Crystal structure of (*E*)-1-(methylthio)-1-(4'-methoxyphenylamino)-2-nitroethene, $C_{10}H_{12}N_2O_3S$

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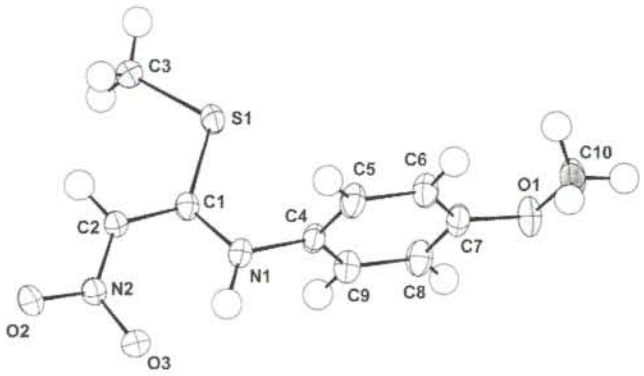

Abstract

$C_{10}H_{12}N_2O_3S$, triclinic, $P\bar{1}$ (No. 2), $a = 6.791(2)$ Å, $b = 8.114(2)$ Å, $c = 10.311(3)$ Å, $\alpha = 88.04(2)°$, $\beta = 86.40(2)°$, $\gamma = 84.87(2)°$, $V = 564.5$ Å^3, $Z = 2$, $R_{gt}(F) = 0.032$, $wR(F) = 0.031$, $T = 293$ K.

Source of material

The title compound was prepared on a conventional way by reacting 1,1-bis(methylthio)-2-nitroethene with one molar equivalent amount of 4-methoxyaniline in warm acetonitrile. Flash chromatography and slow crystallization from dichloromethane afforded the starting material [1-3]. Crystals were grown from dichloromethane.

Discussion

Following our interest for cations in superacids, we were driven to study the behavior of the title compound in trifluoromethanesulfonic acid. In this acidic medium, this compound undergoes a double protonation, one on the C2 bearing the nitro group, and another one on the oxygene of the nitro group. This dication slowly isomerizes into another conformational isomer. From ^{1}H and ^{13}C NMR data of these cations, it was concluded that the neutral precursor compound, in the solid state, is probably (*E*)-configured at the C1=C2 double bond level and that the C2–N2 bond is in the s-*cis* conformation [1]. The present study was undertaken to answer this question. X-ray analysis shows that the double bond C1=C2 and N1, N2 and S1 are coplanar. The planar nitro group is slightly twisted out of the molecular plan (C1–C2–N2–O2: 173.9°). The phenyl ring is twisted out of this plan with a torsion angle close to 75° around the N1–C1 bond. The both phenyl ring and its methoxy group are coplanar together. The atoms N2–C2–C1–N1 are coplanar (torsion angle value 0.1°) wich implies that the double bond is (*E*)-configured. The observed torsion angle C2–C1–N1–C4 (179.7°) indicates that C1–N1 bond is in a *s-cis* conformation relatively to the MeS and PhNH groups. The X-ray structure of the title compound is in agreement with previous structural assumptions from its cationics species in superacid.

Table 1. Data collection and handling.

Crystal:	faint yellow, prism, size 0.20 × 0.25 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	26.7 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, ω/2θ
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3356, 1700
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\ \sigma(I_{obs})$, 1700
$N(param)_{refined}$:	147
Programs:	SHELXS-86 [4], CRYSTALS [5], CAMERON [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	2*i*	–0.0666	1.0770	0.2699	0.079(2)
H(2)	2*i*	0.2993	0.8911	0.0448	0.079(2)
H(5)	2*i*	–0.0139	0.7704	0.4793	0.079(2)
H(6)	2*i*	–0.2651	0.6518	0.6223	0.079(2)
H(8)	2*i*	–0.6959	0.8564	0.3814	0.079(2)
H(9)	2*i*	–0.4449	0.9655	0.2363	0.079(2)
H(31)	2*i*	0.2622	0.4807	0.0452	0.079(2)
H(32)	2*i*	0.3817	0.6399	0.0748	0.079(2)
H(33)	2*i*	0.2104	0.6579	–0.0303	0.079(2)
H(101)	2*i*	–0.7349	0.5695	0.7522	0.079(2)
H(102)	2*i*	–0.5378	0.6684	0.7635	0.079(2)
H(103)	2*i*	–0.5235	0.4980	0.6822	0.079(2)

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	2*i*	0.06695(6)	0.66188(5)	0.18186(4)	0.0535(2)	0.0450(2)	0.0545(2)	–0.0156(2)	0.0153(2)	–0.0007(2)
C(1)	2*i*	0.0667(2)	0.8769(2)	0.1830(1)	0.0334(7)	0.0459(8)	0.0378(7)	–0.0057(6)	–0.0009(6)	0.0019(6)
C(2)	2*i*	0.2025(2)	0.9591(2)	0.1051(1)	0.0377(7)	0.0383(8)	0.0444(8)	–0.0040(6)	0.0033(6)	0.0033(6)
C(3)	2*i*	0.2492(3)	0.6040(2)	0.0551(2)	0.076(1)	0.0416(9)	0.069(1)	–0.0029(8)	0.029(1)	–0.0027(8)
C(4)	2*i*	–0.2112(2)	0.8758(2)	0.3479(1)	0.0379(8)	0.0501(9)	0.0425(8)	–0.0059(6)	0.0090(6)	–0.0025(6)
C(5)	2*i*	–0.1593(2)	0.7867(2)	0.4585(2)	0.0365(8)	0.076(1)	0.0519(9)	–0.0024(7)	0.0034(7)	0.0065(8)
C(6)	2*i*	–0.3034(2)	0.7208(2)	0.5413(2)	0.0489(9)	0.071(1)	0.0442(9)	–0.0043(8)	0.0041(7)	0.0079(8)
C(7)	2*i*	–0.4994(2)	0.7489(2)	0.5130(2)	0.0440(8)	0.058(1)	0.0437(8)	–0.0138(7)	0.0105(6)	–0.0064(7)
C(8)	2*i*	–0.5509(2)	0.8381(2)	0.4018(2)	0.0362(8)	0.075(1)	0.0510(9)	–0.0108(7)	–0.0010(7)	0.0001(8)
C(9)	2*i*	–0.4074(2)	0.9008(2)	0.3189(2)	0.0435(8)	0.060(1)	0.0428(8)	–0.0068(7)	–0.0002(6)	0.0009(7)
C(10)	2*i*	–0.6121(3)	0.6025(3)	0.7037(2)	0.085(1)	0.077(1)	0.052(1)	–0.026(1)	0.022(1)	0.0005(9)
N(1)	2*i*	–0.0668(2)	0.9535(2)	0.2654(1)	0.0424(7)	0.0487(8)	0.0506(7)	–0.0055(6)	0.0121(6)	–0.0006(6)
N(2)	2*i*	0.2124(2)	1.1264(2)	0.1056(1)	0.0414(7)	0.0423(7)	0.0546(8)	–0.0034(5)	0.0059(6)	0.0057(6)
O(1)	2*i*	–0.6549(2)	0.6960(2)	0.5888(1)	0.0514(7)	0.089(1)	0.0600(8)	–0.0233(6)	0.0136(6)	0.0070(7)
O(2)	2*i*	0.3506(2)	1.1870(2)	0.0404(2)	0.0640(8)	0.0466(7)	0.106(1)	–0.0116(6)	0.0349(7)	0.0113(7)
O(3)	2*i*	0.0876(2)	1.2193(1)	0.1707(1)	0.0616(7)	0.0424(6)	0.0727(8)	0.0005(5)	0.0174(6)	–0.0015(5)

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