Na and contributes to two H-bonds. The distances C(1)–O(1) and C(1)–O(2) (1·276 and 1·237 Å) are greater than C(4)–O(5) and C(4)–O(6) (1·270 and 1·248 Å), but the difference is not statistically significant.

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The Crystal Structure of the Hydrochloride of 6,9-*endo*-Methylenehomopseudopelletierine, a Tricyclic Tropane Congener

BY MICHAEL LAING, NEIL SPARROW AND POLLY SOMMERVILLE

Chemistry Department, University of Natal, Durban, South Africa

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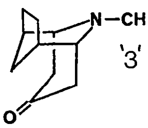
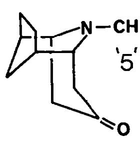
The structure of 6,9-*endo*-methylenehomopseudopelletierine.HCl was determined from film data, and refined by block-diagonal least-squares calculations to $R=0{\cdot}073$ for 1556 observed data. The crystals are orthorhombic, space group *Pbca*, with $a=10{\cdot}69$, $b=10{\cdot}13$, $c=20{\cdot}32$ Å, $Z=8$. The molecule approximates symmetry *m*, with the mirror plane passing through the Cl^- ion and the carbonyl and *N*-methyl groups of the *N*-methyl-γ-piperidone ring which has a flattened chair conformation.

Introduction

The Robinson–Schöpf (Schöpf, 1937) reaction of *cis*-cyclopentane-1,3-dialdehyde, methylamine hydrochloride and acetonedicarboxylic acid in a phosphate-buffered aqueous solution yields a single tricyclic amino ketone in high yield (Alder, Wirtz & Koppelberg, 1956). A detailed study of the stereochemical course of this reaction by n.m.r. spectroscopy (Paquette & Heimaster, 1966) showed that in solution the molecule was 'best described as a mobile equilibrium of conformers' shown below.





The determination of the exact conformation of the *N*-methyl-γ-piperidone ring was of interest, and a crystal structure determination was therefore undertaken.

Experimental

Crystals of the hydrochloride, $C_{11}H_{18}NOCl$, were supplied by Dr Paquette. A well formed rectangular parallelepiped 0·8 × 0·3 × 0·3 mm was used for all X-ray work.

Oscillation, Weissenberg and precession photographs showed the cell to be orthorhombic, space group *Pbca* from systematic absences: $0kl$ for k odd, $h0l$ for l odd, $hk0$ for h odd. Accurate unit-cell dimensions were measured from calibrated zero-layer photographs. $a=10{\cdot}69$ (1), $b=10{\cdot}13$ (1), $c=20{\cdot}32$ (2) Å; $d_{\text{obs}}=1{\cdot}24$ g cm^{-3}, measured by flotation in a chlorobenzene–bromobenzene mixture. $Z=8$.

Integrated multiple-film intensities were collected by the equi-inclination Weissenberg method with Ni-filtered Cu $K\alpha$ radiation for layers $0kl$ to $8kl$; $h0l$, $h1l$ and $hk0$ were collected for scaling purposes. The intensities were measured with a Hilger & Watts densitometer and the weak data estimated visually with a time-calibrated intensity strip. The unobserved data were assigned an intensity of local $I_{\text{min}}/2$. Lorentz and polarization corrections were calculated, and applied to the data by hand.

Determination of the structure

A temperature-sharpened Patterson map was calculated from the 1556 observed data. [The values of the F^2_{obs} were multiplied by the appropriate value of $\exp(8{\cdot}0 \sin^2\theta/\lambda^2)$.] The coordinates of Cl were deduced from the peaks on the Harker lines and sections. A structure factor calculation for the Cl atom alone yielded $R=0{\cdot}62$ ($B=4{\cdot}0$ Å^2) and the Fourier map revealed all 13 light atoms. Their positions were adjusted from the subsequent observed Fourier map ($R=0{\cdot}30$) and the structure was then refined isotropically by block-diagonal least-squares calculations to $R=0{\cdot}13$. The H atoms were now observable in a difference map. These atoms were therefore included in the calculations but their positional parameters were not refined. The Cl and O atoms were made anisotropic, and the structure refined for three cycles ($R=0{\cdot}11$). The C and N atoms were now also made anisotropic and the structure refined for a further five cycles. The refinement converged to $R=0{\cdot}073$ for 1556 observed data (0·091 when the 443 unobserved data are included). A Hughes (1941) weighting scheme was used, with $4\,F_{\text{min}}=8{\cdot}0$. The scattering factors for Cl$^-$, C, N,

Table 2. *Intramolecular bond lengths and non-bonded separations* (±0·01 Å)

Bond lengths are not corrected for thermal motion

C(1)—C(2)	1·52 Å	C(1)····C(3)	2·32 Å
C(2)—C(3)	1·52	C(5)····C(4)	2·45
C(1)—C(6)	1·54	C(2)····C(6)	2·36
C(3)—C(7)	1·53	C(2)····C(7)	2·36
C(6)—C(7)	1·53	C(8)····C(9)	2·58
C(1)—C(5)	1·53	C(2)····C(10)	2·90
C(3)—C(4)	1·53	C(2)····O	3·59
C(4)—N	1·51	C(11)···C(10)	3·34
C(5)—N	1·52		
C(4)—C(9)	1·52	N······Cl	3·11
C(5)—C(8)	1·51	C(11)···Cl	3·35
C(9)—C(10)	1·50	C(6)····Cl	3·56
C(8)—C(10)	1·50	C(7)····Cl	3·56
C(10)–O	1·22	C(6)····N	2·82
N——C(11)	1·49	C(7)····N	2·82
		C(8)····C(11)	2·96
		C(9)····C(11)	2·95

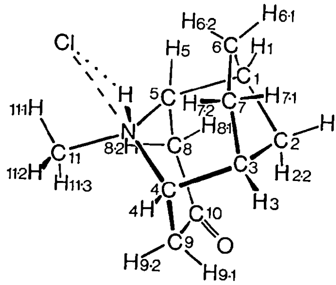


Fig. 1. View of the molecule down x showing the numbering system.

Table 1. *Positional and anisotropic thermal parameters for the heavy atoms; positional parameters for the hydrogen atoms (all $B=4{\cdot}0$ Å^2)*

The general form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$. The estimated standard deviations in the final figure are shown in parentheses. The approximate errors in the hydrogen atom parameters are $x\pm0{\cdot}01, y\pm0{\cdot}01, z\pm0{\cdot}005$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	0·2419 (1)	0·0287 (1)	0·00910 (4)	0·00677 (11)	0·00880 (9)	0·00163 (2)	0·00054 (21)	0·00048 (10)	0·00014 (9)
C(1)	−0·0082 (4)	0·0865 (4)	0·1797 (2)	0·0063 (5)	0·0090 (5)	0·0017 (1)	−0·0010 (7)	−0·0004 (3)	0·0013 (4)
C(2)	0·0239 (4)	0·2028 (5)	0·2235 (2)	0·0074 (5)	0·0127 (6)	0·0013 (1)	−0·0002 (8)	−0·0001 (3)	0·0004 (4)
C(3)	0·1340 (4)	0·2592 (4)	0·1851 (2)	0·0079 (5)	0·0106 (5)	0·0020 (1)	−0·0054 (8)	−0·0008 (4)	0·0000 (4)
C(4)	0·0890 (4)	0·3153 (4)	0·1195 (2)	0·0085 (5)	0·0082 (5)	0·0022 (1)	−0·0046 (8)	0·0002 (4)	−0·0001 (4)
C(5)	−0·0617 (4)	0·1331 (4)	0·1136 (2)	0·0058 (5)	0·0073 (4)	0·0021 (1)	0·0015 (7)	0·0004 (3)	0·0006 (3)
C(6)	0·1214 (5)	0·0207 (5)	0·1722 (2)	0·0100 (6)	0·0111 (5)	0·0022 (1)	0·0031 (9)	0·0005 (4)	0·0029 (4)
C(7)	0·2143 (5)	0·1357 (5)	0·1756 (2)	0·0061 (6)	0·0163 (6)	0·0023 (1)	0·0016 (9)	−0·0011 (4)	0·0007 (5)
C(8)	−0·1720 (4)	0·2251 (4)	0·1204 (2)	0·0061 (5)	0·0108 (5)	0·0026 (1)	0·0004 (8)	−0·0002 (4)	0·0002 (4)
C(9)	−0·0143 (4)	0·4181 (5)	0·1255 (2)	0·0122 (6)	0·0076 (5)	0·0023 (1)	−0·0005 (8)	0·0004 (4)	−0·0008 (4)
C(10)	−0·1404 (4)	0·3619 (5)	0·1426 (2)	0·0098 (5)	0·0117 (6)	0·0016 (1)	0·0065 (9)	0·0007 (4)	−0·0001 (4)
C(11)	0·0052 (4)	0·2454 (5)	0·0092 (2)	0·0106 (5)	0·0113 (5)	0·0014 (1)	0·0042 (8)	−0·0004 (4)	0·0011 (4)
N	0·0412 (3)	0·2046 (3)	0·0766 (1)	0·0056 (4)	0·0086 (4)	0·0015 (1)	0·0005 (6)	0·0005 (2)	0·0003 (3)
O	−0·2168 (3)	0·4281 (4)	0·1725 (2)	0·0117 (4)	0·0158 (5)	0·0025 (1)	0·0131 (7)	0·0005 (3)	−0·0013 (3)

	x	y	z		x	y	z
H(1)	−0·075	0·023	0·197	H(7,1)	0·274	0·123	0·214
H(2,1)	0·047	0·176	0·269	H(7,2)	0·265	0·140	0·134
H(2,2)	−0·049	0·268	0·226	H(8,1)	−0·232	0·184	0·153
H(3)	0·178	0·336	0·207	H(8,2)	−0·215	0·231	0·076
H(4)	0·164	0·357	0·097	H(9,1)	0·011	0·482	0·161
H(5)	−0·038	0·037	0·115	H(9,2)	−0·022	0·467	0·082
H(N)	0·112	0·141	0·070	H(11,1)	0·079	0·288	−0·013
H(6,1)	0·137	−0·044	0·209	H(11,2)	−0·021	0·166	−0·017
H(6,2)	0·128	−0·027	0·129	H(11,3)	−0·065	0·310	0·011

Table 3. *Bond angles in degrees* (± 1°).

C(1)–C(2)–C(3)	100	C(5)–C(8)—C(10)	115
C(2)–C(1)–C(5)	111	C(4)–C(9)—C(10)	114
C(2)–C(3)–C(4)	110	N——C(5)—C(8)	108
C(2)–C(1)–C(6)	101	N——C(4)—C(9)	108
C(2)–C(3)–C(7)	101	C(8)–C(10)–C(9)	119
C(1)–C(6)–C(7)	104	C(5)–N——C(4)	108
C(3)–C(7)–C(6)	105	C(8)–C(10)–O	121
C(4)–C(3)–C(7)	112	C(9)–C(10)–O	120
C(5)–C(1)–C(6)	112	C(5)–N——C(11)	114
C(1)–C(5)–N	108	C(4)–N——C(11)	114
C(3)–C(4)–N	109	C(4)–N——Cl	117
C(1)–C(5)–C(8)	114	C(5)–N——Cl	116
C(3)–C(4)–C(9)	114		

O, H were taken from *International Tables for X-ray Crystallography* (1962). Neither absorption nor extinction corrections were applied. Calculations were done initially on an 8K IBM 1130 computer, and the refinement was carried out on a Burroughs B5700 machine with the local set of programs (Laing, 1972).

The final positional and thermal parameters are given in Table 1. Intramolecular bond lengths and non-bonded separations are given in Table 2, and bond angles in Table 3. The numbering system and molecular shape are illustrated in Fig. 1, while the mode of packing of the molecules and certain of the intermolecular separations are shown in Fig. 2.* The parameters of the thermal vibration ellipsoids were calculated and showed that the r.m.s. amplitudes of vibration were in the range 0·16 to 0·33 Å. Typical results are: Cl$^-$, 0·21 × 0·20 × 0·18 Å; N, 0·21 × 0·18 × 0·17 Å; O, 0·33 × 0·24 × 0·19 Å. The thermal motion analysis shows that the molecule does not approximate a rigid body, hence meaningful **T** and **ω** tensors cannot be obtained.

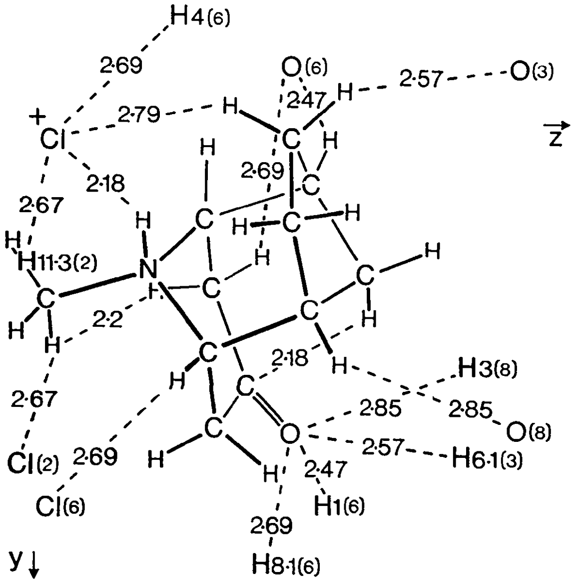


Fig. 2. View down x showing important intermolecular contacts. The numbers in brackets indicate the equivalent positions: (2) $\frac{1}{2}+x, \frac{1}{2}-y, -z$. (3) $-x, \frac{1}{2}+y, \frac{1}{2}-z$. (6) $\frac{1}{2}-x, \frac{1}{2}+y, z$. (8) $\frac{1}{2}+x, y, \frac{1}{2}-z$. Certain H atoms are translated parallel to the cell edges: H(3), $\bar{1}00$; H(8, 1), $\bar{1}00$; H(1), $\bar{1}00$; H(4), $0\bar{1}0$.

Discussion

The symmetry of the molecule as a whole is close to m, with C(2), C(10), C(11), O, N and Cl lying within 0·003 Å of the mirror plane. Deviations of other atoms from this plane are: C(1) −1·15, C(3) 1·16, C(5) −1·23, C(4) 1·22, C(6) −0·76, C(7) 0·77, C(8) −1·29, C(9) 1·29 Å. The *N*-methyl-*γ*-piperidone ring has a flattened chair conformation with the methyl group C(11) oriented pseudo-axially, *i.e.* the molecule is conformer 3 above. The bond lengths are normal and similar to those observed in related compounds (Sutton, 1965); average C–N 1·51 (±0·01), C(sp^3)–C(sp^3) 1·53 (±0·02) Å. There are, however, small but systematic angular distortions which are generated as the molecule adjusts to reduce the strains caused by intramolecular non-bonded interactions. For each large angular distortion there is a related short non-bonded separation. C(2)–C(3)–C(7) and C(2)–C(1)–C(6) (101°) are far smaller than C(4)–C(3)–C(7) and C(5)–C(1)–C(6) (112°) as this angular distortion helps relieve the compressions involving the N atom; N···C(7) and N···C(6) = 2·82 Å. The small value of C(1)–C(2)–C(3) is, in addition, partly due to compression by C(10); C(2)···C(10) = 2·90, H(2,2)···C(10) = 2·18 Å. This strain is also reflected in C(9)–C(4)–C(3) and C(1)–C(5)–C(8) (114°) being opened at the expense of C(9)–C(4)–N and C(8)–C(5)–N (108°). The intramolecular strains caused by C(11) are negligible; C(11)···C(10) = 3·34, C(11)···C(9) and C(11)···C(8) = 2·96 Å.

The methyl group in the neutral ketone is in the least hindered orientation, with the result that the N atom is protonated from the more hindered side in the hydrochloride. This is in accord with the observation that the neutral ketone will not form the methiodide (Paquette & Heimaster, 1966; Sasaki, Eguchi & Kiriyama, 1971) because of the unfavourable steric repulsions that would be generated between the second *N*-methyl group and C(6) and C(7) of the ethano bridge. The N atom is hydrogen bonded to the Cl$^-$ ion (Cl···N = 3·11 Å) which 'snuggles' against the H atoms on C(11), C(7) and C(6); Cl···C(7) and Cl···C(6) = 3·56, Cl···C(11) = 3·35 Å; Cl···H(6,2) and Cl···H(7,2) = 2·8 Å and Cl···H(11,1) and Cl···H(11,2) = 3·1 Å. These interactions with H atoms on the C atoms are simple van der Waals contacts and are not hydrogen bonds.

The intramolecular non-bonded contacts H(9,1)···H(3), H(8,1)···H(1) as well as those between H(11,3)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31117 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

and C(10) determine the conformation of the carbonyl group. If the piperidone ring took up the boat conformation, C(10) would collide with H(11,3) while H(9, 1) and H(8,1) would be forced against H(3) and H(1) respectively, resulting in large compression strains. In all the related compounds whose crystal structures have been determined (Fodor, 1970) the piperidine ring also has the chair conformation.

The mode of packing implies that there is no strong intermolecular hydrogen bonding. The shortest intermolecular contacts range from 2·45 to 2·90 Å between the Cl^- and O atoms of one molecule and the H atoms on surrounding molecules. The O atom is involved in four contacts: 2·47, 2·57, 2·69 and 2·85 Å; Cl^- has two 2·67 and 2·69 Å. None is particularly short and, while these interactions are involved in holding the structure together, they are not hydrogen bonds in the accepted sense (Donohue, 1968).

The unique torsion angles between the H atoms on C atoms 2, 3, 4, 7 and 9 can be used to estimate the coupling constants that will be observed in the n.m.r. spectrum (Jackman & Sternhell, 1969). These values are given in Table 4. A value of 4·5 c.p.s. was observed for $J_{H(3)\cdots H(4)}$ in the free ketone. It thus seems reasonable to conclude that in solution the free ketone retains the conformation found in the solid state for the hydrochloride.

Table 4. *Torsion angles between hydrogen atoms* (± 5°)

H(3) ~ H(2, 1)	56°	H(4) ~ H(9, 1)	74°
H(3) ~ H(2, 2)	67	H(3) ~ H(7, 1)	36
H(3) ~ H(4)	53	H(3) ~ H(7, 2)	85
H(4) ~ H(9, 2)	45		

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The Structure of Halloysite

BY G. B. MITRA AND S. BHATTACHERJEE

Department of Physics, Indian Institute of Technology, Kharagpur, India

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A pure sample of Utah halloysite has been subjected to an X-ray diffraction study. The X-ray line profiles have been studied in the light of a theory of diffraction by curved crystals developed in this paper. It is concluded that metahalloysite has a lath-like cylindrical structure and the kaolin layers are considered to be arranged parallel to one another but shifted parallel to themselves. Experimental results have been compared with the theorctical calculations and a satisfactory model with the values of the lattice parameters has been proposed. Observed and calculated line profiles agree with this model fairly satisfactorily.

Introduction

Halloysite is an important member of the kaolin group of clay minerals and is made up of kaolin layers. Brindley & Robinson (1946) have considered it to be composed of kaolin layers which are stacked more or less regularly along the *c* axis but are displaced at random parallel to the *ab* plane. It has not yet been possible to carry out a detailed structural analysis of halloysite because of the great complexity of the diffraction pattern. However, Brindley & Robinson (1948) have made an attempt to analyse the structure of metahalloysite on the basis of a disordered structure. They observed that the X-ray reflexions could be grouped into two categories: (i) the basal reflexions 00*l* which are the only three-dimensional reflexions and