The Crystal and Molecular Structure of 1-Piperoylpiperidine

By Marc Grynpas and Peter F. Lindley

Department of Crystallography, Birkbeck College, Malet Street, London WC1E 7HX, England

Crystals of 1-piperoylpiperidine, piperine, are monoclinic, space group $P2_1/n$, with $a = 8.743$ (2), $b = 13.364$ (3), $c = 13.147$ (3) Å, $\beta = 108.66$ (1)°. The structure has been refined to $R = 0.056$ for 1626 significant independent reflexions measured on an automated four-circle diffractometer. The 3,4-methylenedioxyphenyl moiety is twisted with respect to the pentadiene chain by an angle of 8.4° owing to repulsions between hydrogen atoms. The piperidine ring adopts the chair conformation and the basal plane of the chair makes a dihedral angle of 66.1° with respect to the pentadiene chain.

Introduction

1-Piperoylpiperidine, referred to hereinafter as piperine, is the piperidine amide of 5-(3,4-methylenedioxyphenyl)-2,4-pentadienoic acid, (piperic acid). The alkaloid occurs in pepper, particularly black pepper (*Piper nigrum*), and is used to impart a pungent taste to brandy. It has also been used as an insecticide (against houseflies) being non-toxic to humans.

Experimental

Pale yellow prismatic crystals of piperine were obtained by extraction of the material with ethanol from an oleoresin of black pepper and subsequent recrystallization using the same solvent. The mass spectrum of the recrystallization product, recorded on an AEI MS902 instrument, showed the parent ion peak at m/e 284 consistent with the molecular formula of piperine, $C_{17}H_{19}O_3N$.

Preliminary unit-cell parameters and space-group information were obtained from precession and Weissenberg photographs taken with copper radiation. A crystal with the dimensions $0.38 \times 0.19 \times 0.19$ mm was mounted parallel to the longest edge, which was found to be the a axis. The data were collected on a Hilger–Watts Y290 automatic four-circle diffractometer with Ni-filtered copper radiation.

Accurate cell parameters were determined from 20 reflexions with 2θ between 24° and 89° by a least-squares technique. Intensity data were collected using the $\omega/2\theta$ scanning method with a step size of 0.01° and a counting time of 1 s per step. The scan width was 0.85° plus a dispersion correction. Stationary background counts were measured before and after each scan for 1/10th of the time taken to scan each reflexion. Three reference reflexions were measured after every 50 reflexions and the sum of these reflexions was used to scale the observed intensities by interpolation between groups of references. The overall variation in the intensities of the reference reflexions during data collection was less than 2.5%.
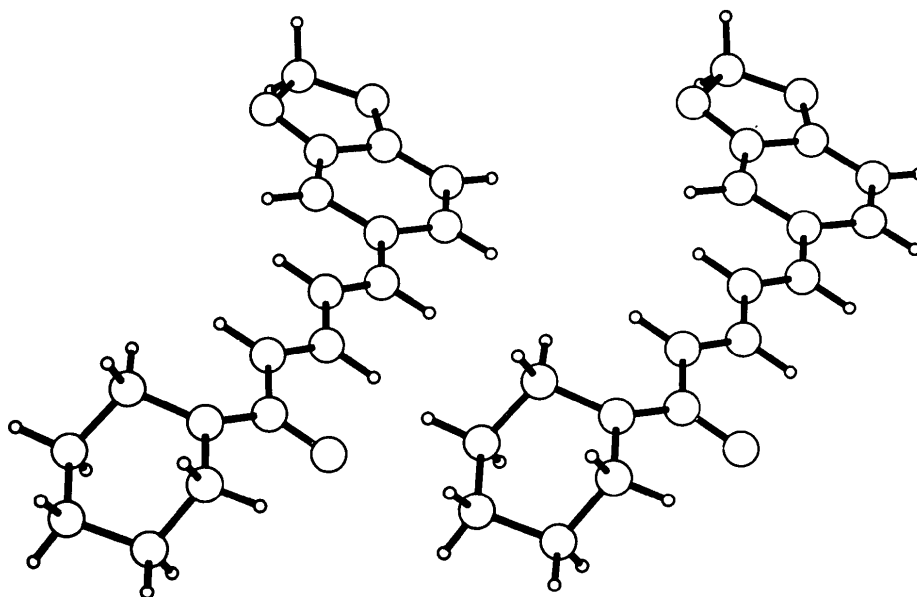

Fig. 1. A stereo drawing of the molecule of piperine viewed along the unit cell a axis.

Intensity data were collected for the hkl and $hk\bar{l}$ reflexions over the range $0° \le \theta \le 70°$. A second set of data was collected for the hkl and $hk\bar{l}$ reflexions over the range $0° \le \theta \le 34\cdot5°$. Averaging of these two sets of data gave 2757 independent reflexions of which 1626 had $I \ge 3\sigma(I)$ and were thereby classified as 'significant'. The overall agreement between the 740 reflexions measured more than once was $1\cdot4\%$. Lorentz and polarization corrections were applied to all reflexions but no corrections were made for absorption. The more important crystal data are given in Table 1. The discrepancy between the measured and calculated densities may be explained by the difficulty in completely separating the crystals from the oleoresin. A set of normalized structure factors was then computed from the observed structure factors using the K-curve method (Karle & Karle, 1965).

Structure solution and refinement

The structure was determined, with some difficulty, using a weighted multisolution tangent refinement

Table 1. *Crystallographic data*

1-Piperoylpiperidine, $C_{17}H_{19}O_3N$
M.W. 285·3
Cell parameters (measured at 20 ± 1 °C)
$\quad a = 8\cdot743$ (2) Å
$\quad b = 13\cdot364$ (3)
$\quad c = 13\cdot147$ (3)
$\quad \beta = 108\cdot66$ (1)°
Cell volume, $V = 1455\cdot4$ Å³
Density, $\varrho_{exp}1\cdot25$ g cm⁻³ (by flotation in aqueous potassium
$\qquad$ iodide solution)
$\quad \varrho$ X-ray $= 1\cdot30$ g cm⁻³
Space group: monoclinic, $P2_1/n$
Four molecules per unit cell
μ(Cu $K\alpha$ radiation) $= 5\cdot05$ cm⁻¹
$E(0,0,0) = 10\cdot3$

Table 2. *Positional and thermal parameters*

(*a*) Positional atomic parameters for the non-hydrogen atoms. Estimated standard deviations are given in parentheses.

	x	y	z
C(1)	0·3381(4)	0·2736 (3)	0·3069 (3)
C(2)	0·4737 (4)	0·2817 (3)	0·3979 (3)
C(3)	0·5622 (4)	0·3677 (2)	0·4242 (2)
C(4)	0·5156 (4)	0·4506 (2)	0·3568 (2)
C(5)	0·3833 (4)	0·4402 (2)	0·2678 (2)
O(6)	0·3159 (3)	0·5099 (2)	0·1909 (2)
C(7)	0·1818 (5)	0·4643 (3)	0·1141 (3)
O(8)	0·1699 (3)	0·3660 (2)	0·1498 (2)
C(9)	0·2964 (4)	0·3543 (3)	0·2431 (2)
C(10)	0·7032 (4)	0·3719 (3)	0·5219 (3)
C(11)	0·8054 (4)	0·4463 (3)	0·5536 (3)
C(12)	0·9369 (4)	0·4495 (3)	0·6528 (2)
C(13)	1·0362 (4)	0·5253 (3)	0·6839 (3)
C(14)	1·1665 (4)	0·5268 (3)	0·7879 (3)
O(15)	1·1880 (3)	0·4549 (2)	0·8478 (2)
N(16)	1·2611 (3)	0·6070 (2)	0·8154 (2)
C(17)	1·2316 (5)	0·7018 (3)	0·7618 (3)
C(18)	1·1831 (6)	0·7766 (3)	0·8306 (4)
C(19)	1·3026 (7)	0·7813 (3)	0·9423 (4)
C(20)	1·3391 (6)	0·6807 (3)	0·9919 (3)
C(21)	1·3861 (4)	0·6103 (3)	0·9197 (3)

Table 2 (*cont.*)

(*b*) Anisotropic thermal parameters $U_{ij} \times 10^3$, for the non-hydrogen atoms. The expression used is:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)] .$$

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(1)	78 (2)	59 (2)	63 (2)	−3 (3)	54 (4)	−21 (4)
C(2)	74 (2)	58 (2)	63 (2)	0 (3)	54 (4)	−11 (4)
C(3)	64 (2)	57 (2)	51 (2)	−5 (3)	47 (3)	0 (3)
C(4)	70 (2)	53 (2)	54 (2)	−4 (3)	31 (3)	−4 (3)
C(5)	68 (2)	53 (2)	54 (2)	7 (3)	48 (3)	5 (3)
O(6)	90 (2)	66 (2)	70 (1)	29 (3)	3 (3)	−14 (3)
C(7)	82 (2)	87 (3)	59 (2)	16 (4)	32 (4)	−14 (4)
O(8)	82 (2)	83 (2)	61 (1)	−10 (3)	18 (3)	−32 (3)
C(9)	64 (2)	61 (2)	50 (2)	−13 (3)	41 (3)	−9 (3)
C(10)	71 (2)	55 (2)	56 (2)	8 (3)	43 (3)	2 (4)
C(11)	74 (2)	56 (2)	54 (2)	−0 (3)	39 (3)	5 (4)
C(12)	73 (2)	59 (2)	49 (2)	−6 (3)	39 (3)	23 (4)
C(13)	80 (2)	53 (2)	59 (2)	−4 (3)	29 (4)	13 (4)
C(14)	70 (2)	60 (2)	53 (2)	1 (3)	38 (3)	23 (4)
O(15)	102 (2)	69 (2)	64 (1)	18 (3)	14 (3)	14 (3)
N(16)	63 (2)	60 (2)	60 (2)	−9 (3)	23 (3)	9 (3)
C(17)	90 (3)	67 (2)	75 (2)	−1 (4)	47 (4)	−23 (4)
C(18)	117 (3)	56 (2)	114 (3)	11 (4)	117 (6)	−4 (5)
C(19)	161 (4)	66 (2)	97 (3)	−32 (5)	145 (6)	−69 (6)
C(20)	116 (3)	92 (3)	68 (2)	−22 (4)	55 (5)	−44 (5)
C(21)	67 (2)	96 (3)	74 (2)	−22 (4)	12 (4)	10 (4)

(*c*) Calculated hydrogen atom positions. All hydrogen atoms were assigned an isotropic thermal parameter, $U = 0\cdot10$ Å². The expression used is $\exp(-8\pi^2 U \sin \theta^2/\lambda^2)$.

	x	y	z
H(1)	0·2762	0·2117	0·2896
H(2)	0·5087	0·2231	0·4457
H(4)	0·5736	0·5148	0·3738
H(71)	0·1971	0·4647	0·0418
H(72)	0·0809	0·5018	0·1098
H(10)	0·7245	0·3121	0·5697
H(11)	0·7874	0·5044	0·5053
H(12)	0·9563	0·3909	0·7020
H(13)	1·0193	0·5841	0·6367
H(171)	1·1436	0·6952	0·6906
H(172)	1·3325	0·7249	0·7486
H(181)	1·0729	0·7581	0·8348
H(182)	1·1725	0·8430	0·7948
H(191)	1·2596	0·8246	0·9882
H(192)	1·4063	0·8106	0·9377
H(201)	1·2382	0·6543	1·0053
H(202)	1·4268	0·6849	1·0632
H(211)	1·4044	0·5442	0·9539
H(212)	1·4908	0·6347	0·9117

(Germain, Main & Woolfson, 1971) to determine phases for 197 reflexions with $|E| > 1\cdot80$. The phase of the reflexion $42\bar{6}$ ($|E| = 3\cdot89$) was fixed as positive by application of the Σ_1 relationship (for $21\bar{3}$ $|E| = 5\cdot23$). The origin-defining reflexions and three others in the starting set were chosen by the authors after an examination of the Σ_2 relationships, as follows:

h	k	l	E	Phase
1	7	9	3·79	+
1	4	9	3·71	+
1	12	$\bar{2}$	3·44	+
2	1	$\bar{2}$	3·73	+, −
2	2	$\bar{3}$	3·16	+, −
4	3	$\bar{5}$	3·04	+, −

The solution with phases −, − and + for the starting set of reflexions respectively gave the second highest figure of merit (1·06) and an E map computed with this phase set revealed 15 of the 21 non-hydrogen atoms in the structure. The remaining six non-hydrogen atoms were then determined from a weighted Fourier synthesis to give an R value of 0·219.

Full-matrix least-squares refinement with all atoms treated isotropically and using only the 1626 'significant' reflexions reduced R to 0·142. A difference Fourier synthesis showed diffuse electron density

maxima, 0·2–0·5 e Å^{-3}, corresponding to the hydrogen atoms in the structure. In subsequent calculations the hydrogen atoms were placed in calculated positions assuming a C–H bond length of 1·0 Å but no attempt was made to refine their positional or thermal parameters.

Further full-matrix refinement with all non-hydrogen atoms treated anisotropically gave final values of $R = 0·056$ and R' $[=(\sum w \Delta^2/\sum w F_o^2)^{1/2}] = 0·063$. The weighting scheme, $w = a_0$ for $|F_o| \leq 20·0$ otherwise $w = [1 - \exp(-a_1 \sin^2 \theta/\lambda^2)]/(a_2 + |F_o| + a_3|F_o|^2)$ with
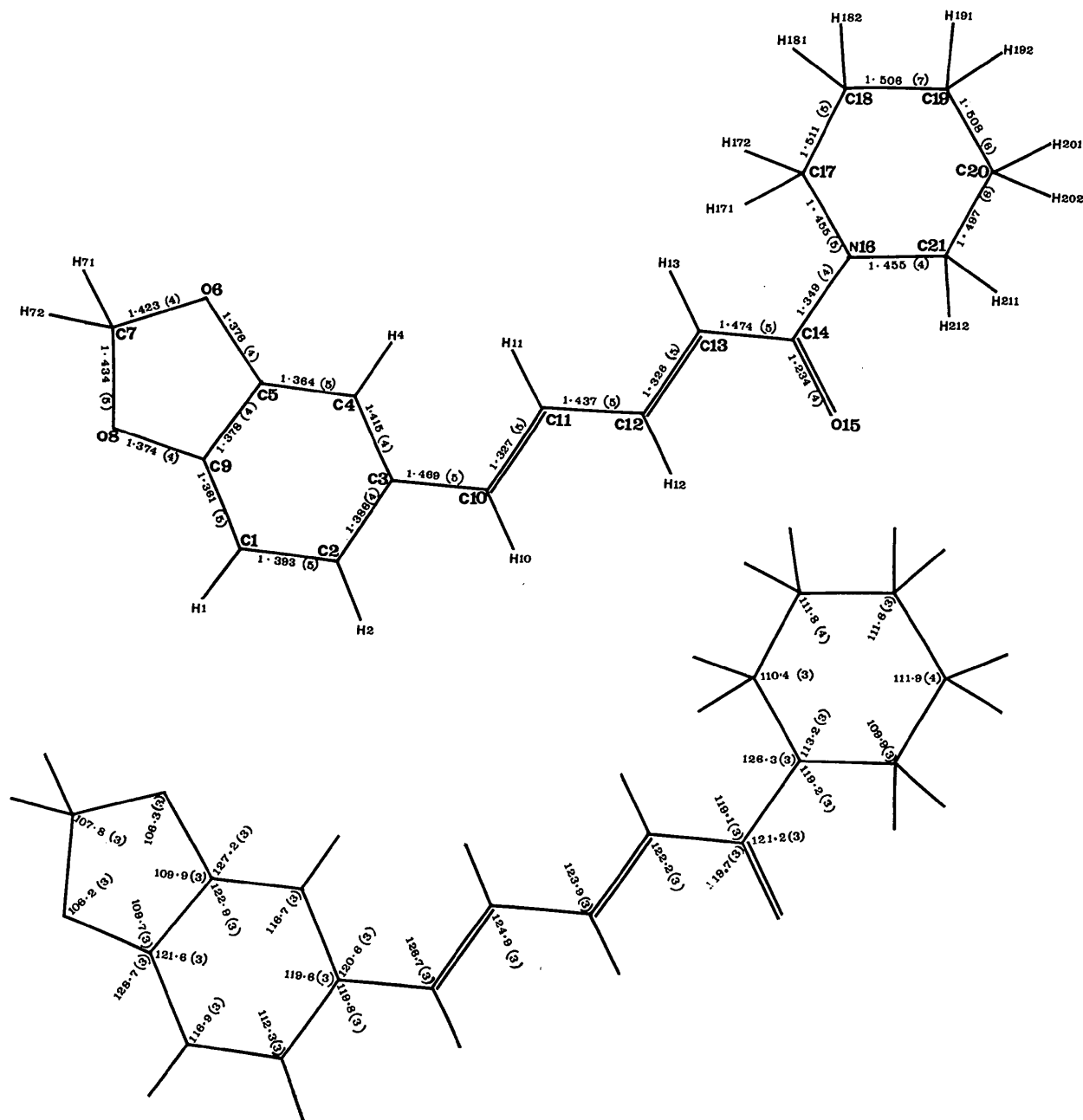

Fig. 2. A schematic drawing of piperine showing the labelling of the atoms and the intramolecular bond lengths and angles together with the corresponding estimated standard deviations (in parentheses).

$a_0 = 0.004$, $a_1 = 20.0$, $a_2 = 50.0$ and $a_3 = 0.003$ was used to make the average values of $w\Delta^2$ uniform when analysed in terms of batches of increasing $|F_o|$ and $\sin\theta/\lambda$. In the last cycle of refinement all parameter shifts were less than the corresponding estimated standard deviations. A final difference Fourier synthesis showed a maximum variation in the residual electron density of ± 0.2 e Å^{-3}. A set of structure factors, computed for the 1131 'insignificant' reflexions, showed no significant discrepancies.

Throughout the structure factor calculations the atomic scattering factors listed by Hanson, Herman, Lea & Skillman (1964) were used. All computations were performed on the CDC 6600 computer at the University of London Computer Centre. The final atomic coordinates and thermal parameters are given in Table 2.* A satisfactory tensor analysis of the anisotropic thermal vibration parameters was obtained for all the non-hydrogen atoms.

Discussion

The crystal structure of piperine consists of discrete molecules, one of which is shown by a stereo drawing in Fig. 1. A schematic drawing of the molecule showing the labelling of the atoms and the intramolecular bond lengths and angles is given in Fig. 2. Further details of the molecular geometry are recorded in Table 3.

The 3,4-methylenedioxyphenyl moiety which is planar within experimental error [see Table 3(a)] is twisted by 8·4° with respect to the least-squares plane defined by the pentadiene chain. This distortion

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31081 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Molecular geometry*

(a) Least-squares planes defined by atomic positions and, in brackets, distances of atoms (Å) from these planes. X, Y, Z refer to orthogonal coordinates (Å) obtained by the transformation

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a\sin\beta & 0 & 0 \\ 0 & b & 0 \\ a\cos\beta & 0 & c \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Plane (1): C(1), C(2), C(3), C(4), C(5), O(6), O(8), C(9)

$$0.5835X - 0.3065Y - 0.7521Z = -1.8300$$

[C(1) −0.003, C(2) 0.004, C(3) −0.003, C(4) −0.004, C(5) 0.002, O(6) 0.002, O(8) −0.002, C(9) 0.001, C(7) 0.023]

Plane (2): C(10), C(11), C(12), C(13), C(14)

$$0.6139X - 0.4223Y - 0.7000Z = -1.8220$$

[C(10) −0.008, C(11) −0.004, C(12) 0.021, C(13) 0.003, C(14) −0.012, O(15) 0.027, N(16) −0.058]

Plane (3): C(17), C(18), C(20), C(21)

$$0.8114X + 0.5464Y - 0.2077Z = 12.1483$$

[C(17) −0.008, C(18) 0.008, C(20) −0.008, C(21) 0.008, C(19) 0.611, N(16) −0.644]

Dihedral angles (°) between the least-squares planes:

plane (1) – plane (2)   8·4
plane (2) – plane (3)   66·1

(b) Non-bonded intramolecular separations (Å)

H(2)—H(10)	2·39	H(12)–O(15)	2·46
H(4)—H(11)	2·11	H(13)–H(171)	1·87
H(10)–H(12)	2·46	O(15)–H(211)	2·31
H(11)–H(13)	2·46		

minimizes the non-bonded contacts H(2)–H(10), 2·39 Å and H(4)–H(11), 2·11 Å.

Within the chain itself the bond lengths are those expected for a 2,4-diene system with the values alternating between an average of 1·460 (5) and 1·327 (5) Å, but the bond angles are widened by an
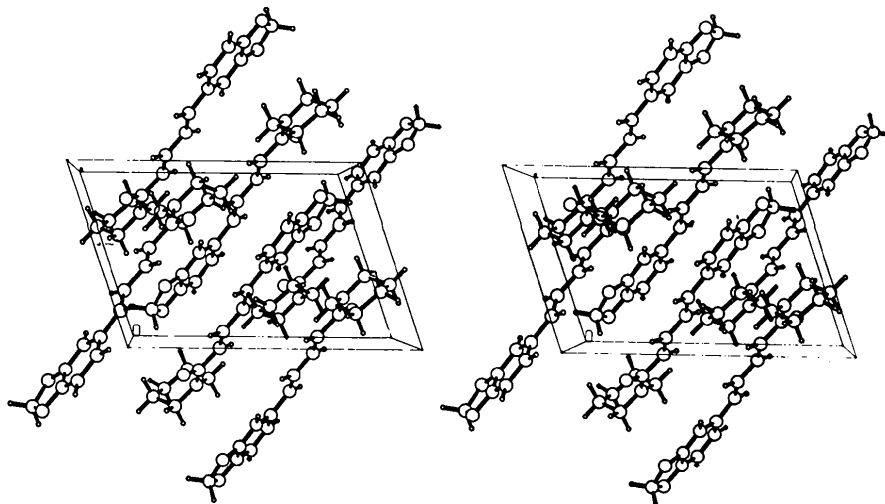

Fig. 3. A stereo drawing of the unit cell contents viewed along the *b* axis.

average of 4·4° from the expected value of 120°. These distortions are similar to those observed in 5-anilino-pentadienylidenanilinium bromide (Brandl, Springer, Narayanan, Preuss, Hoppe & Scheibe, 1974) and are caused by repulsions between hydrogen atoms in the chain [Table 3(*b*)].

The geometry of the portion of the molecule involving the piperidine ring is closely similar to that found in 1-[*p*-(1-oxyminoethyl)phenoxyacetyl]piperidine (Tranqui, Cromer & Boucherle, 1974). The short C(14)–N(16) distance, 1·349 (4) Å, and the small displacement of the N(16) atom, 0·095 Å, out of the plane defined by the atoms C(14), C(17) and C(21) indicate the partial double-bond character of this linkage. The piperidine ring adopts the chair conformation with N(16) and C(19) displaced by −0·644 and 0·611 Å respectively out of the plane defined by the atoms C(17), C(18), C(20) and C(21). The basal plane of the chair makes a dihedral angle of 66·1° with respect to the pentadiene chain.

Fig. 3 is a stereo view of the unit cell contents looking along the *b* axis. The molecules lie approximately in planes parallel to (20$\bar{3}$). There are no intermolecular separations significantly less than the sum of the respective van der Waals radii.

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The Crystal Structure of Tetraphenylarsonium Nitridotetrachlororuthenate(VI): a Square-Pyramidal Ruthenium Complex

BY FREDERICK L. PHILLIPS* AND ANDRZEJ C. SKAPSKI

Chemical Crystallography Laboratory, Imperial College, London SW7 2AY, England

(Ph$_4$As) [RuNCl$_4$] is tetragonal with $a = 12·607$ (3), $c = 7·842$ (2) Å, space group $P4/n$, $Z = 2$. The structure has been determined from diffractometer data, and least-squares refinement with 1188 independent reflexions has reached $R = 0·037$. In the square-pyramidal [RuNCl$_4$]$^-$ anion the Ru and N atoms lie on a fourfold axis, with Ru–N and Ru–Cl 1·570 and 2·310 Å respectively. Electronic repulsion by the nitrido ligand is responsible for the large N–Ru–Cl angles of 104·6°. The cation has $\bar{4}$ (S_4) crystallographic symmetry, with As–C 1·909 Å and two independent C–As–C angles of 104·9 and 111·8°.

Introduction

Complexes containing a terminal nitrido ligand have highly distorted coordinations. The reasons for this may be steric or electronic. We have recently determined the structure of (Ph$_4$As) [OsNCl$_4$] (Fletcher, Griffith, Pawson, Phillips & Skapski, 1973; Phillips & Skapski, 1975), and the geometry found for the anion indicates that in this complex the electronic repulsion by the strongly π-donating nitrido ligand is the predominant factor.

We now report details of the analogous Ru complex.

* Present address; Department of Chemistry, University of Ghana, Legon, Ghana.

Experimental

Tetraphenylarsonium nitridotetrachlororuthenate(VI) was obtained as puce prisms by crystallization from methyl cyanide (Griffith & Pawson, 1973). Preliminary photographs showed the crystal to be tetragonal, with systematic absences $hk0$: $h + k = 2n + 1$ which uniquely determine space group $P4/n$ (No. 85). The distribution of intensities showed the compound to be isostructural with (Ph$_4$As) [OsNCl$_4$].

Measurement of some high-angle α_1 and α_2 reflexions on a diffractometer gave $a = 12·607(3)$, $c = 7·842(2)$ Å, $U = 1246·4$ Å^3, $D_o = 1·70$ (by flotation), $D_c = 1·706$ g cm^{-3} for $Z = 2$ and a molecular formula C$_{24}$H$_{20}$AsCl$_4$NRu; M.W. 640·24, $F(000) = 632$.