Acta Cryst. (1980). B**36**, 2182–2184

Structure of 1,1,3,6,6,8-Hexamethyl-3a,5a,8a,10a-tetraaza-*cis*-10b,10c-perhydropyrene

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(*Received* 22 *January* 1980; *accepted* 21 *April* 1980)

Abstract. $C_{18}H_{34}N_4$, $M_r = 306{\cdot}48$, monoclinic, $P2_1/c$, $Z = 4$, $a = 11{\cdot}508\ (3)$, $b = 11{\cdot}964\ (3)$, $c = 13{\cdot}884\ (4)$ Å, $\beta = 107{\cdot}97\ (2)°$, $V = 1818{\cdot}3$ Å^3, $d_m = 1{\cdot}122$, $d_c = 1{\cdot}085$ Mg m^{-3}, $\mu(\mathrm{Cu}\ K\alpha) = 0{\cdot}52$ mm^{-1}, $F(000) = 680$. 2442 reflections were measured of which 1488 had $I > 2\sigma_I$. These were used for the refinement. The structure was solved by direct methods and refined by the least-squares full-matrix method to a final $R = 0{\cdot}080$ ($R_w = 0{\cdot}058$, weights from counting statistics). The molecule consists of two pairs of fused pyrazine and pyrimidine rings, all possessing the chair conformation. The aminal H atoms are in *cis* configuration, causing the molecule to adopt a folded form. Two methyl substituents at the 3,8 positions are equatorial and remote, whereas the geminal methyl groups are located at the folding of the ring system.

Introduction. 3a,5a,8a,10a-Tetraaza-*cis*-10b,10c-perhydropyrene (PTAP) derivatives, stereochemically very intriguing molecules, were obtained by Choinski (1974) and by Caulkett, Greatbanks, Turner & Jarvis (1977). Spectral examination of some derivatives (Choinski, 1974) as well as crystallographic structure determinations of the 1,6-dimethyl derivative (Krajewski, Urbańczyk-Lipkowska, Bleidelis & Kemme, 1977) and the 1,6-dimethyl-3,8-diphenyl derivatives of PTAP (Caulkett *et al.*, 1977) all reveal that the heterocyclic four-ring system of the compounds consists of two pairs of fused pyrazine and pyrimidine rings, all in the chair conformation, forming a folded ring system with a twofold symmetry axis.

The present X-ray structure determination of the hexamethyl derivative of PTAP was undertaken (i) to confirm the formerly determined overall conformation and (ii) to establish the positions of the methyl substituents on the ring system.

A simple examination of a PTAP model shows two possibilities for 1,3 substitution by geminal and single methyl groups, apart from the conformation involving a single methyl. Positions 1 and 3 are in fact not equivalent, one being at the folding, the other remote (Fig. 1). Therefore, the elucidation of (ii) above is structurally essential.

A well shaped single crystal of the title compound (obtained by slow evaporation of an *n*-hexane solution) of dimensions 0·3 × 0·25 × 0·2 mm was used for diffractometric X-ray data collection. The measurements were made on a Syntex $P2_1$ single-crystal diffractometer (A. Mickiewicz University, Poznań, Poland) using the $\omega/2\theta$ scan method and Cu $K\alpha$ radiation. The measuring range was up to $2\theta_{\max} = 115°$. From 2442 collected intensities 1488 had $I > 2\sigma_I$ and were used (after Lorentz and polarization correction) in the structure refinement.

The monoclinic space group $P2_1/c$ was clearly defined by systematic absences. However, the structure solution by direct methods brought some difficulties. A run of the *SHELX* program (Sheldrick, 1976) afforded three *E* maps of approximately similar quality exhibiting nearly complete ring systems as expected, but with the atomic coordinates shifted on respective maps by large non-systematic values along all three crystal axes. A satisfactory *E* map was obtained when in a subsequent *SHELX* run three reflections of unusually high *E* values (formerly used as the origin) were omitted. It turned out that one of the omitted reflections had a phase inverted with respect to the other two.

All non-hydrogen atoms, except those of two of the methyl groups (one single and one from a geminal pair) were identified from the good *E* map. The missing

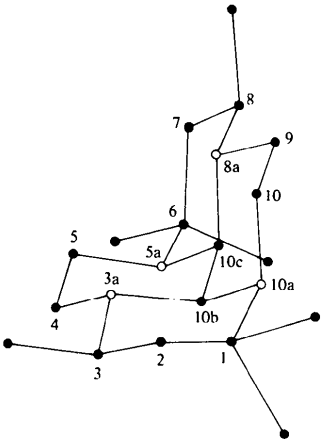

Fig. 1. Conformational view of the molecule (calculated parallel projection) with conventional atomic numbering. N atoms are shown as open circles.

0567-7408/80/092182-03$01.00

Table 1. *Fractional coordinates* (× 10^4) *and* $B_{eq.}$ *values with e.s.d.'s in parentheses*

	x	y	z	$B_{eq.}$(Å^2)*
N(1)	7491 (5)	388 (4)	8333 (4)	3·4 (3)
C(2)	7817 (6)	1482 (5)	8818 (4)	3·7 (3)
C(3)	9195 (6)	1572 (5)	9252 (4)	3·8 (4)
N(4)	9800 (5)	1442 (4)	8467 (4)	3·1 (3)
C(5)	11141 (6)	1425 (6)	8946 (5)	3·9 (4)
C(6)	11772 (6)	1214 (6)	8145 (5)	4·0 (4)
C(7)	11281 (6)	154 (6)	7509 (5)	3·9 (4)
N(8)	9929 (5)	202 (4)	7100 (4)	3·3 (3)
C(9)	9434 (6)	1051 (5)	6298 (4)	3·8 (3)
C(10)	8066 (6)	925 (5)	5897 (4)	3·8 (4)
N(11)	7467 (5)	1088 (4)	6672 (4)	3·1 (3)
C(12)	6134 (6)	890 (6)	6229 (5)	3·9 (4)
C(13)	5535 (6)	902 (6)	7060 (6)	4·3 (4)
C(14)	6137 (6)	146 (6)	7974 (5)	4·2 (4)
C(15)	8003 (5)	284 (5)	7492 (5)	2·9 (3)
C(16)	9406 (6)	377 (5)	7927 (4)	3·0 (3)
C(17)	5599 (6)	377 (7)	8847 (6)	6·3 (5)
C(18)	5959 (6)	−1111 (6)	7704 (5)	5·1 (4)
C(19)	5548 (6)	1788 (6)	5427 (5)	4·8 (4)
C(20)	11828 (6)	77 (6)	6604 (5)	5·6 (4)
C(21)	11679 (6)	−930 (5)	8126 (5)	4·0 (3)
C(22)	11584 (6)	2533 (5)	9470 (5)	5·1 (4)

* Calculated from anisotropic thermal parameters.

positional parameters were then found from a Fourier F_o synthesis. The first isotropic refinement of the non-hydrogen atomic positions by the full-matrix least-squares method [program *CRYLSQ* in the XRAY 70 system (Stewart, Kundell & Baldwin, 1970)] gave the conventional residual R = 0·175 and a reasonable molecular geometry. After several cycles of anisotropic refinement the positional parameters of all 34 H atoms were calculated geometrically [program *XANADU* (Roberts & Sheldrick, 1975)] and added to the atom set. The last step of four anisotropic refinement cycles with statistical weights (H-atomic parameters held invariant) gave the final residuals R = 0·080 and R_w = 0·058. The average shift/error value was then 0·05.

The refined fractional coordinates of the non-hydrogen atoms and their calculated B_{eq} values are listed in Table 1.*

Discussion. Tables 2 and 3 give the intramolecular bond lengths and angles.

As with other X-ray structure determinations of PTAP derivatives (Krajewski *et al.*, 1977; Caulkett *et al.*, 1977) the ring system of the molecule appears in a folded form, all rings being in the chair conformation (Fig. 1). Fig. 2 shows an *ORTEP* (Johnson, 1965) projection of the molecule on the least-squares plane formed by the atoms lying along the folding line of the ring system.

The geminal methyl groups are attached to C atoms at the ends of the folding line. The two remaining single methyl groups are equatorially substituted at remote

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

N(1)–C(2)	1·466 (8)	N(8)–C(9)	1·485 (7)
N(1)–C(14)	1·511 (8)	N(8)–C(16)	1·466 (9)
N(1)–C(15)	1·467 (9)	C(9)–C(10)	1·507 (9)
C(2)–C(3)	1·516 (9)	C(10)–N(11)	1·459 (9)
C(3)–N(4)	1·471 (9)	N(11)–C(12)	1·485 (8)
N(4)–C(5)	1·480 (8)	N(11)–C(15)	1·473 (7)
N(4)–C(16)	1·477 (7)	C(12)–C(13)	1·516 (12)
C(5)–C(6)	1·525 (11)	C(12)–C(19)	1·545 (9)
C(5)–C(22)	1·523 (9)	C(13)–C(14)	1·538 (10)
C(6)–C(7)	1·549 (9)	C(14)–C(17)	1·546 (12)
C(7)–N(8)	1·483 (8)	C(14)–C(18)	1·547 (10)
C(7)–C(20)	1·573 (11)	C(15)–C(16)	1·544 (8)
C(7)–C(21)	1·544 (9)		

Table 3. *Bond angles* (°) *with e.s.d.'s in parentheses*

C(2)–N(1)–C(14)	114·5 (5)	N(8)–C(9)–C(10)	108·9 (5)
C(2)–N(1)–C(15)	109·5 (5)	C(9)–C(10)–N(11)	113·0 (5)
C(14)–N(1)–C(15)	110·4 (5)	C(10)–N(11)–C(12)	109·6 (5)
N(1)–C(2)–C(3)	109·5 (5)	C(10)–N(11)–C(15)	107·6 (5)
C(2)–C(3)–N(4)	112·0 (5)	C(12)–N(11)–C(15)	110·4 (5)
C(3)–N(4)–C(5)	109·5 (5)	N(11)–C(12)–C(13)	109·7 (5)
C(3)–N(4)–C(16)	109·1 (5)	N(11)–C(12)–C(19)	110·7 (6)
C(5)–N(4)–C(16)	109·3 (5)	C(13)–C(12)–C(19)	110·0 (6)
N(4)–C(5)–C(6)	109·8 (5)	C(12)–C(13)–C(14)	115·3 (6)
N(4)–C(5)–C(22)	110·6 (5)	N(1)–C(14)–C(13)	108·3 (6)
C(6)–C(5)–C(22)	109·1 (6)	N(1)–C(14)–C(17)	109·2 (5)
C(5)–C(6)–C(7)	112·3 (6)	N(1)–C(14)–C(18)	108·2 (6)
C(6)–C(7)–N(8)	110·0 (6)	C(13)–C(14)–C(17)	110·8 (6)
C(6)–C(7)–C(20)	109·8 (6)	C(13)–C(14)–C(18)	112·3 (5)
C(6)–C(7)–C(21)	112·2 (5)	C(17)–C(14)–C(18)	108·0 (6)
N(8)–C(7)–C(20)	109·2 (5)	N(1)–C(15)–N(11)	112·6 (5)
N(8)–C(7)–C(21)	109·9 (6)	N(1)–C(15)–C(16)	108·1 (5)
C(20)–C(7)–C(21)	105·7 (6)	N(11)–C(15)–C(16)	113·2 (5)
C(7)–N(8)–C(9)	115·3 (5)	N(4)–C(16)–N(8)	112·6 (5)
C(7)–N(8)–C(16)	110·0 (5)	N(4)–C(16)–C(15)	112·4 (5)
C(9)–N(8)–C(16)	109·5 (5)	N(8)–C(16)–C(15)	108·4 (5)

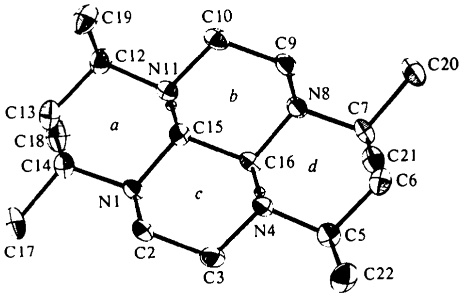

Fig. 2. *ORTEP* (Johnson, 1965) diagram of the molecule (crystallographic numbering of atoms). Parallel projection onto plane (1) (see text). Thermal motion ellipsoids are set at the 40% probability level. H atoms, except those of the aminal, are omitted.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35296 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Torsional angles* (°) *with e.s.d.'s in parentheses* (*methyl substituents not involved*)

C(14)–N(1)–C(2)–C(3)	173·5 (5)	C(5)–N(4)–C(16)–N(8)	−62·7 (6)	C(9)–C(10)–N(11)–C(12)	−177·0 (5)
C(15)–N(1)–C(2)–C(3)	−62·0 (6)	C(3)–N(4)–C(16)–C(15)	54·8 (6)	C(9)–C(10)–N(11)–C(15)	−56·9 (6)
C(2)–N(1)–C(14)–C(13)	70·3 (7)	C(5)–N(4)–C(16)–C(15)	174·5 (5)	C(10)–N(11)–C(12)–C(13)	172·3 (5)
C(15)–N(1)–C(14)–C(13)	−53·7 (7)	N(4)–C(5)–C(6)–C(7)	−53·3 (7)	C(15)–N(11)–C(12)–C(13)	54·0 (7)
C(2)–N(1)–C(15)–N(11)	−64·9 (5)	C(5)–C(6)–C(7)–N(8)	51·9 (7)	C(10)–N(11)–C(15)–N(1)	178·6 (4)
C(14)–N(1)–C(15)–N(11)	62·0 (6)	C(6)–C(7)–N(8)–C(9)	70·0 (7)	C(10)–N(11)–C(15)–C(16)	55·6 (6)
C(2)–N(1)–C(15)–C(16)	60·9 (5)	C(6)–C(7)–N(8)–C(16)	−54·4 (7)	C(12)–N(11)–C(15)–N(1)	−61·9 (6)
C(14)–N(1)–C(15)–C(16)	−172·2 (5)	C(7)–N(8)–C(9)–C(10)	174·8 (5)	C(12)–N(11)–C(15)–C(16)	175·1 (5)
N(1)–C(2)–C(3)–N(4)	59·2 (6)	C(16)–N(8)–C(9)–C(10)	−60·5 (6)	N(11) C(12)–C(13)–C(14)	−51·0 (7)
C(2)–C(3)–N(4)–C(5)	−174·4 (5)	C(7)–N(8)–C(16)–N(4)	61·5 (6)	C(12)–C(13)–C(14)–N(1)	50·4 (7)
C(2)–C(3)–N(4)–C(16)	−54·9 (6)	C(9)–N(8)–C(16)–N(4)	−66·2 (6)	N(1)–C(15)–C(16)–N(4)	−58·4 (6)
C(3)–N(4)–C(5)–C(6)	176·4 (5)	C(7)–N(8)–C(16)–C(15)	−173·5 (5)	N(1)–C(15)–C(16)–N(8)	176·4 (4)
C(16)–N(4)–C(5)–C(6)	56·9 (7)	C(9)–N(8)–C(16)–C(15)	58·8 (6)	N(11)–C(15)–C(16)–N(4)	67·0 (7)
C(3)–N(4)–C(16)–N(8)	177·6 (4)	N(8)–C(9)–C(10)–N(11)	60·5 (6)	N(11)–C(15)–C(16)–N(8)	−58·1 (6)

positions on the pyrazine rings. Examination of bond lengths and angles (Tables 2 and 3) does not reveal any peculiarities.

Considering the atomic positions, the molecule seems to present non-crystallographic C_2 symmetry; the deviations of C_2-related atomic positions from exact C_2 symmetry are within the e.s.d.'s of the distances for these atom pairs. This twofold symmetry axis seems to be nearly parallel to the *b* crystal axes, but lies in a general position with respect to *x* and *z* coordinates.

As in other derivatives of PTAP already investigated, four main least-squares planes may be distinguished in the present molecule: (1) through C(7), N(8), C(16), C(15), N(1) and C(14); (2) C(2), C(3), N(4), C(5), C(6), C(9), C(10), N(11), C(12) and C(13); (3) N(1), C(2), C(16), N(4), C(7) and C(6); (4) N(8), C(9), C(15), N(11), C(14) and C(13). Planes (1) and (2) are almost parallel to each other (dihedral angle <1°); planes (3) and (4) form dihedral angles of about 130° with planes (1) and (2).

The C atoms carrying the geminal methyl groups [C(7) and C(14)] deviate most from plane (1), by about 0·13 Å in the direction of the axial methyl groups. Inspection of the structure of the 7,14-dimethyl derivative of PTAP [one axial and one equatorial methyl substituent (Krajewski *et al.*, 1977)] reveals a similar phenomenon for the C atom substituted by the axial methyl group, but not by the equatorial one. This possibly suggests that the axial substitution of the C atoms in question is responsible for this molecular distortion.

Table 4 presents the torsion angles (not involving methyl substituents) for the fused-ring system. It reveals that the deviations of torsion angles from the C_2 symmetry restrictions seem to be much larger than those observed for the atomic positions. The differences between the symmetry-related torsion angles are mostly greater than their e.s.d.'s, increasing with the distance of the bond from the C_2 axis.

The torsion-angle sums for each six-membered ring deviate from the ideal 360° value. The deviations are apparently larger for rings *a* and *d* (20–26°), than for rings *b* and *c* (*ca* 10°) (Fig. 2).

A more thorough comparative analysis of the molecular conformations of PTAP derivatives will be published in a future paper together with the crystal structure of PTAP itself, which is already under investigation.

The authors are indebted to Dr R. A. Koliński for supplying the samples and for valuable discussions. The courtesy of the Head Manager Mr A. Plenkiewicz, Dr J. Szymczyk and Dr A. Koczyk of the Research and Development Center of Industrial Projecting 'BISTYP', Warszawa, enabled the authors to prepare the *ORTEP* diagram.

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