(14)]

	(I)	(II)
τ_m	18·3	−23·7
q	20·5	31·6
$\sum$	21·8	−195·9
δ	53·6	277·2
α_1	37·7	40·7
α_2	−15·9	123·5

1·350 (4) to 1·425 (3) Å for (I) and from 1·355 (13) to 1·428 (10) Å for (II), similar to those given by Cox & Sim (1979). The orientation of methyl C(16) in (II) is axial.

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References

ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* A**27**, 157–165.
APREDA, M. C., FOCES-FOCES, C., CANO, F. H. & GARCÍA-BLANCO, S. (1978). *Acta Cryst.* B**34**, 2666–2669.
CANO, F. H., FOCES-FOCES, C. & GARCÍA-BLANCO, S. (1977). *Tetrahedron*, **33**, 797–802.
COX, P. J. & SIM, G. A. (1979). *Acta Cryst.* B**35**, 404–410.
FOCES-FOCES, C., CANO, F. H. & GARCÍA-BLANCO, S. (1977). *Acta Cryst.* B**33**, 3957–3959.
GÓMEZ-CONTRERAS, F., LORA-TAMAYO, M., NAVARRO, P. & PARDO, M. (1978). *Tetrahedron*, **34**, 3499–3509.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
LÓPEZ, B., LORA-TAMAYO, M., NAVARRO, P. & SOTO, J. L. (1974). *Heterocycles*, **2**, 649–652.
MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
WINKLER, F. K. & DUNITZ, J. D. (1971). *J. Mol. Biol.* **59**, 169–182.

Acta Cryst. (1980). B**36**, 869–872

Hétérocycles Contenant du Phosphore.
XXXVI. Structure du Sulfure-7 de Diméthyl-6,8 Phénoxy-7 Oxa-3 Tétraaza-1,5,6,8 Phospha-7 Bicyclo[3.3.1]nonane

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Abstract

The structure of the title compound, $C_{11}H_{17}N_4O_2PS$, M_r = 300·2, has been determined by X-ray single-crystal methods. Crystals are monoclinic, space group $P2_1/c$ with a = 8·166 (1), b = 15·495 (3), c = 11·242 (6) Å, β = 94·43 (3)°, Z = 4, V = 1418 Å^3, d_m = 1·37 (4), d_x = 1·40 Mg m^{-3}, μ(Mo $K\alpha$) = 0·342 mm^{-1}, $F(000)$ = 632. The structure has been solved from 2633 independent reflexions with $I > 3\sigma(I)$ and refined by least squares to an R = 0·040 (R_w = 0·058). There is no symmetry plane in the molecule. One of the two six-membered rings exhibits a perfect chair form; the other also has a chair conformation, but is very flattened on the phosphorus side because of steric hindrance.

Introduction

Dans un mémoire (Majoral, Revel & Navech, 1980), nous avons montré que l'action du formaldéhyde sur un phosphodihydrazide (1) conduit, après différents intermédiaires, à un composé auquel l'étude RMN ^{1}H et ^{13}C permettait d'attribuer raisonnablement une structure de type (2). Une étude cristallographique s'imposait pour préciser celle-ci et déterminer ainsi sans ambiguïté la position relative des substituants du phosphore par rapport au reste du bicycle.

Les composés du type bicyclo[3.3.1]nonane posent, par ailleurs, d'intéressants problèmes stéréochimiques au niveau des interactions non-liantes 3–7, comme nous l'avons montré lors de l'étude du dérivé phosphoré (3) (Grand, Robert, Majoral & Navech, 1979). Le composé (2) offrait un bon exemple d'interaction non-liante entre un atome d'oxygène et un atome de

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