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trans-4-[*p*-(*N*,*N*-Diethylamino)styryl]-*N*-methylpyridinium triiodide

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The title compound, $C_{18}H_{23}N_2^+\cdot I_3^-$, was obtained from the reaction of *trans*-4-[*p*-(*N*,*N*-diethylamino)styryl]–*N*-methylpyridinium iodide (DEASPI) and 12-tungstophosphate ($H_3PW_{12}O_{40}$) in ethanol. The compound contains the highly π-conjugated cation $C_{18}H_{23}N_2^+$, in which the pyridyl ring makes a dihedral angle of 4.14 (3)° with the benzene ring. The I_3^- counter-ion is roughly linear [I—I—I = 177.50 (2)°] and the I—I distances are 2.9478 (8) and 2.8849 (8) Å. Adjacent I_3^- anions are connected into I_6^{2-} dimers *via* an I···I contact of 3.852 (8) Å, much shorter than the sum of the van der Waals radii of 4.30 Å.

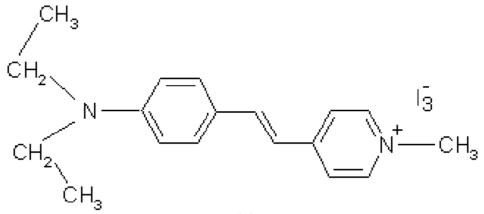
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.011 Å
R factor = 0.043
wR factor = 0.100
Data-to-parameter ratio = 18.3

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

Comment

trans-4-[*p*-(*N*,*N*-Diethylamino)styryl]-*N*-methylpyridinium iodide (DEASPI) has been claimed to have two-photon absorption properties and its two-photon up-conversion efficiency is as high as 10.7% at 2.14 mJ input energy, which is among the largest efficiencies for laser dyes with such a high up-conversion efficiency (Wang *et al.*, 2000). Wang and co-workers have synthesized a series of analogous π-conjugated chromophores and studied systematically the relationships between structure and two-photon properties (Wang, Zhou, Wang *et al.*, 2001; Wang, Zhou, Yu *et al.*, 2001; Wang *et al.*, 2002). However, they have not examined the effects of counter-anions. On the other hand, Marder and co-workers have claimed that finding the correct counter-ions of ionic chromophores in the crystal structure may be a promising approach for the synthesis of new materials with large bulk optical nonlinearities (Marder *et al.*, 1990). Furthermore, DEASPI is a potentially interesting building block for some synthetic metals (Zuo *et al.*, 1995).



(I)

According to the concept of 'molecular engineering', we have designed and synthesized *trans*-4-[*p*-(*N*,*N*-diethylamino)styryl]-*N*-methylpyridinium triiodide (DEASPTI), (I), which can also be regarded as DEAPSI molecularly doped with iodine. This paper deals with the preparation and crystal structure of (I).

The crystal structure determination indicates that, in the title cation (Fig. 1), the pyridyl ring makes a dihedral angle of

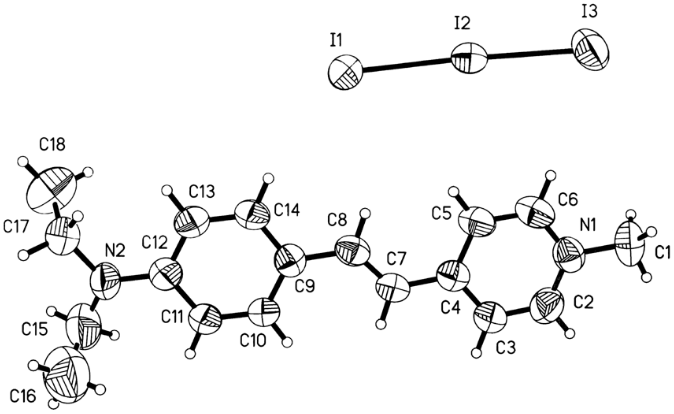


Figure 1
The structure and atom-numbering scheme of the $C_{18}H_{23}N_2^+$ cation and I_3^- anion. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

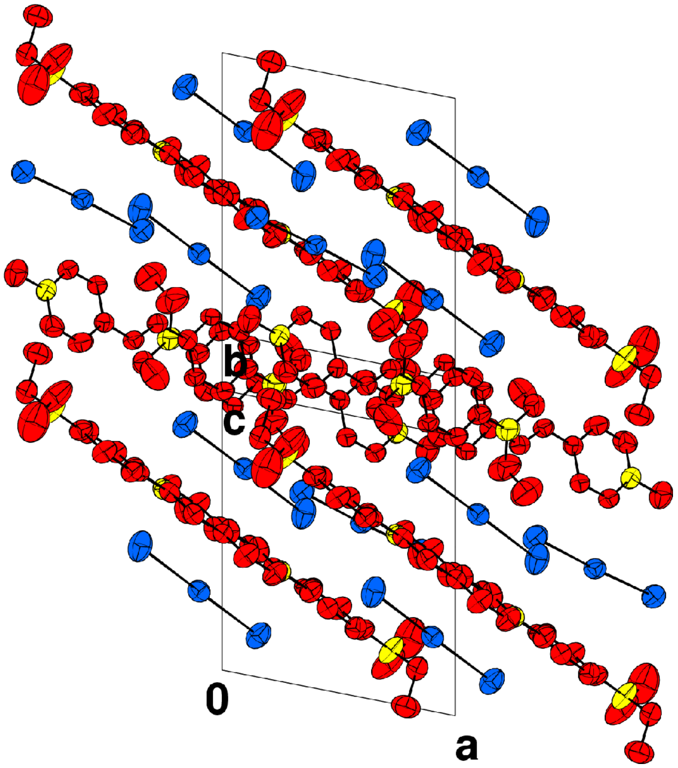


Figure 2
The unit-cell contents, viewed down $[0\bar{2}1]$. This view shows the parallel alignment of the cations and anions.

4.14 (3)° with the benzene ring. The maximum deviations for the non-H atoms from the mean planes of the pyridyl and benzene rings are 0.009 (7) Å for N1 and 0.014 (8) Å for C12, respectively. The near planarity of the backbone of (I) contributes to the high π-conjugation of the whole molecule in the excited state, a necessary condition for two-photon absorption and up-converted fluorescence (Wang, Zhou, Yu *et al.*, 2001).

The I_3^- ion (Fig. 1) is essentially linear [I—I—I = 177.50 (2)°] and the I—I bond lengths [2.9478 (8) and 2.8849 (8) Å] are similar to those found in $C_{20}H_{20}P^+$ salts (Bélanger & Beauchamp, 1993). The difference between the I—I distances, although statistically very significant, is still relatively small; differences of greater than 0.2 Å are observed in compounds where hydrogen bonding and/or strong interionic $I\cdots I$ interactions are found (Tebbe *et al.*, 1985). The I_3^- ions in the title salt are not totally independent; neighbouring ions are connected into I_6^{2-} dimers *via* an $I1\cdots I3^{i}$ contact of 3.852 (8) Å [(i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$], much shorter than the sum of the van der Waals radii of 4.30 Å (Cotton & Wilkinson, 1988). The closest approach of two dimers is 7.324 (9) Å.

In the crystal structure, the cations and I_3^- anions form an interleaved layer arrangement along [103] (Fig. 2), and the shortest distance between the layers (including H atoms) is 3.165 Å. I_3^- anions act as interstitial species at specific sites. The cations of (I) form head-to-tail chains and the nearest chains (2.859 Å apart, including H atoms) have an antiparallel alignment. The crystal structure also reveals that half of the cations are parallel to (378) and the other half are parallel to $(\bar{3}7\bar{8})$.

Experimental

Compound (I) was prepared by reacting a 0.01 mol l^{-1} DEASPI/ethanol solution and a 0.01 mol l^{-1} $H_3PW_{12}O_{40}\cdot 24H_2O$/ethanol solution in a 3:1 molar ratio. The precipitate, a charge-transfer salt between DEASPI and $H_3PW_{12}O_{40}$, was filtered off. On evaporation of the filtrate, brilliant dark-red rod-shaped crystals were obtained, which could be mproved by recrystallization. The remarkable feature of this redox reaction is its convenience and the fact that the structure of the cation is approximately preserved.

Crystal data

$C_{18}H_{23}N_2^+\cdot I_3^-$
M_r = 648.08
Monoclinic, $P2_1/n$
a = 8.8560 (8) Å
b = 17.4364 (19) Å
c = 14.463 (2) Å
β = 105.457 (9)°
V = 2152.6 (4) Å^3
Z = 4
D_x = 2.000 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 35 reflections
θ = 4.9–12.0°
μ = 4.36 mm^{-1}
T = 293 (2) K
Prism, dark red
0.23 × 0.21 × 0.18 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*XSCANS*; Bruker, 1996)
$T_{\min}$ = 0.372, $T_{\max}$ = 0.455
4912 measured reflections
3798 independent reflections
2565 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.025
$\theta_{\max}$ = 25.0°
$h = -10 \rightarrow 1$
$k = -20 \rightarrow 1$
$l = -16 \rightarrow 17$
3 standard reflections every 97 reflections intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.100
S = 1.04
3798 reflections
208 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 2.6762P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.78 e Å^{-3}
$\Delta\rho_{\min}$ = −0.86 e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

C1—N1	1.470 (9)	C10—C11	1.349 (10)
C2—N1	1.335 (9)	C11—C12	1.419 (10)
C2—C3	1.378 (10)	C12—N2	1.395 (9)
C3—C4	1.387 (10)	C12—C13	1.395 (10)
C4—C5	1.393 (9)	C13—C14	1.365 (9)
C4—C7	1.439 (9)	C15—N2	1.472 (11)
C5—C6	1.378 (10)	C15—C16	1.504 (16)
C6—N1	1.345 (9)	C17—N2	1.462 (9)
C7—C8	1.334 (9)	C17—C18	1.518 (11)
C8—C9	1.455 (9)	I1—I2	2.9478 (8)
C9—C10	1.392 (9)	I2—I3	2.8849 (8)
C9—C14	1.406 (9)		
N1—C2—C3	120.9 (7)	N2—C12—C13	123.7 (7)
C2—C3—C4	121.1 (7)	N2—C12—C11	120.8 (7)
C3—C4—C5	116.4 (7)	C13—C12—C11	115.5 (7)
C3—C4—C7	120.5 (6)	C14—C13—C12	122.7 (7)
C5—C4—C7	123.0 (7)	C13—C14—C9	120.7 (6)
C6—C5—C4	120.6 (7)	N2—C15—C16	108.0 (9)
N1—C6—C5	121.0 (7)	N2—C17—C18	114.5 (7)
C8—C7—C4	125.1 (6)	C2—N1—C6	119.8 (7)
C7—C8—C9	127.5 (7)	C2—N1—C1	119.9 (7)
C10—C9—C14	117.2 (6)	C6—N1—C1	120.2 (7)
C10—C9—C8	124.0 (7)	C12—N2—C17	119.4 (6)
C14—C9—C8	118.8 (6)	C12—N2—C15	119.7 (7)
C11—C10—C9	121.7 (7)	C17—N2—C15	117.9 (7)
C10—C11—C12	122.2 (7)	I3—I2—I1	177.50 (2)
N1—C2—C3—C4	0.9 (13)	C11—C12—C13—C14	2.4 (11)
C2—C3—C4—C5	−0.3 (12)	C12—C13—C14—C9	−1.0 (11)
C2—C3—C4—C7	178.5 (7)	C10—C9—C14—C13	−0.9 (10)
C3—C4—C5—C6	0.6 (11)	C8—C9—C14—C13	178.4 (6)
C7—C4—C5—C6	−178.2 (7)	C3—C2—N1—C6	−1.7 (12)
C4—C5—C6—N1	−1.5 (11)	C3—C2—N1—C1	178.7 (8)
C3—C4—C7—C8	179.8 (7)	C5—C6—N1—C2	2.0 (11)
C5—C4—C7—C8	−1.4 (11)	C5—C6—N1—C1	−178.4 (7)
C4—C7—C8—C9	−179.4 (6)	C13—C12—N2—C17	−5.3 (12)
C7—C8—C9—C10	−3.2 (11)	C11—C12—N2—C17	172.7 (7)
C7—C8—C9—C14	177.6 (7)	C13—C12—N2—C15	154.6 (8)
C14—C9—C10—C11	1.3 (11)	C11—C12—N2—C15	−27.5 (12)
C8—C9—C10—C11	−177.9 (7)	C18—C17—N2—C12	87.8 (10)
C9—C10—C11—C12	0.2 (12)	C18—C17—N2—C15	−72.4 (10)
C10—C11—C12—N2	179.9 (8)	C16—C15—N2—C12	100.6 (10)
C10—C11—C12—C13	−2.0 (11)	C16—C15—N2—C17	−99.3 (10)
N2—C12—C13—C14	−179.5 (7)		

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for methyl H atoms and 1.2$U_{\rm eq}$(C) for the other H atoms.

Data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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