

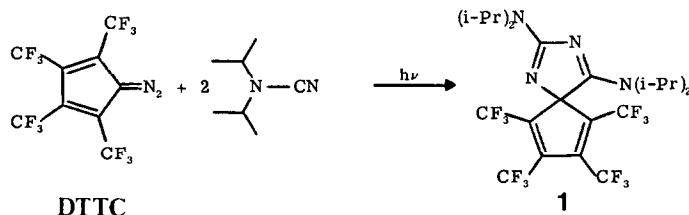
## THE SYNTHESIS AND STRUCTURE OF A STABILIZED NITRILIUM YLIDE

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The X-ray structure of the first stable nitrilium ylide is reported showing the central ylidic system to be essentially linear with only slight bends at the central carbon and nitrogen ( $4^\circ$ ); however MINDO/3 calculations on model compounds suggest the ylide functionality is quite flexible with low deformation energies.

We report an X-ray crystallographic study of the first stable nitrilium ylide. The chemistry of nitrilium ylides has been studied since the early sixties and during this time numerous syntheses have been developed which generate this reactive function under a variety of conditions.<sup>1</sup> The reaction of carbenes with nitriles also provides evidence for the intermediacy of nitrilium ylides.<sup>2</sup> We have previously reported<sup>3</sup> the 1,3-dipolar cycloaddition of a nitrilium ylide generated in this way. In addition to the wealth of syntheses which have been developed, the 1,3- and 1,1-cycloadditions of these nitrilium ylides have been well studied.<sup>1</sup> Yet in the twenty years of active work on this unusual functional group there has been no report of a stable isolable nitrilium ylide. Because of the anion stabilizing ability of the tetrakis(trifluoromethyl)cyclopentadienyl moiety and the previously<sup>3</sup> demonstrated ability of the carbene in this system to form nitrilium ylides, we employed this fluorocarbon group in the quest for a stable ylide. This mode of stabilization is contrary to the most commonly observed charge separation in nitrilium ylides as suggested by both experimental and theoretical<sup>4</sup> data. The regioselectivity of dipolar cycloadditions to nitrilium ylides suggests that the usually preferred charge separation can be reversed by appropriate substitution.<sup>5</sup>

The choice of nitrile for incorporation into the ylidic system is critical since we had previously demonstrated that aryl nitriles give ylides which suffer a rapid cycloaddition of a second molecule of nitrile to give imidazoles.<sup>3</sup> The electronic stabilization of the nitrilium group by amine donors might be expected to give rise to a fairly stable class of nitrilium ylides. However, when diazotetrakis(trifluoromethyl)cyclopentadiene (DTTC) was photolyzed in diisopropyl cyanamide the only ylide derived product<sup>6</sup> was the imidazole, **1**.<sup>7</sup> The ready addition of a second cyanamide in this system may be enhanced by the increased nucleophilicity of the terminal nitrogen. This reaction is similar to that observed with *p*-fluorobenzonitrile.<sup>3</sup>



Whether the addition of a second mole of nitrile proceeds through a concerted  $2\pi + 4\pi$  route or via the carbenoid reactivity<sup>7</sup> of the central nitrilium carbon this reaction should be slowed by steric bulk in the nitrile moiety. The selection of 1-adamantyl nitrile as a precursor allowed the isolation of a stable ylide. The 1-adamantyl nitrilium-N-tetrakis(trifluoromethyl)cyclopentadienylide (**2**) showed a broad  $^{19}\text{F}$  resonance at  $-53.4$  ppm  $\delta$  similar to other ylides derived from this fluorocarbon. The  $^1\text{H}$  NMR showed resonances at 2.27 and 1.83 ppm  $\delta$ , consistent with the ylidic structure.<sup>8</sup> A crystalline sample of this nitrilium ylide melted at  $230\text{-}3^\circ\text{C}$  with decomposition and gave a consistent mass spectrum. A single crystal of **2** was used for X-ray structure determination.<sup>9</sup>

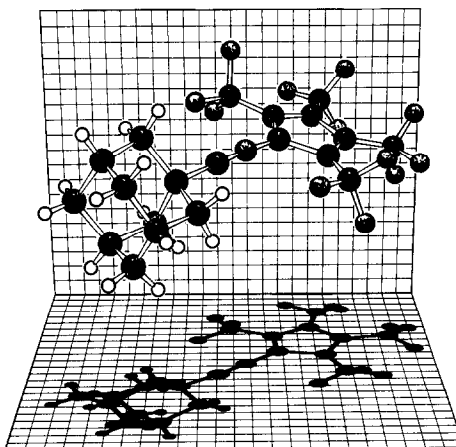
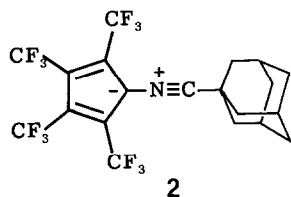
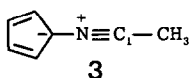


Figure 1. KANVAS<sup>11</sup> drawing of nitrilium ylide, **2**.

The structure of **2** is illustrated in Figure 1. The central ylidic system is very close to linear with only  $4^\circ$  bends at the nitrilium carbon and nitrogen centers (out of plane E arrangement). The nitrogen to cyclopentadienyl bond is fairly short at 138.9(7) pm while the central nitrilium CN bond is only 113.1(8) pm. These bond lengths and angles more closely resemble a nitrile oxide<sup>10</sup> than previously studied theoretical models. This result is not unexpected in view of the anion stabilizing ability of the tetrakis(trifluoromethyl)cyclopentadienyl moiety. MINDO/3 calculations on the acetonitrilium-N-cyclopentadienylide, **3**, show that the linear structure is indeed preferred for this ylide with bond lengths similar to **2** (133 and 117 pm). The structure calculated for **3** is remarkably flexible allowing substantial deformation with little energy required. Table I gives the calculated energy (MINDO/3) required for bending the central ylidic system of **3** in several directions. The slight bending of **2** is probably the result of crystal packing forces in view of the low deformation energies calculated for **3**.

**Table I.** MINDO/3 Energies for Bond Deformation in **3**

Deformation	Energy (cal/mole)
10° bend in plane at N	890
10° bend out of plane at N	1010
10° bend in plane at C <sub>1</sub>	710
10° bend out of plane at C <sub>1</sub>	210
two 10° bends out of plane at C <sub>1</sub> and N (Z arrangement)	380
two 10° bends out of plane at C <sub>1</sub> and N (E arrangement)	2090

The MINDO/3 calculations on **3** also suggest that the charge separation in this system is much like that in an idealized resonance structure for nitrilium ylides (e.g., **3**). The unique cyclopentadienyl carbon had a calculated charge of  $-0.16$  while nitrogen was  $0.36$  and C<sub>1</sub> was  $-0.12$ . The HOMO of **3** has a coefficient of  $0.62$  at the cyclopentadienyl carbon and  $-0.40$  at C<sub>1</sub>. This direction of charge separation explains the regioselectivity observed in cycloadditions of these types of nitrilium ylides.<sup>12</sup> The substitution in **2** and **3** gives a perturbed electronic distribution relative to the simple parent molecule calculated by Houk<sup>13</sup> et al. The model compound **3** has just achieved the charge reversal necessary for an accurate description of the ground states of ylides like **2** and **3**. The high degree of perturbation in **2** no doubt exaggerates these electronic properties.

Further studies are in progress on both the chemistry and structure of these types of stable ylide systems.

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#### References and Notes

- Complete reviews of the literature on nitrilium (nitrile) ylides are available: (a) Padwa, A.; Carlson, P. H. J. "Reactive Intermediates", **2**, Abramovitch, R. A. (Ed.); Plenum Press: New York, 1982. (b) Padwa, A. Acc. Chem. Res. 1976, **9**, 371. (c) Gilgen, P.; Heimgartner, H.; Schmid, H.; Hansen, H. J. Heterocycles 1977, **6**, 143. (d) Hüsigen, R. Mod. Sviluppi Sin. Org., Corso Estivo Chim., 1967, **10**, 259.
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6. The protio anion  $(\text{CF}_3)_4\text{C}_5\text{H}^-$  arising from hydride abstraction is also detected in the product mixture.
  7. The addition of a second nitrile moiety could possibly occur through carbenoid reactivity  $\text{C}_1$  as suggested by Padwa<sup>1a</sup> et al. for 1,1-cycloadditions if this center is sufficiently electrophilic. This would result in the formation of a new nitrilium ylide which can close to the observed imidazole.
  8. The initial 1-cyanoadamantane shows resonances at 2.04 and 1.77 ppm  $\delta$  in  $\text{CD}_2\text{Cl}_2$  so that as expected the ylide shows a downfield shift. The nitrilium ylide, **2**, also shows an IR absorption at  $2210\text{ cm}^{-1}$  ( $\text{C}\equiv\text{N}$ ).
  9. The crystal data were as follows:  $\text{C}_{20}\text{H}_{15}\text{NF}_{12}$ , monoclinic, space group  $\text{P}2_1/m$ ,  $a = 721.0(2)\text{ pm}$ ,  $b = 1442.0(6)\text{ pm}$ ,  $c = 1019.6(4)\text{ pm}$ ,  $\beta = 108.80(2)$ ,  $Z = 4$ ,  $D_c = 1.646\text{ g cm}^{-3}$ , crystal size  $0.48 \times 0.50 \times 0.95\text{ mm}$ . With 1519 reflections greater than  $2.58\sigma$ , the structure was solved by direct methods (MULTAN 80) and standard difference Fourier techniques. The final R factors were  $R = 0.107$  and  $R_w = 0.163$ .
  10. For example 4-methoxy-2,6-dimethylbenzotrile oxide exhibits a CN bond length of 114.7 pm and an NO bond length of 124.9 pm: see Shiro, M.; Yamakawa, M.; Kubota, T.; Koyama, H. *Chem. Commun.* 1968, 1409.
  11. The perspective drawings were made with the E. Keller-A. J. Arduengo Neodimensional Views of Atoms with Shadows (KANVAS) program. The back and shadowed planes are at right angles and bear a 50 pm grid. The lighting source is at infinity so that the shadow size is meaningful.
  12. The p-fluorobenzonitrilium ylide adds a second nitrile to give the 5H imidazole, not the 2H<sup>3</sup>. In a private communication Dr. G. B. Schuster has informed us that acetonitrilium-N-fluorenylide adds carbon dioxide and diethyl oxomalonate to give products suggesting the charge separation calculated for **3**.
  13. In his review<sup>4</sup> Houk suggests strong electron withdrawing groups might have this effect.

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