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N,*N*'-Diethyl-4,4'-bipyridinium diiodide

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Abstract

N,*N*'-Diethyl-4,4'-bipyridinium diiodide ([EV]I_2), $C_{14}H_{18}N_2^{2+}\cdot I_2^{-}$, belongs to a class of compounds that are excellent electron acceptors and are used routinely in studies of electron-transfer reactions. In [EV]I_2, closest contacts from iodide to the $[EV]^{2+}$ dication range from 3.77–4.05 Å with the shortest distances to the nitrogen and *ortho*-carbon [I···N = 3.843 (3) and I···C = 3.770 (4) Å].

Comment

Alkyl viologens are excellent electron acceptors and have proven to be valuable in studies of electron-transfer reactions. Recently, we have prepared several viologens, including the title compound (1), *N*,*N*'-diethyl-4,4'-bipyridinium diiodide (referred to as ethyl viologen diiodide or [EV]I_2). Bond distances and angles of the $[EV]^{2+}$ dication are similar to those reported for the methyl viologen diiodide ([MV]I_2) (Russell & Wallwork 1972). In [EV]I_2, each iodide atom is situated 3.80 Å from the ring centroid of a nearby pyridium ring, with shortest iodide contacts to that ring from 4.02–4.05 Å. However, the closest contacts from iodide to the $[EV]^{2+}$ dication range from 3.77–4.05 Å with shortest distances to the nitrogen and *ortho*-carbon [I1···N1(x, $3/2 - y$, $z - 1/2$) =3.843 (3) and I1···C5(x, $3/2 - y$, $z - 1/2$) =3.770 (4) Å]. These results are consistent with the suggestion of Prout & Murray-Rust (1969) that charge-transfer interactions in bipyridinium halide salts favor orientation of a halogen donor orbital toward the nitrogen or adjacent carbon of the bipyridinium. In other words, one would expect the I···N or I···C_{ortho} interactions to be shortest, as observed for [MV]I_2 (I1···N1 = 3.84 and I1···C_{ortho} = 3.67 Å; Russell & Wallwork, 1972).

Experimental

4,4'-Bipyridine (2.02 g) and a slight excess of ethyl iodide were refluxed in 40 ml of CH_3CN for 2.5 h. The bright orange precipitate was filtered off to give 5.78 g (95.4% yield) of [EV]I_2. Crystals suitable for diffraction studies were grown by slow evaporation from CH_3CN. ^{1}H NMR (250 MHz, DMSO-d_6): δ 1.62 (t, 6H, 7 Hz, –CH_3), 4.73 (q, 4H, 7 Hz, –CH_2–), 8.80 (d, 4H, 6 Hz, pyridinium), 9.42 (d, 4H, 6 Hz, pyridinium) p.p.m.; m.p.: 280–285° C (dec.)

Refinement

Unit-cell dimensions were calculated from 40 reflections lying in a θ range of 5–15°. Intensity data were collected using variable speed (2–30° min^{-1}) θ-2θ scans. A decay correction was applied (minimum 0.987, maximum 1.007) based on three standard reflections monitored every 300 reflections. The data were also corrected for Lorentz, polarization and absorption effects. The absorption correction applied was based on measured ψ scans. The structure was solved by direct methods, expanded by the difference Fourier technique and refined by full-matrix least squares on F^2. Positions of the H atoms were calculated based on geometric criteria (C—H = 0.97 Å, 0.96 and 0.93Å for methylene, methyl and aromatic H atoms, respectively), methyl H atoms were calculated after locating at least one directly from the difference map. All H atoms were treated with a riding model. H-atom isotropic displacement parameters were defined as aU(C) where a = 1.5 for methyl and 1.2 for all others.

Computing details

Data collection: P3/P4-PC (Siemens, 1989); cell refinement: P3/P4-PC; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Crystal data

$C_{14}H_{18}N_2^{2+}\cdot 2I^{1-}$	V = 816.4 (3) Å^3
M_r = 468.10	Z = 2
Monoclinic, $P2_1/c$	Mo $K\alpha$
a = 6.1965 (12) Å	μ = 3.84 mm^{-1}
b = 13.025 (3) Å	T = 298 (2) K
c = 10.419 (2) Å	0.50 × 0.45 × 0.30 mm
β = 103.88 (3)°	

Data collection

Siemens P3 diffractometer	1633 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scans (North et al., 1968)	R_{int} = 0.032
T_{min} = 0.168, T_{max} = 0.316	3 standard reflections
2068 measured reflections	every 300 reflections
1899 independent reflections	intensity decay: minimal

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027	82 parameters
$wR(F^2)$ = 0.068	H-atom parameters constrained
S = 1.11	$\Delta\rho_{max}$ = 0.43 e Å^{-3}
1898 reflections	$\Delta\rho_{min}$ = −0.61 e Å^{-3}

Table 1
Selected geometric parameters (Å, °)

C1—N1	1.342 (5)	C4—C5	1.373 (5)
C1—C2	1.364 (5)	C5—N1	1.318 (4)

C2—C3	1.386 (4)	N1—C7	1.489 (4)
C3—C4	1.393 (4)	C7—C8	1.481 (6)
C3—C3^{i}	1.487 (6)		
N1—C1—C2	121.0 (3)	N1—C5—C4	120.8 (3)
C1—C2—C3	119.8 (3)	C5—N1—C1	120.8 (3)
C2—C3—C4	117.5 (3)	C5—N1—C7	119.5 (3)
C2—C3—C3^{i}	120.9 (3)	C1—N1—C7	119.7 (3)
C4—C3—C3^{i}	121.6 (3)	C8—C7—N1	110.8 (3)
C5—C4—C3	120.1 (3)		

Symmetry codes: (i) $-x+1$, $-y+1$, $-z+2$.

References

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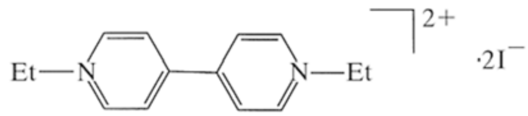
Scheme 1



supplementary materials

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Crystal data

$C_{14}H_{18}N_2^{2+}\cdot 2I^{1-}$	D_x = 1.904 Mg m^{-3}
M_r = 468.10	Melting point: decomposes 280-285°C K
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 6.1965 (12) Å	Cell parameters from 40 reflections
b = 13.025 (3) Å	θ = 5.0–15.0º
c = 10.419 (2) Å	μ = 3.84 mm^{-1}
β = 103.88 (3)º	T = 298 (2) K
V = 816.4 (3) Å^3	Block, orange
Z = 2	0.50 × 0.45 × 0.30 mm
F_{000} = 444	

Data collection

Siemens P3 diffractometer	R_{int} = 0.032
Radiation source: normal-focus sealed tube	θ_{max} = 27.9º
Monochromator: graphite	θ_{min} = 2.6º
T = 298(2) K	h = 0→8
θ–2θ scans	k = 0→17
Absorption correction: ψ scans (North et al., 1968)	l = −13→13
T_{min} = 0.168, T_{max} = 0.316	3 standard reflections
2068 measured reflections	every 300 reflections
1899 independent reflections	intensity decay: minimal
1633 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)]$ = 0.027	H-atom parameters constrained
$wR(F^2)$ = 0.068	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0393P)^2 + 0.4219P]$ where $P = (F_o^2 + 2F_c^2)/3$?
S = 1.11	$(\Delta/\sigma)_{max}$ = −0.001
1898 reflections	$\Delta\rho_{max}$ = 0.43 e Å^{-3}
82 parameters	$\Delta\rho_{min}$ = −0.61 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. A decay correction (min. 0.987, max. 1.007) was applied to the unique reflections based on three standard reflections monitored every 300 reflections.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement on F^2 for ALL reflections except for 1 with very negative F^2 or flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.17762 (3)	0.65401 (2)	0.27396 (2)	0.05198 (10)
C1	0.7453 (6)	0.6353 (3)	0.8426 (3)	0.0482 (7)
H1	0.8774	0.6709	0.8482	0.058*
C2	0.7141 (5)	0.5832 (2)	0.9502 (3)	0.0445 (7)
H2	0.8234	0.5841	1.0289	0.053*
C3	0.5188 (5)	0.5289 (2)	0.9421 (3)	0.0393 (6)
C4	0.3611 (5)	0.5304 (3)	0.8218 (3)	0.0480 (7)
H4	0.2286	0.4944	0.8124	0.058*
C5	0.4010 (6)	0.5850 (3)	0.7172 (3)	0.0493 (7)
H5	0.2946	0.5860	0.6373	0.059*
N1	0.5885 (5)	0.6359 (2)	0.7286 (3)	0.0430 (6)
C7	0.6294 (6)	0.6922 (3)	0.6123 (4)	0.0543 (8)
H7A	0.4884	0.7109	0.5535	0.065*
H7B	0.7108	0.7549	0.6417	0.065*
C8	0.7580 (8)	0.6281 (4)	0.5398 (4)	0.0730 (12)
H8A	0.7826	0.6657	0.4654	0.109*
H8B	0.6764	0.5665	0.5095	0.109*
H8C	0.8985	0.6104	0.5976	0.109*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.04380 (14)	0.04802 (14)	0.0596 (2)	0.00150 (9)	0.00344 (10)	−0.00390 (9)
C1	0.045 (2)	0.048 (2)	0.051 (2)	−0.0115 (13)	0.0103 (14)	−0.0047 (13)
C2	0.043 (2)	0.046 (2)	0.0424 (15)	−0.0111 (13)	0.0062 (12)	−0.0062 (12)
C3	0.0393 (14)	0.0343 (13)	0.0447 (15)	−0.0025 (11)	0.0109 (11)	−0.0079 (12)
C4	0.0369 (14)	0.051 (2)	0.053 (2)	−0.0070 (13)	0.0053 (12)	0.0013 (14)
C5	0.0405 (15)	0.053 (2)	0.051 (2)	−0.0037 (14)	0.0031 (13)	0.0021 (14)
N1	0.0450 (14)	0.0384 (13)	0.0456 (14)	−0.0004 (10)	0.0110 (11)	−0.0016 (10)

C7	0.061 (2)	0.048 (2)	0.052 (2)	−0.004 (2)	0.009 (2)	0.0099 (15)
C8	0.078 (3)	0.083 (3)	0.066 (2)	0.009 (2)	0.032 (2)	0.016 (2)

Geometric parameters (Å, °)

C1—N1	1.342 (5)	C4—C5	1.373 (5)
C1—C2	1.364 (5)	C5—N1	1.318 (4)
C2—C3	1.386 (4)	N1—C7	1.489 (4)
C3—C4	1.393 (4)	C7—C8	1.481 (6)
C3—C3^{i}	1.487 (6)		
N1—C1—C2	121.0 (3)	N1—C5—C4	120.8 (3)
C1—C2—C3	119.8 (3)	C5—N1—C1	120.8 (3)
C2—C3—C4	117.5 (3)	C5—N1—C7	119.5 (3)
C2—C3—C3^{i}	120.9 (3)	C1—N1—C7	119.7 (3)
C4—C3—C3^{i}	121.6 (3)	C8—C7—N1	110.8 (3)
C5—C4—C3	120.1 (3)		
N1—C1—C2—C3	0.8 (5)	C4—C5—N1—C1	0.3 (5)
C1—C2—C3—C4	0.0 (5)	C4—C5—N1—C7	178.5 (3)
C1—C2—C3—C3^{i}	179.7 (3)	C2—C1—N1—C5	−0.9 (5)
C2—C3—C4—C5	−0.5 (5)	C2—C1—N1—C7	−179.1 (3)
C3^{i}—C3—C4—C5	179.7 (3)	C5—N1—C7—C8	−94.6 (4)
C3—C4—C5—N1	0.4 (5)	C1—N1—C7—C8	83.5 (4)

Symmetry codes: (i) $-x+1$, $-y+1$, $-z+2$.