

C(4)C(5)C(5')C(4') and N(1)C(6)C(6')N(1'). The diazacycloheptane ring has a slight twist-chair conformation. All torsion angles around the rings are given in Fig. 2.

A similar geometry was found for the *cis-syn* photodimers of 6-methyluracil (Gibson & Karle, 1971) and thymine trimer (Flippen & Karle, 1971) (Table 3). However, the molecule of the known *cis-syn* photodimer of 1,3-dimethylthymine with substituted N atoms is much more distorted (Camerman & Camerman, 1970).

The bond lengths and angles in the molecule agree well with those for the dimers reported to date (Birnbbaum, 1972 and references cited therein; Leonard *et al.*, 1969; Bremner, Warrener, Adman & Jensen, 1971; Cheng, Hornby, Wong-Ng, Nyburg & Weinblum, 1976).^{*} The short lengths of the bonds C(11)–C(12), C(11')–C(12') are probably due to the thermal motion. The intramolecular distance C(9)···C(9') is only 2.98 Å. The crystal packing is shown in Fig. 3.

^{*} A full list of bond lengths and valency angles of all *cis-syn*, *cis-anti*, *trans-syn*, and *trans-anti* photodimers published to date is available from the authors.

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N-(*N*-Piperidylacetyl)piperidinium Perchlorate

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Abstract. C₁₂H₂₃N₂O₅Cl, orthorhombic, *Pbca*; *a* = 18.699 (2), *b* = 15.456 (2), *c* = 10.302 (1) Å, *V* = 2977 Å³; *Z* = 8, *D_m* = 1.39, *D_c* = 1.39 g cm⁻³; μ(Cu *Kα*) = 24.8 cm⁻¹. *R* = 0.074 for 1672 observed reflexions. The cations are hydrogen bonded and form dimers, each dimer occupying a centre of symmetry.

Introduction. *N*-(*N*-Piperidylacetyl)piperidine is one of various model compounds investigated by Professor M. Wiewiórowski in his study of intramolecular catalysis. The crystals of *N*-(*N*-piperidylacetyl)piperidinium perchlorate were prepared and supplied by him.

Photographs showed systematic absences *Ok**l* for *k* odd, *h**0**l* for *l* odd, *hk**0* for *h* odd. Precise unit-cell-constant determination (by least-squares fit of the setting angles of 15 reflexions) and intensity measurements were carried out on a Syntex P2₁ four-circle computer-

controlled diffractometer using a crystal with dimensions 0.10 × 0.28 × 0.33 mm. Graphite-monochromatized Cu radiation and a variable *θ*–2*θ* scan were used. 2328 independent reflexions were collected in a 2*θ* range up to 114° and, of these, 1673 had *I* > 1.96σ(*I*) and were used in all calculations with the exception of the most intense reflexion, 400, which was excluded from the final stages of least-squares refinement. Structure factors were obtained from the intensities in the usual fashion. No absorption or extinction corrections were applied. The structure was solved by standard heavy-atom Patterson and Fourier methods. An electron density map calculated on the basis of only the Cl atom revealed the positions of all non-hydrogen atoms of the cation and a number of peaks around the Cl atom, the four highest of which were interpreted as O atoms. Attempts to locate the perchlorate group in

another orientation and to refine occupancies of those two sets of O atoms failed and the only acceptable solution was that with the perchlorate ion in one orientation with large temperature factors for the O atoms. All H atoms were located from a three-dimensional ΔF map and each was given an isotropic thermal parameter one unit greater than the isotropic value for the atom to which it was attached. In the final stages of structure refinement positional and anisotropic thermal parameters of all non-hydrogen atoms and positional parameters of the H atoms were refined by the full-matrix least-squares method. The function minimized was $\Sigma w(F_o - F_c)^2$, where the weight w was based on counting statistics: $w = (\sigma^2 + c^2 F^2)^{-1}$ (Stout & Jensen, 1968) with $c = 0$. When the refinement ceased, c was calculated by least-squares analysis of the expression $\sigma^2 + c^2 F^2 = (\Delta F)^2$. The value of $c = 0.04$ was then applied in three more cycles of full-matrix least-squares refinement of the same set of variables except for the positional parameters of H(N2), which were kept fixed, to give the following agreement indices for the final model: $R = \Sigma \|F_o\| - |F_c| / \Sigma |F_o| = 0.074$ (including unobserved data $R = 0.085$), $R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2} = 0.101$, goodness-of-fit = $[\Sigma w(F_o - F_c)^2 / (\text{NO} - \text{NV})]^{1/2} = 2.1$.

All calculations were carried out with the Syntex XTL programs for structure determination (*Syntex XTL Operation Manual*, 1973) except for the program for the least-squares calculation of c , which was written by one of us (MJ). Final positional and thermal parameters are given in Tables 1 and 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32437 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final fractional atomic coordinates* ($\times 10^4$; $\times 10^5$ for chlorine) *for non-hydrogen atoms*

	<i>x</i>	<i>y</i>	<i>z</i>
Cl	14946 (7)	2738 (8)	16330 (13)
C(1)	917 (2)	-3927 (3)	296 (4)
C(2)	1407 (3)	-4699 (3)	344 (5)
O(1)	264 (2)	-4034 (2)	397 (3)
N(1)	1213 (2)	-3147 (2)	193 (4)
C(12)	1974 (3)	-2986 (4)	-72 (6)
C(13)	2052 (3)	-2508 (4)	-1333 (5)
C(14)	1616 (3)	-1681 (3)	-1340 (6)
C(15)	838 (3)	-1876 (4)	-1029 (6)
C(16)	782 (3)	-2358 (3)	230 (5)
N(2)	1037 (2)	-5474 (2)	880 (4)
C(22)	1487 (3)	-6262 (3)	668 (6)
C(23)	1134 (3)	-7063 (3)	1219 (6)
C(24)	952 (3)	-6959 (4)	2622 (6)
C(25)	498 (3)	-6166 (3)	2825 (6)
C(26)	859 (3)	-5366 (3)	2302 (5)
O(2)	1905 (5)	849 (5)	2301 (7)
O(3)	1647 (6)	-538 (4)	1982 (8)
O(4)	868 (5)	483 (9)	2044 (18)
O(5)	1635 (5)	434 (5)	340 (6)

Table 2. *Final hydrogen-atom fractional coordinates* ($\times 10^3$) *and isotropic temperature factors used in the least-squares calculations*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)
H(1)	219 (3)	-353 (4)	-16 (5)	4.3
H(2)	213 (3)	-259 (3)	65 (5)	4.3
H(3)	196 (3)	-288 (3)	-207 (5)	4.3
H(4)	253 (3)	-238 (3)	-146 (5)	4.3
H(5)	163 (3)	-143 (3)	-225 (5)	4.4
H(6)	180 (3)	-127 (4)	-72 (5)	4.4
H(7)	60 (3)	-136 (4)	-93 (5)	4.6
H(8)	62 (3)	-226 (3)	-165 (5)	4.6
H(9)	28 (3)	-253 (3)	46 (5)	4.0
H(10)	102 (3)	-199 (3)	97 (5)	4.0
H(11)	156 (3)	-627 (3)	-12 (5)	3.6
H(12)	194 (3)	-616 (3)	115 (5)	3.6
H(13)	146 (3)	-746 (4)	107 (5)	3.9
H(14)	79 (3)	-724 (3)	69 (5)	3.9
H(15)	138 (3)	-688 (3)	319 (5)	4.7
H(16)	80 (3)	-739 (4)	292 (6)	4.7
H(17)	5 (3)	-625 (3)	233 (5)	4.3
H(18)	42 (3)	-607 (3)	368 (5)	4.3
H(19)	66 (2)	-489 (3)	235 (5)	3.2
H(20)	123 (3)	-528 (3)	264 (5)	3.2
H(21)	184 (3)	-460 (3)	90 (5)	3.4
H(22)	158 (2)	-486 (3)	-65 (5)	3.4
H(N2)	66 (3)	-553 (3)	50 (5)	3.0

Discussion. The labelling sequence, bond lengths and bond angles in the cation are given in Fig. 1. Bond angles containing H atoms, except for H(N2), are not shown. The C-C and C-N distances in the piperidine rings are in good agreement with those found in other compounds containing piperidine systems (Hite & Craven, 1973; Hite & Soares, 1973; Ruble, Blackmond & Hite, 1976; Ruble, Hite & Soares, 1976*a,b*), the mean value of the C-C bond length in the piperidine rings being 1.507 Å. Both piperidine rings adopt chair conformations and this as well as other geometrical features of the piperidine-ring arrangement is easily seen from Table 3, which gives the summary of the least-squares planes calculations.

& Jeffrey, 1960). The numerous peaks found around the Cl atom on F and ΔF maps attest to the fact that the very large temperature factors of perchlorate O atoms are due not only to high thermal motion but also to the disorder of the perchlorate ion. Because these two phenomena are intimately linked, the temperature factors of the O atoms are not accurate and no librational corrections to the Cl-O bonds have been calculated. Perchlorate anions are very often found to be disordered and some recent papers report structures containing perchlorate groups with extremely large thermal parameters for O atoms (Clark, Waters & Whittle, 1975; Kistenmacher & Szalda, 1975).

The geometry of the perchlorate anion is given in Table 4. The Cl-O distances are considerably shorter than the accepted value of 1.46 Å (Truter, Cruickshank

The cations are linked by hydrogen bonds and form dimers, each dimer occupying a centre of symmetry.

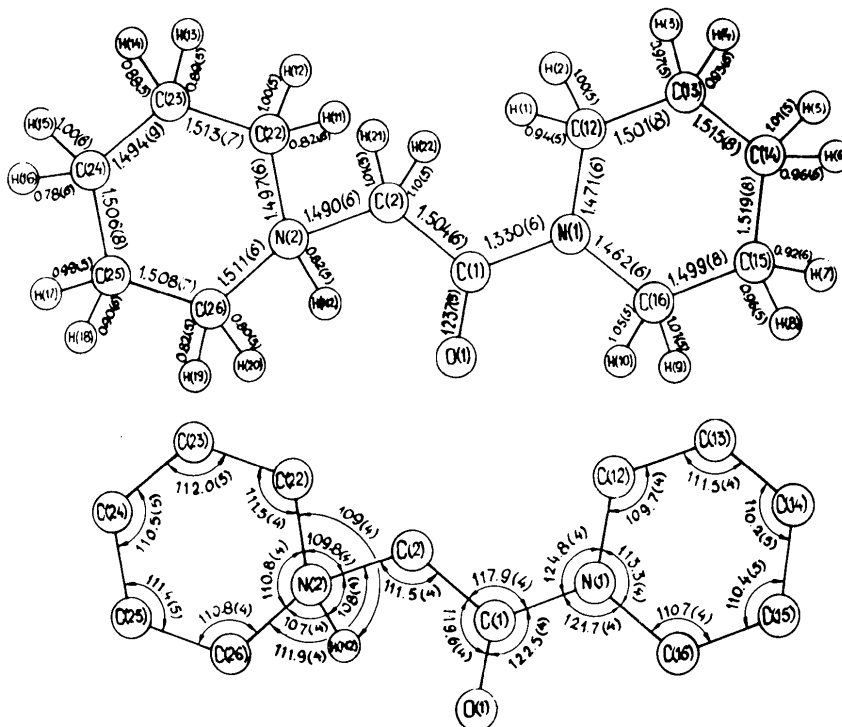


Fig. 1. Bond distances (Å) and angles (°) in the cation. Bond angles containing H atoms except for H(N2) are not shown.

Table 3. Planarity of some groups of atoms in the molecule

The equation of the weighted least-squares plane is expressed as $PX + QY + RZ = S$; X, Y, Z are in Å and are referred to crystal axes. Deviations (Å) of atoms are shown in square brackets.

Plane	Atoms defining the plane	P	Q	R	S	χ^2
A	C(12), C(13), C(15), C(16)	-0.4013	-0.7778	-0.4837	2.1348	0.64
		[C(12)-0.0027 (65), C(13) 0.0025 (65), C(15) -0.0028 (67), C(16) -0.0024 (61), C(14) -0.6560 (64), N(1) -0.6526 (44)]				
B	C(22), C(23), C(25), C(26)	-0.7593	0.1264	-0.6383	-3.7762	6.03
		[C(22) 0.0081 (67), C(23) -0.0089 (69), C(25) 0.0084 (67), C(26) -0.0071 (61), C(24) -0.6602 (69), N(2) 0.6564 (44)]				

Angle between normals to planes A and B: 59°.

Table 4. Bond distances (Å) and angles (°) in the perchlorate anion

Cl-O(2)	1.361 (8)	O(2)-Cl-O(3)	110.9 (5)
Cl-O(3)	1.335 (7)	O(2)-Cl-O(4)	100.5 (7)
Cl-O(4)	1.288 (11)	O(2)-Cl-O(5)	105.3 (5)
Cl-O(5)	1.381 (6)	O(3)-Cl-O(4)	109.9 (7)
		O(3)-Cl-O(5)	112.8 (5)
		O(4)-Cl-O(5)	116.5 (7)

2.700 (5) Å is appreciably shorter than the intermolecular N(2)···O(1ⁱ) distance. H(N2)···O(1), however, is 2.43 (5) Å, which is considerably longer than H(N2)···O(1ⁱ). Hamilton (1968) gave an upper limit of 2.4 Å for the H···O distance in a hydrogen bond. Comparison of H(N2)···O(1) with this limit and

The geometry of the hydrogen bond is given in Fig. 2 and Table 5. The arrangement of hydrogen-bonded molecules in the structure is shown in Fig. 3 which depicts the packing of the structure as viewed down the *c* axis. The intramolecular N(2)···O(1) distance of

Table 5. Geometry of the hydrogen bond

O(1 ⁱ)···N(2)	2.868 (5) Å	O(1 ⁱ)···H(N2)-N(2)	167 (5)°
O(1 ⁱ)···H(N2)	2.06 (5)		
N(2)-H(N2)	0.82 (5)		

Symmetry code: (i) -x, -y, -z.

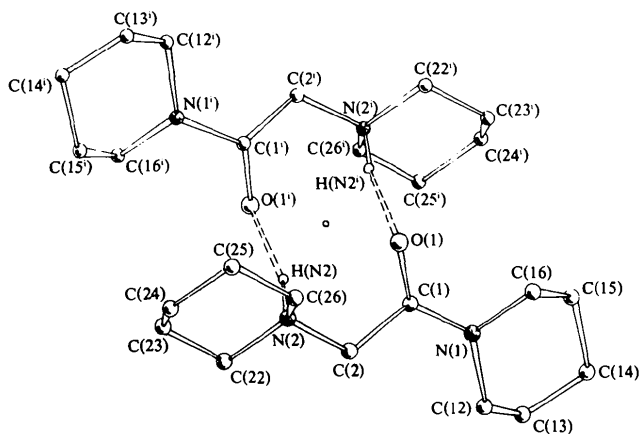


Fig. 2. Arrangement of hydrogen-bonded cations. All H atoms attached to C atoms have been omitted.

the fact that the angle $N(2)-H(N2)\cdots O(1)$ of $101(4)^\circ$ is very unfavorable for hydrogen-bond formation lead to the conclusion that this short contact is probably better classified as a short van der Waals contact rather than a very weak hydrogen bond.

There are no short contacts between the perchlorate O atoms and atoms of the cation. All intermolecular distances are greater than the sums of the appropriate van der Waals radii.

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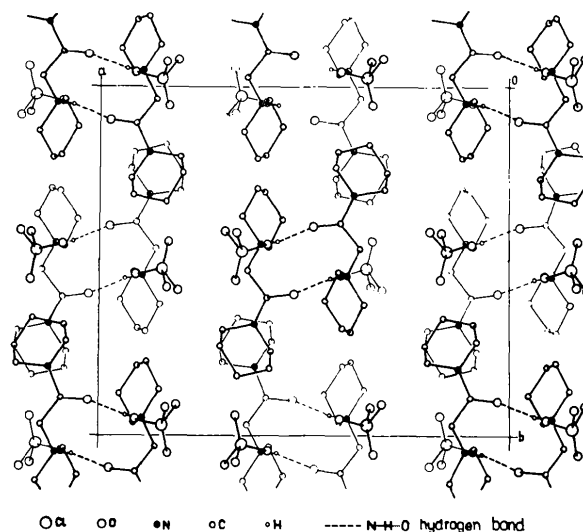


Fig. 3. Projection of the structure down the c axis. All H atoms attached to C atoms have been omitted.

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Bis(ethylenediamine)triiododimercury(II) Triiodomercurate(II)

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Abstract. $Hg_3I_6(en)_2$ ($en = ethylenediamine, C_2H_8N_2$), triclinic, $P\bar{1}$, $a = 15.170(6)$, $b = 8.999(3)$, $c = 8.561(4)$ Å, $\alpha = 83.52(5)$, $\beta = 84.12(5)$, $\gamma =$

$78.69(4)^\circ$, $V = 1134.8$ Å³. $M_r = 1483.4$, $\mu(Mo K\alpha) = 289$ cm⁻¹, $D_m = 4.213$ (pycnometrically), $D_x = 4.341$ g cm⁻³, $Z = 2$. The structure is built up of trigonal