Table 2. *The influence of substituents in position* 4 *on the distortion of the piperidine ring in pentamethylpiperidine derivatives*

Standard deviations of individual torsion angles are in the range 0·6–0·8°.

| Compounds | Mean torsion angle | Mean CCCC angle | Mean CNCC angle | $C_{ax}\cdots C_{ax}$ | $C_{ax}\cdots O$ | ∠CNC | Intermolecular O···N | Number of hydrogen bonds | m.p. |
|---|---|---|---|---|---|---|---|---|---|
| PMPE(a) | 51·6° | 49·0° | 54·5° | 3·214 (5) Å | 3·14 (1) Å | 116·6 (3)° | 3·074 (5) Å | 2 | 395 K |
| PMPM(b) | 51·0 | 59·6 | 52·3 | 3·271 (7) | 3·05 (1) | 116·0 (4) | 2·941 (7) | 1 | 366 |
| PMPV(c) | 50·5 | 49·0 | 51·8 | 3·264 (6) | 3·08 (1) | 116·8 (3) | 3·240 (6) | – | 343 |
| PMPTB(d) | 50·0 | 51·6 | 48·2 | 3·383 (5) | 3·00 (1) | 118·7 (3) | 3·161 (5) | – | 324 |

(*a*) 4-Ethyl-1,2,2,6,6-pentamethyl-4-piperidinol (Cygler, 1980).
(*b*) 1,2,2,4,6,6-Hexamethyl-4-piperidinol (this paper).
(*c*) 1,2,2,6,6-Pentamethyl-4-vinyl-4-piperidinol (Cygler, Dobrynin & Perrin, 1980).
(*d*) 4-*tert*-Butyl-1,2,2,6,6-pentamethyl-4-piperidinol (Cygler, Markowicz, Skolimowski & Skowroński, 1980).

intermolecular distance between O and N atoms depends on the size and orientation of the substituent at C(4) (Table 2). In the case of ethynyl and methyl substituents this distance is close enough for the formation of a hydrogen bond. The vinyl substituent, which is intramolecularly hydrogen-bonded to the hydroxyl O atom, as well as the *tert*-butyl substituent shield the O atom, precluding a close approach by the N atom. Consequently, in these two compounds a hydrogen bond is not formed. The melting points listed in Table 2 provide a good indication of the differences in intermolecular interactions.

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# (−)-Iodolupinane Perchlorate

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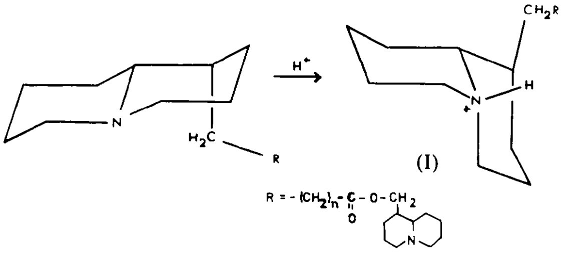
**Abstract.** $C_{10}H_{19}IN^+.ClO_4^-$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}961$ (2), $b = 12{\cdot}504$ (3), $c = 14{\cdot}112$ (4) Å, $Z = 4$, $D_c = 1{\cdot}79$ Mg m$^{-3}$, $\mu$(Mo $K\alpha$) = 2·5 mm$^{-1}$. The structure was solved by the heavy-atom method and refined to $R = 0{\cdot}047$. The iodomethyl group is axially oriented with respect to the *trans*-quinolizidine nucleus. The ammonium N atom forms hydrogen bonds with two $ClO_4^-$ O atoms.

**Introduction.** This work is part of a series of studies on the conformations of substituted lupinine molecules.

The protonation of bislupinine esters leads to an inversion of the *trans*-quinolizidine ring and results in a *cis* system with the $-CH_2R$ group in the equatorial position (I) (Sadykov, Aslanov & Kushmuradov, 1975). It was our interest to see whether similar configurational changes might occur on protonation of *trans*-quinolizidine systems with a bulky substituent at C(11). The aim of the present work was to verify this suggestion in the case of (–)-iodolupinane perchlorate.



(I)

A crystal with dimensions 0·55 × 0·35 × 0·40 mm was mounted on a Syntex $P2_1$ diffractometer. Intensities were collected using Mo $K\alpha$ radiation in the $\theta$–$2\theta$ scan mode to $2\theta_{max}$ = 47°. The scan rate was proportional to the intensity and varied from 1·89 to 29·30° min$^{-1}$. No background measurements were made. The background and integrated intensity for each reflexion were determined using the peak-profile-analysis program *PRAN* (Jaskólski, 1979) based on the Lehmann & Larsen (1974) method. 1151 unique reflexions were collected of which 927 were considered observed $[I/\sigma(I) \geq 1\cdot96]$ and used in the calculations. Corrections were made for Lorentz and polarization effects but not for absorption.

The position of the I atom was determined from a Patterson synthesis. The Cl atom was located on a Fourier map with iodine phasing and the next $F$ map showed all the remaining non-hydrogen atoms. The structure was refined with anisotropic temperature factors using the full-matrix least-squares method. Positions of all H atoms were calculated from the geometry of the cation and they were allowed to contribute to $F_c$ with $B_{iso}$ = 5·5 Å$^2$, their parameters being fixed. Templeton's scattering corrections for I and Cl were incorporated in the structure factor calculation. In the least-squares refinement the reflexions were weighted as follows: $w = (F_o/11\cdot0)^2$ if $|F_o| < 11\cdot0$, $w = 1$ if $11\cdot0 \leq |F_o| \leq 60\cdot0$ and $w = (60\cdot0/F_o)^2$ if $|F_o| > 60\cdot0$. The final $R$ and $R_w$ values are 0·047 and 0·054, respectively. The final $\Delta F$ synthesis showed a few peaks less than 0·60 e Å$^{-3}$ located near the I and Cl atoms. Positional parameters are given in Table 1.*

Table 1. *Positional atomic parameters for non-hydrogen atoms* (×10$^4$) *and their isotropic thermal parameters* (Å$^2$)

| | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| I | 5005 (2) | 2172 (1) | 4423 (1) | 4·95 (5) |
| C(11) | 5094 (29) | 1739 (10) | 5912 (8) | 4·0 (6) |
| C(1) | 5593 (19) | 567 (13) | 6052 (10) | 4·0 (8) |
| C(2) | 4441 (21) | –253 (12) | 5586 (11) | 4·6 (9) |
| C(3) | 2776 (25) | –301 (13) | 6098 (12) | 5·0 (9) |
| C(4) | 3073 (26) | –598 (15) | 7136 (13) | 5·7 (10) |
| N(5) | 4200 (18) | 190 (11) | 7613 (9) | 3·7 (6) |
| C(6) | 4511 (23) | –173 (15) | 8631 (11) | 5·2 (10) |
| C(7) | 5616 (23) | 593 (15) | 9150 (11) | 5·0 (9) |
| C(8) | 7274 (23) | 721 (17) | 8666 (12) | 5·6 (10) |
| C(9) | 6999 (21) | 1077 (14) | 7628 (11) | 4·6 (8) |
| C(10) | 5878 (20) | 299 (12) | 7101 (11) | 3·2 (7) |
| Cl | 6665 (5) | 2509 (3) | 1694 (3) | 4·0 (2) |
| O(I) | 8226 (17) | 2421 (10) | 2167 (10) | 6·9 (8) |
| O(II) | 5562 (24) | 1822 (18) | 1983 (13) | 14·5 (15) |
| O(III) | 6921 (27) | 2472 (19) | 732 (10) | 13·2 (13) |
| O(IV) | 6227 (25) | 3588 (17) | 1852 (21) | 15·2 (17) |

Table 2. *Bond lengths* (Å)

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1·53 (2) | C(9)–C(10) | 1·52 (2) |
| C(2)–C(3) | 1·51 (3) | C(10)–C(1) | 1·54 (2) |
| C(3)–C(4) | 1·53 (3) | C(1)–C(11) | 1·53 (2) |
| C(4)–N(5) | 1·49 (2) | C(11)–I | 2·17 (1) |
| N(5)–C(10) | 1·53 (2) | | |
| N(5)–C(6) | 1·53 (2) | Cl–O(I) | 1·42 (1) |
| C(6)–C(7) | 1·49 (3) | Cl–O(II) | 1·30 (2) |
| C(7)–C(8) | 1·50 (3) | Cl–O(III) | 1·37 (1) |
| C(8)–C(9) | 1·55 (2) | Cl–O(IV) | 1·41 (2) |

Table 3. *Bond angles* (°)

E.s.d.'s are in the range 1·0–1·5°.

| | | | |
|---|---|---|---|
| C(1)–C(2)–C(3) | 110·3 | C(9)–C(10)–N(5) | 109·9 |
| C(2)–C(3)–C(4) | 109·4 | C(9)–C(10)–C(1) | 114·9 |
| C(3)–C(4)–N(5) | 111·4 | C(10)–C(1)–C(11) | 111·8 |
| C(4)–N(5)–C(10) | 111·8 | C(2)–C(1)–C(11) | 115·6 |
| N(5)–C(10)–C(1) | 110·3 | C(1)–C(11)–I | 111·9 |
| C(10)–C(1)–C(2) | 111·0 | | |
| C(4)–N(5)–C(6) | 109·0 | O(I)–Cl–O(II) | 113·3 |
| C(10)–N(5)–C(6) | 109·3 | O(I)–Cl–O(III) | 109·5 |
| N(5)–C(6)–C(7) | 111·5 | O(I)–Cl–O(IV) | 102·5 |
| C(6)–C(7)–C(8) | 111·5 | O(II)–Cl–O(III) | 113·0 |
| C(7)–C(8)–C(9) | 109·7 | O(II)–Cl–O(IV) | 114·7 |
| C(8)–C(9)–C(10) | 111·3 | O(III)–Cl–O(IV) | 103·0 |

**Discussion.** Bond lengths and angles are given in Tables 2 and 3, respectively. The torsion angles given in Table 4 indicate that both rings of the cation have almost ideal chair conformations. The –CH$_2$I group is axial and thus no conformation inversion is observed. The torsion angle I–C(11)–C(1)–C(2) (Fig. 1) differs from the corresponding angle in the lupinine cation, O(1)–C(11)–C(1)–C(2), in (–)-lupinine.HCl (Kozioł, Gdaniec & Kosturkiewicz, 1980) by ~9°. This is the only conformational modification resulting from the presence of the bulky substituent.

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* Lists of structure factors, anisotropic thermal parameters for non-hydrogen atoms and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35401 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Torsion angles* (°)

E.s.d.'s are in the range 1·0–2·1 °.

| | | | | | |
|---|---|---|---|---|---|
| C(4)–N(5)–C(10)–C(1) | 54 | N(5)–C(6)–C(7)–C(8) | −58 | I–C(11)–C(1)–C(2) | −59 |
| C(10)–C(1)–C(2)–C(3) | 58 | C(6)–C(7)–C(8)–C(9) | 56 | I–C(11)–C(1)–C(10) | 173 |
| C(1)–C(2)–C(3)–C(4) | −59 | C(7)–C(8)–C(9)–C(10) | −56 | N(5)–C(10)–C(1)–C(11) | 76 |
| C(2)–C(3)–C(4)–N(5) | 59 | C(8)–C(9)–C(10)–N(5) | 57 | C(3)–C(2)–C(1)–C(11) | −71 |
| C(3)–C(4)–N(5)–C(10) | −57 | C(9)–C(10)–N(5)–C(6) | −57 | C(4)–N(5)–C(6)–C(7) | −179 |
| N(5)–C(10)–C(1)–C(2) | −55 | C(10)–N(5)–C(6)–C(7) | 58 | C(9)–C(10)–C(1)–C(2) | −179 |

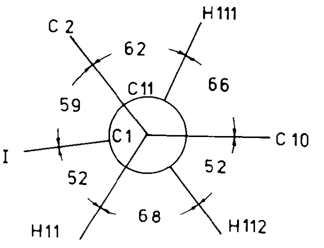
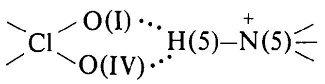


Fig. 1. A Newman projection along the C(1)–C(11) bond, showing some torsion angles (°).

Table 5. *Hydrogen-bond geometry*

| | | | |
|---|---|---|---|
| N(5)–O(1) | 3·10 (2) Å | N(5)–H(5)···O(1) | 160° |
| N(5)–O(IV) | 2·92 (3) | N(5)–H(5)···O(IV) | 132 |
| N(5)–H(5) | 0·98 | | |
| H(5)–O(I) | 2·16 | | |
| H(5)–O(IV) | 2·16 | | |

The packing of the molecules in the crystal is shown in Fig. 2. Two $ClO_4^-$ groups interact with each cation. One is involved in a bifurcated hydrogen bond  $>Cl<^{O(I)\cdots}_{O(IV)\cdots}H(5)-\overset{+}{N}(5)\lessgtr$ (the geometry of this bond is given in Table 5) while the other interacts with the I atom [I···O(II) 3·50 (2) Å]. A similar bifurcated hydrogen-bond system was found in the quinoline.$HClO_4$ structure (Rychlewska, 1976).

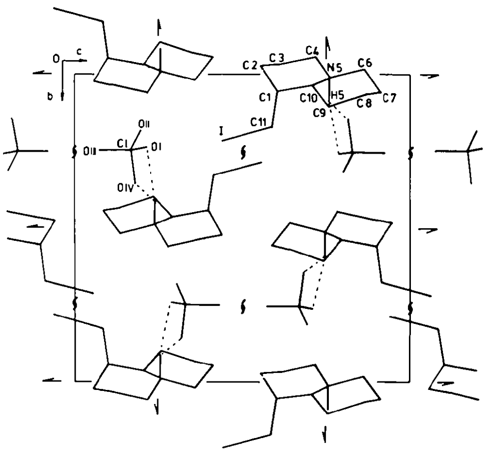


Fig. 2. Projection of the structure along the *a* axis. H atoms, except H(5), are omitted for clarity.

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