chains parallel to the *a* axis, occurs between the amino group and the carbonyl oxygen, with N$\cdots$O and H$\cdots$O separations of 2·834 (2) and 1·97 (3) Å, and a subtended N—H$\cdots$O angle of 168 (2)°. These chains interact through a weaker hydrogen-bonding contact which involves the amino function and the N(2) ring atom [N(3)$\cdots$N(2) = 3·238 (2), H$\cdots$N(2) = 2·41 (3) Å, $\angle$N(3)—H$\cdots$N(2) = 149 (2)°].

We thank the Centro Interdipartimentale Grandi Strumenti of Modena University for X-ray data collection, and the Centro Interdipartimentale di Calcolo Automatico e Informatica Applicata for computer facilities.

References

ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, S1–S19.

FURBERG, S., GRØGAARD, J. & SMEDSRUD, B. (1979). *Acta Chem. Scand. Ser. B*, **33**, 715–724.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

PECORARI, P., RINALDI, M. & COSTI, M. P. (1989). *J. Heterocyl. Chem.* **26**, 1701–1705.

PECORARI, P., RINALDI, M., COSTI, M. P. & ANTOLINI, L. (1991). *J. Heterocycl. Chem.* In the press.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1986). *SHELXS86*. Program for crystal structure solution. Univ. of Göttingen, Germany.

TAYLOR, R. & KENNARD, O. (1982). *J. Mol. Struct.* **78**, 1–28.

Acta Cryst. (1991). C**47**, 2415–2417

Tris[(2-pyridinium)methyl]amine Perchlorate

BY DOYLE BRITTON, RICHARD E. NORMAN AND LAWRENCE QUE JR

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA

(*Received* 5 *February* 1991; *accepted* 29 *May* 1991)

Abstract. Nitrilotrismethylenetri-2-pyridinium perchlorate, $C_{18}H_{21}N_4^{3+}.3ClO_4^-$, M_r = 591·74, cubic, $P2_13$, a = 13·289 (3) Å, V = 2347 (2) Å^3, Z = 4, D_x = 1·675 (2) g cm^{-3}, λ(Mo Kα) = 0·71069 Å, μ = 4·60 cm^{-1}, F(000) = 1216, T = 189 (3) K, R = 0·056 for 1073 unique observed reflections with $I > \sigma(I)$. All four ions lie on threefold axes. The perchlorate ions are nearly regular tetrahedra. The bond lengths and angles in the ions are normal. As the name implies, the cation is protonated on the pyridine N atoms and not on the amine N atom. Each H atom attached to an N atom is part of a three-centered hydrogen bond in which the H-atom acceptors are O atoms on two different perchlorate ions.

Introduction. $[Fe_2TPA_2\{O_2P(OPh)_2\}](ClO_4)_3$, where TPA = tris(2-pyridylmethyl)amine and $O_2P(OPh)_2$ = diphenylphosphate, was synthesized by the reaction of $TPA.HClO_4$, $Fe(ClO_4)_3.10H_2O$, the diphenyl ester of phosphoric acid and triethylamine in methanol, yielding dark-green crystals (Norman, Yan, Que, Backes, Ling, Sanders-Loehr, Zhang, & O'Connor, 1990). Upon further standing a second pale-yellow crystalline product formed in low yield. These crystals were thought, at first, to be a different iron-containing complex and an X-ray diffraction study was begun. It quickly became clear that they did not contain iron but that they were probably a salt of the ligand. The cubic symmetry, which is relatively rare for crystals of large molecules, and the question of the location of the protons on the cation were the reasons for completing the structure determination. This determination, which also served as the chemical analysis, showed the compound to be the perchlorate salt of the triply protonated ligand.

Experimental. Crystals suitable for X-ray diffraction were found in the original sample. D_m was not measured. A light-yellow crystal, 0·2 × 0·2 × 0·6 mm, elongated along [111] was used for the data collection. Data were collected on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator. 25 reflections with $12 < \theta < 19°$ were used to determine the cell parameters. Systematic extinctions (h00, h odd) plus the Laue symmetry, $m3$, uniquely determined the space group. Data were collected, using ω scans, in the range $0 < \theta < 30°$ for most of one octant (h and k, 0 to 18; l, 0 to 11). The intensities of 2885 different reflections were measured. Three check reflections measured every 6000 s of exposure time showed no systematic change with time. After absorption corrections were made using *DIFABS* (Walker & Stuart, 1983; transmission factors 0·84–1·06), equivalent reflections were combined to give 1281 independent reflections (R_{int} = 0·052) of which the 1073 with $I > \sigma(I)$ were used in the calculations. The structure was solved by direct methods (*MITHRIL*; Gilmore, 1984) and refined with full-

0108-2701/91/112415-03$03.00

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}(Å^2)
Cl(1)	0·90502 (8)	0·90502 (8)	0·90502 (8)	2·1430 (3)
Cl(2)	0·58938 (8)	0·58938 (8)	0·58938 (8)	2·5133 (4)
Cl(3)	0·21428 (8)	0·21428 (8)	0·21428 (8)	2·2007 (4)
O(11)	0·8423 (3)	0·8423 (3)	0·8423 (3)	3·084 (1)
O(12)	0·8798 (3)	1·0089 (2)	0·8875 (3)	3·0 (1)
O(21)	0·6516 (3)	0·6516 (3)	0·6516 (3)	5·557 (2)
O(22)	0·6342 (3)	0·5811 (3)	0·4923 (3)	3·8 (2)
O(31)	0·1522 (2)	0·1522 (2)	0·1522 (2)	3·007 (1)
O(32)	0·1579 (3)	0·2498 (2)	0·3006 (2)	2·8 (1)
N(1)	0·4000 (3)	0·4000 (3)	0·4000 (3)	2·016 (1)
N(2)	0·2844 (3)	0·2295 (3)	0·4787 (3)	2·1 (1)
C(1)	0·3544 (3)	0·2799 (3)	0·5319 (3)	2·0 (2)
C(2)	0·4054 (4)	0·2282 (4)	0·6049 (3)	2·8 (2)
C(3)	0·3824 (4)	0·1268 (4)	0·6219 (4)	3·5 (2)
C(4)	0·3090 (4)	0·0797 (3)	0·5682 (4)	2·9 (2)
C(5)	0·2605 (3)	0·1328 (4)	0·4943 (4)	2·6 (2)
C(6)	0·3702 (3)	0·3886 (3)	0·5067 (3)	2·3 (2)
H(2N)	0·244 (4)	0·264 (4)	0·444 (4)	4 (1)

Table 2. *Bond lengths* (Å) *and angles* (°)

Cl(1)	O(12)	1·440 (3)	N(2)	C(5)	1·339 (6)
Cl(1)	O(11)	1·444 (6)	N(2)	C(1)	1·347 (5)
Cl(2)	O(22)	1·426 (4)	C(1)	C(2)	1·368 (6)
Cl(2)	O(21)	1·433 (7)	C(1)	C(6)	1·498 (6)
Cl(3)	O(31)	1·428 (6)	C(2)	C(3)	1·400 (7)
Cl(3)	O(32)	1·448 (3)	C(3)	C(4)	1·361 (7)
N(1)	C(6)	1·481 (5)	C(4)	C(5)	1·370 (7)
N(2)	H(2N)	0·84 (5)	H(2N)	O(32)	2·23 (5)

O(12)	Cl(1)	O(12)	109·9 (1)	C(5)	N(2)	C(1)	124·0 (4)
O(12)	Cl(1)	O(11)	109·0 (1)	N(2)	C(1)	C(2)	117·7 (4)
O(22)	Cl(2)	O(22)	109·9 (2)	N(2)	C(1)	C(6)	117·3 (4)
O(22)	Cl(2)	O(21)	109·0 (2)	C(2)	C(1)	C(6)	125·0 (4)
O(31)	Cl(3)	O(32)	110·3 (1)	C(1)	C(2)	C(3)	119·3 (5)
O(32)	Cl(3)	O(32)	108·6 (2)	C(4)	C(3)	C(2)	120·9 (5)
C(6)	N(1)	C(6)	109·1 (3)	C(3)	C(4)	C(5)	118·5 (4)
H(2N)	N(2)	C(5)	117 (4)	N(2)	C(5)	C(4)	119·6 (5)
H(2N)	N(2)	C(1)	117 (4)	N(1)	C(6)	C(1)	110·5 (4)
N(2)	H(2N)	O(32)	139 (5)				

matrix least-squares refinement on F's. All non-H atoms were given anisotropic thermal parameters, the H atom attached to N(2) was refined with an isotropic thermal parameter, and the remaining H atoms were included at idealized positions with isotropic B values 20% larger than the equivalent isotropic B of the attached C atom. Refinement converged with $R = 0{\cdot}056$, $wR = 0{\cdot}049$ and $S = 1{\cdot}25$ (refinement of the opposite enantiomer converged with $R = 0{\cdot}057$, $wR = 0{\cdot}050$ and $S = 1{\cdot}29$); $w = 1/\sigma^2(F)$ was calculated from $\sigma^2(I) = \sigma^2(I)_c + (0{\cdot}03I)^2$, where $\sigma(I)_c$ is the standard deviation in I based on counting statistics alone. In the final cycle of refinement $(\Delta/\sigma)_{max} = 0{\cdot}01$, $(\Delta\rho)_{max} = 0{\cdot}47$ and $(\Delta\rho)_{min} = -0{\cdot}34$ e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections for all atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The computer programs used were from *TEXSAN* (Molecular Structure Corporation, 1985).

Discussion. The final positional parameters are given in Table 1.* The thermal ellipsoids and the labeling of the atoms in the cation and one of the anions are shown in Fig. 1. Bond lengths and angles are given in Table 2; they are normal within experimental error. The ring is planar within experimental error. All the perchlorate ions have close to regular tetrahedral symmetry. The cation has only threefold symmetry. The conformation around the C(6)—N(1) bond is staggered, approximately [torsion angles: C(1)—C(6)—N(1)—C(6′), −75·9 (4)°; C(1)—C(6)—N(1)—C(6′), 165·0 (4)°], and the C(6)—N(1) bond is rotated out of the plane of the pyridinium ring [torsion

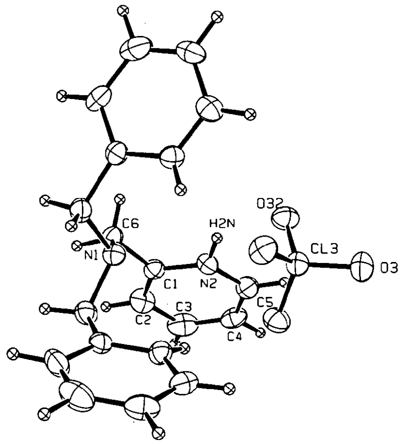

Fig. 1. The $N(CH_2C_5NH_5)_3^{3+}$ cation and the ClO_4^- anion, which is hydrogen bonded to three H atoms in the amine molecule. Thermal ellipsoids are drawn at the 50% probability level. H atoms are shown with arbitrary radius. Both ions lie on a threefold axis along the line connecting N(1) and O(31).

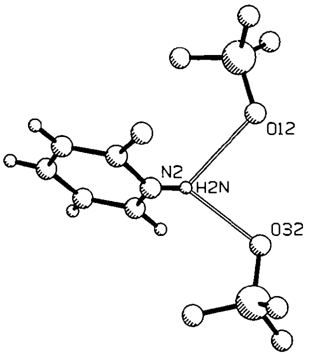

Fig. 2. The three-center hydrogen-bond arrangement. The H atom is 0·27 (5) Å out of the N(2)···O(12)···O(32) plane.

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and deviations from the mean plane of the pyridine ring have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54291 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

angles: N(1)—C(6)—C(1)—C(2), 121·2 (5)°; N(1)—C(6)—C(1)—N(2), −59·1 (5)°]. These rotations move the H(2N) atoms away from the N(1) atom so that the H(2N)···N(1) distance is 2·81 (5) Å; there is no indication of intramolecular hydrogen bonding in the cation. Our result, that the three pyridine N atoms are protonated and the aliphatic N atom is not, is in agreement with the conclusions reached by Anderegg, Hubmann, Podder & Wenk (1977) on the basis of pH measurements and confirmed by Anderegg, Popov & Pregosin (1986) by ^{15}N NMR studies.

The H(2N) atoms are involved in three-center hydrogen bonds with the O(12) and O(32) atoms (Fig. 2).* Distances are H(2N)···O(12), 2·42 (5); H(2N)···O(32), 2·23 (5); N(2)···O(12), 3·040 (5); N(2)···O(32), 2·916 (5) Å. The H atom is 0·27 (5) Å out of the N(2)···O(12)···O(32) plane. These distances fit the criteria for three-center hydrogen bonds given by Jeffrey (1987).

This work was supported in part by grant GM-33162 from the National Institutes of Health.

---

* We are indebted to a referee for pointing this out.

References

Anderegg, G., Hubmann, E., Podder, N. G. & Wenk, F. (1977). *Helv. Chim. Acta*, **60**, 123–140.

Anderegg, G., Popov, K. & Pregosin, P. S. (1986). *Helv. Chim. Acta*, **69**, 329–332.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

Jeffrey, G. A. (1987). In *Patterson and Pattersons*, edited by J. P. Glusker, B. K. Patterson & M. Rossi, pp. 193–213. Oxford Univ. Press.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.

Norman, R. E., Yan, S., Que, L. Jr, Backes, G., Ling, J., Sanders-Loehr, J., Zhang, J. H. & O'Connor, C. J. (1990). *J. Am. Chem. Soc.* **112**, 1554–1562.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1991). C**47**, 2417–2419

Structure and Photochemistry of a Cyclohexenone* and its Solid-State Photoproduct†

By Jianxin Chen, Christine Hwang, John R. Scheffer and James Trotter

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

(*Received* 14 *February* 1991; *accepted* 29 *May* 1991)

Abstract. $C_{18}H_{15}BrO$, $M_r = 327·23$, $T = 294$ K, Mo $K\alpha_1$, $\lambda = 0·70930$ Å. Cyclohexenone, monoclinic, $P2_1/c$, $a = 16·157$ (2), $b = 9·189$ (3), $c = 9·996$ (3) Å, $\beta = 95·80$ (2)°, $V = 1476$ (1) Å^3, $Z = 4$, $D_m = 1·46$, $D_x = 1·472$ g cm^{-3}, $F(000) = 664$, $\mu = 27·5$ cm^{-1}, $R = 0·051$ for 1807 reflections. Photoproduct, monoclinic, $I2/a$, $a = 17·607$ (4), $b = 8·213$ (2), $c = 19·976$ (5) Å, $\beta = 93·09$ (3)°, $V = 2884·5$ (12) Å^3, $Z = 8$, $D_x = 1·507$ g cm^{-3}, $F(000) = 1328$, $\mu = 28·1$ cm^{-1}, $R = 0·038$ for 1651 reflections. In the cyclohexenone molecule the six-membered cyclohexene ring has a C5-sofa conformation with the *p*-bromophenyl substituent in a pseudo-axial site; the structure exhibits disorder, with the enantiomers randomly distributed (75:25 occupancies) at one site. Formation of the photoproduct involves migration of the *p*-bromophenyl substituent from position 4 to 3, and 2—4 bonding (cyclohexenone numbering); the detailed molecular structure of the photoproduct can be derived with minimum atomic movement from that of the cyclohexenone reactant.

Introduction. Photolysis in solution of 4,4-diaryl substituted cyclohexenones (Fig. 1) gives photoproducts resulting from migration of one of the substituents and 2—4 bond formation (Zimmerman & Wilson, 1964; Zimmerman, Rieke & Scheffer, 1967; Schuster, 1980); for unsymmetrically substituted compounds there are two possible photoproducts (Fig. 1). The present work involves a study of the photolysis reaction in the solid state, and the crystal structures of the *p*-bromophenyl compound and of its major solid-state photoproduct have been determined to obtain quantitative information on the proposed reaction mechanism (Fig. 1).

Experimental. Crystals of the cyclohexenone were grown from diethyl ether/petroleum ether; the photoproduct sample was obtained by photolysis in

---

* 4-(4-Bromophenyl)-4-phenylcyclohex-2-en-1-one.

† *trans*-6-(4-Bromophenyl)-5-phenylbicyclo[3.1.0]hexan-2-one.

0108-2701/91/112417-03$03.00