

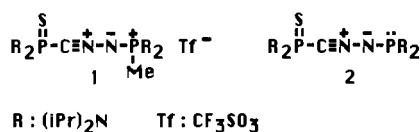
Communications

X-ray Crystal Structure and Reactivity of an *N*-Phosphonio-Substituted Nitrilimine: A Stable Electrophilic Nitrilimine

In a famous review, Huisgen pointed out that 1,3-dipoles are ambivalent nucleophiles and electrophiles, which is of key importance in understanding the mechanism, reactivity sequences, and regiochemistry of 1,3-dipolar cycloaddition.¹ The Sustmann plots of the logarithms of the relative rates of reaction of nitrilimines versus the IP's of the dipolarophiles have a U-shape with the slender branch on the side of electron-poor dipolarophiles.² Not surprisingly, it was calculated that strong electron-withdrawing substituents would lower the LUMOs of the dipoles increasing their electrophilicity.³ On the other hand, for the parent nitrilimine, theoretical calculations predicted that the planar heteropropargylic structure A and the bent heteropseudoallene structure B have similar stabilities but that placing electron-withdrawing groups at the nitrogen terminus would favor the planarization of nitrilimines.^{3c,d}



Here, we wish to report the reactivity and X-ray crystal structure of *C*-[bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(diisopropylamino)methylphosphonio]nitrilimine (**1**)⁴ and to



compare the results with those obtained for the *N*-phosphanyl-nitrilimine analogue **2**.⁵ The steric factors are quite comparable,

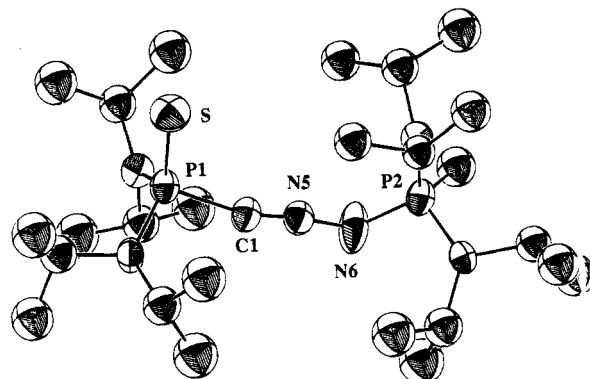


Figure 1. ORTEP view of the cationic part of **1**, showing the atom-numbering scheme of the heaviest elements.

but there is an electron-withdrawing group (a phosphonio group) and an electron-releasing substituent (a phosphanyl group) at the nitrogen terminus of **1** and **2**, respectively.

We have recently shown that the *N*-phosphonio nitrilimine **1** (white crystals, mp 100–102 °C)⁴ can be easily prepared by treatment of *C*-[bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(diisopropylamino)phosphanyl]nitrilimine (**2**)⁵ with a stoichiometric amount of methyl trifluoromethanesulfonate.

A single crystal of **1**, suffering from disorder in the anionic part, grown from a THF/ether solution, has been used for X-ray structure analysis.⁶ **1** crystallizes in the triclinic system, space group $P\bar{1}$ with $Z = 2$. Thus, there are two enantiomers present in the crystal, and they are related by a center of symmetry. The ORTEP view of one of the enantiomers is shown in Figure 1 along with the atom-numbering scheme. The pertinent metric parameters of **1** are compared in Table I with those of nitrilimine **2**^{5c} and those calculated for the parent nitrilimine.^{3c} In **1**, the CNNP skeleton is almost linear (178°), and the carbon–nitrogen bond length is shorter and the nitrogen–nitrogen bond length is longer than in **2**. Concerning the angles, the most dramatic change

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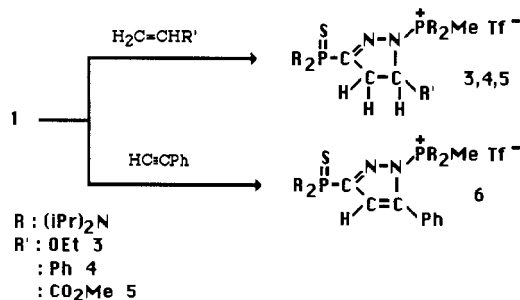
- (6) Nitrilimine **1** ($C_{27}H_{59}F_3N_6O_3P_2S_2$) crystallizes in the triclinic system, space group $P\bar{1}$ with $Z = 2$. The cell constants were determined from 20 independent reflexions in the range $20^\circ < 2\theta < 28^\circ$ on a 4-circle Siemens diffractometer (AED): $a = 9.798$ (5), $b = 13.327$ (7), $c = 16.151$ (9) Å; $\alpha = 103.09$ (4), $\beta = 104.92$ (4), $\gamma = 101.47$ (4)°; $V = 1909$ Å³. Mo $K\alpha$ radiation was used with a graphite monochromator. LP corrections have been performed but no absorption corrections (due to the low absorption coefficient $\mu = 2.29$ cm⁻¹). A total of 5853 reflections have been measured ($3 < 2\theta < 45^\circ$), 3668 have been classified as observed ($F_o \geq 3\sigma_{F_o}$). The structure was solved by direct methods and was refined (340 parameters) by using scattering factors of the program.¹³ The hydrogen atoms of the methyl groups have been calculated as fixed (tetrahedral geometry; C–H = 1.08 Å), and anisotropic temperature factors have been attributed to all non-carbon (besides C(1) and C(27)) and non-hydrogen atoms. The CF₃ group is highly disordered. No splitting model was successful; we finally took the high anisotropic values, since the rest of structure refined nicely with $R = 0.086$ ($R_w = 0.075$); $w = 4.25/\sigma_{F_o}^2$.

Table I. Metric Parameters (Å and deg) of Nitrilimines **1** and **2**^{5c} (X-ray Analysis) Compared to the Calculated Planar and Bent Structures of the Parent Nitrilimine^{3d}

param	MINDO/3		X-ray	
	bent	planar	2	1
∠XCN	126	159	138.2 (4)	163.5 (6)
∠CNN	167	177	173.6 (3)	169.6 (6)
∠NNY	115	116	115.0 (2)	123.6 (5)
∠XCNN	141	180	121	84.1
∠CNNY	120	180	152	177.7
r(CN)	1.20	1.17	1.177 (6)	1.143 (7)
r(NN)	1.19	1.20	1.240 (5)	1.285 (7)
r(PC)			1.771 (7)	1.815 (7)
r(NP)			1.777 (3)	1.623 (6)

compared to **2** is observed for PCN, which tends toward linearity (163.5°). The nitrogen–phosphorus bond length is considerably shorter (1.623 Å) than in **2** (1.777 Å), confirming the stabilization of the negative charge on nitrogen by the phosphorus cation (there are no significant interactions between the cation and the anion). The only striking difference between the calculated propargylic structure and that of **1** is the nonplanarity of **1**, which induces a chiral axis. There is a dihedral angle of 84° between the PCN and CNN planes; however, since the PCN angle is large (163.5°), the λ⁵-phosphorus atom is not so far from the CNNP plane. This small deviation from the theoretical structure may be due to steric factors. In valence bond terminology, a $\text{C}\equiv\text{N}^+-\text{N}^-$ propargylic structure represents the electronic structure of **1** fairly well, while a $\text{C}=\text{N}^+=\text{N}^-$ cumulenic structure best illustrates **2**. The differences observed in the X-ray diffraction studies of **1** and **2** are corroborated by the infrared frequencies (**1**, 2170 cm⁻¹; **2**, 2040 cm⁻¹), which is in good agreement with the increased CN bond order of **1** (note that the IR frequency of the corresponding nitrile (R₂N)₂P(S)CN is 2180 cm⁻¹).⁷

In contrast with all the known transient^{1,8} and stable^{5,9} nitrilimines, **1** is strongly electrophilic. It reacts with an electron-rich olefin such as ethyl vinyl ether at room temperature, while styrene requires 14 h at 60 °C, and 20 h at 80 °C is necessary for the electron-poor olefin methyl acrylate. Reaction with phenylacetylene is complete after 10 h at 55 °C. The dipolarophilic activity series of **1** was confirmed by competition experiments. The dipole and two dipolarophiles were mixed together in a 1/2/2 ratio in a benzene solution. The results are given in Table II and clearly demonstrate the strong electrophilic character of nitrilimine **1**.¹⁰ All these reactions occurred with complete regioselectivity (according to NMR spectroscopy¹¹), yielding the 5-substituted pyrazolines **3–5** or pyrazole **6** in good yield.¹² This is not sur-



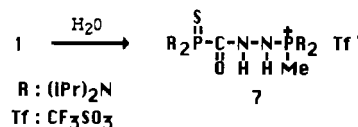
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Table II. Comparison of Dipolarophilic Activities of Various Carbon–Carbon Multiple-Bonded Compounds with **1**

dipolarophiles	products	ratio
EtO–CH=CH ₂ /PhCH=CH ₂	3/4	100/0
PhCH=CH ₂ /MeO ₂ C–CH=CH ₂	4/5	85/15
Ph–C≡CH/Ph–CH=CH ₂	6/4	100/0

prising, since the presence of an electron-withdrawing substituent decreases the HOMO and LUMO energies of the dipole. The cycloaddition is thus LUMO (dipole) controlled, which was predicted to favor the 5-substituted regioisomer.³

Last, nitrilimine **1** reacted with water by a 1,3-addition process leading to **7**.¹² This is in marked contrast with the behavior of **2** where the phosphorus–nitrogen bond was cleaved by water leading to the (thioxophosphoranyl)diazomethane and the phosphane oxide.^{5b,c}



It is clear from these results that, both electrophilic and nucleophilic, stable nitrilimines can be prepared. In good agreement with calculations, the geometry of the nitrilimine skeleton can be quite different, depending on the nature of the substituents.

Supplementary Material Available: Tables of bond lengths and angles, atomic coordinates with *B* values and anisotropic temperature factors and a figure of the cation and anion (4 pages); a table of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

- (12) All compounds were isolated and fully characterized. Selected spectroscopic data are as follows. **3**: 85% yield; ³¹P NMR (CDCl₃) δ = +55.77, +47.60, J(PP) = 1.7 Hz; ¹H NMR (CDCl₃) δ = 2.30 (d, J(PH) = 14.4 Hz, 3 H, CH₃P), 3.30 (m, 2 H, CH₂(ring)), 5.64 (dd, J(HH) = 4.6 and 2.8 Hz, 1 H, CH(ring)); ¹³C NMR (CDCl₃) δ = 14.98 (s, CH₃CH₂), 15.08 (d, J(PC) = 100.4 Hz, CH₃P); 43.93 (dd, J(PC) = 18.7 and 6.1 Hz, CH₂(ring)), 62.02 (s, CH₂O), 88.85 (m, CH(ring)), 120.74 (q, J(CF) = 320.7 Hz, CF₃), 160.08 (dd, J(PC) = 140.0 and 11.2 Hz, C=N). **4**: 84% yield; ³¹P NMR (CDCl₃) δ = +49.73, +57.43, J(PP) = 2.4 Hz; ¹H NMR (CDCl₃) δ = 2.01 (d, J(PH) = 14.0 Hz, 3 H, CH₃P), 3.33 (dd, J(HH) = 4.3 and 18.3 Hz, 1 H, CH₂(ring)), 3.89 (dd, J(HH) = 11.9 and 18.3 Hz, 1 H, CH₂(ring)), 5.47 (ddd, J(HH) = 4.4 and 11.9 Hz, J(PH) = 2.9 Hz, 1 H, CH(ring)); ¹³C NMR (CDCl₃) δ = 15.21 (d, J(PC) = 102.2 Hz, CH₃P), 63.97 (dd, J(PC) = 7.0 and 2.9 Hz, CH(ring)), 120.94 (q, J(CF) = 320.2 Hz, CF₃), 160.55 (dd, J(PC) = 139.3 and 11.2 Hz, C=N). **5**: 77% yield; ³¹P NMR (CDCl₃) δ = +49.91, +56.91, J(PP) = 2.0 Hz; ¹H NMR (CDCl₃) δ = 2.23 (d, J(PH) = 14.1 Hz, CH₃P), 5.11 (ddd, J(HH) = 3.6 and 12.8 Hz, J(PH) = 2.2 Hz, CH(ring)); ¹³C NMR (CDCl₃) δ = 14.37 (d, J(PC) = 101.9 Hz, CH₃P), 43.54 (dd, J(PC) = 3.1 and 21.0 Hz, CH₂(ring)), 53.22 (s, OCH₃), 59.61 (dd, J(PC) = 3.5 and 8.1 Hz, CH(ring)), 120.33 (q, J(CF) = 319.7 Hz, CF₃), 159.48 (dd, J(PC) = 136.7 and 10.4 Hz, C=N), 171.2 (s, CO). **6**: 82% yield; ³¹P NMR (CDCl₃) δ = +49.52, +56.53, J(PP) = 1.6 Hz; ¹H NMR (CDCl₃) δ = 1.93 (d, J(PH) = 14.2 Hz, 3 H, CH₃P), 6.72 (d, J(PH) = 2.5 Hz, 1 H, CH(ring)); ¹³C NMR (CDCl₃) δ = 17.50 (d, J(PC) = 102.2 Hz, CH₃P), 116.11 (dd, J(PC) = 16.6 and 5.1 Hz, CH(ring)), 120.9 (q, J(CF) = 320.2 Hz, CF₃), 150.31 (dd, J(PC) = 10.6 and 6.0 Hz, C(ring)), 157.97 (dd, J(PC) = 147.2 and 10.6 Hz, C=N). **7**: 91% yield; ³¹P NMR (CDCl₃) δ = +53.16, +52.30, J(PP) = 2.5 Hz; ¹H NMR (CDCl₃) δ = 1.93 (d, J(PH) = 14.7 Hz, 3 H, CH₃P), 7.67 (d, J(PH) = 20.5 Hz, 1 H, NH), 9.60 (s, 1 H, NH); ¹³C NMR (CDCl₃) δ = 14.57 (d, J(PC) = 102.0 Hz, CH₃P); 120.24 (q, J(CF) = 319.6 Hz, CF₃), 170.61 (d, J(PC) = 142.7 Hz, CO); IR (CDCl₃) 1685 cm⁻¹ (CO).
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