

Hydrated Form of 4-N,N-Dimethylamino-4'-N'-Methyl- Stilbazolium Tosylate, $C_{16}H_{19}N_2(C_7H_7SO_3 \cdot H_2O)$

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4-N,N-Dimethylamino-4'-N'-Methyl-stilbazolium tosylate의 水化物

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Abstract

The crystal structure of the title compound consists of discrete 4-N,N-dimethylamino-4'-N'-methyl-stilbazolium, $C_{16}H_{19}N_2$, and tosylate, $C_7H_7SO_3$, dimer. The 4-N,N-dimethylamino-4'-N'-methyl-stilbazolium molecule has a trans conformation at the central C=C double bond: the dihedral angle between the phenyl and the pyridyl rings is $5.7(2)^\circ$ and the whole molecule is planar within $0.138(8)\text{\AA}$. Tosylate molecules display hydrogen-bonded dimers with the O-H...O distances of $2.855(9)$ and $2.899(8)\text{\AA}$, respectively. The shortest intermolecular contact is the distance $3.10(1)\text{\AA}$ between O(3) and C(16).

要 約

表題化合物的 結晶構造는 4-N,N-dimethylamino-4'-N'-methyl-stilbazolium, $C_{16}H_{19}N_2$ 와 tosylate, $C_7H_7SO_3$ 의 不連續한 二分子體로 構成되어 있다. 4-N,N-dimethylamino-4'-N'-methyl-stilbazolium 分子는 中間에 있는 C=C double bond에서 trans conformation을 가지고 있으며 phenyl 및 pyridyl ring들간의 二面角은 $5.7(2)^\circ$ 을 이루어 全分子는 $0.138(8)\text{\AA}$ 丙에서 平面을 이루고 있다. Tosylate 分子들은 距離가 各各 $2.855(9)$ and $2.899(8)\text{\AA}$ 인 O-H...O 水素結合으로 連結된 二分子體를 나타내고 있다. 이 두 分子간의 가장 가까운 距離는 O(3)와 C(16) 原子間的 $3.10(1)\text{\AA}$ 이다.

1. Introduction

Organic materials with large second-order non-linear optical (NLO) effects are of great interest because of their potential applications in frequency conversion and electro-optic modulation.¹⁻³⁾ Much effort has been made to search for novel molecular crystalline materials

composed of stable chromophoric molecules with larger molecular hyperpolarizabilities with an optimized orientation for large macroscopic NLO properties. 4-N,N-dimethylamino-4'-N'-methyl-stilbazolium tosylate (DAST) is reported to have one of the highest value of electro-optic coefficient, $r_{11}=400 \text{ pm/V}$.⁴⁾

DAST crystals which exhibit second harmonic

generation has a non-centrosymmetric structure. However when DAST crystals absorb water, the structure changes and the crystals do not show second harmonic generation any longer. The color of the DAST crystals is greenish dark red, but the color of the DAST·H₂O crystals changes into orange.

The structure of DAST crystals has been determined by Marder *et al.*⁵⁾ So it is very interesting to investigate the structure of hydrated form of DAST.

DAST was synthesized by the condensation of 4-methyl-N-methyl pyridinium tosylate of 4-N, N-dimethylamino-benzaldehyde in the presence of piperidine.⁶⁾ DAST·H₂O was purified by recrystallization from water and methanol, and orange colored crystals were obtained by evaporating methanol solution.

2. Experimental

The crystallographic data of the title compound (I) are listed in Table 1. The accurate cell parameters were refined from setting angles of only 8 reflections with $11.41 < \theta < 12.24^\circ$ because they gave the least estimated standard deviations. Cell refinement, data collection and data reduction were done using SDP.⁷⁾ The structure of the compound was solved by using SHELX86⁸⁾ and refined by full-matrix least squares with SHELX76.⁹⁾ All H atom positions except for water molecules were calculated geometrically (C-H: 1.08Å) and H-atoms of water were found from difference Fourier map. All H-atoms were refined isotropically. Fractional atomic coordinates are given in Table 2. Softwares used for molecular graphics were

Table 1. Experimental details of the X-Ray diffraction study of C₂₃H₂₆N₂SO₃·H₂O

Crystal data	
C ₂₃ H ₂₆ N ₂ SO ₃ ·H ₂ O	
M _r =430.563	
Triclinic	
P1	
a=9.640(4)Å	
b=14.805(6)Å	
c=8.09(2)Å	
α=79.29(7)°	
β=78.75(7)°	
γ=81.21(3)°	
V=1105.1Å ³	
Z=2	
Data collection	
Enraf-Nonius CAD-4 diffractometer	
ω/2θ scans	
absorption correction: none	
No. of measured reflections: 3109	
No. of independent reflections: 3070	
No. of observed reflections: 2129	
criterion for observed reflections: F _o ≥ 3σ(F _o)	
Refinement	
Refinement on F	
Final R=0.058	
ωR=0.058	
S=1.0461	
383 parameters	
	Mo Kα radiation
	λ=0.71069 Å
	Cell parameter determination
	from 8 reflections
	θ=11.41-12.24°
	μ=0.13 mm ⁻¹
	T=297 K
	Light red
	Rectangular plate
	0.50×0.20×0.12 mm
	D _{calc} =1.29 Mg m ⁻³
	θ _{max} =23°
	h= → -10-10
	k= → -15-16
	l= → 0-8
	3 standard reflections
	monitored every 180 minutes
	intensity variation <2.1%
	ω=unit weights
	(Δ/ρ) _{max} =0.354
	Δρ _{max} =0.222 eÅ ⁻³
	Δρ _{min} =-0.250 eÅ ⁻³
	Atomic scattering factors
	were provided in SHELX76

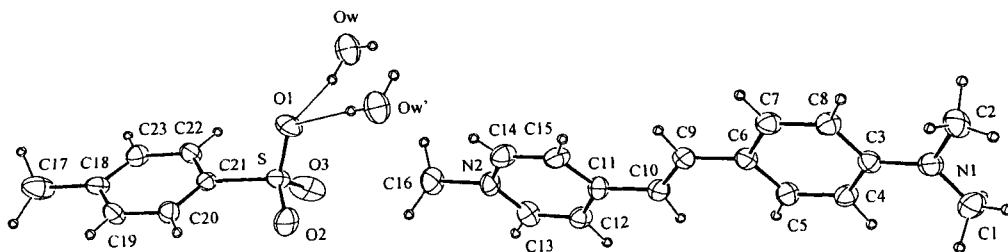
Table 2. Positional and equivalent isotropic thermal parameters (\AA^2) for non-hydrogen atoms of $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_4\text{S}$

	x	y	z	Ueq
S	0.2836(2)	0.6676(1)	-0.6671(2)	0.048
O(1)	0.4250(4)	0.6225(3)	-0.6503(5)	0.073
O(2)	0.2274(5)	0.7259(3)	-0.5406(5)	0.074
O(3)	0.1880(5)	0.6044(3)	-0.6771(5)	0.084
O(W)	0.4963(6)	0.4318(5)	-0.6854(8)	0.077
N(1)	0.1980(5)	0.1010(3)	1.1460(5)	0.058
N(2)	0.1515(5)	0.4241(3)	-0.1497(5)	0.051
C(1)	0.0670(8)	0.0726(6)	1.2456(9)	0.071
C(2)	0.3242(8)	0.0841(6)	1.2243(9)	0.064
C(3)	0.2057(5)	0.1399(3)	0.9773(6)	0.045
C(4)	0.0881(6)	0.1500(4)	0.8927(7)	0.046
C(5)	0.0958(6)	0.1912(4)	0.7255(7)	0.048
C(6)	0.2196(5)	0.2243(4)	0.6293(6)	0.045
C(7)	0.3373(6)	0.2119(4)	0.7126(7)	0.055
C(8)	0.3312(6)	0.1709(4)	0.8799(7)	0.050
C(9)	0.2291(6)	0.2730(4)	0.4553(7)	0.048
C(10)	0.1229(6)	0.2943(4)	0.3655(7)	0.049
C(11)	0.1360(6)	0.3411(4)	0.1884(6)	0.046
C(12)	0.0234(6)	0.3472(4)	0.1000(7)	0.051
C(13)	0.0340(7)	0.3871(4)	-0.0658(7)	0.053
C(14)	0.2623(7)	0.4219(5)	-0.0685(8)	0.063
C(15)	0.2557(6)	0.3816(5)	0.0990(7)	0.060
C(16)	0.1637(10)	0.4704(6)	-0.3322(8)	0.071
C(17)	0.3347(11)	0.9198(8)	-1.3563(12)	0.086
C(18)	0.3218(5)	0.8567(4)	-1.1844(7)	0.050
C(19)	0.2960(6)	0.8923(4)	-1.0356(8)	0.054
C(20)	0.2852(6)	0.8359(4)	-0.8769(8)	0.049
C(21)	0.3016(5)	0.7423(4)	-0.8675(6)	0.040
C(22)	0.3307(6)	0.7040(4)	-1.0165(7)	0.051
C(23)	0.3396(6)	0.7610(5)	-1.1738(7)	0.054

NRCVAX¹⁰ and ORTEP.¹¹

3. Discussion

Fig. 1 is a view of the molecule showing the

**Fig. 1. Molecular structure showing 40% probability displacement ellipsoids.****Table 3. Bond lengths, angles, selected torsion angles and hydrogen bonds with e.s.d.s in parentheses**

(1) Bond lengths (\AA)			
S-O(1)	1.443(4)	C(6)-C(9)	1.451(7)
S-O(2)	1.434(4)	C(7)-C(8)	1.371(8)
S-O(3)	1.433(5)	C(9)-C(10)	1.335(8)
S-C(21)	1.779(5)	C(10)-C(11)	1.462(7)
N(1)-C(1)	1.435(9)	C(11)-C(12)	1.395(8)
N(1)-C(2)	1.447(9)	C(11)-C(15)	1.392(8)
N(1)-C(3)	1.372(6)	C(12)-C(13)	1.353(8)
N(2)-C(13)	1.340(8)	C(14)-C(15)	1.369(9)
N(2)-C(14)	1.352(8)	C(17)-C(18)	1.520(12)
N(2)-C(16)	1.499(8)	C(18)-C(19)	1.367(8)
C(3)-C(4)	1.410(7)	C(18)-C(23)	1.389(9)
C(3)-C(8)	1.400(7)	C(19)-C(20)	1.391(9)
C(4)-C(5)	1.370(8)	C(20)-C(21)	1.360(8)
C(5)-C(6)	1.395(7)	C(21)-C(22)	1.389(7)
C(6)-C(7)	1.402(7)	C(22)-C(23)	1.386(8)

atom-numbering scheme.

In (I), the bond lengths N(1)-C(1) [1.435(9) \AA] and N(1)-C(2) [1.447(9) \AA] are in good agreement with the comparable bonds in 1,1'-methylenebis(4,4'-dimethylaminopyridinium) iodide.¹²

As shown in Table 3, the eleven C-C bond lengths in the aromatic phenyl and pyridyl rings range from 1.353(8) to 1.410(7) \AA with mean value 1.386 \AA which is comparable with the normal C-C resonance bond distance of 1.395 \AA (13), and valence angles from 116.2(5) $^\circ$ to 122.3(5) $^\circ$ with mean value 120 $^\circ$.

The bonds connecting the phenyl and pyridyl rings [C(9)-C(10)=1.335(8) \AA , average bond distance 1.457 \AA of C(6)-C(9) and C(10)-C(11)] show double- and single-bond character, respectively. The torsion angle of C(6)-C(9)-C(10)-C(11) is -178(1) $^\circ$.

Table 3. Continued

(2) Bond angles (°)			
O(1)-S-O(2)	112.4(3)	C(3)-C(8)-C(7)	121.4(5)
O(1)-S-O(3)	112.8(3)	C(6)-C(9)-C(10)	126.0(5)
O(2)-S-O(3)	113.0(3)	C(9)-C(10)-C(11)	125.0(5)
O(1)-S-C(21)	106.0(2)	C(10)-C(11)-C(12)	119.6(5)
O(2)-S-C(21)	106.2(3)	C(10)-C(11)-C(15)	124.0(5)
O(3)-S-C(21)	105.7(2)	C(12)-C(11)-C(15)	116.4(5)
C(1)-N(1)-C(2)	118.8(5)	C(11)-C(12)-C(13)	121.1(5)
C(1)-N(1)-C(3)	120.9(5)	N(2)-C(13)-C(12)	121.2(6)
C(2)-N(1)-C(3)	120.2(5)	N(2)-C(14)-C(15)	120.5(6)
C(13)-N(2)-C(14)	119.9(5)	C(11)-C(15)-C(14)	120.9(5)
C(13)-N(2)-C(16)	121.9(5)	C(17)-C(18)-C(19)	121.0(6)
C(14)-N(2)-C(16)	118.2(5)	C(17)-C(18)-C(23)	121.0(6)
N(1)-C(3)-C(4)	121.8(4)	C(19)-C(18)-C(23)	118.0(5)
N(1)-C(3)-C(8)	121.6(4)	C(18)-C(19)-C(20)	122.0(5)
C(4)-C(3)-C(8)	116.6(5)	C(19)-C(20)-C(21)	119.6(5)

(3) Selected torsion angles (°)	
O(1)-S-C(21)-C(20)	-109.8(5)
O(1)-S-C(21)-C(22)	71.2(5)
O(2)-S-C(21)-C(20)	9.9(5)
O(2)-S-C(21)-C(22)	-169.0(5)
O(3)-S-C(21)-C(20)	130.2(5)
O(3)-S-C(21)-C(22)	-48.8(4)
C(1)-N(1)-C(3)-C(4)	-2.8(5)
C(1)-N(1)-C(3)-C(8)	177.8(8)
C(2)-N(1)-C(3)-C(4)	174.4(8)
C(2)-N(1)-C(3)-C(8)	-5.1(5)
C(5)-C(6)-C(9)-C(10)	1.4(6)
C(7)-C(6)-C(9)-C(10)	-175.7(9)
C(6)-C(9)-C(10)-C(11)	-178.1(9)
C(9)-C(10)-C(11)-C(12)	170.4(9)
C(9)-C(10)-C(11)-C(15)	-9.9(6)

(4) Hydrogen-bonding geometry (Å, °)				
D-H...A	D-H	H...A	D...A	D-H...A
O(W)-H(w1)...O(1)	0.95(8)	1.9(8)	2.855(9)	163(7)
O(W)-H(w2)...O(1) ⁱ	0.66(8)	2.3(8)	2.899(8)	165(10)
H(w1)-O(W)-H(w2)				106(8)

Symmetry code: (i) 1-x, 1-y, -1-z.

0.138(8)Å, with C(1) and C(2) deviating 0.26(1) and 0.02(1)Å, respectively, from the best plane. The dihedral angle between the nitrophenyl and pyridyl rings is 5.7(2)°.

To diminish repulsions between C(5) and C(10) and between C(9) and C(15), the angles 123.7(5)° of C(5)-C(6)-C(9) and 124.0(5)° of C(10)-C(11)-C(15) are larger than 120.0(5)° of C(7)-C(6)-C(9) and 119.6(5)° of C(10)-C(11)-C(12). All of this conformations are comparable with those of 4-methoxy-3-methyl-4'-nitrostilbene¹⁴ and 2-methoxy-5-(4-nitrostyryl)phenol.¹⁵

The phenyl ring of the p-toluenesulfonate is approximately perpendicular to the dimethylaminostilbene plane with the dihedral angle 99.4(2)° and the angles around S atom are very close to the tetrahedral angle as shown in Table 3. The distance C(21)-S [1.779(5)Å] is in good agreement with the value quoted for a C(sp³)-S single bond (1.8Å).¹⁶

O(1) atom of the p-toluenesulfonate molecule participates in two hydrogen bonds with a water molecule and with another water molecule related by an inversion center. Therefore The p-toluenesulfonates form hydrogen-bonded dimers.

As shown in the molecular packing diagram (Fig. 2), the structure is highly layered with the shortest contact 3.10(1)Å between O(3) and C(16).

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The stilbene moiety in (I) is planar to within

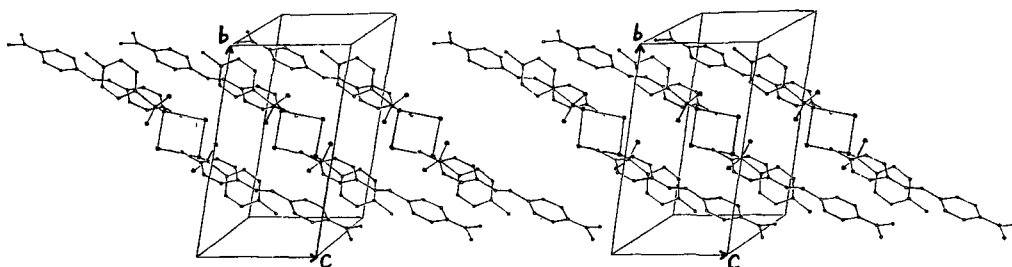


Fig. 2. A stereoview of a unit-cell packing for the molecule: origin, lower left; c-axis, horizontal; b-axis, vertical.

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References

- 1) Williams, D. J. ed., Nonlinear Optical Properties of Organic and Polymeric Materials, ACS Symp. Ser., Vol. 233. Am. Chem. Soc., Washington, DC, 1983.
- 2) Chemla, D. S. and Zyss, J. ed., Nonlinear Optical Properties of Organic Molecules and Crystals, Academic Press, Orlando, FL, Vol. 1 and 2, 1987.
- 3) Marder, S. R., Sohn, J. E. and Stucky, G. D. ACS Symp. Ser., Vol. 455, *Am. Chem. Soc.*, Washington, DC, 1991.
- 4) Marder, S. R., Perry, J. W. and Schaefer, W. P. *J. Mater. Chem.* **2**, 985, 1992.
- 5) Marder, S. R. and Schaefer, W. P. The Structure of P-Dimethyl Amino, P-Methyl Stilbazolium Tosylate. Personal communication.
- 6) Marder, S. R., Perry, J. W. and Schaefer, W. P. *Science*. **245**, 626, 1989.
- 7) Frenz, B. A. Enraf-Nonius, SDP, Structure Determination Package, Enraf-Nonius, Delft, The Netherlands, 1985.
- 8) Sheldrick, G. M. SHELX86. Program for Crystal Structure Solution. University of Göttingen, Germany, 1985.
- 9) Sheldrick, G. M. SHELX76. System of Crystallographic Computer Program: University of Cambridge, England, 1976.
- 10) Gabe, E. J., Le Page, Y., Charland, J. P., Lee, F. L. and White, P. S. *J. Appl. Cryst.*, **22**, 384-387, 1989.
- 11) Johnson, C. K. ORTEP. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA, 1971.
- 12) Munavalli & Poziomek, E. J. *Acta Cryst.* **C44**, 272-275, 1988.
- 13) Hand book of Chemistry and Physics, 70th ed., CRC Press, Inc. Boca Raton, Florida, USA. 1989-1990.
- 14) Suh, I. H., Lim, S. S., Lee, J. H. Ryu, B. Y., Kim, M. J. Yoon, C. S. Hong, H. K. and Lee K. S. *Acta Cryst.* **C50**, 1768-1770, 1994.
- 15) Li, Z. D. & Su, G. *Acta Cryst.* **C51**, 311-313, 1995.
- 16) Khan, M. A., Taylor, R. W., Lehn, J.-M. & Dietrich, B. *Acta Cryst.* **C44**, 1928-1931, 1988.