

***trans*-4-[4-(Dimethylamino)phenyl-
iminomethyl]-*N*-phenylpyridinium
hexafluorophosphate**Benjamin J. Coe,^{a*} James A. Harris,^a Thomas Gelbrich^b
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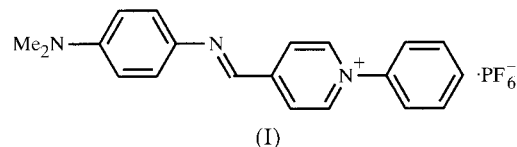
The crystal structure of the dipolar chromophoric title compound, $C_{20}H_{20}N_3^+ \cdot PF_6^-$, is described. The phenylene and pyridyl rings are almost coplanar [dihedral angle $7.5(2)^\circ$], but the phenyl substituent forms a dihedral angle of $56.6(1)^\circ$ with the pyridyl ring. The compound crystallizes in the non-centrosymmetric space group *Cc* and is a likely candidate for the display of quadratic non-linear optical effects.

Comment

The discovery of new molecular materials possessing non-linear optical (NLO) properties is crucial for the development of future optoelectronic and photonic devices (Bosshard *et al.*, 1995; Chemla & Zyss, 1987; Nalwa & Miyata, 1997). It is well established that the creation of efficient quadratic NLO materials requires the optimization of both molecular and bulk properties. The majority of promising candidates consist of dipolar donor- π -acceptor (*D*- π -*A*) molecules which must exist in a non-centrosymmetric macroscopic arrangement if quadratic NLO effects, such as frequency doubling (second harmonic generation, SHG), are to be observed.

Although NLO organics are usually neutral molecules, various charged compounds also exhibit NLO behaviour. Hemicyanine dyes, such as the *p*-toluenesulfonate salt of *trans*-4'-(dimethylamino)-*N*-methyl-4-stilbazolium (DAST), are particularly attractive for quadratic NLO applications (Marder *et al.*, 1989, 1994). The NLO properties of related Schiff base chromophores such as *trans*-4-[4-(dimethylamino)phenyliminomethyl]-*N*-methylpyridinium have also been studied (Coradin *et al.*, 1996). We have recently found that the molecular quadratic NLO responses of *N*-aryl-stilbazolium chromophores are larger than those of their *N*-methyl counterparts (Coe *et al.*, 2000). Hence, dipolar *N*-arylpyridinium Schiff base derivatives are also of interest as potential novel NLO materials. The title compound, (I), was

synthesized by a base-catalyzed condensation reaction of *N*-phenylpicolinium chloride hydrate [prepared from the reaction of picoline with 2,4-dinitrochlorobenzene, followed by treatment with aniline, according to a procedure previously published by Coe *et al.* (1998)] with *N,N'*-dimethyl-4-nitroso-aniline, and its structure is presented here.

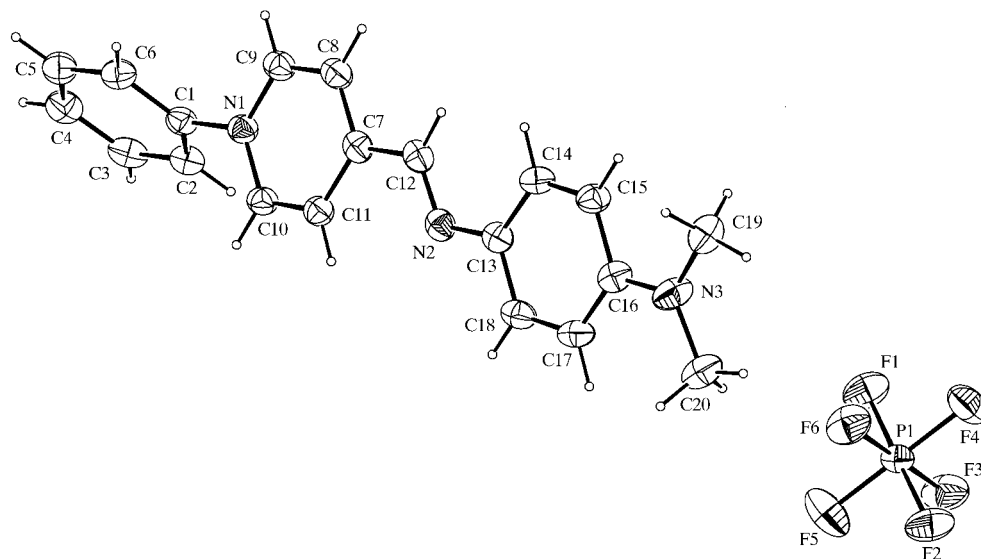


The cation in (I) is a *D*- π -*A* molecule and shows an intense visible absorption band at $\lambda_{\max} = 534$ nm in acetonitrile. By comparison with existing related molecules, this band is ascribed to a $\pi \rightarrow \pi^*$ intramolecular charge transfer (ICT) from the highest occupied molecular orbital (primarily localized on the electron-rich NMe_2 group) to the lowest unoccupied molecular orbital, localized on the electron-deficient pyridinium unit. Such low-energy ICT bands are typically associated with large molecular quadratic NLO responses (Bosshard *et al.*, 1995; Chemla & Zyss, 1987; Nalwa & Miyata, 1997). The ICT band in (I) is red-shifted by *ca* 0.14 eV, but is roughly half as intense when compared with the corresponding absorption in *trans*-4'-(dimethylamino)-*N*-phenyl-4-stilbazolium hexafluorophosphate (Coe *et al.*, 2000; data in acetonitrile).

The molecular structure of the cation in (I) is as indicated by ¹H NMR spectroscopy, with the phenylene and pyridyl rings adopting the expected *trans* disposition about the iminomethyl group. The small dihedral angle of $7.5(2)^\circ$ defined by the ring planes C13-C18 and N1/C7-C11 is consistent with substantial π -electronic coupling through the *D*- π -*A* framework. The phenyl substituent is twisted with respect to the pyridyl ring, with a dihedral angle of $56.6(1)^\circ$ between the planes N1/C7-C11 and C1-C6. As expected, the dipolar cation in (I) shows some evidence for polarization in the ground state, both the pyridyl and phenylene rings being partially quinoidal. For example, the average of the distances C14-C15 and C17-C18 is *ca* 0.03 Å less than the average of the other phenylene C-C distances. Also, N3-C16 shows appreciable double-bond character, being *ca* 0.08 Å shorter than N1-C1.

To the best of our knowledge, no crystallographic studies of purely organic compounds closely related to (I) have been reported previously. The only structures containing 4-[(4-*R*-phenyl)iminomethyl]-*N*-*R'*-pyridinium fragments (*R* and *R'* are any substituent) are cluster complexes of Rh (Lahoz *et al.*, 1991) or Os (Wong *et al.*, 1995, 1996). The geometric parameters of the diaryl Schiff base unit in (I) are similar to those found in [Os₃(μ -H)₂(CO)₉(μ_3 -CNC₅H₄CH=NC₆H₄-4-O-*n*-C₁₆H₃₃)] (Wong *et al.*, 1996).

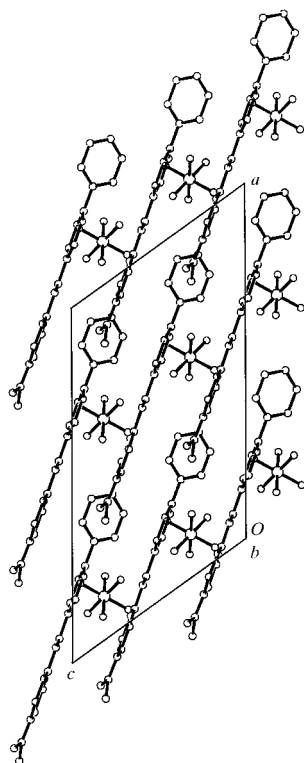
The crystal packing structure of (I) is of primary importance in relation to quadratic NLO properties. The well studied compound DAST crystallizes in the non-centrosymmetric space group *Cc* and is highly SHG active (Marder *et al.*, 1989). Although the presence of *p*-toluenesulfonate anions generally


Figure 1

A representation of the molecular structure of (I), with 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

appears to encourage stilbazolium salts to adopt packing motifs favourable for quadratic NLO effects (Marder *et al.*, 1994), the PF_6^- salt (I) also crystallizes in *Cc*.

The pseudo-planar *trans*-4-[4-(dimethylamino)phenylimino-methyl]pyridinium portions of the cations of (I) align head-


Figure 2

A crystal packing diagram for (I), viewed along the *b* axis.

to-tail and stack in an essentially parallel fashion, forming polar sheets within a macroscopically polar structure. The plane of the pyridinium ring (N1/C7–C11) in a given molecule and the phenylene ring plane (C13–C18) in the adjacent molecule generated by the symmetry operation $(x, 1 - y, z + \frac{1}{2})$ form an angle of 1.5° with an interplanar separation of 3.29 \AA , suggestive of π -stacking interactions. The PF_6^- anions lie in between the cationic sheets and are located close to the electron-deficient pyridinium moieties. The shortest intermolecular contact involving the PF_6^- anion is $\text{C9}-\text{H}\cdots\text{F3}(x, y + 1, z - 1)$, with $\text{H}\cdots\text{F3} = 2.43 \text{ \AA}$. The anions are arranged in channels which run parallel to the *c* axis. Similar packing structures

have been observed in DAST and related compounds, in which it has been suggested that the intervening anions act to reduce dipole–dipole interactions which would otherwise cause the polar cationic sheets to align antiparallel (Marder *et al.*, 1989, 1994).

In (I), the angle θ_m between the dipolar axis (approximated as the N1–N3 vector) and the crystallographic *b* axis is 74.33° . The optimal θ_m value for SHG phase matching in the *m* symmetry point group is 35.26° (Zyss & Oudar, 1982). Hence, although the structure is not optimized for SHG, it is anticipated that (I) will exhibit substantial bulk quadratic NLO effects, especially electro-optic behaviour.

Experimental

A solution of *N*-phenylpicolinium chloride hydrate (220 mg, 0.878 mmol), *N,N'*-dimethyl-4-nitrosoaniline (Aldrich; 219 mg, 1.458 mmol) and piperidine (Lancaster Synthesis; 2 drops) in methanol (Merck; 15 ml) was heated under reflux for 1.5 h. The resulting purple solution was reduced to dryness on a rotary evaporator. The crude chloride salt was metathesized to the PF_6^- salt by precipitation from water/aqueous NH_4PF_6 (Acros) and purified by column chromatography [silica gel, 70–230 mesh (Aldrich), acetone (Merck)/dichloromethane (Merck) 1:10], followed by precipitation from acetone/diethyl ether (yield 59 mg, 14%). Analysis calculated for $\text{C}_{20}\text{H}_{20}\text{F}_6\text{N}_3\text{P}$: C 53.69, H 4.51, N 9.39%; found: C 53.99, H 4.57, N 9.21%. Spectroscopic analysis, ^1H NMR (200 MHz, CD_3CN , δ , p.p.m.): 9.31 (2H, *d*, $J = 7.0$ Hz, $\text{C}_3\text{H}_4\text{N}$), 9.07 (1H, *s*, CH), 8.66 (2H, *d*, $J = 7.0$ Hz, $\text{C}_3\text{H}_4\text{N}$), 8.01–7.96 (2H, *m*, Ph), 7.84–7.79 (3H, *m*, Ph), 7.61 (2H, *d*, $J = 9.1$ Hz, C_6H_4), 6.87 (2H, *d*, $J = 9.2$ Hz, C_6H_4), 3.11 (6H, *s*, NMe_2); MS, *m/z*: 302: $[\text{M}-\text{PF}_6^-]^+$; $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{ dm}^3$): 534 (32,900), 284 (16,500). Crystals of (I) suitable for single-crystal X-ray diffraction measurements were obtained by slow evaporation of an acetonitrile (Rathburn) solution at room temperature.

Crystal data

C₂₀H₂₀N₃⁺·PF₆⁻M_r = 447.36

Monoclinic, Cc

a = 19.3044 (4) Å

b = 10.6009 (3) Å

c = 11.6549 (3) Å

β = 125.527 (2)°

V = 1941.10 (8) Å³

Z = 4

D_x = 1.531 Mg m⁻³

Mo Kα radiation

Cell parameters from 3729 reflections

θ = 2.9–40.2°

μ = 0.210 mm⁻¹

T = 150 (2) K

Block, black

0.1 × 0.1 × 0.1 mm

Data collection

Nonius KappaCCD area-detector diffractometer

φ scans and ω scans to fill Ewald sphere

Absorption correction: multi-scan (SORTAV; Blessing, 1995)

T_{min} = 0.979, T_{max} = 0.979

6150 measured reflections

1909 independent reflections (with 1331 Friedel-related reflections)

2945 reflections with I > 2σ(I)

R_{int} = 0.028θ_{max} = 25.98°

h = -23 → 23

k = -12 → 13

l = -13 → 12

Refinement

Refinement on F²R[F² > 2σ(F²)] = 0.036wR(F²) = 0.092

S = 0.998

3240 reflections

292 parameters

H-atom parameters constrained

w = 1/[σ²(F_o²) + (0.0611P)²]where P = (F_o² + 2F_c²)/3(Δ/σ)_{max} < 0.001Δρ_{max} = 0.22 e Å⁻³Δρ_{min} = -0.21 e Å⁻³

Extinction correction: SHELXL97

(Sheldrick, 1997)

Extinction coefficient: 0.0126 (13)

Absolute structure: Flack (1983)

Flack parameter = 0.01 (9)

Table 1

Selected geometric parameters (Å, °).

N1—C9	1.353 (3)	N2—C13	1.392 (3)
N1—C10	1.361 (3)	N3—C16	1.363 (3)
N1—C1	1.443 (3)	N3—C20	1.445 (4)
N2—C12	1.288 (3)	N3—C19	1.459 (3)
C9—N1—C10	119.8 (2)	N1—C9—C8	120.7 (2)
C9—N1—C1	120.8 (2)	N1—C10—C11	121.2 (2)
C10—N1—C1	119.3 (2)	N2—C12—C7	119.5 (2)
C12—N2—C13	121.9 (2)	N2—C13—C18	116.7 (2)
C16—N3—C20	120.3 (2)	N2—C13—C14	126.2 (2)
C16—N3—C19	121.1 (2)	N3—C16—C17	122.4 (2)
C20—N3—C19	118.6 (2)	N3—C16—C15	120.4 (2)

All H atoms were refined in idealized positions using a riding model (C—H 0.93 and 0.96 Å) and their isotropic displacement parameters were allowed to refine freely.

Data collection: DENZO (Otwinowski & Minor, 1997) and COLLECT (Hooft, 1998); cell refinement: DENZO and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1113). Services for accessing these data are described at the back of the journal.

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