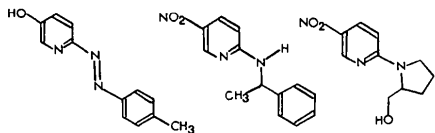


also be obtained from the intermolecular hydrogen-bonding arrangement (Fig. 2) where the phenolic O(1) of  $(x, y, z)$  is situated 2.693 Å from the heterocyclic N(3) of  $(\frac{1}{2} + x, \frac{1}{2} - y, -z)$ . Such a hydrogen-bonding scheme is only consistent with the  $-O-H \cdots N$  grouping, that is with the hydroxyazo tautomer.

An additional point of interest is the non-centrosymmetric space group of the title compound. Currently there is much interest in obtaining non-centrosymmetric molecular crystals since these may show appreciable second harmonic generation (SHG) or frequency doubling effects. A trivial means of ensuring adoption of such a space group is to use resolved materials but these are often difficult to obtain or very expensive. Much effort has been focused therefore on compounds which, though showing no optical activity in solution, resolve spontaneously on crystallization. The title compound belongs to this category.

In general, not much is known about molecular features which favour such spontaneous resolution. In this context, it is curious to note a certain similarity in the molecular framework of the title compound and the two others shown below:



These two other compounds are among those which show some of the largest SHG effects known today (Twieg & Jain, 1983).

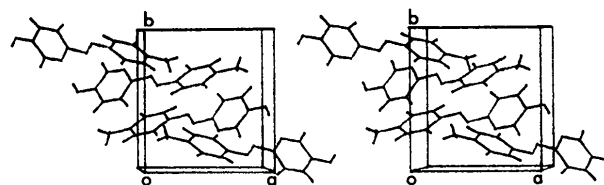


Fig. 2. Stereoscopic view of the crystal structure down the  $c$  axis.

We thank the UGC, New Delhi, for financial assistance and Dr W. Jones, Department of Physical Chemistry, University of Cambridge, for the use of the diffractometer for data collection.

#### References

- DESIRAJU, G. R. (1983). *J. Chem. Soc. Perkin Trans. 2*, pp. 1025–1030.
- GUGGENBERGER, L. J. & TEUFER, G. (1975). *Acta Cryst.* **B31**, 785–790.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99–102. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- KURAHASHI, M. (1976). *Bull. Chem. Soc. Jpn.*, **49**, 2927–2933.
- MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J.-P. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MORGAN, K. J. (1961). *J. Chem. Soc.* pp. 2151–2159.
- PENDERGRASS, D. B. JR, CURTIN, D. Y. & PAUL, I. C. (1972). *J. Am. Chem. Soc.* **97**, 8730–8737.
- SAEVA, F. D. (1971). *J. Org. Chem.* **36**, 3842–3843.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- TWIEG, R. & JAIN, K. (1983). *ACS Symp. Ser.* No. 233.
- ZOLLINGER, H. (1961). *Azo and Diazo Chemistry*. New York: Interscience.

*Acta Cryst.* (1986). **C42**, 1248–1251

### Absolute Conformation of 3-(*N*-Methyl-*N*-benzyl)carbamoil-1,2,4-trimethylpyridinium Iodide (I) and Absolute Configuration of 3-[*N*-Methyl-*N*-(*R*)- $\alpha$ -methylbenzyl]carbamoil-1,2,4-trimethylpyridinium Iodide (II)

BY J. A. KANTERS AND F. H. VAN DER STEEN

*Laboratorium voor Kristal- en Structuurchemie, Rijksuniversiteit Utrecht, Transitorium 3, Padualaan 8, 3584 CH Utrecht, The Netherlands*

AND L. A. M. BASTIAANSEN AND J. A. C. DE GRAAF

*Laboratorium voor Organische Chemie, Technische Hogeschool Eindhoven, Eindhoven, The Netherlands*

(Received 28 November 1985; accepted 4 March 1986)

**Abstract.** (I):  $C_{17}H_{21}N_2O^+ \cdot I^-$ ,  $M_r = 396.27$ , orthorhombic,  $P2_12_12_1$ ,  $a = 7.183$  (3),  $b = 8.769$  (2),  $c = 28.093$  (6) Å,  $V = 1769.5$  (9) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.47$  (1),  $D_x = 1.487$  g cm<sup>-3</sup>,  $MoK\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 16.73$  cm<sup>-1</sup>,  $F(000) = 792$ ,  $T = 294$  K, final  $R = 0.035$  for 2347 observed reflections. (II):

0108-2701/86/091248-04\$01.50

© 1986 International Union of Crystallography

$C_{18}H_{23}N_2O^+I^-$ ,  $M_r = 410.30$ , orthorhombic,  $P2_12_12_1$ ,  $a = 7.209$  (7),  $b = 8.877$  (5),  $c = 28.698$  (1) Å,  $V = 1836$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.47$  (1),  $D_x = 1.484$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 16.13$  cm<sup>-1</sup>,  $F(000) = 824$ ,  $T = 294$  K,  $R = 0.030$  for 3181 observed reflections. (I) is chiral because of conformational dissymmetry and isostructural with (II), which has a chiral center at C(7). The molecules contain three nearly planar parts: the pyridinium and phenyl rings and the *N,N*-dimethylcarbamoyl fragments. The I<sup>-</sup> ion has a short contact with N(2) of the pyridinium ring: 3.666 (5) (I) and 3.699 (3) Å (II).

**Introduction.** The restricted rotation about the C(aryl)—C(O) bond in alkylated 3-carbamoyl-1,2,4-trimethylpyridinium halides was demonstrated recently by the enantiomeric resolution of the *N,N*-diethyl substituted compound (van Hooff, van Lier, Bastiaansen & Buck, 1982). During investigations in the unsymmetrically disubstituted series we were able to isolate an amide rotamer of the title compound (I).

An analogous amide rotamer, with additional carbon chirality in the amide side chain (II), was prepared to study the influence of this chirality on the orientation of the carbonyl group with respect to the pyridinium ring. We now report the crystal structures of the title compounds (I) and (II).

**Experimental.** Crystals of (I) obtained by slow crystallization from water. Rod-shaped crystal  $0.28 \times 0.20 \times 0.28$  mm. Lattice parameters by least-squares refinement of 24 reflections ( $5.2 < \theta < 8.2^\circ$ ), CAD-4F automated diffractometer, Zr-filtered Mo  $K\alpha$  radiation,  $\omega$ - $2\theta$  scan with  $\omega = (0.60 + 0.35 \tan \theta)^\circ$ . Within one octant of the reflection sphere ( $h$  0–10,  $k$  0–12,  $l$  0–39) with  $2\theta_{\max} = 60^\circ$ , 2952 intensities, 2347 above the  $2.5\sigma(I)$  level. Three periodically measured standard reflections ( $2\bar{2}5$ ,  $\bar{2}25$ ,  $225$ ) showed an average deviation of 1.1%. Correction for Lorentz–polarization effects and absorption (min. transmission 0.619, max. 1.413). Structure solved by Patterson and Fourier methods. H atoms placed at calculated positions (C–H 1.08 Å) with isotropic thermal parameters equal to those of their carrier atoms. Anisotropic, weighted full-matrix refinement on  $F$  (190 parameters) gave  $R = 0.035$ ,  $wR = 0.039$ ,  $w = [\sigma^2(F_o) + 0.000291F_o^2]^{-1}$ ,  $S = 1.05$ , max.  $\Delta/\sigma = 0.165$ . Final difference synthesis showed max. density of  $0.68 \text{ e } \text{Å}^{-3}$  at about  $0.8 \text{ Å}$  from I<sup>-</sup> and a min. density of  $-0.36 \text{ e } \text{Å}^{-3}$ .

Crystals of (II) from an aqueous solution at room temperature. Needle-shaped crystal,  $0.5 \times 0.13 \times 0.03$  mm. Lattice parameters by least-squares refinement of 23 reflections ( $5.7 < \theta < 16.4^\circ$ ). CAD-4F diffractometer, Zr-filtered Mo  $K\alpha$  radiation,  $\omega$ - $2\theta$  scan with  $\omega = (0.60 + 0.35 \tan \theta)^\circ$ . Within one quadrant of the reflection sphere ( $h$  0–9,  $k$  0– $\pm 11$ ,  $l$  0–36) with  $2\theta_{\max} = 53^\circ$ ,  $hkl$  and  $h\bar{k}l$  pairs were measured, 4148

intensities, 3181 above the  $2.5\sigma(I)$  level. Equivalent reflections not merged because of determination of absolute configuration. Three periodically measured standard reflections (200, 040, 008) showed an average deviation of 1.18%. Correction for Lorentz–polarization effects and absorption (min. transmission 0.839, max. 1.154). Structure solved by Patterson and Fourier methods. H atoms at calculated positions with constant isotropic thermal parameters equal to those of the carrier atoms. Anisotropic, weighted full-matrix refinement on  $F$  (199 parameters) gave  $R = 0.030$ ,  $wR = 0.031$  with  $w = [\sigma^2(F_o) + 0.000158F_o^2]^{-1}$ ,  $S = 2.29$ , max.  $\Delta/\sigma = 0.05$ . Final difference Fourier synthesis showed max. density of  $0.77 \text{ e } \text{Å}^{-3}$  at about  $0.8 \text{ Å}$  from I<sup>-</sup> and a min. density of  $-0.59 \text{ e } \text{Å}^{-3}$ .

The absolute conformation of (I) in the crystal and the absolute configuration of (II) were ascertained by refinement of the inverted models which resulted in  $R = 0.040$ ,  $wR = 0.045$  for (I) and  $R = 0.035$  and  $wR = 0.037$  for (II). For (I) about 20 Friedel pairs, which displayed maximal calculated differences in intensity, were measured with Cu  $K\alpha$  radiation and the absolute conformation of (I) was confirmed by the Bijvoet differences of these reflections. For (II) the absolute configuration was confirmed by examination of 22 selected Friedel pairs from the original (Mo  $K\alpha$ ) data set. As (I) unlike (II) has no chiral center but rather a dissymmetric molecular conformation, it is apparent that (I) displays spontaneous resolution on crystallization in a conglomerate of enantiomeric crystals. Densities were measured by flotation in a mixture of dibromoethane and toluene. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Calculations performed with *SHELX76* (Sheldrick, 1976) (structure determination and refinement), the *EUCLID* package (Spek, 1982) and *ORTEP* (Johnson, 1976) (illustrations and molecular geometry) on the CDC Cyber-175 of the University of Utrecht.

**Discussion.** Atomic coordinates and equivalent isotropic thermal parameters of (I) and (II) are listed in Table 1 and the molecular geometries are given in Table 2.\* Fig. 1 shows a perspective view of (I) and (II) and includes the atom numbering. As has already been pointed out in *Experimental*, (I) has a dissymmetric molecular conformation. The CD spectrum of a methanolic solution of the crystal of (I) that was used for the structure analysis revealed that

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42991 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>) for (I) and (II) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

Compound (I)	x	y	z	U <sub>eq</sub>
I	0.66297 (6)	0.26134 (4)	0.17428 (1)	0.0601 (1)
O	0.2736 (6)	0.7893 (5)	0.1414 (2)	0.057 (1)
N(1)	0.2056 (6)	0.5705 (6)	0.1028 (2)	0.047 (1)
N(2)	-0.1764 (7)	0.6150 (5)	0.2305 (2)	0.046 (1)
C(1)	-0.1455 (9)	0.5342 (8)	0.0309 (3)	0.069 (3)
C(2)	-0.196 (1)	0.543 (1)	-0.0158 (4)	0.090 (3)
C(3)	-0.115 (2)	0.463 (1)	-0.0506 (3)	0.094 (4)
C(4)	0.032 (1)	0.373 (1)	-0.0396 (2)	0.077 (3)
C(5)	0.097 (1)	0.3625 (9)	0.0063 (2)	0.060 (2)
C(6)	0.0120 (9)	0.4433 (7)	0.0435 (2)	0.049 (2)
C(7)	0.0851 (9)	0.4413 (7)	0.0935 (2)	0.049 (2)
C(8)	0.3867 (9)	0.571 (1)	0.0800 (3)	0.067 (2)
C(9)	0.1674 (7)	0.6815 (6)	0.1346 (2)	0.041 (1)
C(10)	-0.0145 (7)	0.6821 (6)	0.1615 (2)	0.038 (1)
C(11)	-0.1563 (7)	0.7796 (6)	0.1476 (2)	0.042 (1)
C(12)	-0.137 (1)	0.8815 (7)	0.1054 (2)	0.061 (2)
C(13)	-0.3121 (7)	0.7890 (7)	0.1759 (2)	0.051 (2)
C(14)	-0.3229 (8)	0.7036 (7)	0.2167 (2)	0.049 (2)
C(15)	-0.197 (1)	0.5376 (8)	0.2777 (2)	0.068 (3)
C(16)	-0.0258 (8)	0.5978 (6)	0.2035 (2)	0.039 (1)
C(17)	0.125 (1)	0.4918 (7)	0.2193 (2)	0.056 (2)
Compound (II)				
I	0.66450 (4)	0.24899 (4)	0.17560 (1)	0.0589 (1)
O	0.2798 (4)	0.7679 (4)	0.1466 (1)	0.062 (1)
N(1)	0.2014 (5)	0.5572 (4)	0.1064 (1)	0.046 (1)
N(2)	-0.1822 (5)	0.6032 (3)	0.2315 (1)	0.046 (1)
C(1)	-0.1374 (8)	0.5464 (5)	0.0322 (2)	0.075 (2)
C(2)	-0.188 (1)	0.5693 (7)	-0.0126 (3)	0.105 (3)
C(3)	-0.092 (1)	0.4983 (8)	-0.0479 (2)	0.106 (3)
C(4)	0.050 (1)	0.4009 (7)	-0.0381 (2)	0.089 (3)
C(5)	0.1039 (8)	0.3784 (6)	0.0078 (2)	0.066 (2)
C(6)	0.0110 (7)	0.4527 (4)	0.0441 (2)	0.052 (2)
C(7)	0.0661 (6)	0.4358 (4)	0.0944 (1)	0.045 (1)
C(8)	0.3824 (6)	0.5532 (6)	0.0844 (2)	0.065 (2)
C(9)	0.1693 (6)	0.6670 (4)	0.1384 (1)	0.043 (1)
C(10)	-0.0119 (5)	0.6688 (4)	0.1643 (1)	0.037 (1)
C(11)	-0.1495 (5)	0.7684 (4)	0.1506 (1)	0.044 (1)
C(12)	-0.1308 (7)	0.8706 (5)	0.1099 (2)	0.064 (2)
C(13)	-0.3114 (6)	0.7760 (4)	0.1785 (2)	0.052 (2)
C(14)	-0.3228 (8)	0.6915 (5)	0.2176 (2)	0.053 (1)
C(15)	-0.2024 (8)	0.5219 (5)	0.2769 (2)	0.073 (2)
C(16)	-0.0269 (6)	0.5872 (4)	0.2054 (1)	0.041 (1)
C(17)	0.1214 (7)	0.4835 (5)	0.2229 (2)	0.056 (2)
C(18)	0.1425 (7)	0.2836 (4)	0.1070 (2)	0.063 (2)

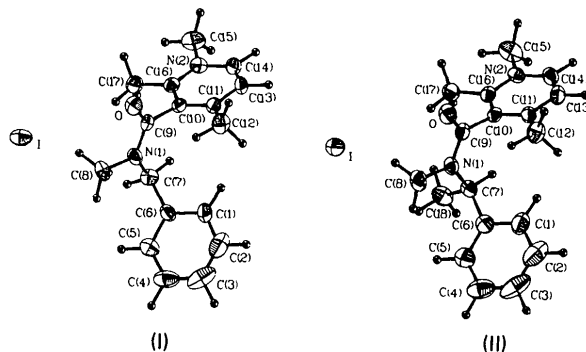


Fig. 1. ORTEP diagrams (Johnson, 1976) and atom-numbering schemes. Non-H ellipsoids at 50% probability level, H atoms depicted as 0.1 Å radius spheres.

(i) steric hindrance between the methylene and methyl group H atoms, and

(ii) the rotation barrier of the N–C amide bond.

The molecules (I) and (II) consist of three nearly planar fragments, the pyridinium, the *N,N*-dimethylcarbamoyl and phenyl parts, as follows from their  $\sigma_{\text{plane}}$  values  $\{\sigma_{\text{plane}} = [\sum_{i=1}^N a_i^2 / (N-3)]^{1/2}\}$  of 0.023, 0.032, 0.020 Å for (I) and 0.025, 0.028 and 0.016 Å for (II), respectively.

The bulky pyridinium and phenyl rings are attached to the planar *N,N*-dimethylcarbamoyl fragment, such that the pyridinium and benzyl groups approach a *cis* position with respect to the N(1)–C(9) bond, as follows from the C(10)–C(9)–N(1)–C(7) torsion angle,  $-3.4$  (8) for (I) and  $0.6$  (5)° for (II). The conformations of (I) and (II) are very similar, the mean deviation of a molecular fit of corresponding atoms amounts to 0.078 (1) Å. Both compounds show the same orientation of the carbonyl group with respect to the pyridinium ring. As stated above, the batch of (I) consists of both enantiomers, while that of (II) contains only one enantiomer. Therefore, it can be concluded that the orientation of the carbonyl group is governed by the chirality in the amide side chain. The configuration of the chiral center at C(7) in (II) is (*R*) in accordance with that of its synthetic precursor.

The geometries of (I) and (II) show a satisfactory general agreement; the mean deviations of corresponding distances, angles and chain torsion angles are 0.01 (1) Å, 1.2 (9) and 3 (2)°, respectively. The largest discrepancies of the geometries (Table 2) involve C(7) which carries an additional methyl group in (II) and atoms C(2), C(3) and C(4) of the benzene rings which display a large thermal motion.

The crystal structures of (I) and (II) can be considered as an ionic network with the pyridinium ion interacting with two symmetry-related I<sup>-</sup> ions. These

the dissymmetric conformer is stable in solution at room temperature for a prolonged time. Accordingly, CD spectra of carefully selected single crystals from the batch, showed that crystals containing either enantiomer are present (de Kok *et al.*, 1986). The transformation of (I) into its enantiomer can be achieved by rotations about the C(9)–C(10) and N(1)–C(7) bonds of about  $-140$  and  $160$ °, respectively. However, such a rotation about the C(9)–C(10) bond is sterically impossible, because it results in contact distances between H atoms of C(7) and C(12) of less than 0.6 Å. The only way to circumvent this crowding would be a concerted process involving also a rotation about the N(1)–C(9) acid amide bond, which is known to have a high barrier of rotation in *N,N*-dialkylpyridinamides (Sattler & Schunack, 1975). So two factors seem to be responsible for the observed stability of the dissymmetric conformer of (I) in solution:

Table 2. *Interatomic distances (Å), bond angles (°) and selected torsion angles (°)*

O—C(9)	(I) 1.230 (7)	(II) 1.222 (5)	C(1)—C(6)	(I) 1.428 (9)	(II) 1.397 (7)	C(9)—C(10)	(I) 1.509 (7)	(II) 1.503 (5)
N(1)—C(7)	1.449 (8)	1.494 (5)	C(2)—C(3)	1.34 (1)	1.38 (1)	C(10)—C(11)	1.386 (7)	1.386 (5)
N(1)—C(8)	1.450 (8)	1.450 (6)	C(7)—C(18)		1.503 (5)	C(10)—C(16)	1.395 (8)	1.388 (4)
N(1)—C(9)	1.349 (8)	1.359 (5)	C(3)—C(4)	1.35 (1)	1.37 (1)	C(11)—C(12)	1.491 (8)	1.485 (6)
N(2)—C(14)	1.364 (8)	1.342 (6)	C(4)—C(5)	1.374 (8)	1.388 (8)	C(11)—C(13)	1.375 (7)	1.417 (6)
N(2)—C(15)	1.497 (8)	1.497 (6)	C(5)—C(6)	1.402 (9)	1.403 (8)	C(13)—C(14)	1.371 (8)	1.352 (7)
N(2)—C(16)	1.330 (8)	1.354 (5)	C(6)—C(7)	1.500 (8)	1.505 (6)	C(16)—C(17)	1.495 (9)	1.498 (6)
C(1)—C(2)	1.36 (1)	1.35 (1)						
	(I)	(II)		(I)	(II)		(I)	(II)
C(7)—N(1)—C(8)	117.3 (6)	118.0 (3)	C(1)—C(6)—C(5)	116.2 (6)	117.6 (5)	C(10)—C(11)—C(12)	121.7 (5)	123.2 (4)
C(7)—N(1)—C(9)	124.2 (5)	124.2 (3)	C(1)—C(6)—C(7)	121.1 (6)	119.7 (4)	C(12)—C(11)—C(13)	120.0 (5)	119.4 (4)
C(8)—N(1)—C(9)	118.2 (5)	117.7 (4)	C(5)—C(6)—C(7)	122.7 (6)	122.6 (4)	C(10)—C(11)—C(13)	118.2 (5)	117.4 (3)
C(14)—N(2)—C(15)	115.7 (5)	117.8 (4)	N(1)—C(7)—C(6)	111.6 (5)	108.8 (3)	C(11)—C(13)—C(14)	119.8 (5)	119.5 (4)
C(14)—N(2)—C(16)	122.0 (5)	121.4 (3)	O—C(9)—N(1)	122.1 (5)	123.0 (4)	N(2)—C(14)—C(13)	120.3 (5)	121.7 (4)
C(15)—N(2)—C(16)	122.3 (5)	120.8 (3)	O—C(9)—C(10)	117.2 (5)	117.6 (3)	N(2)—C(16)—C(10)	118.0 (5)	118.7 (3)
C(2)—C(1)—C(6)	118.7 (7)	121.9 (5)	N(1)—C(9)—C(10)	120.7 (5)	119.3 (3)	N(2)—C(16)—C(17)	119.4 (5)	118.0 (3)
C(1)—C(2)—C(3)	123.9 (8)	119.6 (6)	C(9)—C(10)—C(11)	119.8 (5)	119.2 (3)	C(10)—C(16)—C(17)	122.6 (5)	123.4 (4)
C(2)—C(3)—C(4)	118.6 (8)	120.9 (6)	C(9)—C(10)—C(16)	118.2 (5)	118.8 (3)	N(1)—C(7)—C(18)		110.7 (3)
C(3)—C(4)—C(5)	121.2 (7)	119.7 (6)	C(11)—C(10)—C(16)	121.5 (5)	121.2 (3)	C(6)—C(7)—C(18)		114.7 (3)
C(4)—C(5)—C(6)	121.2 (7)	120.2 (5)						
	(I)	(II)		(I)	(II)		(I)	(II)
C(8)—N(1)—C(7)—C(6)	-71.0 (7)	-66.8 (5)	O—C(9)—C(10)—C(11)	74.9 (7)	77.1 (4)			
C(9)—N(1)—C(7)—C(6)	115.7 (6)	116.6 (4)	O—C(9)—C(10)—C(16)	-97.1 (6)	-93.4 (4)			
C(7)—N(1)—C(9)—O	-180.0 (6)	-177.7 (3)	N(1)—C(9)—C(10)—C(11)	-101.9 (6)	-101.3 (4)			
C(7)—N(1)—C(9)—C(10)	-3.4 (8)	0.6 (5)	N(1)—C(9)—C(10)—C(16)	86.1 (7)	88.3 (4)			
C(8)—N(1)—C(9)—O	6.8 (9)	5.8 (6)	C(8)—N(1)—C(7)—C(18)		60.0 (5)			
C(8)—N(1)—C(9)—C(10)	-176.6 (6)	-176.0 (3)	C(9)—N(1)—C(7)—C(18)		-116.5 (4)			
C(1)—C(6)—C(7)—N(1)	-82.1 (7)	-87.7 (5)	C(1)—C(6)—C(7)—C(18)		147.7 (4)			
C(5)—C(6)—C(7)—N(1)	95.2 (7)	91.8 (5)	C(5)—C(6)—C(7)—C(18)		-32.7 (6)			

Table 3. *Intermolecular contacts involving I<sup>-</sup>*

	(I)	(II)
I <sup>1</sup> ...N(2)	3.666 (5)	3.699 (3)
C(16)	3.792 (5)	3.833 (4)
C(15)	3.914 (6)	3.904 (5)
C(14)	4.059 (6)	4.110 (5)
C(17)	4.086 (7)	4.126 (5)
C(7)	4.103 (6)	4.070 (4)
C(18)		3.980 (5)
I <sup>II</sup> ...C(14)	3.950 (6)	3.965 (5)
C(15)	4.107 (7)	4.125 (5)
I <sup>III</sup> ...C(4)	4.073 (6)	
I <sup>IV</sup> ...C(17)	4.103 (6)	4.052 (5)

Symmetry operations on I<sup>-</sup>: (i)  $-1+y, y, z$ ; (ii)  $-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (iii)  $-\frac{1}{2}+x, \frac{1}{2}-y, -z$ ; (iv)  $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ .

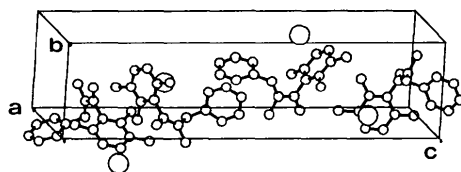


Fig. 2. View of the unit cell of compound (I), approximately along a.

two I<sup>-</sup> ions have contact distances with N(2) of 3.666 (5) and with C(14) of 3.950 (6) Å in (I), and 3.699 (3) and 3.965 (5) Å in (II) (Table 3). The I<sup>-</sup> ion at  $1-x, y, z$  with the shorter distance lies 3.59 (1) Å above

the pyridinium plane near N(2) and C(16) in (I); in (II) this distance is 3.62 (1) Å. The symmetry-related I<sup>-</sup> ion at  $-x, \frac{1}{2}+y, \frac{1}{2}-z$  is nearly in the plane of the pyridinium ring [distance 0.87 (1) in (I) and 0.91 (1) Å in (II)] having a short contact with C(14) of the cation (Table 3) in (I) and (II). This anion-cation arrangement resembles that reported for the structure of *N*-methylpyridinium iodide (Lalancette, Furey, Costanzo, Hemmes & Jordan, 1978). As the stacking of (I) and (II) in these unit cells is almost identical, only that of (I) is shown in Fig. 2.

### References

- HOOFF, H. J. G. VAN, VAN LIER, P. M., BASTIAANSEN, L. A. M. & BUCK, H. M. (1982). *Recl Trav. Chim. Pays-Bas*, **101**, 191–192.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- KOK, P. M. T. DE, DONKERSLOOT, M. C. A., VAN LIER, P. M., MEULENDIJKS, G. H. W. M., BASTIAANSEN, L. A. M., VAN HOOFF, H. J. G., KANTERS, J. A. & BUCK, H. M. (1986). *Tetrahedron*, **42**, 941–959.
- LALANCETTE, R. A., FUREY, W., COSTANZO, J. N., HEMMES, P. R. & JORDAN, F. (1978). *Acta Cryst.* **B34**, 2950–2953.
- SATTLER, H. J. & SCHUNACK, W. (1975). *Chem. Ber.* **108**, 730–734.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SPEK, A. L. (1982). *Computational Crystallography*, edited by D. SAYRE, p. 528. Oxford: Clarendon Press.