trans-4-[(4-Dimethylaminophenyl)-iminomethyl]-N-methylpyridinium para-toluenesulfonate

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In the title compound, $C_{15}H_{18}N_3^+ \cdot C_7H_7O_3S^-$, the phenylene and pyridyl rings are somewhat twisted with respect to each other, forming a dihedral angle of 23.49 (6)°. The compound contains a dipolar chromophoric cation, but crystallizes in the centrosymmetric space group $P2_1/n$ and is thus not expected to display quadratic non-linear optical effects.

Comment

Much effort continues to be devoted to the discovery of new molecular compounds which exhibit non-linear optical (NLO) properties because such materials are expected to form the basis of emerging optoelectronic and photonic technologies (Bosshard et al., 1995; Chemla & Zyss, 1987; Nalwa & Miyata, 1997). The design of efficient quadratic (second order) NLO materials involves the optimization of both molecular and bulk-level properties. Most promising candidate compounds consist of dipolar donor-π-acceptor (D-π-A) molecules, which must be arranged in a non-centrosymmetric macroscopic structure in order to display bulk quadratic NLO effects, such as frequency doubling (second harmonic generation, SHG).

Amongst known NLO compounds, stilbazolium salts are especially attractive for use in devices (Lee & Kim, 1999). Early studies showed that trans-4'-(dimethylamino)-N-methyl-4-stilbazolium para-toluenesulfonate (DAST) exhibits very pronounced bulk quadratic NLO activity, as evidenced by a powder SHG efficiency from a 1907 nm laser of ca 1000 times that of a urea reference (Marder et al., 1989, 1994). At the molecular level, quadratic NLO activity is governed by first hyperpolarizabilities β, and static ('off-resonance') first hyperpolarizabilities β_0 are generally used when comparing active molecules. A hyper-Rayleigh scattering investigation of DAST using a 1064 nm laser afforded a large β_0 value of 364 × 10^{-30} e.s.u. (Duan et al., 1995). Hence, DAST has been intensively investigated in recent years (Meier et al., 2000), leading to the growth of large high-quality single crystals (Pan, Wong et al., 1996; Adachi et al., 1999; Sohma et al., 1999) and

the fabrication of prototype NLO devices for parametric interactions and electro-optical modulation (Pan, Knöpfle et al., 1996; Meier et al., 1998; Bhowmik et al., 2000).

D-π-A molecules exhibit intense low-energy absorption bands due to $\pi \to \pi^*$ intramolecular charge-transfer (ICT) excitations from the HOMO (highest occupied molecular orbital) primarily localized on the electron-rich D group to the LUMO (lowest unoccupied molecular orbital) localized on the electron-deficient A unit. According to the two-state model (Oudar & Chemla, 1977; Zyss & Oudar, 1982), β_0 is proportional to the square of the ICT transition dipole moment but inversely proportional to the square of the ICT energy. Hence, β_0 increases as the ICT absorption intensity increases and as the energy decreases. The ICT band in the title compound, (I), is red-shifted by ca 0.16 eV, but roughly half as intense when compared with the corresponding absorption in DAST (λ_{max} = 476 nm, ε = 42 100 M^{-1} dm^3 in methanol). Hence, the β_0 value of (I) may be similar to that of DAST, potentially giving rise to pronounced bulk quadratic NLO effects. We have previously reported the synthesis and structure of the related compound trans-4-[(4-dimethylaminophenyl)iminomethyl]-N-phenylpyridinium hexafluorophosphate, (II) (Coe et al., 2000).

(I)

(II)
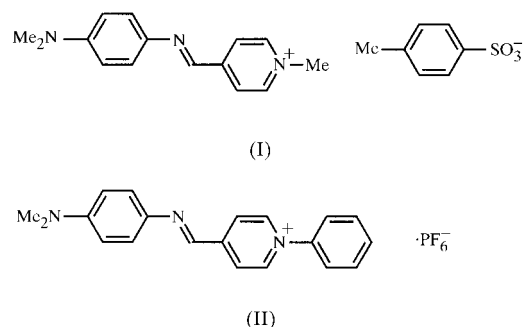
The molecular structure of the cation in (I) is as indicated by [1]NMR spectroscopy, with the two aryl rings adopting the expected trans arrangement about the iminomethyl linkage. The dihedral angle of 23.49 (6)° defined by these ring planes (C10–C15 and N3/C17–C21) is larger than that found in (II) [7.5 (2)°; Coe et al., 2000]. This difference in dihedral angles may arise from weaker π-electronic coupling through the D-π-A framework in (I), consistent with the larger molar extinction coefficient for the ICT band of (II) (λ_{max} = 534 nm, ε = 32 900 M^{-1} dm^3 in acetonitrile; Coe et al., 2000). The dipolar cation in (I) shows a small degree of ground-state polarization, with both the pyridyl and phenylene rings being partially quinoidal. For example, the average of the C11—C12 and C14—C15 distances is 0.025 Å less than the average of the other phenylene C—C distances. With the exception of the phenylene/pyridyl dihedral angle, the geometric parameters of the diaryl Schiff base unit in (I) are similar to those found in (II) (Coe et al., 2000).

The crystal packing structure of (I) is of interest with regard to quadratic NLO properties. The closely related compound DAST crystallizes in the non-centrosymmetric space group Cc (Marder et al., 1989), as does (II) (Coe et al., 2000). Unfortunately, (I) adopts the centrosymmetric space group $P2_1/n$ and hence is not expected to display bulk NLO effects. Clearly,

organic compounds

replacement of the ethylene unit in DAST with an iminomethyl group alters the crystallization behaviour. By contrast, (II) and *trans*-4′-(dimethylamino)-*N*-phenyl-4-stilbazolium hexafluorophosphate are isostructural (Coe *et al.*, 2001). Although the present structure is somewhat disappointing, it is quite possible that salts of the cation in (I) with other anions may adopt different crystal structures more favourable for bulk NLO behaviour.
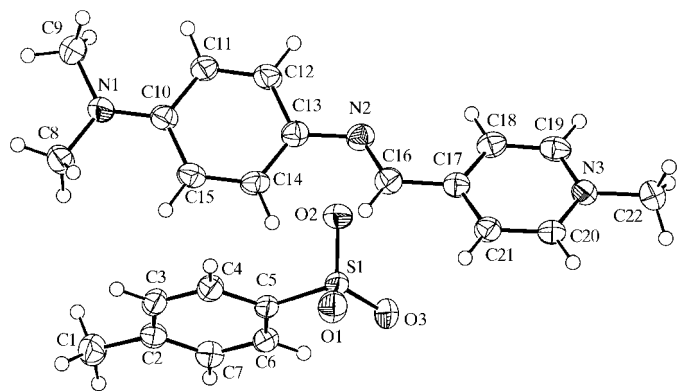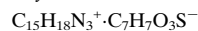

Figure 1
A representation of the molecular structure of (I) shown with 50% probability displacement ellipsoids.

Experimental

trans-4-[(4-Dimethylaminophenyl)iminomethyl]-*N*-methylpyridinium iodide was synthesized as described previously (Matsui *et al.*, 1992) and metathesized to (I) by precipitation from water/aqueous sodium *para*-toluenesulfonate (Acros). Crystals suitable for single-crystal X-ray diffraction measurements were obtained by slow diffusion of diethyl ether (BDH) vapour into a methanol (BDH) solution of (I) at room temperature; note that the same method is used to produce SHG-active crystals of DAST (Marder *et al.*, 1994). The crystals of (I) were hygroscopic and were therefore protected from air prior to and during the crystallographic analysis. NMR and UV–vis data are available in the CIF.

Crystal data

$C_{15}H_{18}N_3{}^+\cdot C_7H_7O_3S^-$	$D_x = 1.345$ Mg m^{-3}
$M_r = 411.51$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 18 258
$a = 7.0956\ (14)$ Å	reflections
$b = 19.035\ (4)$ Å	$\theta = 2.9$–$27.5°$
$c = 15.312\ (3)$ Å	$\mu = 0.19$ mm^{-1}
$\beta = 100.61\ (3)°$	$T = 150\ (2)$ K
$V = 2032.8\ (7)$ Å^3	Block, black
$Z = 4$	$0.14 \times 0.08 \times 0.04$ mm

Data collection

Nonius KappaCCD area-detector diffractometer	4634 independent reflections
φ and ω scans to fill Ewald sphere	2549 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scans	$R_{int} = 0.076$
(*SORTAV*; Blessing, 1995)	$\theta_{max} = 27.5°$
$T_{min} = 0.974,\ T_{max} = 0.993$	$h = -9 \rightarrow 9$
16 234 measured reflections	$k = -24 \rightarrow 24$
	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0506P)^2]$
$R(F) = 0.049$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.115$	$(\Delta/\sigma)_{max} = 0.014$
$S = 0.94$	$\Delta\rho_{max} = 0.23$ e Å^{-3}
4634 reflections	$\Delta\rho_{min} = -0.26$ e Å^{-3}
267 parameters	Extinction correction: *SHELXL*97
H-atom parameters constrained	Extinction coefficient: 0.0044 (8)

Table 1
Selected geometric parameters (Å, °).

C10—N1	1.365 (3)	C19—N3	1.351 (3)
C13—N2	1.413 (3)	C20—N3	1.341 (2)
C16—N2	1.283 (2)	C22—N3	1.476 (3)
C16—C17	1.461 (3)		
N1—C10—C11	121.98 (18)	C18—C17—C16	121.53 (18)
N1—C10—C15	121.11 (18)	C21—C17—C16	120.46 (18)
C12—C13—N2	117.29 (18)	C16—N2—C13	120.27 (18)
C14—C13—N2	125.27 (18)	C20—N3—C22	119.66 (17)
N2—C16—C17	119.97 (19)	C19—N3—C22	119.33 (17)

H atoms were included in idealized positions with their displacement parameters tied to those of their parent atoms.

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: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990).

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