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N,*N*-Dimethyl-5-dimethylamino-3-(1-pyrrolyl)-2,4-pentadieniminium tetrafluoroborate

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In the crystal structure of the title salt, $C_{13}H_{20}N_3^+\cdot BF_4^-$, the asymmetric unit has two independent cations and anions. The cations have similar markedly non-planar pentamethinecyanine moieties with a *trans–cis–cis–trans* conformation of the pentamethinecyanine NC_5N chain. The pyrrole substituents are rotated 21.14 (9) and 23.43 (19)° from planarity with the adjacent atoms in the pentamethinecyanine chains.

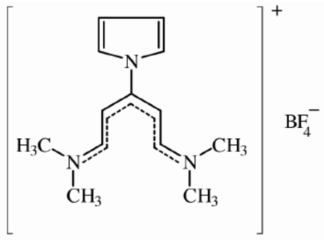
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
Disorder in solvent or counterion
R factor = 0.061
wR factor = 0.220
Data-to-parameter ratio = 10.9

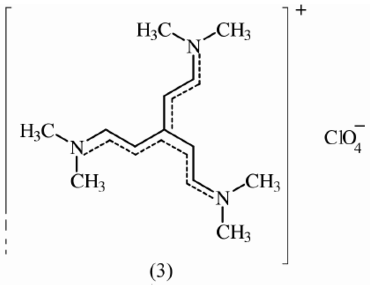
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

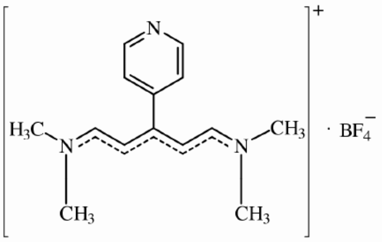
The title salt, (1), containing the relatively electron-rich 1-pyrrolyl substituent was prepared in order to determine what effect the 1-pyrrolyl substitution would have on the conformation of the pentamethinecyanine moiety of the cation.



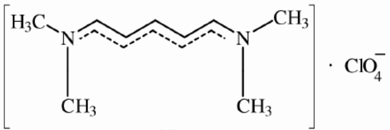
(1)



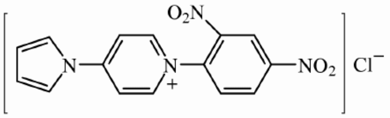
(3)



(2)



(4)



(5)

There are two independent cations and anions in the asymmetric unit of (1) with each of the anions disordered over two sites. The pentamethinecyanine moieties in the cations (Figs. 1 and 2) have similar, markedly non-planar, *trans–cis–cis–trans* conformations, with torsion angles $Cn1—Cn2—Cn3—Cn4$ and $Cn2—Cn3—Cn4—Cn5$ having values −22.8 (6), −30.7 (6), and −27.2 (6) and −26.4 (6)° for n = 1 and 2, respectively. It is interesting to compare these conformations with those found for the pentamethinecyanine moieties in 5-dimethylamino-*N*,*N*-dimethyl-3-(4-pyridyl)-2,4-pentadieniminium tetrafluorobate [(2); all-*trans*; Ferguson *et al.*, 2001] and in tris(2-dimethylaminoethenyl)methylium per-

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chlorate [(3); *trans–trans–cis–trans*; Dale *et al.*, 1988]. In (2), the relatively electron-poor 4-pyridyl substitutent is not conjugated with the pentamethinecyanine, and these two moieties form a dihedral angle of 60.58 (9)°. In (3), which may be regarded as a pentamethinecyanine carrying an electron-rich 2-dimethylaminoethenyl substituent at the central carbon, conjugative interaction results in a change in the conformation of the pentamethincyanine moiety in order to avoid a potentially severe steric interaction between C1—H (or C5—H) and C2—H of the 2-dimethylaminoethenyl substituent. In addition, the cation in (3), which has a threefold symmetry axis, is not planar but adopts a twisted-propeller shape.

In spite of their different conformations, bond lengths within the pentamethinecyanine moiety of (1) do not differ significantly from those reported for the all-*trans* pentamethinecyanine moieties in the simple parent salt (4) (Honda *et al.*, 1986) and the 3-(4-pyridyl) derivative (2) (Ferguson *et al.*, 2001). The bond lengths within the 1-pyrrolyl substituent of (1) are very similar to those reported (Ferguson & McAlees, 1990) for the 1-pyrrolyl fragment in the pyridinium salt (5), consistent with direct conjugation between the relatively electron-rich 1-pyrrolyl substituent and the electron-poor pentamethinecyanine and pyridinium moieties in (1) and (5), respectively. Such conjugation is also suggested by the relatively short bond between the pyrrole and pentamethinecyanine moieties [C13—N13 1.399 (5) Å and C23—N23 1.409 (5) Å]. With the pentamethinecyanine chain in the all-*trans* conformation, coplanarity with the pyrrole would result in severe steric interactions between the pyrrole α-H atoms and C1—H and C5—H. These and other interactions are avoided in (1) by adoption of the *trans–cis–cis–trans* conformation along with out-of-plane twisting as found for (3) (Dale *et al.*, 1988).

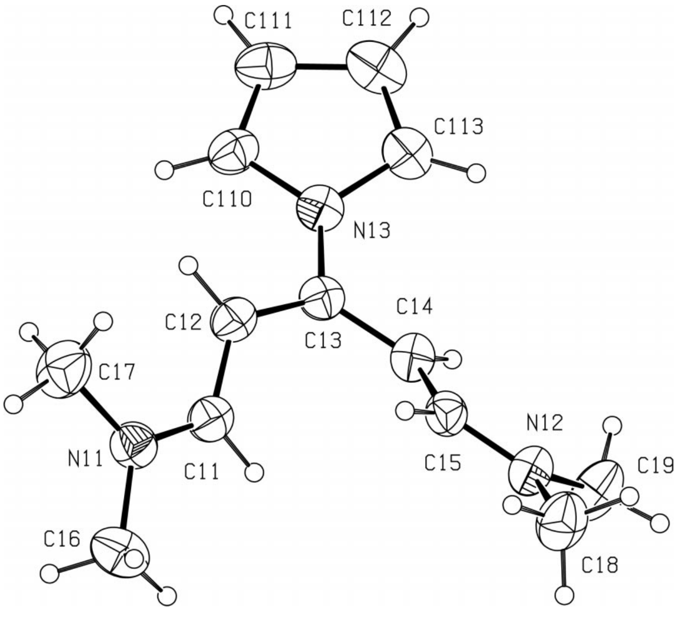

Figure 1
View of one of the two independent cations of (1) with our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

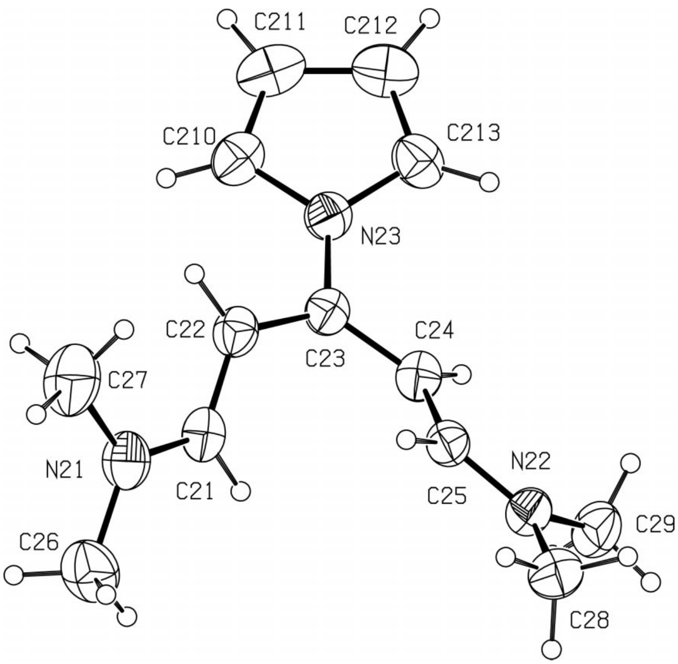

Figure 2
Views of the second of the two independent cations of (1) with our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

A solution of dimethylamine (0.98 g, 22 mmol) in ethanol (7 ml) was added to a suspension of *N*-(2,4-dinitrophenyl)-4-(1-pyrrolyl)-pyridinium chloride [(5); 3.47 g, 10.0 mmol; Ferguson & McAlees, 1990] in ethanol (20 ml) and the mixture was stirred at ambient temperature for 16 h. The resulting mixture was filtered, and the collected green–yellow powder (2,4-dinitroaniline) was washed with ethanol (3 × 10 ml). The combined filtrate and washings were evaporated *in vacuo* to leave a clear orange gum which was taken up in water (50 ml) and filtered to remove yellow insoluble material. The aqueous filtrate was then washed with chloroform (3 × 25 ml) and treated with an aqueous solution (10 ml) of $NaBF_4$ (1.2 g, 11.0 mmol). The resulting mixture was extracted with dichloromethane (3 × 30 ml), the combined extracts were dried (Na_2SO_4) and the solvent was evaporated to leave an orange–red gum. Crystallization from ethanol gave yellow hexagonal plates of (1) (2.32 g, 76% yield; m.p. 397.5–398.5 K).

Crystal data

$C_{13}H_{20}N_3^+\cdot BF_4^-$
$M_r = 305.13$
Monoclinic, $P2_1/c$
$a = 14.882$ (3) Å
$b = 10.366$ (2) Å
$c = 24.064$ (3) Å
$\beta = 121.987$ (11)°
$V = 3148.7$ (10) Å^3
$Z = 8$

$D_x = 1.287$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.4$–12.8°
$\mu = 0.11$ mm^{-1}
$T = 293$ (1) K
Plate, yellow
0.43 × 0.43 × 0.30 mm

Data collection

Nonius CAD-4 diffractometer
θ–2θ scans
5728 measured reflections
4505 independent reflections
2271 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\rm max} = 25.0°$

$h = -17 \rightarrow 15$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 28$
3 standard reflections
frequency: 120 min
intensity decay: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.220$
$S = 1.09$
4505 reflections
414 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1129P)^2 + 0.6033P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.45$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0060 (12)

Table 1
Selected geometric parameters (Å, °).

N11—C11	1.310 (5)	N21—C21	1.310 (5)
N11—C16	1.447 (5)	N21—C26	1.452 (6)
N11—C17	1.444 (6)	N21—C27	1.444 (6)
N12—C15	1.308 (5)	N22—C25	1.316 (5)
N12—C18	1.455 (5)	N22—C28	1.462 (5)
N12—C19	1.454 (6)	N22—C29	1.461 (5)
N13—C13	1.399 (5)	N23—C23	1.409 (5)
N13—C110	1.390 (5)	N23—C210	1.387 (5)
N13—C113	1.390 (5)	N23—C213	1.368 (5)
C11—C12	1.387 (6)	C21—C22	1.381 (5)
C12—C13	1.389 (6)	C22—C23	1.389 (5)
C13—C14	1.396 (5)	C23—C24	1.387 (6)
C14—C15	1.374 (5)	C24—C25	1.383 (5)
C110—C111	1.345 (6)	C210—C211	1.343 (6)
C111—C112	1.417 (7)	C211—C212	1.406 (7)
C112—C113	1.330 (6)	C212—C213	1.359 (6)
N11—C11—C12—C13	174.6 (4)	N21—C21—C22—C23	171.4 (4)
C11—C12—C13—C14	−22.8 (6)	C21—C22—C23—C24	−27.2 (6)
C12—C13—C14—C15	−30.7 (6)	C22—C23—C24—C25	−26.4 (6)
C13—C14—C15—N12	−179.3 (4)	C23—C24—C25—N22	175.6 (4)

Compound (1) crystallized in the monoclinic system; space group $P2_1/c$ from the systematic absences. H atoms were treated as riding atoms with C—H 0.93 and 0.96 Å. Difference maps showed that methyl H atoms at C17, C19 and C29 were disordered and they were modelled using six H sites, each with occupancy 0.50, mutually offset by 60°. The H atoms of the other methyl groups were modelled with free rotation about the relevant C—C bond. It was also apparent that the F atoms of the BF_4^- ions were disordered over major and minor occupancy sites with common B atoms. The geometry of these tetrahedral BF_4^- anions was restrained to be near to tetrahedral by use of *DFIX* commands with an overall restrained B—F distance. The minor occupancy F atoms were allowed for with overall isotropic displacement parameters.

Data collection: *CAD*-4-*PC Software* (Nonius, 1992); cell refinement: *SET*4 and *CELDIM* (Nonius, 1992); data reduction: *HELENA* in *PLATON* (Spek, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON*; software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PREP*8 (Ferguson, 1998).

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