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1-(4-Chloro-2-nitrophenyl)-4,4′-bipyridinium triiodide

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Key indicators

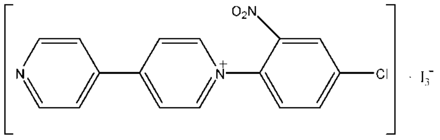
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.018 Å
R factor = 0.069
wR factor = 0.179
Data-to-parameter ratio = 15.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{16}H_{11}ClN_3O_2^+\cdot I_3^-$, consists of a bipyridinium cation and a triiodide anion. The two pyridine rings of the cation are not coplanar, with a dihedral angle of 28.83 (4)°. The benzene ring is also twisted out of the mean plane of the adjoining pyridine ring by 64.27 (5)°. The I_3^- anions are slightly bent and asymmetric, with an I—I—I angle of 178.24 (5)° and I—I bond distances of 2.937 (2) and 2.957 (2) Å. The packing shows a columnar arrangement, with parallel stacks of bipyridinium and I_3^- ions along the b axis.

Comment

Owing to their potential as prototypical electron-transfer reagents (Willner *et al.*, 1990), herbicides (Summers, 1980) and materials for electrochromic displays (ECD) (Bruinink *et al.*, 1977; Yasuda *et al.*, 1987), viologens (N,N'-disubstituted 4,4′-bipyridinium dications) have been extensively studied in the past decade. In order to incorporate the viologen-specific function into a coordination polymer, there have been several viologen derivative ligands prepared by nucleophilic substitution reactions (Ashton *et al.*, 1994). In particular, viologen derivatives which are π-conjugated exhibit photo-electrochemical activity and a change of spin multiplicity upon external stimuli (Iyoda *et al.*, 1999). Their fascinating functions are attracting considerable attention from chemists. We report here the synthesis and structure of a new π-conjugated viologen derivative made up of a bipyridinium cation and a triiodide anion.



(I)

There is one crystallographically independent bipyridinium cation and one crystallographically independent triiodide anion, lying in general positions (Fig. 1). In the crystal structure, the bipyridinium cation is twisted, with an interplanar angle of 28.83 (4)° between the two pyridine rings, and a larger dihedral angle of 64.27 (5)° between the benzene ring and the adjacent pyridine ring. Because of the 2-nitro-4-chlorophenyl substituent on one side of the bipyridine core, the two pyridine rings within the bipyridine nucleus are asymmetric, there are great differences between the corresponding C—N and C—C bond lengths. The N1—C7 [1.366 (2) Å] and N1—C11 [1.371 (2) Å] distances of the substituted pyridine ring are typically longer than N2—C14 [1.333 (18) Å] and N2—C15

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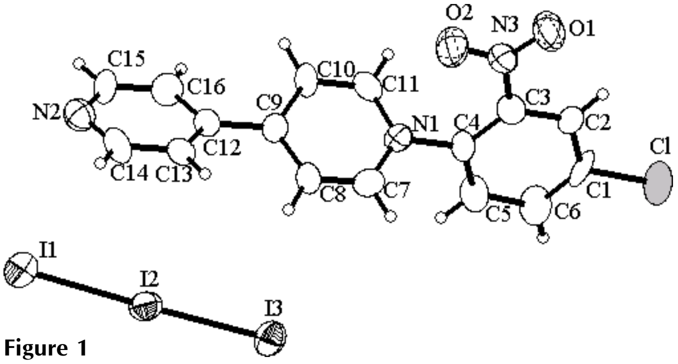

Figure 1
The cation and anion in the structure of the title compound, with the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level.

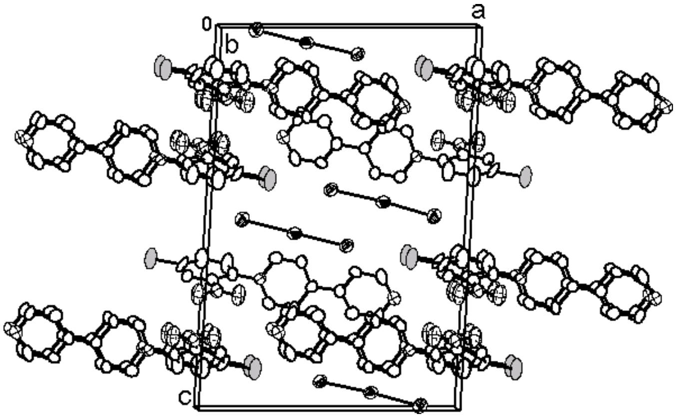

Figure 2
Packing diagram, viewed along the *b* axis. H atoms have been omitted for clarity.

[1.357 (17) Å] of the unsubstituted one, due to the electron delocalization with the nitrophenyl moiety.

The counter-ions appear in the structure in the form of slightly asymmetrical I_3^- ions, which can be described as a donor-acceptor or hypervalent I^-–I_2 interaction. The I—I bond distances in I_3^- are 2.937 (2) and 2.957 (2) Å. The shorter I—I bond distance in this asymmetrical I_3^- ion is longer than in pure iodine [2.666 (2) Å in the gas phase (Karle, 1955) and 2.715 (6) Å in the solid state at 110 K (van Bolhuis *et al.*, 1967)]. This elongation is attributable to the donation of electron density from I^- to the σ*-antibonding LUMO of the I_2 molecule (Blake *et al.*, 1998; Purcell & Kotz, 1977). I_3^- is not exactly linear, the angle I1—I2—I3 being 178.24 (5)°. The packing diagram (Fig. 2) shows a columnar arrangement, with parallel stacks of bipyridinium and I_3^- ions along the *b* axis.

Experimental

2 ml DMF was added to a mixture of 4,4′-bipyridine (1.56 g, 10 mmol) and 2,5-dichloronitrobenzene (0.96 g, 5 mmol), and the solution was refluxed at 403 K under nitrogen for 8 h. The solvent was reduced to a small volume in vacuum, benzene was added, and the precipitate was filtered off and washed with benzene, then dried to afford a brown solid. The brown solid (0.0348 g, 0.1 mmol) was added to a solution of KI (0.066 g, 1 mmol) in water. The resulting yellow solution was allowed to stand at room temperature for several days to form brown block crystals.

Crystal data

$C_{16}H_{11}ClN_3O_2^+\cdot I_3^-$
$M_r = 693.43$
Monoclinic, $P2_1/c$
$a = 13.658$ (3) Å
$b = 7.5018$ (15) Å
$c = 19.936$ (4) Å
$\beta = 93.37$ (3)°
$V = 2039.1$ (7) Å^3
$Z = 4$
$D_x = 2.259$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 210 reflections
$\theta = 1.5$–25.1°
$\mu = 4.74$ mm^{-1}
$T = 293$ (2) K
Block, brown
0.54 × 0.14 × 0.12 mm

Data collection

Siemens SMART CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.455$, $T_{\max} = 0.566$
5930 measured reflections
3492 independent reflections
2394 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$
$\theta_{\max} = 25.1°$
$h = -16 \rightarrow 15$
$k = -8 \rightarrow 8$
$l = -23 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.179$
$S = 1.18$
3492 reflections
226 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2 + 19.8577P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.02$ e Å^{-3}
$\Delta\rho_{\min} = -1.06$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

I2—I3	2.937 (2)	N2—C15	1.357 (17)
I2—I1	2.957 (2)	C7—C8	1.362 (18)
N1—C7	1.366 (16)	C11—C10	1.392 (17)
N1—C11	1.371 (16)	C8—C9	1.397 (18)
N2—C14	1.333 (18)	C10—C9	1.415 (17)
I3—I2—I1	178.24 (5)	N1—C11—C10	119.7 (11)
C7—N1—C11	121.3 (11)	C7—C8—C9	121.1 (12)
C14—N2—C15	116.6 (12)	C11—C10—C9	119.5 (12)
C8—C7—N1	120.1 (12)	C8—C9—C10	118.2 (12)

All H atoms were positioned geometrically and included as riding atoms, with C—H = 0.93 Å. The highest peak and deepest hole are 0.97 Å from I1 and 1.03 Å from I2, respectively.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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