(Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: CF1035). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-(2-Pyridyl)pyridinium Triiodide

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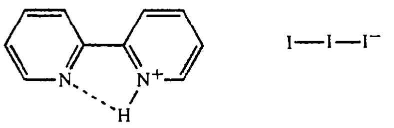
Abstract

The title structure, $C_{10}H_9N_2^+.I_3^-$, consists of 2-(2-pyridyl)pyridinium cations and near-symmetric essentially linear triiodide anions [I—I = 2.902 (1) and 2.920 (1) Å, and I—I—I = 177.88 (5)°]. The cation has a *syn* configuration, with an intramolecular N—H···N hydrogen bond: H—N2 and H···N1 = 1.13 (11) and 1.83 (10) Å, respectively, and N2—H···N1 = 124 (8)°. The two heterocyclic rings are not coplanar, the angle between the rings being 9.6 (8)°.

Comment

The title compound, (I), was obtained from a reaction scheme which involved the sequential addition to 4,5-dibenzoylthio-1,3-dithiole-2-thione in MeOH of NaOMe, 2,2′-bipyridyl and SnI_4, and after a work-up which involved acidification and fractional crystallization from MeOH. The X-ray crystallography was carried out to identify the unexpected product unambiguously.



(I)

The title compound exists as an ionic species, with discrete cations and anions. The heterocyclic rings in the 2-(2-pyridyl)pyridinium cation have a *syn* arrangement (Fig. 1), with an angle of 9.6 (8)° between the perpendiculars of the planes of the two rings. The acidic H atom, bonded to N2, is intramolecularly hydrogen bonded to N1, with bond lengths for H—N2 and H—N1 of 1.13 (11) and 1.83 (10) Å, respectively, and an N2—H···N1 angle of 124 (8)°. The intramolecular N1···N2 separation is 2.64 (2) Å.

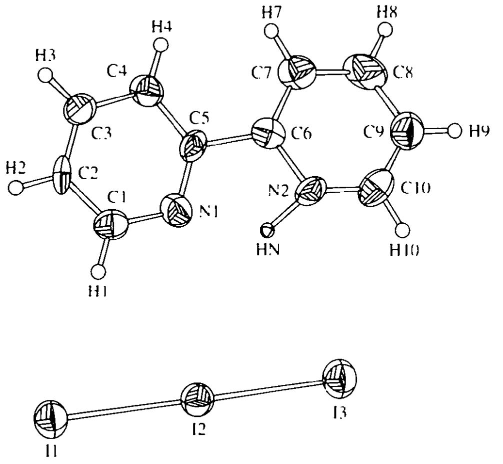


Fig. 1. The asymmetric unit of $C_{10}H_9N_2^+.I_3^-$ showing the atom-numbering scheme. Displacement ellipsoids of non-H atoms are at the 40% probability level and H atoms are shown as spheres of arbitrary radii.

There are a number of (2-pyridyl)pyridinium compounds listed in the Cambridge Structural Database (Allen & Kennard, 1993). (2-Pyridyl)pyridinium cations have generally been shown to have *syn* structures in ionic complexes, with intramolecular N—H···N hydrogen bonds, and with small angles between the planes of the two aromatic rings (see, for example, Figgis, Skelton & White, 1978; Khan, Kumar & Tuck, 1984; Chantler & Maslen, 1989; Decurtins, Schmalle, Schneuwly & Oswald, 1993).

The triiodide anion is almost linear [I3—I2—I1 = 177.88 (5)°] and almost symmetrical, with I—I bond lengths of 2.920 (1) (I2—I1) and 2.902 (1) Å (I2—I3).

These values are in agreement with the general finding (Hon, Mak & Trotter, 1982) that linear and symmetrical I_3^- ions are associated with large cations, *e.g.* the 1,4,6,7-tetramethylquinoxalinium cation (Hausen, Schulz & Kaim, 1993), in contrast to the asymmetric bent I_3^- anions found with small asymmetric or highly charged cations. Of interest, the I_3^- ion in 1-methylcytosinium triiodide is unsymmetrical [I—I = 2.794 (1) and 3.123 (1) Å] with I—I—I = 177.6 (1)° (Rossi, Marzilli & Kistenmacher, 1978).

The packing diagram for the title compound is shown in Fig. 2. The shortest N···N intermolecular separation between cations is 4.04 (2) Å; the closest intermolecular N···I approach between an anion and a cation is 3.67 (1) Å, and the shortest I···I distance between anions is 4.452 (2) Å. Both the N···I and I···I distances are close to the sums of the appropriate van der Waals radii, 3.65 and 4.30 Å, respectively (Cotton & Wilkinson, 1972).

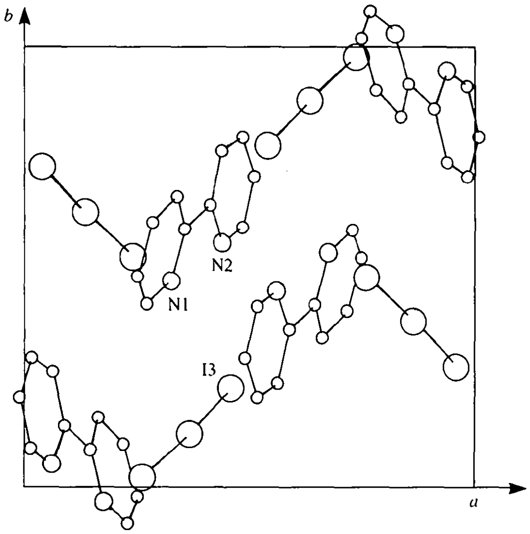


Fig. 2. The unit cell of $C_{10}H_9N_2^+.I_3^-$ viewed down the *c* axis. Atoms are represented by circles of arbitrary size increasing in radius in the order C, N and I. Some atoms of the asymmetric unit are labelled. H atoms have been omitted for clarity.

The large features in the difference map are associated with the triiodide ion. The positive peak is 1.89 Å from I3 and the negative hole is 2.18 and 1.95 Å from I1 and I2, respectively.

Experimental

The title compound was isolated from a reaction scheme which involved the sequential addition to 4,5-dibenzoylthio-1,3-dithiole-2-thione in MeOH of NaOMe, 2,2′-bipyridyl and SnI_4 (see *Comment*).

Crystal data

$C_{10}H_9N_2^+.I_3^-$
M_r = 537.91
Monoclinic
$P2_1/n$
a = 11.222 (5) Å
b = 10.725 (8) Å
c = 12.002 (8) Å
β = 98.03 (5)°
V = 1430 (2) Å^3
Z = 4
D_x = 2.498 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 14 reflections
θ = 11–14°
μ = 6.46 mm^{-1}
T = 298 K
Needle
0.6 × 0.2 × 0.06 mm
Brown

Data collection

Nicolet *P*3 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min}$ = 0.172, $T_{\max}$ = 0.596
2825 measured reflections
2269 independent reflections
1683 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int}$ = 0.036
$\theta_{\max}$ = 25°
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 14$
2 standard reflections monitored every 50 reflections
intensity decay: 3.0 and 3.8%

Refinement

Refinement on F
R = 0.057
wR = 0.067
S = 0.61
1683 reflections
141 parameters
H-atom treatment: see below
$w = 1/[\sigma^2(F) + 0.020383F^2]$

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 1.00 e Å^{-3}
$\Delta\rho_{\min}$ = −1.64 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
I1	0.26086 (11)	0.02242 (12)	0.55879 (9)	0.0646 (4)
I2	0.36426 (9)	0.12119 (9)	0.36675 (8)	0.0482 (3)
I3	0.45903 (12)	0.22481 (12)	0.17371 (9)	0.0660 (4)
N1	0.3237 (14)	0.4682 (13)	0.4378 (12)	0.064 (5)
N2	0.4394 (11)	0.5540 (12)	0.2770 (11)	0.050 (4)
C1	0.2704 (17)	0.4170 (16)	0.5176 (15)	0.063 (5)
C2	0.2498 (16)	0.4789 (18)	0.6120 (14)	0.066 (6)
C3	0.2823 (15)	0.5990 (15)	0.6241 (13)	0.055 (5)
C4	0.3373 (15)	0.6587 (16)	0.5443 (11)	0.053 (5)
C5	0.3538 (11)	0.5851 (14)	0.4499 (11)	0.040 (4)
C6	0.4111 (12)	0.6404 (13)	0.3551 (12)	0.044 (4)
C7	0.4374 (17)	0.7629 (17)	0.3388 (14)	0.062 (5)
C8	0.484 (2)	0.7946 (18)	0.2448 (16)	0.082 (8)
C9	0.5102 (18)	0.7047 (18)	0.1645 (15)	0.066 (6)
C10	0.4840 (16)	0.5894 (18)	0.1852 (14)	0.062 (6)

Table 2. *Selected geometric parameters (Å, °)*

I2—I1	2.920 (1)	I3—I2	2.902 (1)
C1—N1	1.32 (2)	C5—N1	1.30 (2)
C6—N2	1.39 (2)	C10—N2	1.33 (2)
C2—C1	1.36 (2)	C3—C2	1.34 (2)
C4—C3	1.37 (2)	C5—C4	1.41 (2)
C6—C5	1.50 (2)	C7—C6	1.37 (2)
C8—C7	1.35 (3)	C9—C8	1.42 (3)
C10—C9	1.30 (3)		

I3—I2—I1	177.88 (5)	C5—N1—C1	117.2 (15)
C10—N2—C6	121.2 (14)	C2—C1—N1	123.3 (16)
C3—C2—C1	118.9 (15)	C4—C3—C2	121.1 (15)
C5—C4—C3	114.9 (14)	C4—C5—N1	124.5 (14)
C6—C5—N1	115.3 (12)	C6—C5—C4	120.3 (13)
C5—C6—N2	114.3 (12)	C7—C6—N2	118.1 (15)
C7—C6—C5	127.6 (15)	C8—C7—C6	118.6 (18)
C9—C8—C7	122.4 (19)	C10—C9—C8	116.1 (18)
C9—C10—N2	123.5 (17)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*—H···*A*
N2—HN···N1	1.13 (11)	1.83 (10)	124 (8)

All non-H atoms were refined anisotropically. H atoms attached to C atoms were placed in calculated positions with C—H = 0.95 Å and refined riding upon the C atom to which they were attached with a common group $U_{\rm iso}$. The H atom attached to N2 was found in a difference map and refined isotropically. All computations were performed on the Sun SPARCserver (UNIX operating system) of the Computing Centre of the University of Aberdeen.

Data collection: *Nicolet P3 Software* (Nicolet XRD Corporation, 1980). Cell refinement: *Nicolet P3 Software*. Data reduction: *RDNIC* (Howie, 1980). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEX* (McArdle, 1994). Software used to prepare material for publication: *XPUB* (Low, 1980).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1051). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-Methylbenzylammonium 4-Methylbenzylcarbamate

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Abstract

The title structure, $C_8H_{12}N^+.C_9H_{10}NO_2^-$, consists of infinite bilayers, parallel to the *ab* plane, incorporating both cations and anions. Within each bilayer, anions and cations are stacked in a herringbone fashion and the layers are generated by three N—H···O hydrogen bonds. The NHCOO⁻ moiety displays near-planar geometry.

Comment

The chemical properties of organic carbamates have been studied widely, especially in view of their use as herbicides (Machemer & Pickel, 1994*b*) and insecticides (Machemer & Pickel, 1994*a*). The general synthetic route to carbamates is well established (Schering, 1901) and they are now easily prepared through the reaction of primary, secondary or aromatic amines with carbon dioxide. Furthermore, the reactions can be carried out at ambient temperature and pressure. Despite the ease with which organic carbamates can be made, there is a severe lack of X-ray single-crystal studies on organic compounds containing the *R*NHCOO⁻ moiety. A search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) uncovered only three organic compounds containing the uncoordinated *R*NHCOO⁻ function, *i.e.* ammonium carbamate (Adams & Small,

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