

Indole- and carbazole-substituted pyridinium iodide salts: a rare case of conformational isomerism in crystals

Zheng Wang,^a Vladimir N. Nesterov,^a Oleg Ya. Borbulevych,^a Ronald D. Clark,^a Mikhail Yu. Antipin^{a,b} and Tatiana V. Timofeeva^{a*}

^aDepartment of Chemistry, New Mexico Highlands University, Las Vegas, NM 87701, USA, and ^bInstitute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St., B-334 Moscow, Russia
Correspondence e-mail: tanya@kremlin.nmhu.edu

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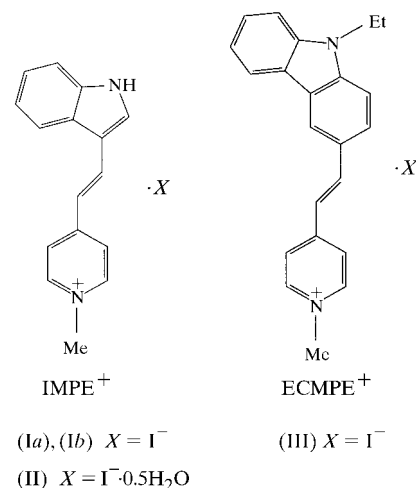
A series of indole- and carbazole-substituted pyridinium iodide salts has been synthesized and characterized. X-ray analysis revealed that the iodide salt of the indole-substituted cation (*E*)-4-(1*H*-indol-3-ylvinyl)-*N*-methylpyridinium (IMPE⁺), C₁₆H₁₅N₂⁺·I⁻, (I), has two polymorphic modifications, (*Ia*) and (*Ib*), and a hemihydrate structure, C₁₆H₁₅N₂⁺·I⁻·0.5H₂O, (II). Until now, only one crystal modification has been identified for the (*E*)-4-(9-ethyl-9*H*-carbazol-3-ylvinyl)-*N*-methylpyridinium (ECMPE⁺) iodide salt, C₂₂H₂₁N₂⁺·I⁻, (III). Crystals of (*Ia*) and (*Ib*) comprise stacks of antiparallel cations with iodide anions located in the channels between the stacks. Due to the presence of the water molecules, the packing in (II) is quite different to that found in (*Ia*) and (*Ib*), and positional disorder involving a statistical superposition of two rotamers of IMPE⁺, with different orientations of the indole fragment, was found. Crystals of (III) contain two independent ECMPE⁺ rotamers with different orientations of their carbazole substituents. The cations are packed in stacks, with the iodide anions located in the channels between the stacks. In (III), the iodide was found to be disordered over two sites, with occupancies of 0.83 and 0.17.

Comment

In a search for potential non-linear optical (NLO) materials, we have carried out the synthesis and characterization of several indole- and carbazole-substituted pyridinium salts. In many cases, organic salts were found to be significantly more active as NLO materials than compounds containing neutral organic molecules. We plan to use long-tail analogues of the salts described in this paper in the preparation of Langmuir–Blodgett films. The NLO properties of several pyridinium and quinolinium salts which form Langmuir–Blodgett films have been described previously (Hu, 1993; Xu *et al.*, 1997; Ashwell *et al.*, 1998; Johal *et al.*, 1999). To our knowledge, no pyridin-

ium salts with indole or carbazole substituents have been previously structurally characterized.

Crystallization of (*E*)-4-(1*H*-indol-3-ylvinyl)-*N*-methylpyridinium iodide (IMPE⁺·I⁻) from dimethyl sulfoxide (DMSO) solution resulted in the formation of two types of crystals, namely orange square-prismatic crystals, (*Ia*), and thin yellow needles, (*Ib*). By crystallization of the same compound from ethanol, yellow hexagonal prismatic crystals of (*E*)-4-(1*H*-indol-3-ylvinyl)-*N*-methylpyridinium iodide hemihydrate, (II), were obtained. Structural analysis revealed that (*Ia*) and (*Ib*) are triclinic and monoclinic polymorphs of IMPE⁺·I⁻, respectively, while (II) is a monoclinic hemihydrate (IMPE⁺·I⁻·0.5H₂O) of the same salt.



In all four structures reported here, the cations are nearly planar (Table 1), the largest deviations from planarity being found for (II). The bond lengths and angles in the cation of

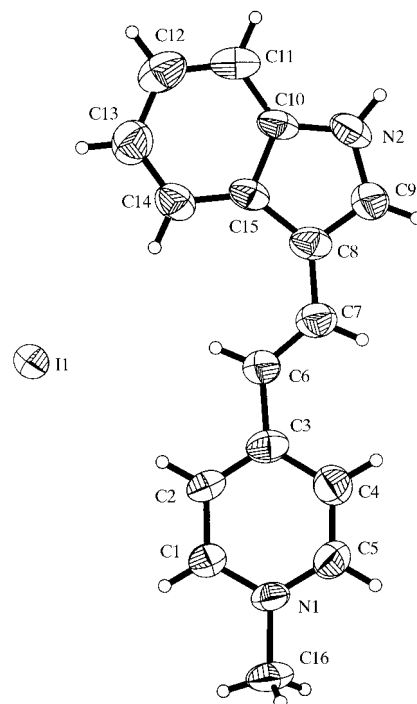


Figure 1
View of (*Ia*) with displacement ellipsoids for the non-H atoms at the 50% probability level.

(*Ia*) are close to standard values and to those found in (*Ib*), except for the bridging C3—C6=C7—C8 fragment (Figs. 1 and 2, and Table 1). The C6=C7 double bond in (*Ib*) [1.271 (8) Å] is considerably shorter not only than that in (*Ia*) [1.346 (8) Å] but also than the typical C=C bond length (1.34 Å; Allen *et al.*, 1987). Moreover, the C3—C6 and C7—C8 bonds in (*Ib*) are elongated to 1.487 (8) and 1.497 (9) Å, respectively, compared with the corresponding bond lengths in (*Ia*) [1.465 (6) and 1.435 (7) Å]. Several similar examples, with a discussion of the reasons for the shortening of both the C=C and N=N bonds in *trans*-stilbene (Bernstein, 1975; Hoekstra *et al.*, 1975), 2,2'-dimethylstilbene (Ogawa *et al.*, 1988, 1992) and several substituted azobenzenes (Harada *et al.*, 1997; Atroshchenko *et al.*, 2000), have appeared in the literature. For instance, the X-ray investigation of (*E*)-2,2'-

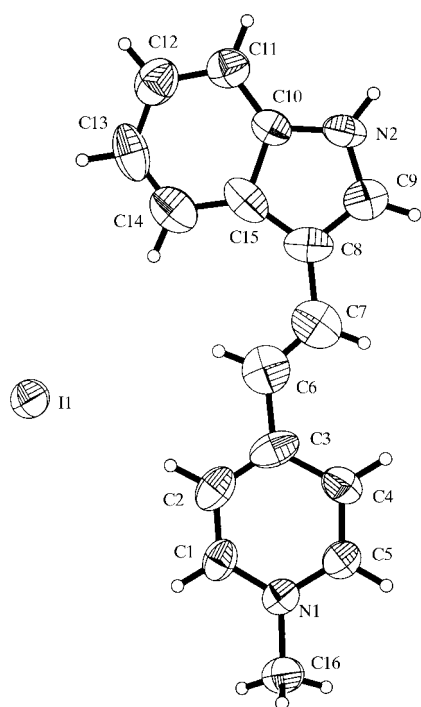


Figure 2
View of (*Ib*) with displacement ellipsoids for the non-H atoms at the 50% probability level.

dimethylstilbene (Ogawa *et al.*, 1988) reveals that the C=C bond at room temperature (1.281 Å) is significantly shorter than at 118 K (1.324 Å). Recent multi-temperature investigations of this phenomenon (Harada *et al.*, 1995, 1997) led to the conclusion that shrinkage of the C=C double bond is an artifact of torsion vibration of the C(or N)—Ph bond. If the amplitude of the torsion vibration is large enough it gives rise to conformational interconversion and hence to dynamic disorder in the crystal. However, such dynamic disorder cannot usually be resolved in a routine experiment due to the low resolution of the X-ray data and the low population of one of the conformers (Harada *et al.*, 1997). Therefore, the assumption is made that, even at 200 K, the unusual bond lengths in the bridging group of (*Ib*) are artifacts related to crystal disorder.

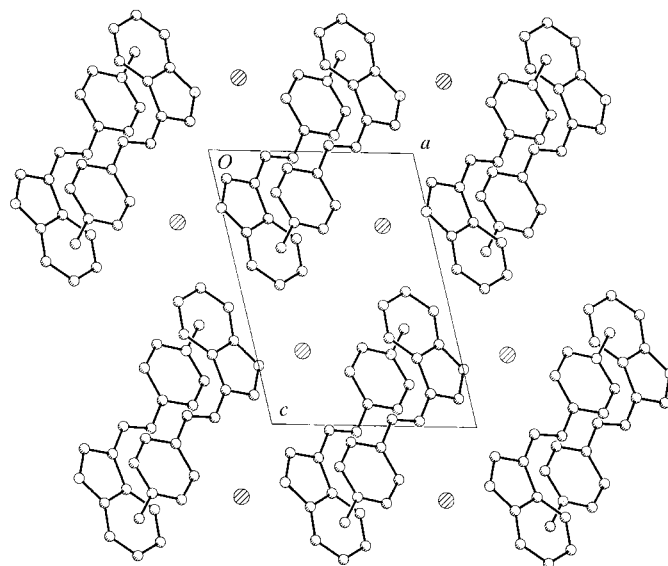


Figure 3
Projection of the crystal packing of (*Ia*) along the *b* axis.

The crystal packing of (*Ia*) and (*Ib*) share some similar features. In both crystal phases, organic cations are packed in stacks. The stacks extend along [010] in (*Ia*) and along [100] in (*Ib*) by the inversion operations $(-1-x, 2-y, 2-z; -1-x, 1-y, 2-z)$ and $(-1-x, 1-y, -z; -x, 1-y, -z)$, respectively (Figs. 3 and 4). The corresponding IMPE⁺ interplanar distances in these stacks are 3.36 (1) and 3.17 (1) Å for (*Ia*), and 3.31 (1) and 3.36 (1) Å for (*Ib*). In (*Ia*) (Fig. 3), stacks are packed in parallel, and in (*Ib*) in a herring-bone manner (Fig. 4). The iodide anions are located in the channels between these stacks.

An alternative way to describe the packing in these polymorphs is by reference to a sheet [a structure-building motif according to Desiraju (1989, 1991)] of cations and to the relative positions of the anions. It is possible to identify planar sheets of cations along [110] in (*Ia*) and slightly corrugated sheets along $[\bar{1}01]$ in (*Ib*). We define a sheet plane as a plane that goes through the centers of mass of the corresponding molecules. The angles between the least-squares mean planes

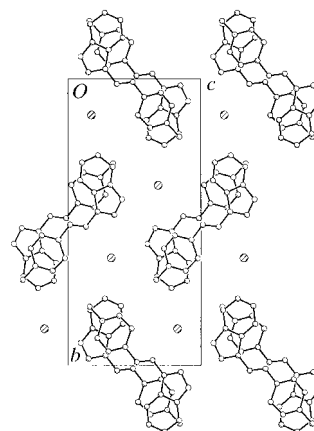


Figure 4
Projection of the crystal packing of (*Ib*) along the *a* axis.

of the cations and the relevant crystal planes [110] and $[\bar{1}01]$ are 6.3 and 11.5° in (Ia) and (Ib), respectively.

In (Ia), there is an alternation of intersheet distances, with separations of 3.09 and 3.33 Å. There are no iodides between the sheets with the shorter separation. In (Ia), all iodides are located between sheets with separations of 3.33 Å and their

displacements from the nearest sheet are 0.898 Å. Four short contacts of the H···I type shorter than 3.18 Å have been found in (Ia) (Table 2). The sum of the van der Waals radii of the I and H atoms is 3.18 Å (Bondi, 1964) and the length of the mean statistical H···I contact (3.13 Å; Rowland & Taylor, 1996) lies close to this value. In this structure, the iodide coordination environment within a sphere of 3.6 Å includes ten contacts of the types N—H···I and C—H···I. All four short contacts are related to interaction of the anion with the same sheet of cations. The shortest contact is formed between an iodide and the acid H atom of the indole substituent (Table 2).

In (Ib), all intersheet distances are of 3.24 Å. Iodide anions are located between each pair of sheets, with a displacement from the sheet plane of 0.613 Å. There are nine I···H contacts in the environment of the anion within a sphere of 3.6 Å. Four of these are shorter than 3.18 Å and the shortest H···I contact is of the same type as in (Ia). The iodide has one short contact (less than 3.18 Å) with one of the sheets, H16A···I1ⁱⁱ [symmetry code: (ii) $-x, -y, -z$], and three contacts with another adjacent sheet (Table 3).

Two crystallographically independent molecules (A and B) are found in (II) (Figs. 5a and 5b). Organic cation A is equally disordered over two sites (Fig. 5a). The two cations forming 'a disordered pair' are rotamers with opposite orientations of the indole substituents around the C7—C8 bond (Fig. 5a). The

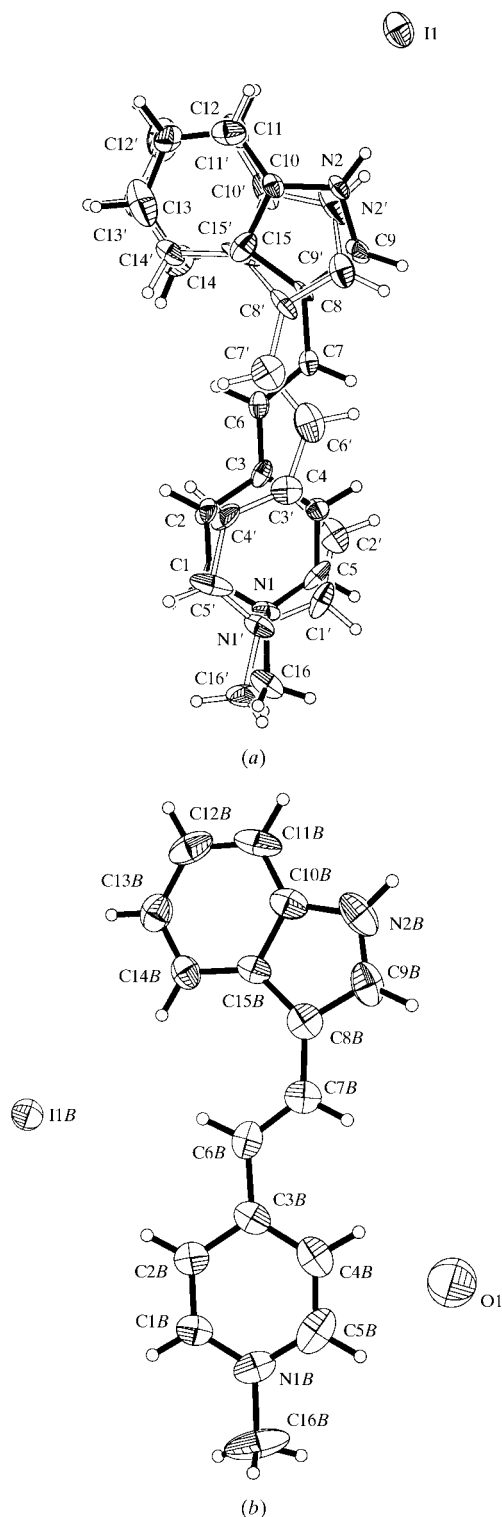


Figure 5
Views of ion pairs (a) A and (b) B of (II). Displacement ellipsoids for the non-H atoms are at the 50% probability level.

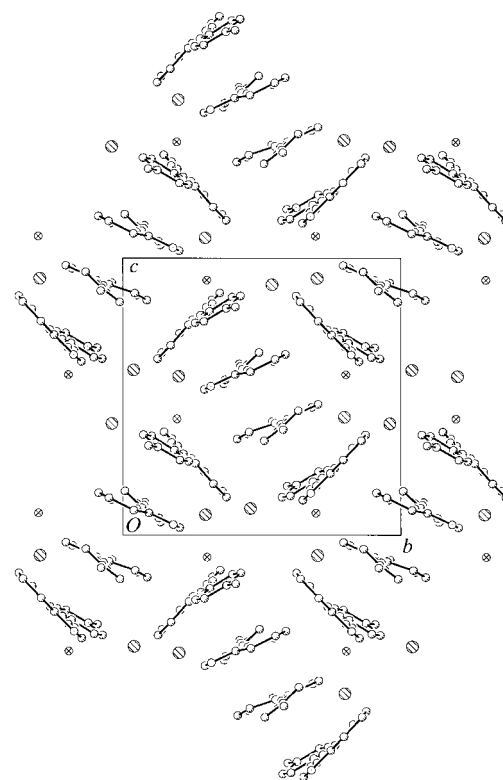


Figure 6
Projection of the crystal packing of (II) along the *a* axis. Only one molecule of a disordered pair is shown and, for clarity, all H atoms have been omitted. O atoms are shown as crossed-hatched circles and iodides are shown as shaded circles. Each infinite stack is surrounded by four others which are almost perpendicular to it.

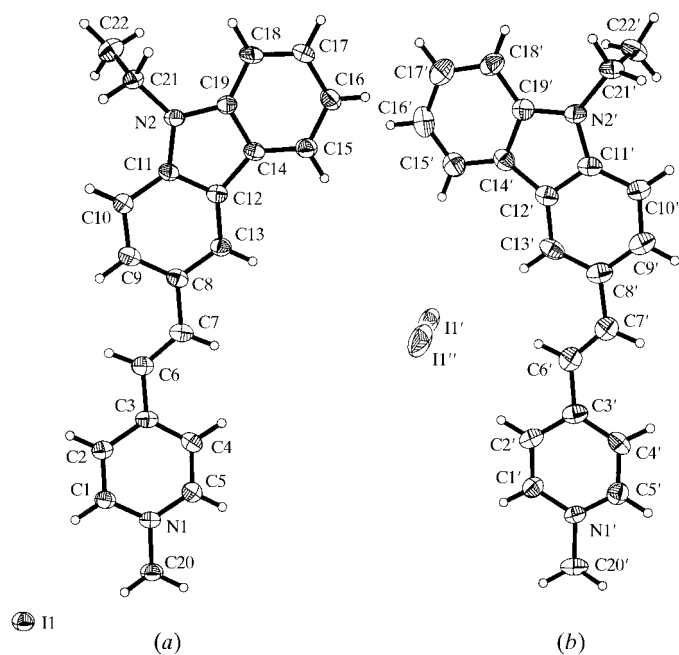


Figure 7
Views of ion pairs (a) *A* and (b) *B* of (III). Displacement ellipsoids for the non-H atoms are at the 50% probability level.

corresponding torsion angles C6–C7–C8–C9 and C6'–C7'–C8'–C9' are $-172(1)$ and $13(3)^\circ$, respectively. This type of disorder (Fig. 5*a*) is similar to that found in disordered diazabenzene or stilbene compounds. Although the disorder results in less precise geometry for cation *A*, bond lengths and valence angles for cation *B* in (II) do not differ considerably from the standard values (Allen *et al.*, 1987) or from those in (I*a*). Coplanar cations *A* and *B* form four-cation infinite stacks. Every such stack is surrounded by four others; within these, the mean planes of the cations are oriented almost perpendicular to those in the reference pack (Fig. 6).

The water molecule is involved in the formation of an N–H...O hydrogen bond with the indole fragment of cation *B*. The quality of the X-ray data did not allow location of the H atoms of the water molecule. Nevertheless, the distances between the O atoms and iodide ions [I1...O1ⁱ 3.643(7) Å and I1*B*...O1 3.398(7) Å; symmetry code: (i) $x - 1, -y + \frac{3}{2}, z + \frac{1}{2}$] allow us to infer the presence of H...I interactions involving the water H atoms. Due to the complexity of the structure of (II), only those H...I contacts below 3.18 Å are listed in Table 4. Short H...I contacts (Table 4) with H atoms of the indole substituents involve both iodides in (II); these interactions are similar to those seen in (I*a*) and (I*b*).

In (III), there are also two independent ion pairs (*A* and *B*), for which different orientations of the carbazole moiety with respect to the C7–C8 bond are observed (Figs. 7*a* and 7*b*, and Table 1). Moreover, the ethyl group has a different orientation in the two cations; the relevant torsion angles are $-101.3(3)^\circ$ for C11–N2–C21–C22 in cation *A* and $85.1(4)^\circ$ for C11'–N2'–C21'–C22' in cation *B*. The distribution of bond lengths and angles is essentially the same as in (I*a*), (I*b*) and (II), and both cations in (III) are almost planar. R.m.s. deviations from

the planes passing through all non-H atoms (except for the C atoms of the ethyl group) are 0.035 (for ion-pair *A*) and 0.043 Å (for ion-pair *B*). One of the iodides in (III) is statistically disordered over two sites, with occupancies of 0.83 and 0.17. The crystal packing of (III) is similar to that observed in (I*a*) and (I*b*). Cations in (III) form stacks along [100] and anions are located in channels between the stacks. Cations *A* and *B* alternate within these stacks, with interplanar distances of 3.31 (1) and 3.60 (1) Å. However, no sheets of cations are observed in (III). H...I short contacts of less than 3.18 Å are listed in Table 5.

The rare phenomenon of co-existence in one crystal of two conformers (rotamers) was observed for the crystals of related compounds (II) and (III). While in (II), the second rotamer was found only as part of a 'disordered pair', in (III), the two rotamers were observed in the asymmetric unit.

In spite of the drastic difference in molecular packing in polymorphs (I*a*) and (I*b*), hemihydrate (II) and carbazole derivative (III), in the majority of these structures [*viz.* (I*a*), (II) and (III)], the long axis of the molecules have a parallel orientation that is important for their potential application as liquid crystalline and/or Langmuir–Blodgett materials.

Experimental

The salts IMPE⁺I[−], (I), and ECMPE⁺I[−], (III), were obtained by reaction of equimolar amounts of 1,4-dimethylpyridinium iodide (0.005 mol) with indole-3-carboxaldehyde (0.005 mol) [for the preparation of compound (I)] or *N*-ethyl-3-carbazolecarboxaldehyde (0.005 mol) [for the preparation of (III)], in the presence of catalytic amounts of piperidine, in ethanol solution under reflux for 5 h (Marder *et al.*, 1990, 1994). The precipitates were collected by vacuum filtration and recrystallized from acetonitrile. The yields of final products were: (I) 79%, m.p. 533 K; (III) 90%, m.p. 578 K. In (I), a trace amount of the *cis* isomer was found. Crystals of (I*a*) and (I*b*) were both grown from a DMSO solution of (I), while (II) was obtained from a solution in ethanol. Crystals of (III) were grown from acetonitrile. Crystallization gave orange and yellow crystals, of which only the yellow crystals were suitable for X-ray analysis. Data for the *trans* isomer of compound (I), ¹H NMR (unisol): δ (p.p.m) 9.92 (*s*, HN), 8.62 (*d*, *J* = 6.62 Hz, HC1, HC5), 8.13 (*d*, *J* = 16.18 Hz, HC7), 8.03 (*t*, *J* = 4.05 Hz, HC14), 7.96 (*d*, *J* = 6.62 Hz, HC2, HC4), 7.83 (*d*, *J* = 2.94 Hz, HC9), 7.50 (*dd*, *J* = 4.42 Hz, HC13), 7.30–7.23 (*m*, HC11, HC12), 7.16 (*d*, *J* = 16.18 Hz, HC6), 4.28 (*s*, CH₃); ¹³C NMR (unisol): δ (p.p.m) 153.83 (C3), 142.47 (C1 and C5), 136.72 (C15), 136.34 (C7), 131.51 (C10), 123.79 (C9), 122.02 (C2 and C4), 120.72 (C6), 120.36 (C12), 119.14 (C13), 115.06 (C14), 112.72 (C8), 111.56 (C11), 45.36 (−CH₃); UV–vis (ethanol): λ_{max} 444 nm. Data for compound (III), ¹H NMR (unisol): δ (p.p.m) 8.80 (*d*, *J* = 6.62 Hz, HC1, HC5), 8.47 (*s*, HC13), 8.15 (*d*, *J* = 7.72 Hz, HC10), 8.09 (*d*, *J* = 6.98 Hz, HC2, HC4), 8.03 (*d*, *J* = 7.73 Hz, HC18), 7.84 (*d*, *J* = 6.62 Hz, HC15), 7.53 (*d*, *J* = 16.18 Hz, HC7), 7.53–7.43 (*m*, HC16, HC17), 7.37 (*d*, *J* = 16.18 Hz, HC6), 7.32–7.21 (*m*, HC9), 4.46 (*q*, *J* = 7.72 Hz, H₂C21), 4.35 (*s*, H₃C20), 1.46 (*t*, H₃C22); ¹³C NMR (unisol): δ (p.p.m) 152.88, 125.41 (C9), 125.32 (C17), 125.18 (C12), 124.60 (C14), 122.13 (C13), 122.00 (C2 and C4), 121.31 (C15), 119.33 (C6), 118.71 (C10), 117.94 (C16), 108.08 (C18), 45.75 (C20), 36.53 (C21), 12.64 (C22); UV–vis (ethanol): λ_{max} 442 nm.

Table 1

Comparison of molecular geometry parameters (Å, °) and characteristics of planarity for compounds (Ia), (Ib), (II) and (III).

Parameter	(Ia)	(Ib)	(IIA)	(IIA')	(IIB)	(IIIA)	(IIIB)
C3—C6	1.465 (6)	1.487 (8)	1.39 (2)	1.449 (2)	1.458 (6)	1.457 (4)	1.475 (5)
C6—C7	1.346 (8)	1.271 (8)	1.35 (1)	1.339 (2)	1.334 (7)	1.344 (5)	1.325 (5)
C7—C8	1.435 (7)	1.497 (9)	1.46 (2)	1.43 (2)	1.420 (7)	1.466 (4)	1.476 (5)
C4—C3—C6—C7	−4.2 (8)	5 (1)	7 (2)	6 (2)	4.5 (7)	−4.6 (5)	−2.7 (5)
C6—C7—C8—C15 ^a	−0.8 (9)	0 (1)	12 (2)	−167 (2)	6.3 (8)	−174.0 (3)	1.1 (5)
R.m.s deviation ^b	0.039	0.037	0.163	0.168	0.159	0.044	0.044
Maximum deviation ^{b,c}	−0.094 (4)	0.088 (6)	−0.32 (2)	−0.34 (1)	0.316 (4)	0.101 (3)	−0.089 (2)

Notes: C6—C7—C8—C13 in (III); (b) for the planes passing through all the non-H atoms of the cations of (Ia), (Ib), (IIA), (IIA') and (IIB), and all non-H atoms except for the ethyl C atoms of the cations of (IIIA) and (IIIB); (c) maximum deviations for atoms C2, C4, C5, C2', C2B, C2 and N2' in the cations of (Ia), (Ib), (IIA), (IIA'), ethyl (IIB), (IIIA) and (IIIB).

Compound (Ia)*Crystal data*

C₁₆H₁₅N₂⁺·I[−]
M_r = 362.20
 Triclinic, *P*1̄
a = 8.097 (3) Å
b = 9.223 (4) Å
c = 10.906 (4) Å
 α = 76.71 (3)°
 β = 73.12 (3)°
 γ = 75.25 (3)°
V = 742.8 (5) Å³

Data collection

Siemens P3 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
T_{min} = 0.414, *T_{max}* = 0.566
 3121 measured reflections
 2902 independent reflections
 2385 reflections with *I* > 2σ(*I*)

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.053
wR(*F*²) = 0.142
S = 1.04
 2902 reflections
 173 parameters

Z = 2
D_x = 1.619 Mg m^{−3}
 Mo *K*α radiation
 Cell parameters from 24 reflections
 θ = 10–11°
 μ = 2.14 mm^{−1}
T = 293 (2) K
 Square prism, orange
 0.50 × 0.40 × 0.30 mm

R_{int} = 0.021
 θ_{\max} = 26.1°
 h = 0 → 10
 k = −11 → 11
 l = −12 → 13
 2 standard reflections
 every 98 reflections
 intensity decay: 3.2%

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.1081P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.26 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.82 \text{ e } \text{Å}^{-3}$

Table 2

H···I interaction geometry (Å, °) for (Ia).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H2N···I1 ⁱ	0.86	2.81	3.609 (5)	155
C2—H2···I1	0.93	3.09	4.015 (5)	171
C14—H14···I1	0.93	3.18	4.040 (6)	155
C16—H16A···I1 ⁱⁱ	0.96	3.10	4.021 (6)	161

Symmetry codes: (i) 1 + *x*, *y* − 1, *z*; (ii) *x*, *y*, 1 + *z*.**Compound (Ib)***Crystal data*

C₁₆H₁₅N₂⁺·I[−]
M_r = 362.20
 Monoclinic, *P*2₁/*c*
a = 7.3189 (17) Å
b = 20.960 (5) Å
c = 10.009 (2) Å
 β = 102.597 (6)°
V = 1498.5 (6) Å³
Z = 4

D_x = 1.605 Mg m^{−3}
 Mo *K*α radiation
 Cell parameters from 4500 reflections
 θ = 2–24°
 μ = 2.13 mm^{−1}
T = 200 (2) K
 Needle, yellow
 0.30 × 0.10 × 0.10 mm

Data collection

Bruker SMART CCD area-detector
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 1998)
T_{min} = 0.568, *T_{max}* = 0.816
 8032 measured reflections

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.048
wR(*F*²) = 0.118
S = 0.82
 3248 reflections
 173 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0588P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.02 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.55 \text{ e } \text{Å}^{-3}$

Table 3

H···I interaction geometry (Å, °) for (Ib).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H2N···I1 ⁱ	0.88	2.79	3.592 (4)	153
C2—H2···I1	0.95	2.94	3.882 (6)	175
C16—H16A···I1 ⁱⁱ	0.98	3.07	3.997 (6)	158
C16—H16C···I1 ⁱⁱⁱ	0.98	3.06	3.931 (6)	149

Symmetry codes: (i) 1 + *x*, *y*, 1 + *z*; (ii) −*x*, −*y*, −*z*; (iii) −*x*, *y* − ½, ½ − *z*.**Compound (II)***Crystal data*

C₁₆H₁₅N₂⁺·I[−]·0.5H₂O
M_r = 370.20
 Monoclinic, *P*2₁/*c*
a = 15.3795 (19) Å
b = 13.8324 (17) Å
c = 14.1690 (17) Å
 β = 100.816 (2)°
V = 2960.7 (6) Å³
Z = 8

D_x = 1.661 Mg m^{−3}
 Mo *K*α radiation
 Cell parameters from 765 reflections
 θ = 2–24°
 μ = 2.16 mm^{−1}
T = 110 (2) K
 Hexagonal prism, yellow
 0.50 × 0.30 × 0.20 mm

Data collection

Bruker SMART CCD area-detector
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 1998)
T_{min} = 0.412, *T_{max}* = 0.672
 30 042 measured reflections

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.051
wR(*F*²) = 0.139
S = 1.05
 6728 reflections
 517 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0966P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 3.86 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.06 \text{ e } \text{Å}^{-3}$

Table 4
H...I interaction geometry (Å, °) for (II).

D—H...A	D—H	H...A	D...A	D—H...A
N2B—H2BN...O1 ⁱ	0.88	2.31	3.072 (9)	145
N2—H2N...I1	0.88	2.66	3.427 (13)	146
N2'—H2'N...I1	0.88	3.11	3.814 (15)	138
N2B—H2BN...I1B ⁱⁱ	0.88	2.99	3.674 (4)	136
C1B—H1B...I1	0.95	3.08	3.965 (5)	156
C5'—H5'...I1B ⁱⁱ	0.95	3.14	3.92 (3)	140
C5B—H5B...I1 ⁱⁱⁱ	0.95	3.06	3.924 (5)	151
C16'—H16E...I1 ^{iv}	0.98	3.58	4.152 (18)	120
C16B—H16H...I1 ^v	0.98	3.05	3.823 (6)	137

Symmetry codes: (i) $-x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iv) $x - 1, y, z$; (v) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

Compound (III)

Crystal data

C₂₂H₂₁N₂⁺I⁻ Z = 4
M_r = 440.31 *D_x* = 1.497 Mg m⁻³
 Triclinic, P1̄ Mo Kα radiation
 a = 7.554 (2) Å Cell parameters from 547 reflections
 b = 16.046 (6) Å
 c = 16.295 (5) Å
 α = 82.27 (3)°
 β = 87.36 (2)°
 γ = 87.42 (3)°
 V = 1953.5 (10) Å³ μ = 1.65 mm⁻¹
 T = 110 (2) K
 Needle, yellow
 0.50 × 0.10 × 0.10 mm

Data collection

Bruker SMART CCD area-detector 8901 independent reflections
 diffractometer 6571 reflections with *I* > 2σ(*I*)
 φ and ω scans *R*_{int} = 0.025
 Absorption correction: multi-scan θ_{max} = 27.5°
 (SADABS; Bruker, 1998) *h* = -9 → 9
*T*_{min} = 0.493, *T*_{max} = 0.853 *k* = -20 → 20
 15 654 measured reflections *l* = -20 → 21

Refinement

Refinement on *F*² H-atom parameters constrained
R[*F*² > 2σ(*F*²)] = 0.041 *w* = 1/[σ²(*F_o*²) + (0.0531*P*)²]
wR(*F*²) = 0.096 where *P* = (*F_o*² + 2*F_c*²)/3
S = 0.91 (Δ/σ)_{max} = 0.002
 8901 reflections Δρ_{max} = 1.76 e Å⁻³
 464 parameters Δρ_{min} = -0.53 e Å⁻³

The accuracy of structure (II) is limited by disorder; modeling of this required the application of extensive distance restraints in the affected region. No sign of disorder was seen for the I and O atoms, for example, in the shapes of their ellipsoids. The residual density of 3.86 e Å⁻³ suggests some further disorder not accommodated by the

Table 5
H...I interaction geometry (Å, °) for (III).

D—H...A	D—H	H...A	D...A	D—H...A
C1—H1...I1	0.95	3.15	3.921 (3)	140
C20—H20C...I1	0.98	3.17	4.100 (4)	159
C5'—H5'...I1 ⁱ	0.95	3.17	3.951 (4)	140
C21'—H21D...I1 ⁱⁱ	0.99	3.15	4.105 (4)	163
C21—H21A...I1 ⁱⁱⁱ	0.99	3.17	4.069 (3)	152
C20—H20A...I1 ⁱ	0.98	2.95	3.911 (4)	168
C6'—H6'...I1 ⁱ	0.95	3.09	4.017 (4)	166
C13'—H13'...I1 ⁱ	0.95	3.11	4.055 (4)	174
C2'—H2'...I1 ⁱⁱ	0.95	3.07	3.970 (5)	159
C6'—H6'...I1 ⁱⁱ	0.95	3.17	4.049 (5)	155
C17'—H17'...I1 ⁱⁱⁱ	0.95	3.11	3.973 (6)	151
C20'—H20F...I1 ⁱⁱⁱ	0.98	2.90	3.806 (5)	154

Symmetry codes: (i) 1 - *x*, 1 - *y*, -*z*; (ii) -*x*, 1 - *y*, 1 - *z*; (iii) *x* - 1, *y*, 1 + *z*.

refinement model, but this peak is located very close (0.05 Å) to I1B. Methyl H atoms were located from difference Fourier syntheses and refined as part of a rigid group, which was allowed to rotate but not tip or distort, and with *U*_{iso}(H) = 1.5*U*_{eq}(C). Other H atoms were placed geometrically and refined using a riding model with *U*_{iso}(H) = 1.2*U*_{eq}(C,N). The following distance restraints were applied: N—H = 0.86, C—H(methyl) = 0.96 and other C—H = 0.93 Å in (Ia); N—H = 0.88, C—H(methyl) = 0.98 and other C—H = 0.95 Å in (Ib) and (II); C—H(methylene) = 0.99, C—H(methyl) = 0.98 and other C—H = 0.95 Å in (III).

For compound (Ia), data collection: P3 (Siemens, 1989); cell refinement: P3; data reduction: XDISK (Siemens, 1991); for compounds (Ib), (II) and (III), data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 1998). For all compounds, program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL97 (Sheldrick, 1997b).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1458). Services for accessing these data are described at the back of the journal.

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