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# Structure and Conformation of 5-Methyl-1,3,4,6-tetraoxoperhydropyrrolo[3,4-*c*]pyridine

By A. Amorese, E. Gavuzzo and F. Mazza

*Istituto di Strutturistica Chimica 'G. Giacomello' CNR, CP n.* 10–00016 *Monterotondo Stazione, Roma, Italy*

and G. Casini and M. Ferappi

*Istituto di Chimica Farmaceutica e Tossicologica, Università di Bari, V. Amendola* 173, *Bari, Italy*

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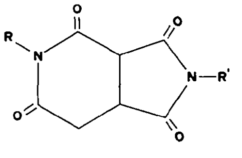
**Abstract.** $C_8H_8N_2O_4$, $M_r = 196{\cdot}16$, monoclinic, $P2_1/c$, $a = 11{\cdot}227\,(5)$, $b = 6{\cdot}177\,(1)$, $c = 12{\cdot}828\,(5)$ Å, $\beta = 111{\cdot}68\,(3)°$, $V = 826{\cdot}7\,(5)$ Å$^3$, $Z = 4$, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu(\mathrm{Mo}\ K\alpha) = 1{\cdot}38$ mm$^{-1}$, $D_c = 1{\cdot}57$, $D_m = 1{\cdot}57$ Mg m$^{-3}$ by flotation in chloroform–bromoform mixture. $R = 0{\cdot}064$ and $R_w = 0{\cdot}102$ for 1501 independent reflections with $I > 1{\cdot}5\sigma(I)$. The fusion between the two rings is of the *cis* type. The penta- and hexaatomic rings are in an envelope and sofa conformation respectively.

**Introduction.** Purine structural analogs are of interest as antimetabolites (Hitchings & Ellion, 1963). When these are *N*-methylated and present different carbonyl groups, they become structurally related to xanthine compounds such as theophylline and caffeine and can show pharmacological interference with them. Some of us (Ferappi, Carotti, Casini, De Laurentis, Giardinà, Cingolani, Gavuzzo & Mazza, 1982) have prepared several tetracarbonyl derivatives (I) of the fully hydrogenated pyrrolo[3,4-*c*]pyridine which, although not planar, might be considered partial isosters (Casini, Schimberni & Zevi, 1959; Bonamico, Coppola & Giacomello, 1960) with respect to the purine nucleus. The presence of the hydrogenated junction in the series (I) makes possible a *cis–trans* stereoisomerism which is not easily solvable by NMR spectroscopy. Therefore, we undertook a crystal-structure analysis of the title compound which is a member of that series.



R,R'=H,CH$_3$,CH$_2$-ϕ

(I)

Prismatic crystals were obtained by slow evaporation of an ethanol solution. Approximate unit-cell dimensions and the space group were determined from oscillation and Weissenberg photographs. A crystal of 0·25 × 0·25 × 0·15 mm was used for crystal data and intensity measurements on an automatic Syntex $P2_1$ diffractometer equipped with a graphite monochromator. Refined unit-cell parameters were obtained by a least-squares fit of the angular settings of 15 reflections. Intensities were recorded up to a maximum $2\theta$ value of 58·0° by the $\theta$–$2\theta$ technique. Three standard reflections, measured after every 50, showed only small random deviations from their means. Of the 2430 independent reflections recorded, 1501 with $I > 1{\cdot}5\sigma(I)$ were considered observed and used for the calculations. Lorentz and polarization corrections were applied, but intensities were not corrected for extinction and absorption. The structure was solved by *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). 200 reflections and 1396 $\sum_2$ relationships were used in the phase-determining procedure. An *E* map computed with the phases from the set with the highest figures of merit revealed peaks for all non-H atoms. These positions were refined isotropically then anisotropically by the full-matrix least-squares method. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = (a + |F_o| + c|F_o|^2)^{-1}$ with $a$ and $c$ of the order of $2F_{o(\min)}$ and $2/F_{o(\max)}$ respectively. A difference Fourier map computed at this stage showed all the H atoms in stereochemically feasible positions. The H positional parameters together with isotropic thermal values derived from the carrier atoms were included and kept fixed in the refinement. The final $R$ and $R_w$ are 0·064 and 0·102 respectively for all the observed reflections. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All the calculations were carried out on the HP 21MX minicomputer (Cerrini & Spagna, 1977) of the CNR Research Area and on the Univac 1100/80 computer of the University of Rome. Final atomic coordinates are given in Table 1.*

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* Lists of structure factors, anisotropic thermal parameters and H positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38043 (13 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 coordinates with e.s.d.'s in parentheses and $B_{eq}$ (Å$^2$) for non-*H *atoms*

| | $x$ | $y$ | $z$ | $B_{eq}$* |
|---|---|---|---|---|
| C(1) | 0·2180 (3) | 0·1294 (6) | 0·5521 (3) | 2·6 |
| N(2) | 0·1606 (3) | −0·0714 (5) | 0·5405 (2) | 2·6 |
| C(3) | 0·0965 (3) | −0·1328 (5) | 0·4316 (3) | 2·3 |
| C(4) | 0·2036 (3) | −0·0650 (5) | 0·3003 (2) | 2·2 |
| N(5) | 0·3294 (2) | −0·0086 (5) | 0·3325 (2) | 2·4 |
| C(6) | 0·3828 (4) | 0·1792 (6) | 0·3938 (3) | 2·8 |
| C(7) | 0·2932 (4) | 0·3331 (6) | 0·4159 (3) | 3·1 |
| C(8) | 0·1827 (3) | 0·2270 (5) | 0·4365 (3) | 2·4 |
| C(9) | 0·1211 (3) | 0·0405 (5) | 0·3559 (2) | 2·1 |
| C(10) | 0·4108 (4) | −0·1391 (7) | 0·2890 (4) | 3·5 |
| O(1) | 0·2832 (3) | 0·2085 (5) | 0·6407 (2) | 3·6 |
| O(3) | 0·0333 (3) | −0·2945 (4) | 0·4022 (2) | 3·5 |
| O(4) | 0·1578 (3) | −0·2092 (4) | 0·2318 (2) | 3·0 |
| O(6) | 0·4962 (3) | 0·2159 (6) | 0·4205 (3) | 4·3 |

* $B_{eq} = 8\pi^2(U_1U_2U_3)^{1/3}$.

**Discussion.** The numbering scheme adopted is shown in Fig. 1, together with related bond lengths and angles. As can be seen from Fig. 2, the fusion between the two rings is of the *cis* type, so that the overall shape of the molecule is bent. The pentaatomic ring, although presenting small internal torsion angles (see Table 2), adopts a flattened $C_s$—C(9) envelope conformation. The displacements of the atoms C(3), N(2), C(1) and C(8) from their least-squares plane are 0·012 (4), −0·020 (4), 0·019 (4) and −0·010 (4) Å respectively, while C(9) is 0·214 (4) Å apart from this plane on the side of the hexaatomic ring.

The conformation of the hexaatomic ring can be approximated to a sofa. The C(6), N(5), C(4), C(9) and C(8) atoms are displaced by −0·059 (4), 0·089 (3), −0·052 (3), −0·007 (3) and 0·029 (3) Å respectively from their least-squares plane, whereas C(7) is −0·508 (4) Å out of this plane on the opposite side of the pentaatomic ring.

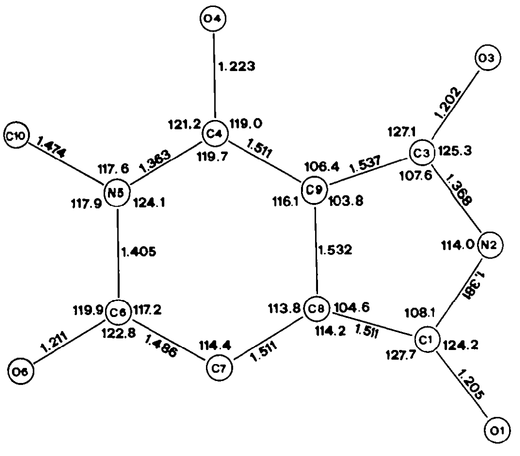

Fig. 1. Bond distances (Å) and angles (°) for non-H atoms with the atomic-numbering scheme adopted. E.s.d.'s are in the ranges 0·004–0·006 Å and 0·3–0·4° respectively.

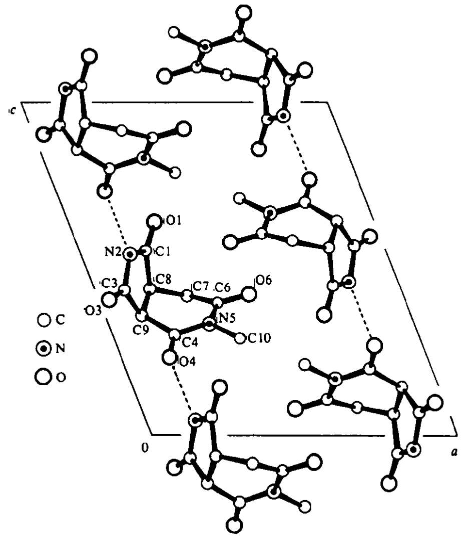

Fig. 2. The crystal packing viewed along the *b* axis. Dashed lines represent hydrogen bonds.

Table 2. *Endocyclic and relevant torsion angles* (°) *with e.s.d.'s in parentheses*

The convention of Klyne & Prelog (1960) has been adopted for the torsion angles.

| | | | |
|---|---|---|---|
| Pentaatomic ring | | | |
| C(3)–N(2) | 5·1 (4) | C(8)–C(9) | 13·4 (3) |
| N(2)–C(1) | 4·0 (4) | C(9)–C(3) | −11·6 (4) |
| C(1)–C(8) | −11·1 (4) | | |
| Hexaatomic ring | | | |
| C(6)–N(5) | −5·3 (5) | C(9)–C(8) | 22·3 (4) |
| N(5)–C(4) | −16·9 (5) | C(8)–C(7) | −43·1 (4) |
| C(4)–C(9) | 7·2 (4) | C(7)–C(6) | 35·8 (4) |
| Amidic groups | | | |
| O(1)–C(1)–N(2)–C(3) | −176·8 (4) | O(4)–C(4)–N(5)–C(10) | −4·8 (5) |
| O(3)–C(3)–N(2)–C(1) | −175·2 (4) | C(7)–C(6)–N(5)–C(10) | 167·2 (3) |
| C(9)–C(4)–N(5)–C(10) | 170·7 (3) | O(6)–C(6)–N(5)–C(4) | 179·0 (3) |
| O(4)–C(4)–N(5)–C(6) | 167·6 (3) | O(6)–C(6)–N(5)–C(10) | −8·6 (5) |

The angle between the least-squares plane of the five-membered ring and that of the hexaatomic ring, excluding C(7), is 108·2 (4)°.

The sum of the bond angles around the N of the hexaatomic ring is 359·6 (5)° and the distance between this N and the plane of its three substituents is 0·052 (3) Å.

The crystal packing shown in Fig. 2 is characterized by an intermolecular hydrogen bond of 2·813 (4) Å between N(2) and O(4) atoms of glide-related molecules. The H(N2)···O(4) distance is 1·81 Å; the C(4)—O(4)···H(N2) and C(4)—O(4)···N(2) angles are 141·7 and 147·2 (2)° respectively; the O(4)···H(N2)—N(2) angle is 161·4°; finally, the N(2)—H(N2)···O(4)—C(4) torsion angle is 146·8°.

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# Structure of 8-[1,2-Dicarba-*closo*-dodecaboran(12)-3-yl]-5,6-dicarba-*nido*-decaborane(12)

BY V. ŠUBRTOVÁ AND A. LÍNEK

*Institute of Physics, Czechoslovak Academy of Sciences,* 180 40 *Praha* 8, *Czechoslovakia*

AND J. HAŠEK

*Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,* 162 06 *Praha* 6, *Czechoslovakia*

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**Abstract.** *iso*-$C_4H_{22}B_{18}$, $M_r = 265{\cdot}02$, monoclinic, $C2/c$, $Z = 8$, $a = 21{\cdot}099\,(9)$, $b = 7{\cdot}081\,(2)$, $c = 22{\cdot}065\,(9)$ Å, $\beta = 94{\cdot}27\,(3)^\circ$, $U = 3287{\cdot}4$ Å$^3$, $D_x = 1{\cdot}071$ Mg m$^{-3}$, $\mu(\mathrm{Cu}\ K\alpha) = 0{\cdot}254$ mm$^{-1}$. The structure was solved by direct methods and refined to $R = 0{\cdot}054$ for 2108 counter reflections. The molecule represents the first-known case of an uncharged combination of a *nido*- and *closo*-carbaborane.

**Introduction.** Two isomeric carbaboranes, *neo*-$C_4H_{22}B_{18}$ and *iso*-$C_4H_{22}B_{18}$, were isolated in the oxidation of the 7,8-$C_2H_{12}B_9^-$ anion with chromic acid (Janoušek, 1973; Plešek & Heřmánek, 1974). The molecule of the former isomer consists of two identical, mutually coupled *nido*-7,8-$C_2H_{11}B_9$ units (Janoušek, Heřmánek, Plešek & Štibr, 1974; Sklenář & Hašek, 1978).

For the constitution of the second *iso*-$C_4H_{22}B_{18}$ isomer a linkage of two different moieties, 1,2-$C_2H_{11}B_{10}$ and 5,6-$C_2H_{11}B_8$, was proposed from the mass and NMR spectral data (Janoušek, Plešek, Štíbr & Heřmánek, 1982). The X-ray study on *iso*-$C_4H_{22}B_{18}$ has been undertaken in order to clarify the way in which these two dicarbaborane units are connected and to determine the geometry of the molecule. The distances and angles in the 5,6-$C_2H_{11}B_8$ part of the molecule are also of great interest because unsubstituted 5,6-$C_2H_{12}B_8$ has proved to be the important readily available compound from which many new derivatives have been prepared (Štíbr, Plešek & Heřmánek, 1974; Janoušek, Plešek & Plzák, 1979; Jung & Hawthorne, 1980; Colquhoun, Greenhough & Wallbridge, 1980).

A crystal 0·35 × 0·40 × 0·60 mm was used for data collection on a Syntex $P2_1$ diffractometer with graphite-monochromated Cu $K\alpha$ radiation. The cell parameters were determined by least squares from 25 high-order reflections. Systematic extinctions indicated space group $Cc$ or $C2/c$; the latter has been confirmed by a statistical test. The intensities of 2244 independent reflections ($\theta \leq 57^\circ$) were measured in the $\omega/2\theta$ scan mode, of which 2108 with $I > 1{\cdot}96\sigma(I)$ were considered as observed and included in further calculations. Reflections were corrected for Lorentz and polarization effects but not for absorption or extinction.

The structure was solved with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). For the solution the known configuration of the 12 atoms in the icosahedral carbaborane cage was used (Šubrtová, Línek & Hašek, 1980), with random position and orientation. The $E$ map showed the positions of all non-H atoms. The refinement was carried out by block-diagonal least squares with a modified *NRC*-10 program (Ahmed, Hall, Pippy & Huber, 1966). The function minimized was $w(|F_o| - |F_c|)^2$, with $w^{-1} = \sigma^2(F) + (0{\cdot}022F_o)^2$. A difference map showed all H atoms including two in the hydrogen bridges. Least-squares calculations, with isotropic thermal parameters for H and anisotropic parameters for the other atoms, reduced $R$ ($\sum ||F_c| - |F_o||/\sum |F_o|$) to a final

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