HARKER, D. & KASPER, J. S. (1948). *Acta Cryst.* 1, 70.
KARLE, J. (1966). *Acta Cryst.* 21, 273.
KARLE, J. (1968). *Acta Cryst.* B24, 182.
KARLE, J. & HAUPTMAN, H. (1950). *Acta Cryst.* 3, 181.
KARLE, J. & HAUPTMAN, H. (1953). *Acta Cryst.* 6, 473.
KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* 9, 635.
KARLE, J. & KARLE, I. L. (1966a). *Acta Cryst.* 21, 849.
KARLE, I. L. & KARLE, J. (1966b). *Acta Cryst.* 21, 860.
LIPSCOMB, W. N., REEKE, G. N., HARTSUCK, J. A., QUI-OCHO, F. A. & BETHGE, P. H. (1969). *Proc. Roy. Soc.* B. In the press.

PERUTZ, M. F. & SCATTURIN, V. (1954). *Acta Cryst.* 7, 799.
REEKE, G. N., HARTSUCK, J. A., LUDWIG, M. L., QUIOCHO, F. A., STEITZ, T. A. & LIPSCOMB, W. N. (1967). *Proc. nat. Acad. Sci. Wash.* 58, 2220.
ROSSMANN, M. G., JEFFERY, B. A., MAIN, P. & WARREN, S. (1967). *Proc. nat. Acad. Sci. Wash.* 57, 515.
SAYRE, D. (1952). *Acta Cryst.* 5, 60.
STEITZ, T. A. (1968). *Acta Cryst.* B24, 504.
WEINZIERL, J. E., EISENBERG, D. & DICKERSON, R. E. (1969). *Acta Cryst.* B25, 380.
ZACHARIASEN, W. H. (1952). *Acta Cryst.* 5, 68.

The Molecular Structure of N-Phenyl-2,4,6-Trimethylpyridinium Perchlorate

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N-Phenyl-2,4,6-trimethylpyridinium perchlorate exhibits the nuclear magnetic resonance peak due to the α-methyl protons at higher field than the peak due to the γ-methyl protons, unlike 2,4,6-trimethyl derivatives of pyridine or N-alkylpyridinium salts. The compound crystallizes in space group $P2_1/a$ with unit-cell dimensions $a = 16\cdot619 \pm 0\cdot004$, $b = 12\cdot110 \pm 0\cdot007$, $c = 8\cdot340 \pm 0\cdot003$ Å, $\beta = 114\cdot44 \pm 0\cdot03°$. The structure has been refined to an R value of $0\cdot061$ using diffractometer data. The planes of the phenyl and pyridinium rings are rotated $83\cdot5°$ with respect to each other and the C–N bridge bond length after correction for thermal motion is $1\cdot470$ Å. These results indicate that the shielding of the α-methyl protons is due to the ring current induced in the N-phenyl ring and not to any resonance effect. 14% of the perchlorate ions have disordered oxygen positions and as a result all Cl–O bonds appear shorter than usual.

Introduction

The reaction of pyrylium salts (Balaban, Schroth & Fischer, 1968) with primary amines represents a convenient method for preparing pyridinium salts, especially with N-aryl groups, which cannot be obtained by direct quaternization (Brody & Ruby, 1960). Thus 2,4,6-trimethylpyrylium perchlorate and aniline afford in high yield N-phenyl-2,4,6-trimethylpyridinium perchlorate (I). Unlike 2,4,6-trimethyl derivatives of pyridine, N-alkylpyridinium, or pyrylium salts whose α-methyl groups give rise to n.m.r. peaks at lower fields than the γ-methyl group (Toma & Balaban, 1966; Balaban, Bedford & Katritzky, 1964), compound (I) exhibits the n.m.r. peak due to the six α-methyl protons at higher field than the peak due to the three γ-methyl protons. This supplementary shielding of the α-methyl groups in (I) could be due either to a marked perturbation of the π-electron density in the pyridinium ring, by interaction with the phenyl ring electron cloud, or to an effect of the ring current induced in the phenyl group (Pople, Schneider & Bernstein, 1959) which

CH₃ ... (I)
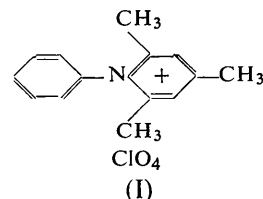
owing to steric hindrance is presumably tilted out of the plane of the pyridinium ring.

In order to test these alternatives, an X-ray diffraction analysis of N-phenyl-2,4,6-trimethylpyridinium perchlorate was undertaken. As far as we are aware no other structure determination of an N-alkyl or N-aryl pyridinium salt has been published.

Experimental

N-Phenyl-2,4,6-trimethylpyridinium perchlorate was prepared (Toma & Balaban, 1966) from 2,4,6-trimethylpyrylium perchlorate and aniline in ethanol. Large yellow prismatic single crystals elongated along b were grown from ethanol, m.p. 128–129°C. For intensity measurements an approximately cubic crystal

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of dimension 0·35 mm was cut from a larger specimen.

Unit-cell constants were determined by least-squares minimization of the difference between calculated and observed θ values for 13 reflections measured at both $+2\theta$ and -2θ with Mo $K\alpha$ radiation using a four-circle diffractometer. The crystal density was measured by the flotation method in a mixture of chloroform and cyclohexanone. The crystallographic data are summarized below:

N-Phenyl-2,4,6-trimethylpyridinium perchlorate, $C_{14}H_{16}NClO_4$. M.W. 297·75. Space group $P2_1/a$ from systematic absences: $h0l$ when h odd, $0k0$ when k odd.

$$a = 16\cdot619 \pm 0\cdot004 \text{ Å} \qquad Z = 4$$
$$b = 12\cdot110 \pm 0\cdot007 \qquad D_m = 1\cdot32 \text{ g.cm}^{-3}$$
$$c = 8\cdot340 \pm 0\cdot003 \qquad D_x = 1\cdot30 \text{ g.cm}^{-3}$$
$$\beta = 114\cdot44 \pm 0\cdot03° \qquad F(000) = 624 .$$

An alternative space group, $P2_1/n$ may also be chosen with $a = 15\cdot20$, $b = 12\cdot11$, $c = 8\cdot34$ Å, $\beta = 95\cdot5°$. For the convenience of working with an a-glide rather than an n-glide, the former space group was chosen even though β is more obtuse.

Preliminary Weissenberg photographs indicated that the intensities fall off rather sharply beyond $\sin\theta/\lambda = 0\cdot5$. Intensities were therefore measured only

Table 1. *Fractional coordinates and anisotropic temperature parameters* (Å^2) *for the non-hydrogen atoms*

Estimated standard deviations are given in parentheses.
The anisotropic thermal parameters are in the form $\exp[-0\cdot25(h^2B_{11}a^{*2}\ldots 2klB_{23}b^*c^*)]$.

	x	y	z	B_{11}	B_{22}	B_{23}	B_{12}	B_{13}	B_{23}
Cl(1)	0·2047 (1)	0·0470 (1)	0·2701 (1)	5·27	5·42	5·11	−0·26	1·38	0·24
O(2)	0·1950 (2)	0·1530 (3)	0·3284 (5)	10·72	10·26	11·36	−0·59	3·48	−4·95
O(3)	0·2438 (2)	−0·0357 (3)	0·3832 (5)	13·11	14·82	10·72	0·73	0·89	6·33
O(4)	0·1211 (2)	0·0136 (3)	0·1425 (3)	7·97	6·46	9·58	−0·42	1·15	−0·30
O(5)	0·2550 (3)	0·0668 (3)	0·1756 (5)	11·67	12·30	16·28	2·09	8·99	3·43
O(6′)	0·1855 (15)	0·0481 (32)	0·4211 (22)	12·09	23·13	6·05	9·99	5·69	4·95
O(7′)	0·2891 (18)	0·0010 (30)	0·3231 (48)	4·80	14·29	29·14	5·21	2·38	−7·44
O(8′)	0·2035 (35)	0·1553 (36)	0·2066 (70)	45·74	18·23	41·37	−8·60	10·82	−15·83
O(9′)	0·1420 (22)	−0·0181 (28)	0·1354 (45)	23·68	21·21	10·69	16·54	−3·43	−7·49
N(6)	0·1907 (2)	0·3183 (3)	−0·0270 (5)	5·08	5·69	4·88	0·37	2·31	0·80
C(7)	0·2499 (3)	0·2704 (4)	−0·0792 (6)	6·18	6·75	6·29	0·52	3·27	0·63
C(8)	0·3379 (3)	0·2798 (5)	0·0267 (8)	6·15	9·61	7·78	0·91	3·78	1·70
C(9)	0·3678 (3)	0·3371 (5)	0·1817 (7)	5·41	9·83	6·57	−0·55	2·25	2·66
C(10)	0·3057 (4)	0·3818 (4)	0·2333 (6)	7·22	8·23	5·55	−1·21	2·05	0·12
C(11)	0·2164 (3)	0·3722 (4)	0·1302 (6)	6·12	7·02	5·12	−0·32	2·12	0·09
C(12)	0·1504 (3)	0·4178 (5)	0·1871 (7)	6·97	12·93	6·96	1·04	2·30	−3·05
C(13)	0·4655 (3)	0·3490 (6)	0·2927 (8)	6·25	19·26	11·71	−3·25	2·22	3·47
C(14)	0·2165 (3)	0·2106 (5)	−0·2514 (7)	8·27	12·36	8·64	1·24	5·08	−2·03
C(15)	0·0968 (3)	0·3134 (4)	−0·1439 (5)	5·22	6·08	4·37	0·02	2·26	0·32
C(16)	0·0479 (3)	0·2226 (4)	−0·1429 (6)	6·68	5·96	5·89	−0·21	2·80	0·38
C(17)	−0·0409 (3)	0·2198 (4)	−0·2578 (7)	6·64	8·56	6·73	−1·82	3·35	−0·35
C(18)	−0·0791 (3)	0·3070 (5)	−0·3687 (6)	5·57	10·24	6·13	−0·59	2·54	0·27
C(19)	−0·0291 (3)	0·3985 (4)	−0·3622 (6)	6·00	9·30	6·55	1·34	2·48	2·15
C(20)	0·0595 (3)	0·4017 (4)	−0·2504 (6)	6·08	7·09	6·33	0·02	2·69	1·57

Table 2. *Fractional coordinates, isotropic temperature parameters* (Å^2) *and bond distances* (Å) *for the hydrogen atoms*

Estimated standard deviations are given in parentheses.

	x	y	z	B	C–H distance
H(8)	0·379 (2)	0·241 (3)	−0·012 (4)	10·1	0·98 (4)
H(10)	0·316 (2)	0·418 (2)	0·333 (5)	6·8	0·90 (4)
H(16)	0·078 (2)	0·157 (3)	−0·087 (4)	8·1	0·95 (3)
H(17)	−0·075 (2)	0·159 (3)	−0·260 (4)	9·2	0·93 (4)
H(18)	−0·154 (2)	0·296 (2)	−0·448 (3)	6·1	1·15 (3)
H(19)	−0·063 (2)	0·456 (2)	−0·439 (5)	7·4	0·95 (3)
H(20)	0·092 (2)	0·459 (2)	−0·247 (4)	4·7	0·87 (4)
H(12·1)	0·105 (3)	0·385 (3)	0·157 (5)	7·0	0·77 (4)
H(12·2)	0·105 (3)	0·469 (3)	0·107 (6)	8·7	0·99 (4)
H(12·3)	0·173 (3)	0·440 (3)	0·316 (7)	10·1	1·04 (6)
H(13·1)	0·488 (3)	0·266 (4)	0·362 (7)	15·9	1·14 (5)
H(13·2)	0·471 (3)	0·405 (4)	0·363 (7)	14·1	0·86 (5)
H(13·3)	0·489 (3)	0·384 (3)	0·263 (7)	8·6	0·70 (6)
H(14·1)	0·176 (2)	0·259 (3)	−0·340 (5)	9·3	0·96 (3)
H(14·2)	0·261 (3)	0·201 (3)	−0·280 (6)	12·7	0·88 (6)
H(14·3)	0·174 (2)	0·154 (3)	−0·200 (5)	13·5	1·18 (5)

Table 3. *Comparison of observed and calculated structure factors for N-phenyl-2,4,6-trimethylpyridinium perchlorate*

The data are listed in groups of constant k and l. The three columns within each group are h, $10F_o$ and $10F_c$. Reflections whose measured intensities are less than 2σ are indicated with an asterisk and were treated as unobserved reflections.

to $2\theta = 45°$, corresponding to an interplanar spacing of 0·9 Å. The $\theta - 2\theta$ scan technique with Nb-filtered Mo $K\alpha$ ($\lambda = 0·71069$ Å) radiation was employed. A total of 1985 independent reflections were measured. Of these, 1549 had intensity greater than $2\sigma_c$, where $\sigma_c = (N_{B1} + N_{Pk} + N_{B2})^{1/2}$, N_{B1} and N_{B2} are the background counts on each side of the peak, and N_{Pk} is the scan count. Frequently measured standard reflections suggested the diffractometer reliability to be $\pm 1\%$, hence the estimated error in the intensity of each reflection is $\sigma_I = [\sigma_c^2 + (0·01\sigma_c^2)^2]^{1/2}$. Structure factors were obtained from the intensities in the usual fashion; weights were taken as $\sqrt{\omega} = 1/\sigma_F$. No absorption corrections were applied. The linear absorption coefficient for Mo $K\alpha = 4·7$ cm^{-1}.

Solution of the structure

A three-dimensional sharpened Patterson function was calculated from which the chlorine atom position was located. Structure factors phased on the chlorine atom only gave an R of 0·54 and a three-dimensional Fourier synthesis was computed. Careful study of this map yielded the positions of all other non-hydrogen atoms and structure factors based on these positions had an R of 0·37. The scattering factors used were the following: O, N and C, Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955); H, Stewart, Davidson & Simpson (1965); Cl, Viervoll & Øgrim (1949).

Refinement proceeded *via* full-matrix least-squares; two cycles using isotropic temperature factors reduced R to 0·16 and two more cycles with anisotropic temperature factors reduced R to 0·095. A three-dimensional ΔF map was calculated from which the 16 hydrogen

positions were obtained. Two cycles of least-squares refinement of all the atoms using isotropic temperature factors for the hydrogen atoms reduced R to 0·072.

At this point another three-dimensional ΔF map was calculated. This map confirmed the correctness of the hydrogen atom positions but showed residual electron density near the oxygen positions of the perchlorate ion. Four peaks arranged tetrahedrally about the chlorine atom position stood out higher than the background with the highest peak approximately 2 electrons and the other three somewhat less. Accordingly, these sites were adopted as alternative positions for the oxygen atoms of the perchlorate ion, keeping the chlorine atom position unchanged. A least-squares refinement of the occupancies of the resultant eight oxygen positions, assigning to each oxygen atom a B of 8·0, revealed that the four major oxygen sites have occupancies of 0·86 whereas the four minor sites range from 0·10 to 0·30, averaging 0·15. Hence, the oxygen positions in the major ClO_4^- orientation were assigned occupancies of 0·86 and those in the minor orientation, 0·14.

Four cycles of least-squares refinement of the coordinates and anisotropic thermal parameters of the chlorine atom and eight oxygen atoms reduced R to 0·058. However, a bond length calculation showed the Cl–O distances in the minor orientation position of the perchlorate ion to be chemically unreasonable (1·1 – 1·2 Å) with only the oxygen atom positioned on the highest peak of the ΔF map, O(6'), having an acceptable Cl–O distance (1·42 Å). It was decided to accept this latter oxygen atom position and to fix the other three minor oxygen sites so as to most closely fit the peaks in the ΔF map and yet maintain chemically reasonable Cl–O distances. Having chosen suitable

Table 4. *Bond angles and estimated standard deviations*

	Angle	e.s.d.		Angle	e.s.d.
O(2)–Cl(1)–O(3)	121·9	0·2	C(10)–C(9)—C(13)	121·7	0·5
O(2)–Cl(1)–O(4)	107·7	0·2	C(9)—C(10)–C(11)	121·5	0·5
O(2)–Cl(1)–O(5)	102·8	0·2	C(9)—C(10)–H(10)	126·6	1·4
O(3)–Cl(1)–O(4)	110·7	0·3	C(11)–C(10)–H(10)	111·9	1·5
O(3)–Cl(1)–O(5)	107·4	0·2	N(6)—C(11)–C(10)	117·9	0·5
O(4)–Cl(1)–O(5)	104·9	0·2	N(6)—C(11)–C(12)	120·7	0·4
			C(10)–C(11)–C(12)	121·4	0·5
O(6')–Cl(1)–O(7')	106·7	2·1	N(6)—C(15)–C(16)	120·1	0·4
O(6')–Cl(1)–O(8')	110·5	2·0	N(6)—C(15)–C(20)	118·4	0·4
O(6')–Cl(1)–O(9')	110·3	2·7	C(16)–C(15)–C(20)	121·5	0·4
O(7')–Cl(1)–O(8')	110·2	3·1	C(15)–C(16)–C(17)	118·7	0·4
O(7')–Cl(1)–O(9')	110·0	3·1	C(15)–C(16)–H(16)	118·9	1·5
O(8')–Cl(1)–O(9')	109·2	2·3	C(17)–C(16)–H(16)	120·5	1·3
			C(16)–C(17)–C(18)	120·6	0·5
C(7)—N(6)–C(11)	122·1	0·4	C(16)–C(17)–H(17)	120·2	1·3
C(7)—N(6)–C(15)	119·0	0·4	C(18)–C(17)–H(17)	119·2	1·3
C(11)–N(6)–C(15)	118·9	0·4	C(17)–C(18)–C(19)	119·3	0·4
N(6)–C(7)–C(8)	118·8	0·5	C(17)–C(18)–H(18)	112·7	1·1
N(6)–C(7)–C(14)	119·0	0·4	C(19)–C(18)–H(18)	127·7	0·9
C(8)–C(7)–C(14)	122·2	0·6	C(18)–C(19)–C(20)	120·6	0·5
C(7)–C(8)–C(9)	121·8	0·6	C(18)–C(19)–H(19)	111·9	1·4
C(7)–C(8)–H(8)	116·6	1·3	C(20)–C(19)–H(19)	127·4	1·4
C(9)–C(8)–H(8)	121·6	1·3	C(15)–C(20)–C(19)	119·3	0·5
C(8)–C(9)–C(10)	117·9	0·5	C(15)–C(20)–H(20)	119·4	1·2
C(8)—C(9)–C(13)	120·5	0·6	C(19)–C(20)–H(20)	121·3	1·2

coordinates for the oxygen atoms, three cycles of least-squares refinement were run on the chlorine and eight oxygen atom parameters keeping the position of O(6′)–O(9′) fixed, followed by one cycle in which all parameters were varied. The final R index is 0·061.

Programs used in the structure determination and refinement were from the X-ray 63 system (Stewart, 1964).

Results

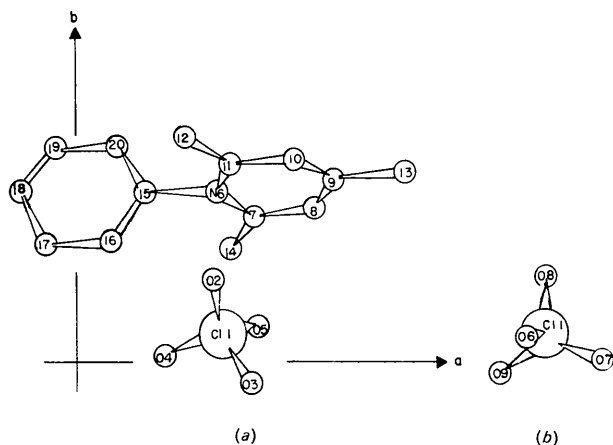Fractional coordinates and temperature parameters for the non-hydrogen atoms and for the hydrogen atoms

Fig. 1. (a) Projection of the structure of N-phenyl-2,4,6-tri-methylpyridinium perchlorate on (001). The perchlorate ion is in its preferred orientation. (b) Alternate positions of the oxygen atoms in the disordered perchlorate.

are given in Tables 1 and 2 respectively. Table 2 also lists the carbon–hydrogen distances. Observed and calculated structure factors are listed in Table 3. The molecule is shown in Fig. 1 and the non-hydrogen atom bond-lengths in Fig. 2. Table 4 lists the bond angles. Least-squares planes were calculated through the atoms of the 2,4,6-trimethylpyridinium and phenyl rings and the deviations of the atoms from these planes are listed in Table 5. The angle between the two planes is 83·5°.

Table 5. *Deviations of atoms from least-squares planes*

	Plane I		Plane II
	Δ		Δ
N(6)	−0·034 Å	C(15)	−0·009 Å
C(7)	0·011	C(16)	0·002
C(8)	0·029	C(17)	0·012
C(9)	−0·006	C(18)	−0·019
C(10)	−0·001	C(19)	0·012
C(11)	−0·006	C(20)	0·002
C(12)	0·020	*N(6)	−0·033
C(13)	−0·010	†σ(II)	0·015
C(14)	−0·003		
*C(15)	−0·138		
†σ(I)	0·023		

* These atoms were not used in calculating the plane.
† The standard deviations from planes I and II of atoms defining these planes are σ(I) and σ(II) respectively.

Discussion

Molecular structure

The C–N bridge bond-length is 1·470 ± 0·005 Å and the angle between the phenyl and pyridinium rings is 83·5°, indicating no interaction between the π electron
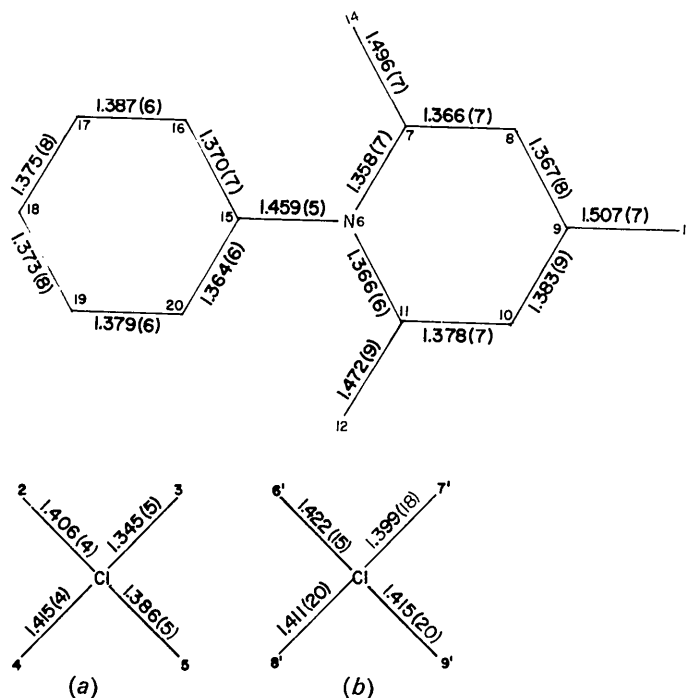

Fig. 2. Bond distances with estimated standard deviations in parentheses.

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clouds of the two rings. This conforms with the results found for biphenyl and biphenyl derivatives (Fowweather, 1952; Hargreaves & Rizvi, 1962; Young, Tollin & Sutherland, 1968).

As the nitrogen atom has only one *p* electron and that involved in the pyridinium π electron cloud, and the large angle between the two rings essentially precludes resonance over the system, the C–N bridge bond has no multiple bond character and is a single $C(sp^2)$–$N(sp^2)$ sigma bond. Hence, we suggest $1\cdot470 \pm 0\cdot005$ Å to be an acceptable value for the σ bond between trigonal carbon and trigonal nitrogen atoms (Camerman, 1969). Bonds between trigonal carbon and trigonal nitrogen significantly shorter than $1\cdot470$ Å exhibit some double bond character.

The lack of interaction between the phenyl and pyridinium rings clearly indicates that the shielding of the α-methyl groups in the n.m.r. spectrum of *N*-phenyl-2,4,6-trimethylpyridinium perchlorate is not due to perturbation of the π-electron density in the pyridinium ring by the phenyl group, but rather originates in the ring current induced in the phenyl group. As seen in Fig. 1, the two α-methyl groups lie on either side of the plane of the phenyl ring. It would be interesting to see in an *N*-phenylpyridinium salt where non-coplanarity is not compulsory on steric grounds, whether or not the two rings are coplanar, in order to compare this type of compound with biphenyl.

With suitably substituted pyridinium and phenyl rings, atropisomerism, caused by hindered rotation about the *N*-phenyl bond, should be possible in *N*-arylpyridinium salts. The present results also suggest that purely inductive effects of *m*- or *p*-substituents on the phenyl ring on chemical shifts of the γ-methyl in *N*-aryl-2,4,6-trimethylpyridinium salts can be studied and compared; conjugative and/or hyperconjugative effects of substituents should be destroyed by the mutually perpendicular orientation of the two rings.

Fig. 3 illustrates the relative magnitudes and shapes of the thermal ellipsoids of the carbon and nitrogen atoms. Analysis of the individual atomic thermal ellipsoids in terms of rigid-body tensors was performed using the method of Schomaker & Trueblood (1968). Calculations were carried out for the molecule as a whole and for two connected rigid bodies: N(6)–C(14) and N(6)+C(15)–C(20). The differences between the $U(I,J)$ derived from the input $B(I,J)$ and those calculated from the rigid-body parameters indicated that the latter model was more nearly correct. Root mean square $\Delta U(I,J)$'s for the two rigid bodies, N(6)–C(14) and N(6)+C(15)–C(20), are $0\cdot0045$ and $0\cdot0024$ Å respectively. Table 6 lists the r.m.s. amplitudes of libration, translation and screw motion along the principal axes of the libration, the reduced translation and reduced screw motion tensors and the direction cosines of the respective axes referred to the orthogonalized axes a, b and c^*.

Rotational corrections were applied to the bond lengths for the *N*-phenyl-2,4,6-trimethylpyridinium ion and the corrected distances are shown in Fig. 4.

Bond lengths for pyridine have previously been reported from microwave (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958) and electron-diffraction (Schomaker & Pauling, 1939) experiments and for pyridine hydrochloride from X-ray diffraction (Rérat, 1962). A comparison between present results and the previous values is shown in Table 7.

Perchlorate ion

Approximately 80–90% of the perchlorate ions are ordered but the others have their oxygen atoms occupying disordered positions. The minor oxygen sites are not of equal occupancy, as evidenced from both the ΔF map and the occupancy parameters from the least-squares refinement, but are the four statistically-heaviest occupied positions in a continuum of randomly oriented perchlorate ion tetrahedra. The chlorine atom apparently exhibits no site disorder. However, small deviations in the chlorine position not readily detectable in the ΔF map may be the major
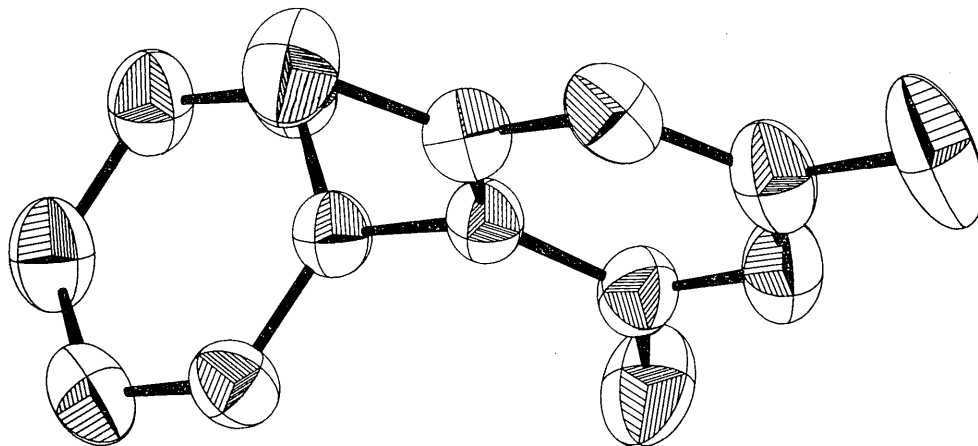

Fig. 3. Thermal ellipsoids for the *N*-phenyl-2,4,6-trimethylpyridinium ion.

factor contributing to the somewhat unsatisfactory resolution of the perchlorate ion behavior.

There are disturbing aspects of the perchlorate ion parameters, e.g. the O(2)–Cl–O(3) angle is too large, the Cl–O(3) distance too short, and there are distances of only 2·7 Å between O(8′)–N(6) and O(8′)–C(11). Nevertheless the very evident improvement in the ΔF map upon introduction of the minor oxygen sites and the decrease in R from 0·072 to 0·061 are strong evidence that the disordered perchlorate is a more nearly appropriate description of the ion than is the ordered one. The phenomenon of oxygen atom disorder in perchlorate ions has been observed in other structures (Sundaralingam & Jensen, 1966; Coulter, Gantzel & McCullough, 1963; McCullough, 1964), and we suggest that final ΔF maps should be calculated for all crystals containing perchlorate ions even when the R index is as low as 0·07.

The Cl–O bond lengths are considerably shorter than the accepted value of 1·46 Å (Cruickshank, 1961), primarily due to the disorder and high thermal motion of the oxygen atoms. Because these two phenomena are intimately linked, the temperature factors of the oxygen atoms are not accurate and no librational corrections to the Cl–O bonds have been calculated.

Note added in proof:- The structure of 1,1′ethylene -2,2′-bipyridylium dibromide has been recently reported (Derry & Hamor, 1969). In this structure two pyridylium nuclei are rotated only 19·7° from coplanarity and there is no evidence of resonance interaction. The lengths and central C—N—C angle are similar to those found for the pyridinium ring in this paper.

Intermolecular distances

All intermolecular contacts are longer than the van der Waals distances between atoms, assuming van der Waals radii of 1·80, 1·60, 1·50 and 1·40 Å for Cl, C, N, and O atoms respectively (Pauling, 1960). There are no hydrogen bonds and the crystals are soft and may be easily cut in any direction.

References

BAK, B., HANSEN-NYGAARD, L. & RASTRUP-ANDERSEN, J. (1958). *J. Mol. Spectr.* **2**, 361.
BALABAN, A. T., BEDFORD, G. R. & KATRITZKY, A. R. (1964). *J. Chem. Soc.* p. 1646.
BALABAN, A. T., SCHROTH, W. & FISCHER, G. (1968). In *Advances in Heterocyclic Chemistry*. Vol. 10. Edited by A. R. KATRITZKY. New York: Academic Press.
BERGHUIS, J., HAANAPPELL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. A. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
BRODY, F. & RUBY, P. R. (1960). In *Pyridine and its Derivatives*, Part I, p. 210. Edited by KLINGSBERG. New York: Interscience.
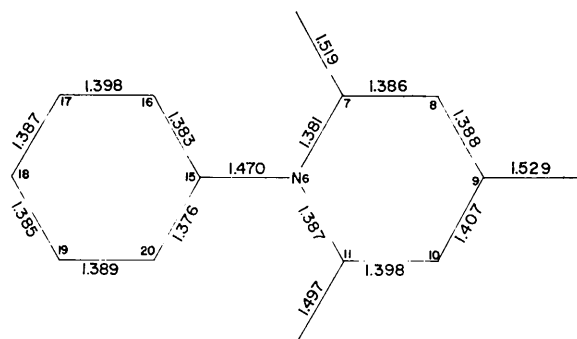

Fig.4. Thermally corrected bond lengths in the N-phenyl-2,4,6-trimethylpyridinium ion.

Table 6. *Principal-axis r.m.s. amplitudes of libration* **L** *and translation* **T** *and the cross-tensor* **S**, *and direction cosines referred to the orthogonalized axes a, b and c**

Rigid body		Atoms N(6)–C(14)				Atoms N(6)+C(15)–C(20)		
	7·92°	−0·635	−0·113	−0·765	6·58°	0·702	0·019	0·712
L and direction cosines	6·44	−0·768	−0·016	0·640	4·13	0·712	−0·066	−0·699
	3·69	−0·085	0·993	−0·072	2·60	0·034	0·998	−0·060
	0·265 Å	0·150	−0·952	−0·269	0·264 Å	−0·132	−0·936	−0·326
T and direction cosines	0·232	−0·865	−0·006	−0·502	0·238	−0·762	0·305	−0·571
	0·199	0·479	0·308	−0·822	0·206	0·634	0·173	−0·754
	0·007	−0·547	−0·221	0·807	0·002	0·506	0·552	0·663
S and direction cosines	0·000	0·834	−0·227	0·503	0·000	−0·235	−0·652	0·721
	−0·007	0·072	0·949	0·309	−0·002	0·830	−0·521	−0·200

Table 7. *Bond distances in the pyridine nucleus*

	N(6)–C(7)	C(7)–C(8)	C(8)–C(9)
Electron diffraction (pyridine)	1·37	1·39	1·39
Microwave (pyridine)	1·3402	1·3945	1·3944
X-ray diffraction (pyridine HCl)	1·32	1·42	1·40
*X-ray diffraction (present results)	1·384	1·392	1·397

* Chemically equivalent bonds have been averaged.

CAMERMAN, A. (1969). To be published.
COULTER, C. L., GANTZEL, P. K. & McCULLOUGH, J. D. (1963). *Acta Cryst.* **16**, 676.
CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* p. 5486.
DERRY, J. E. & HAMOR, T. A. (1969). *Nature, Lond.* **181**, 446.
FOWWEATHER, F. (1952). *Acta Cryst.* **5**, 820.
HARGREAVES, A. & RIZVI, S. H. (1962). *Acta Cryst.* **15**, 365.
McCULLOUGH, J. D. (1964). *Acta Cryst.* **17**, 1067.
PAULING, L. (1960). In *The Nature of the Chemical Bond*, p. 260. Ithaca: Cornell Univ. Press.
POPLE, J. A., SCHNEIDER, W. G. & BERNSTEIN, H. J. (1959). In *High Resolution Nuclear Magnetic Resonance*, p. 180. New York: McGraw-Hill.
RÉRAT, C. (1962). *Acta Cryst.* **15**, 427.

SCHOMAKER, V. & PAULING, L. (1939). *J. Amer. Chem. Soc.* **61**, 1769.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63.
STEWART, J. M. (1964). *Crystal Structure Calculations System.* Computer Science Center, Univ. of Maryland.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
SUNDARALINGAM, M. & JENSEN, L. H. (1966). *J. Amer. Chem. Soc.* **88**, 198.
TOMA, C. & BALABAN, A. T. (1966). *Tetrahedron*, Supplement 7, 9.
VIERVOLL, H. & ØGRIM, O. (1949). *Acta Cryst.* **2**, 277.
YOUNG, D. W., TOLLIN, P. & SUTHERLAND, H. H. (1968). *Acta Cryst.* **B24**, 161.

The Crystal and Molecular Structure of Siccanin *p*-Bromobenzenesulphonate

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The crystal structure of siccanin *p*-bromobenzenesulphonate, $C_{28}H_{33}O_5SBr$, has been determined in order to elucidate the molecular structure and absolute configuration of siccanin, $C_{22}H_{30}O_3$, an antibiotic isolated from the cultured broth of *Helminthosporium siccans* Drechsler. The unit cell is orthorhombic with dimensions, $a = 11 \cdot 06$, $b = 22 \cdot 87$, $c = 10 \cdot 34$ Å, containing four molecules. The space group is $P2_12_12_1$. The structure was solved by the heavy atom method and refined by the method of block-matrix least-squares for 1537 observed reflexions including anisotropic thermal parameters. The final *R* value was 0·12. It was revealed that siccanin is a triprenylphenol compound involving a bicyclic sesquiterpene moiety and a phenolic ring. The former consists of a *cis*-fused decalin system, which is the first example found in natural products having a drimane carbon skeleton.

Introduction

Ishibashi (1962) isolated a phenolic antibiotic, siccanin, from cultured broth of *Helminthosporium siccans* Drechsler. It was reported that this substance exhibits inhibitory activities against various fungi, especially strongly against *Trichophyton interdigitale* and *T. asteroids* (Ishibashi, 1962). In the present study, the molecular structure of siccanin is determined by an X-ray crystal structure analysis of siccanin *p*-bromobenzenesulphonate, a heavy atom derivative of siccanin. A preliminary short note on this work has already been published (Hirai, Nozoe, Tsuda & Iitaka, 1967).

Experimental

Direct bromination of siccanin was first attempted but it failed in obtaining a crystalline derivative suitable for X-ray work. The *p*-bromobenzenesulphonyl ester of siccanin was then prepared by the treatment of siccanin with *p*-bromobenzenesulphonyl chloride in pyridine. The crystals were grown from a mixture of methanol and n-hexane. These crystals are orthorhombic colourless prisms elongated along the *c* axis. The lattice constants were determined from *a* and *b* axis equatorial precession photographs taken with Cu *Kα* radiation. The density was measured by flotation in aqueous solutions of potassium iodide.

Crystal data

Siccanin *p*-bromobenzenesulphonate, $C_{28}H_{33}O_5SBr$, M.W. 561·5, m.p. 156°C .
Orthorhombic,
$a = 11 \cdot 06 \pm 0 \cdot 04$, $b = 22 \cdot 87 \pm 0 \cdot 03$, $c = 10 \cdot 34 \pm 0 \cdot 03$ Å;
$U = 2615 \cdot 4$ Å³.
$D_m = 1 \cdot 42$ g.cm⁻³, $D_x = 1 \cdot 42$ g.cm⁻³.
$F(000) = 1168$, $Z = 4$.
μ(Cu *Kα*) = 35·4 cm⁻¹.
Absent spectra, (*h*00) when *h* is odd, (0*k*0) when *k* is odd, (00*l*) when *l* is odd.
Space group $P2_12_12_1$.

Three-dimensional intensity data were recorded on multiple-film equi-inclination Weissenberg photographs