

β -Cyanoethyl Anion: *Lusus Naturae*

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Abstract: A stable $E1_{cb}$ intermediate, β -cyanoethyl anion (1β), has been synthesized in the gas phase at room temperature under thermal conditions via the fluoride-induced desilylation of 3-(trimethylsilyl)propionitrile. The reactivity and thermodynamic properties of this ion are reported. The cyano group is found to lower the proton affinity of 1β by 29 ± 6 kcal/mol, which represents a particularly large substituent effect. High-level ab initio and density functional calculations have been carried out on 1β and several related species. The computational results are compared to each other, and their accuracy is evaluated.

Elimination reactions are common processes which have been extensively examined.^{1–3} Mechanistic investigations indicate that a range of pathways from $E1_{cb}$ to $E1$ can take place, as originally described by Cram^{2c} and Bunnett^{2a,b} in what is commonly referred to as the variable $E2$ transition state model.³ Reactive intermediates are formed in both of these limiting cases, and in the latter instance they (carbenium ions) can be generated as long-lived species in non-nucleophilic and nonbasic media.⁴ In the $E1_{cb}$ pathway, carbanions with a β leaving group are produced. These ions usually are unstable, and this makes them very difficult to study. The transient nature of these species could be an intrinsic limitation, but it may be just an environmental effect. Computations and gas-phase experiments are of interest in this regard. The latter approach is particularly promising since elusive species in solution can often be generated in the gas phase. For example, we have made thiomethyl anion ($^-\text{CH}_2\text{SH}$),⁵ diazirinyl anion (c-CHN_2^-),⁶ dehydrophenoxide ($\text{C}_6\text{H}_3\text{O}^-$),⁷ and a cyclopropenyl anion ($\text{c-C}_3\text{H}_2\text{R}^-$)⁸ in the gas phase, whereas these ions are either unknown or highly elusive in condensed media.

An $E1_{cb}$ intermediate of the form $^-\text{CH}_2\text{CH}_2\text{X}$, where X is a leaving group, is a β -substituted alkyl anion. The related unsubstituted species are difficult to prepare in the gas phase because they are extremely strong bases and tend to be unstable with respect to their corresponding radicals. For example, ethyl, *n*-propyl, isopropyl, and *tert*-butyl anions are all unbound. These ions can be stabilized relative to their corresponding radicals and conjugate acids, however, by incorporating an electron-withdrawing substituent. Leaving groups invariably are electron withdrawing, so the electron binding energy of a substituted anion will be larger, its basicity will be less, and if there is a large enough barrier to elimination, then a stable ion will result. We now report a rare instance of a stable β -substituted alkyl anion in the gas phase which can undergo elimination (i.e., an $E1_{cb}$ intermediate).^{10–12}

Experimental Section

The gas-phase experiments reported in this work were carried out with a variable temperature flowing afterglow apparatus which has been described previously.^{5,13} Briefly, ions are generated by electron ionization and are carried down a 1 m long tube by a rapidly moving stream of helium buffer gas ($\bar{v}_{\text{He}} = 8\text{--}10000$ cm/s, $P \sim 0.4$ Torr). Neutral reagents can be added to the system at numerous points along the 1 m long reaction region so that a sequence of ion/molecule reactions can be carried out. The charged products are subsequently mass filtered and detected with a triple quadrupole-conversion dynode/electron multiplier setup.

Amide (NH_2^-), hydroxide (OH^-), and fluoride (F^-) were generated via electron ionization upon addition of ammonia (NH_3), nitrous oxide (N_2O) and methane (CH_4 , 1:2), and nitrogen trifluoride (NF_3), respectively. Propionitrile ($\text{CH}_3\text{CH}_2\text{CN}$, Aldrich) was deprotonated with amide or hydroxide to afford α -cyanoethyl anion (1α) while the β ion (1β) was produced by fluoride-induced desilylation of 3-(trimethylsilyl)propionitrile (i.e., the DePuy reaction¹⁴). Liquid samples

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Table 1. Computed MP2/6-31+G(d) Structures for Propionitrile, α -Cyanoethyl Anion (**1 α**), β -Cyanoethyl Anion (**1 β**), and the Latter Ion's Elimination Transition Structure (**1TS**)^a

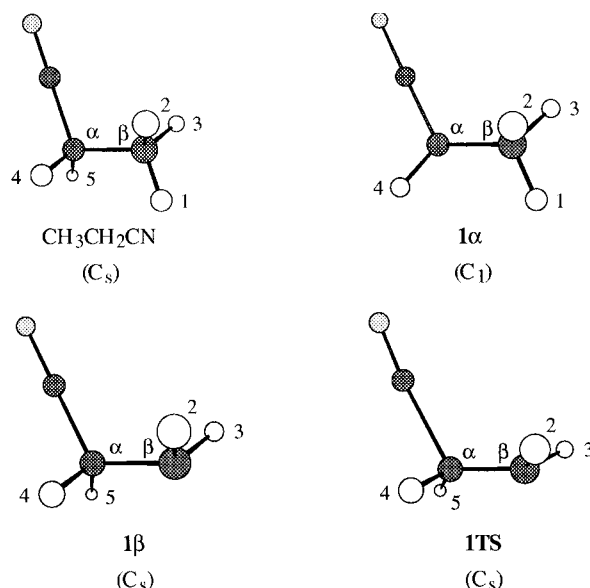
structural param	propionitrile	1α	1β	1TS
C β -H ₁	1.093	1.100		
C β -H ₂	1.093	1.111	1.102	1.092
C β -H ₃	1.093	1.100	1.102	1.092
C α -C β	1.533	1.516	1.527	1.431
C α -H ₄	1.095	1.091	1.100	1.091
C α -C _N	1.468	1.398	1.497	1.806
C \equiv N	1.182	1.205	1.188	1.197
H ₁ -C β -C α	109.8	110.5		
H ₂ -C β -C α	110.8	115.8	109.9	116.4
H ₃ -C β -C α	110.8	110.7	109.9	116.4
C β -C α -C	112.0	117.3	117.4	117.3
H ₄ -C α -C β	110.7	114.9	110.9	115.6
N-C-C α	178.9	177.0	175.8	157.2
H ₁ -C β -C α -C	180.0	-169.4		
H ₂ -C β -C α -C	60.2	69.2	59.8	68.6
H ₃ -C β -C α -C	-60.2	-51.7	-59.8	-68.6
H ₄ -C α -C β -C	120.7	141.8	121.3	114.8

^a Distances are in angstroms, and angles are in degrees.

were obtained from the following sources: D₂O (Isotec), CH₃OD (Aldrich), CH₃CH₂OD (Aldrich), and (CH₃)₃COD (Aldrich); they were used as supplied. Noncondensable impurities, however, were removed by carrying out several freeze-pump-thaw cycles. Gas purities (minimum) and sources were as follows: He (Genex, 99.9995%), NH₃ (Linde, 99.995%), N₂O (Air Products, 99.0%), CH₄ (Air Products, 99.99%), NF₃ (Air Products, 99.0%), and SO₂ (Linde, 99.98%).

3-(Trimethylsilyl)propionitrile (1). A modified procedure to the one reported by Fleming et al. was employed.¹⁵ Freshly prepared LDA was generated at 0 °C under a nitrogen atmosphere by adding 8.0 mL of *n*-BuLi (2.5 M in hexanes) to 1.98 g (19.6 mmol) of diisopropylamine in 20 mL of dry THF. After cooling of the LDA solution to -78 °C, 0.80 g (19.6 mmol) of acetonitrile in 10 mL of THF was added dropwise to it. The resulting solution was stirred for an additional 3.5 h at -78 °C, and then 1.9 g (15.7 mmol) of (chloromethyl)trimethylsilane in 10 mL of THF was slowly added. The resulting reaction mixture was allowed to warm to room temperature overnight before being quenched with 100 mL of 1 M HCl. Separation of the two phases and extraction of the aqueous layer with 3 \times 40 mL of ether was followed by successive washings of the combined organic material with 40 mL portions of saturated sodium bicarbonate, water, and brine. The ethereal solution was dried with anhydrous magnesium sulfate, and the bulk of the solvent was removed under reduced pressure with a rotary evaporator. Distillation of the residue under vacuum afforded 1.2 g (62%) of **1** (bp 65–70 °C at 15 mmHg). ¹H NMR (200 MHz, CDCl₃): δ 2.30 (t, 2H, *J* = 8.2 Hz), 0.90 (t, 2H, *J* = 8.2 Hz), 0.60 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 121.3 (s), 12.7 (t), 11.9 (t), -2.1 (q).

All of the reported computations were carried out using Gaussian 92/DFT¹⁶ on a UNIX-based workstation or a Cray supercomputer at the Minnesota Supercomputer Institute. Systematic isomeric and conformational analyses were carried out on C₃H₅N, C₃H₄N⁺, C₃H₄N⁻, and transition structures converting one species into another at the MP2-(UMP2)/6-31+G(d)/RHF(UHF)/6-31+G(d) and MP2(UMP2)/6-31+G(d)/MP2(UMP2)/6-31+G(d) levels of theory (Table 1, Figure 1, and supporting information).^{17,18} Force constants were also determined at these levels of theory for each stationary point in order to determine

**Figure 1.** Calculated MP2/6-31+G(d) structures for CH₃CH₂CN, **1 α** , **1 β** , and **1TS**.

the curvature of the potential energy surface and the zero-point energies (ZPE). The latter quantities were scaled throughout by 0.9135 (HF) and 0.9646 (MP2), as previously recommended.¹⁹ The resulting lowest energy minima and their connecting transition states were subsequently examined at the MP2(UMP2)/aug-cc-pVTZ//MP2(UMP2)/aug-cc-pVDZ²⁰ and DFT/aug-cc-pVTZ//DFT/aug-cc-pVDZ (DFT functionals: B-VWN5, B-LYP, and Becke3-LYP)^{21–24} levels of theory (Table 2 and supporting information). Force constants were again calculated for each optimized geometry, but the DFT ZPEs were used without employing any empirical scaling factor.²⁵

The density functionals employed in this study are representative of the range of those commonly used. These functionals, B-VWN5, B-LYP, and Becke3-LYP, differ in their respective exchange and correlation components.^{21–24} The first two methods make use of Becke's nonlocal correction to Slater's local exchange functional. They differ from each other in that the former's correlation functional is entirely local in nature, whereas the latter has a nonlocal correction added to the local functional. Becke3-LYP, on the other hand, is a "hybrid" method with both Hartree-Fock and density functional (local with a nonlocal correction) exchange as well as a correlation term. Moreover, the components which make up this method were parametrically fitted to an empirical data set.

(17) For references dealing with the 6-31+G(d) basis set and Møller-Plesset perturbation theory, see: (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (c) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163. (d) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265. (e) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294. (f) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (g) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 281.

(18) Alternative structures to **1 β** were considered, and a few of them were examined computationally. In particular, $\text{CH}_2\text{CH}_2\text{NC}$, $\text{CH}_2\text{CH}_2\text{C}\equiv\text{N}^-$, $\text{CH}_2\text{CH}_2\text{C}^-\equiv\text{N}$, and $\text{CH}_2\text{CH}_2\text{N}=\text{C}^-$ were found to be 16.4, 22.5, 30.2, and 94.5 kcal/mol less stable than **1 β** at the MP2/6-31+G(d)/HF/6-31+G(d) level. Isomerization to one of these anions, therefore, is unlikely. For further information on these ions, structures, and absolute energies, see the supporting information.

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Table 2. Calculated Energies^a for Propionitrile, α - and β -Cyanoethyl Anion (**1** α and **1** β), α - and β -Cyanoethyl Radical (**2** α and **2** β), the E1_{cb} Transition Structure (**1TS**), and Related Species

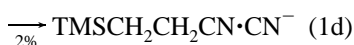
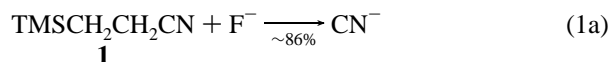
species	B-VWN5 ^b	B-LYP ^b	Becke3-LYP ^b	MP2 ^c	MP2/6-31+G(d) ^d	MP2/aug-cc-pVTZ ^d	G2+ (MP2)	G2+
CH ₃ CH ₂ CN	-172.919 86	-171.989 89	-172.061 93	-171.434 74	-171.439 68	-171.650 22	-171.682 23	-171.745 19
CH ₃ CH ⁻ CN (1 α)	-172.321 99	-171.402 74	-171.469 30	-170.837 99	-170.841 40	-171.053 80	-171.085 15	-171.145 42
⁻ CH ₂ CH ₂ CN (1 β)	-172.286 04	-171.366 68	-171.431 98	-170.800 58	-170.805 30	-171.019 78	-171.050 76	-171.111 87
CH ₃ CHCN ^e (2 α)	-172.264 14	-171.359 11	-171.422 75	-170.794 17	-170.792 81	-170.990 21	-171.028 89	-171.095 13
	(0.759; 0.750)	(0.758; 0.750)	(0.766; 0.750)	(0.913; 0.766)	(0.888; 0.761)	(0.890; 0.762)	(0.888; 0.761)	(0.888; 0.761)
[*] CH ₂ CH ₂ CN ^e (2 β)	-172.242 05	-171.336 29	-171.401 62	-170.788 16	-170.793 05	-170.988 82	-171.019 67	-171.080 89
	(0.754; 0.750)	(0.753; 0.750)	(0.754; 0.750)	(0.762; 0.750)	(0.762; 0.750)	(0.763; 0.750)	(0.762; 0.750)	(0.762; 0.750)
E1 _{cb} TS ^f (1TS)	-172.283 90	-171.363 27	-171.425 47	-170.792 10	-170.797 89	-171.009 27	-171.039 70	-171.102 84
	(391i)	(393i)	(450i)	(511i)	(469i)	(467i)	(465i)	(465i)
C ₂ H ₄	-79.014 40	-78.526 50	-78.572 88	-78.240 54	-78.241 22	-78.354 47	-78.374 80	-78.414 52
CN ⁻	-93.311 91	-92.871 78	-92.890 47	-92.595 49	-92.599 04	-92.688 35	-92.703 27	-92.728 56
CH ₂ =CHCN	-171.672 92	-170.793 19	-170.848 15	-170.252 94	-170.259 68	-170.444 48	-170.476 44	-170.533 48

^a In hartrees. ^b DFT/aug-cc-pVTZ//DFT/aug-cc-pVDZ (e.g., BVWN5/aug-cc-pVTZ/BVWN5/aug-cc-pVTZ). Unscaled zero-point energies are included. ^c MP2/6-31+G(d)//HF/6-31+G(d) + (0.9135)ZPE. ^d Energies and structures were obtained with the indicated basis set. Scaled (0.9646) ZPEs are included. ^e Spin contamination ($\langle S^2 \rangle$) in the wavefunction before and after projection is given in parentheses. ^f The imaginary frequencies have been scaled (0.8929 (HF) and 0.9427 (MP2)) and are in cm⁻¹.

Several minima and transition structures pertinent to the experimental results were investigated at the G2+ and G2(MP2)+ levels of theory.^{26–29} These calculations effectively correspond to QCISD(T)/6-311+G(3df,2p)/MP2/6-31+G(d,p) + ZPE energies and represent the highest levels of theory employed in the present study. Calculations of this type generally reproduce experimental energetics to within 2–3 kcal/mol.^{26,27}

Results and Discussion

3-(Trimethylsilyl)propionitrile (**1**), synthesized from acetonitrile and (chloromethyl)trimethylsilane, reacts with fluoride ion at room temperature in our flowing afterglow device to afford cyanide (m/z 26) as the predominate product ion. Smaller amounts of the $M - \text{TMS}$ (m/z 54), $M - 1$ (m/z 126), and $M + \text{CN}^-$ (m/z 153) ions are also produced (eq 1).³⁰ The relative abundance of the m/z 54 ion (**1** β) is only about 5%, but the absolute intensity is sufficient to characterize this species and assign its structure (signal-to-noise ratios of ≥ 100 –1000:1 were obtained in a single scan).



α -Cyanoethyl anion (**1** α), the $M - 1$ ion of propionitrile, was produced by deprotonation of propionitrile with hydroxide

(26) For a description of the G2 procedure, see: Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

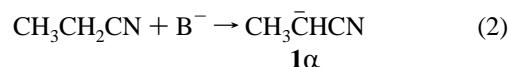
(27) For a description of the G2(MP2) method, see: Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

(28) For a discussion of the G2+ approach, see: Gronert, S. *J. Am. Chem. Soc.* **1993**, *115*, 10258.

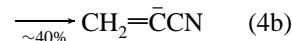
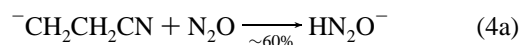
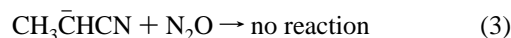
(29) In contrast to the literature procedure which calls for MP2(full)/6-31+G(d,p) geometries for anions, MP2(full)/6-31G(d,p) geometries for neutrals and scaled HF frequencies, we used MP2(FC)/6-31+G(d,p) optimizations for all structures and scaled (0.9646) MP2 frequencies. Our G2+ energies were then obtained as follows: $E(\text{G2+}) = E(\text{MP4(SDTQ)}/6-311+G(2\text{df,p})) + (E(\text{QCISD(T)}/6-311+G(d,p)) - E(\text{MP4(SDTQ)}/6-311+G(d,p))) + (E(\text{MP2}/6-31+G(3\text{df},2\text{p})) - E(\text{MP2}/6-311+G(2\text{df},\text{p}))) + E(\text{HLC}) + \text{scaled MP2 ZPE}$.

(30) Additional ions at m/z 46, 80, 89, 91, 93, 116, 130, and 146 were also observed.

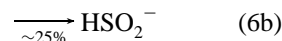
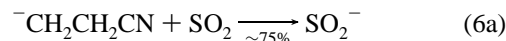
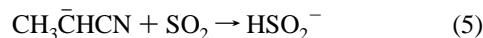
or amide (eq 2). In addition to the $M - 1$ ion (m/z 54), a small



amount of CN⁻ and a $M + (M - 1)$ cluster (m/z 109) are also formed. The α -anion (**1** α) was readily distinguished from its less stable β -isomer (**1** β) on the basis of the following observations: (1) Nitrous oxide does not react with **1** α but affords characteristic products, HN₂O⁻ (m/z 45) and CH₂=C⁻CN (m/z 52), with **1** β (eqs 3 and 4).³¹ The product ions also are in



keeping with the structure of **1** β and the previously reported behavior of N₂O.³² (2) Sulfur dioxide reacts with **1** α to give HSO₂⁻ (m/z 65) while **1** β affords SO₂⁻ (m/z 64) and HSO₂⁻ in approximately a 3:1 ratio, respectively (eqs 5 and 6). These



results indicate that the electron affinity of the α -cyanoethyl radical (**2** α) is greater than 25.5 kcal/mol (1.11 eV),³³ and the β -cyanoethyl radical (**2** β) has a smaller electron affinity than this value. In accord with this conclusion, the literature value

(31) It is worth noting that, given the large background signal at m/z 26, the formation of CN⁻ would go undetected in all of the transformations of **1** β that were studied.

(32) (a) Kass, S. R.; Filley, J.; Van Doren, J. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 2849. (b) Bierbaum, V. M.; DePuy, C. H.; Schmitt, R. H. *J. Am. Chem. Soc.* **1977**, *99*, 5800.

(33) Celotta, R. J.; Bennett, R. A.; Hall, J. L. *J. Chem. Phys.* **1974**, *60*, 1740.

(34) All thermodynamic data, unless otherwise noted, comes from Lias et al. (Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1) or the slightly updated form available on a personal computer: *NIST Negative Ion Energetics Database* (Version 3.00, 1993); *NIST Standard Reference Database 19B*.

Table 3. Summary of Proton Transfer and Hydrogen–Deuterium Exchange Data for **1α** and **1β**^a

ref acid	$\Delta H^\circ_{\text{acid}}$ (kcal/mol) ^a	1α	1β
(CH ₃) ₃ COD	374.6 ^b	D ⁺ transfer	
CH ₃ CH ₂ OD	377.4 ^b	1 H/D exchange	
CH ₃ OD	383.5	1 H/D exchange	D ⁺ transfer + 2 H/D exchanges ^c
H ₂ O	390.7		H ⁺ transfer (small)
D ₂ O	392.0	1 H/D exchange	2 H/D exchanges ^d
(CH ₃) ₂ NH	396.3		no H ⁺ transfer

^a The acidity data comes from refs 34 and 36. ^b Value for protic acid. ^c Incorporation of the second deuterium only occurs to a small extent. ^d The possible presence of DO[−] (*m/z* 18) was obscured by the large F[−] (*m/z* 19) signal.

for the electron affinity of **2α** is 28.6 ± 2.3 kcal/mol (1.24 ± 0.10 eV).³² (3) Deuterium oxide reacts with **1α** by exchanging one hydrogen for a deuterium while **1β** undergoes two H/D exchanges (eqs 7 and 8). On the basis of these results it is



apparent that **1α** and **1β** have different structures, and with the aid of ab initio calculations (vide infra) we assign the β-cyanoethyl anion structure to **1β**.^{18,35}

The reactivities of the α- and β-cyanoethyl anions (**1α** and **1β**) with a series of acids of known strength were examined in order to establish their proton affinities. By observing the occurrence or nonoccurrence of proton transfer it was possible to bracket their proton affinities. The results from these experiments are summarized in Table 3 and indicate that PA(**1α**) = 376 ± 2 kcal/mol and PA(**1β**) = 391 ± 5 kcal/mol.^{34,36} The former value is in excellent agreement with the literature proton affinity of 375.1 ± 2.1 kcal/mol and our computed ab initio acidity (376.4 kcal/mol (G2+), Table 4). The latter quantity is also in reasonable agreement with our calculated value (397.4 kcal/mol (G2+)) although the computations suggest that the β-acidity is toward the higher end of our range.

The large difference in the acidity of the α and β sites in propionitrile, 15 ± 5 kcal/mol, accounts for the different hydrogen–deuterium (H/D) exchange behavior of **1α** and **1β**. The former anion reacts with a deuterated acid such as deuterium oxide to replace the unique hydrogen at the charged site with a deuterium via a deuteron transfer–proton abstraction sequence (eq 7).³⁷ The β-cyanoethyl anion also undergoes an initial deuteron transfer, to the β-position in this case (eq 8), but the subsequent proton abstraction now occurs at the α site. This acid-catalyzed isomerization results in the formation of a monodeuterated α-cyanoethyl anion, CH₂DCH[−]CN, which still has an exchangeable hydrogen at the α-position. Consequently, two H/D exchanges can take place for the β-anion.

Ab initio and density functional theory (DFT) calculations have been carried out on **1α**, **1β**, and a number of related species.¹⁸ Optimizations were performed at the Hartree–Fock

(35) A cluster ion between CN[−] and ethylene (C₂H₄·CN[−] or C₂H₄·NC[−]) is more stable than **1β**, but can be excluded on the basis of the observed reactivity of the M – TMS ion, the measured thermodynamic properties, and the reported computational results.

(36) Barlow, S. E.; Dang, T. T.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1990**, *112*, 6832.

(37) For excellent descriptions of the gas-phase exchange process, see: (a) Grabowski, J. J.; DePuy, C. H.; Van Doren, J. V.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1985**, *107*, 7384. (b) Nibbering, N. M. M. *Adv. Phys. Org. Chem.* **1988**, *24*, 1 and references therein.

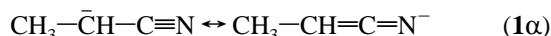
Table 4. Calculated Thermochemical Data^a for **1α**, **1β**, and the Elimination Reaction of the Latter Ion

quantity ^b	B-VWN5 ^c	B-LYP ^c	Becke3-LYP ^c	MP2 ^d	MP2/6-31+G(d) ^e	MP2/aug-cc-pVTZ ^e	G2+ (MP2)	G2+	expt
PA (1α)	375.2	368.4	371.9	374.5	375.4	374.3	374.4	376.4	375.1 ± 2.1
PA (1β)	397.9	391.1	395.3	397.9	398.1	395.6	396.3	397.4	391 ± 5
EA (2α) ^f	36.2 (1.57)	27.4 (1.19)	29.3 (1.27)	27.4 (1.19)	30.4 (1.32)	39.9 (1.73)	35.3 (1.53)	31.6 (1.37)	28.6 ± 2.3 (1.24 ± 0.10)
EA (2β) ^f	27.7 (1.20)	19.1 (0.83)	19.1 (0.83)	7.8 (0.34)	7.6 (0.33)	19.4 (0.84)	19.6 (0.85)	19.4 (0.84)	≤ 25.6 (1.11)
HA(α) ^g	76.1 (48.7)	51.3 (50.7)	58.6 (53.6)	35.9	33.9	51.2	50.8	52.8	57.0 ± 2.2
HA(β) ^g	53.6 (26.2)	28.7 (28.1)	35.2 (30.2)	12.5	11.2	29.9	29.2	31.8	41 ± 5
ΔH°	1.3	2.1	4.1	5.3	4.6	6.6	6.9	5.7	
$\Delta H^\circ_{\text{elim}}(\beta)$ ^h	−25.3 (−14.1)	−19.8 (−14.1)	−19.7 (−14.8)	−22.2 (−14.8)	−21.9 (−14.1)	−14.5 (−12.7)	−17.1 (−13.3)	−19.6 (−12.4)	-8 ± 5

^a In kilocalories/mole. ^b PA = proton affinity, EA = electron affinity, and HA = hydride affinity of acrylonitrile (CH₂=CHCN). ^c DFT/aug-cc-pVTZ/DFT/aug-cc-pVDZ (e.g., BVWN5/aug-cc-pVTZ//BVWN5/aug-cc-pVTZ). Unscaled ZPEs are included. ^d MP2/6-31+G(d)/HF/6-31+G(d) + (0.9135)ZPE. ^e MP2 energies and structures were obtained with the indicated basis set. Scaled (0.9646) ZPEs are included. ^f These electron affinities were calculated directly (i.e., eq 9), and parenthetical values are in electronvolts. ^g The exact energy of H[−], −0.52775 hartrees, was used. DFT results using the calculated hydride energies (−0.57142 (B-VWN5), −0.52873 (B-LYP), and −0.53567 (Becke3-LYP) hartrees) are given in parentheses. ^h Parenthetical values were obtained using eq 14c as described in the text.

(HF) level using the 6-31+G(d) basis set and at the MP2 (frozen core) level with both the 6-31+G(d) and aug-cc-pVDZ basis sets.^{17,20} Three diverse DFT functionals (B-VWN5, B-LYP, and Becke3-LYP) were also used with the latter basis set.^{21–24} The resulting geometries are generally in good agreement with each other (≤ 0.02 Å and $\leq 2^\circ$) except for the C≡N bond length, which elongates by approximately 0.05 Å in going from the HF to the MP2 level. The effect of the basis set, MP2/6-31+G(d) vs MP2/aug-cc-pVDZ, also is small (< 0.015 Å and $< 2^\circ$) except for the C_α–CN distance in the transition structure for cyanide expulsion (**1TS**), which increases by 0.028 Å with the larger basis set. Therefore, only the MP2/6-31+G(d) geometries are given in Figure 1 and Table 1 and are discussed below (all of the structural data can be found in the supporting information).

Deprotonation of propionitrile at the α-position results in a 0.070 Å shortening of the C_α–CN bond and a 0.023 Å lengthening of the C≡N distance as expected for a delocalized carbanion. The C_α–C_β distance also contracts somewhat (0.017 Å) in accord with a formal hybridization change from sp³ to sp² at the α-carbon (C_α).



The β-anion (**1β**) flattens out slightly at C_β (2.2°)³⁸ and has a longer C_α–CN bond than its conjugate acid (0.029 Å) in accord with a species stabilized by negative hyperconjugation. These trends are further accentuated in the elimination transition structure; the C_α–CN distance is 0.309 Å longer, the β-carbon



is 18.9° flatter, and the C_α–C_β bond length is 0.096 Å shorter than in **1β** due to the formation of carbon–carbon double bond character. It is also interesting that the N–C–C angle deviates from linearity by 22.9° and is 15.8° smaller than in **1β**. Presumably, this orientation reduces the electrostatic repulsion between the incipient nitrile (CN[−]) and the negatively charged β-carbon.

The proton affinities of **1α** and **1β** were calculated at several levels of theory, and all of them, with the exception of the B-LYP result, are in good accord with the experimental values and each other (Table 4). These results, in combination with the experimental acidity of ethane ($\Delta H^\circ_{\text{acid}} = 420$ kcal/mol),^{9b} reveal that the C≡N group decreases the proton affinity of **1α** and **1β** by 45 (experiment, 44 (G2+)) and 29 (experiment, 23 (G2+)) kcal/mol, respectively.³⁵ The bigger interaction at the α-position is consistent with **1α** being resonance stabilized, while the latter value indicates that β-substituent effects can be considerable. It is worth adding that cyclization of **1β** to a three- or four-membered-ring isomer is energetically quite unfavorable and this is not responsible for the large β-effect.¹⁸ A preliminary analysis of the observed stabilization in terms of the field effect, resonance, polarization, and the inductive effect indicates that the first two contributors are the dominant factors.

Another commonly used measure of the stability of an anion is its electron binding energy. This quantity, more typically referred to as the electron affinity (EA), is the enthalpic difference between an anion and its corresponding radical. Unfortunately, this thermodynamic property is more difficult to calculate accurately than a proton affinity because of spin contamination in unrestricted wavefunctions of open-shell systems (e.g., UHF or UMP2) and a greater need to account

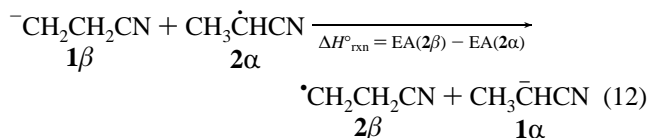
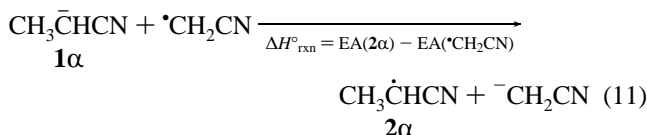
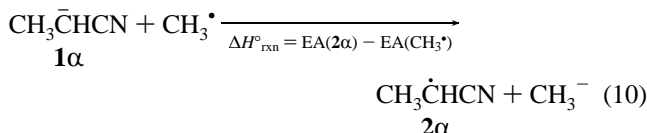
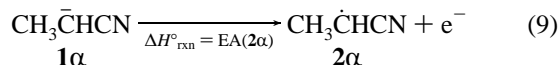
(38) The pyramidalization angle at C_β was defined as the acute angle formed by the line going through C_β and C_α and the line bisecting the H–C_β–H angle.

Table 5. Calculated Electron Affinities^a for α- and β-Cyanoethyl Radicals (**2α** and **2β**) Using Several Approaches^b

compd	level of theory	eq 9	eq 10	eq 11	eq 12	av
2α	B-VWN5	1.57				1.57
	B-LYP	1.19				1.19
	Becke3-LYP	1.27				1.27
	MP2 ^c	1.19	1.74			1.47
	G2+(MP2)	1.53	1.53	1.26		1.44
	G2+	1.37	1.38	1.27		1.34
	expt					1.24 ± 0.09
2β	B-VWN5	1.20				1.20
	B-LYP	0.83				0.83
	Becke3-LYP	0.83				0.83
	MP2 ^c	0.34	0.89		0.39	0.54
	G2+(MP2)	0.85	0.85	0.58	0.56	0.71
	G2+	0.84	0.86	0.74	0.71	0.79

^a In electronvolts. ^b Scaled and unscaled ZPEs are included in the ab initio and DFT results, respectively. Experimental values for the electron affinities of •CH₃, •CH₂CN, and CH₃CH(CN)•, see refs 34 and 41, were used in eqs 10–12, respectively. ^c MP2/6-31+G(d)//HF/6-31+G(d) energies.

for electron correlation.³⁹ The latter requirement is a result of the fact that the number of electron pairs differs in an anion and its corresponding radical. As a result, high levels of theory are needed to calculate electron affinities directly. A computationally less demanding approach which has met with success is to make use of isogyric reactions, transformations in which the number of paired and unpaired electrons are preserved.⁴⁰ Both methods were utilized in calculating the electron affinities of **2α** and **2β** as illustrated for the former compound in eqs 9–11 (Table 5).⁴¹ The latter quantity was also calculated



making use of the known electron affinity of **2α** (eq 12).³⁴ For both compounds the G2+ energies span a narrow range (≤ 0.15 eV) and the average values, 1.34 and 0.79 eV, respectively, were employed. Our computed results are in good agreement with the measured electron affinity of the α-radical (1.24 ±

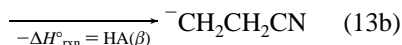
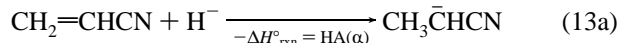
(39) Baker, J.; Nobes, R. H.; Radom, L. *J. Comput. Chem.* **1986**, 7, 349.

(40) (a) Pople, J. A.; Schleyer, P. v. R.; Kaneti, J.; Spitznagel, G. W. *Chem. Phys. Lett.* **1988**, 145, 359. (b) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley and Sons: New York, 1986.

(41) The G2+ and G2+(MP2) electron affinities of CH₃• and •CH₂CN were calculated directly and are in good accord with experiment: EA(CH₃•) = 0.065 (G2+), 0.082 (G2+(MP2)), and 0.080 ± 0.030 eV (experiment); EA(•CH₂CN) = 1.64 (G2+), 1.81 (G2+(MP2)), and 1.543 ± 0.014 eV (experiment). For the experimental data, see: (a) Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, 100, 2556 (CH₃•). (b) Moran, S.; Ellis, H. B., Jr.; DeFrees, D. J.; McLean, A. D.; Ellison, G. B. *J. Am. Chem. Soc.* **1987**, 109, 5996 (•CH₂CN).

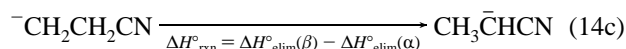
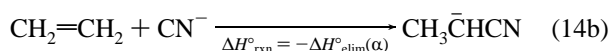
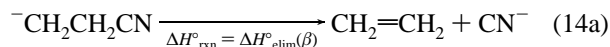
0.09 eV), and they account for why **1** β transfers an electron to sulfur dioxide (EA = 1.11 eV)³³ while **1** α does not; the former reaction is exothermic whereas the latter one is endothermic. It is also worth noting that B-LYP and Becke3-LYP do a very good job on the electron affinities but at a fraction of the computational time required for the G2+ results.

The hydride affinity (HA) of acrylonitrile at the α - and β -positions (eq 13) provides another measure of the stability of **1** α and **1** β . These energies were calculated at several levels of



theory (Table 4), although in each case the exact energy of H^- , -0.52775 hartrees, was used. The reason for this is that the basis sets which were employed, as is usually the case, are more flexible for heavy atoms than for hydrogen; consequently, hydride is badly described computationally. Smith, Pople, Curtiss, and Radom circumvented this problem by defining the exact energy of H^- as its G2 (and thus G2+) value, and we have adopted this proposal.^{42,43} At the G2+ level, $\text{HA}(\alpha) = 52.8$ kcal/mol, which is in reasonable accord with the experimental value of 57.0 ± 2.2 kcal/mol.³⁴ The β -hydride affinity, $\text{HA}(\beta) = 31.8$ kcal/mol, is in poor agreement with experiment (41 ± 5 kcal/mol), but this is largely a reflection of the 6.4 kcal/mol discrepancy in the acidity.⁴⁴ In any case, these results suggest that hydride transfer from **1** α to nitrous oxide is slightly endothermic (+3 kcal/mol) whereas it is exothermic with **1** β (-14 kcal/mol);⁴⁵ this accounts for the formation of HN_2O^- in the latter case.

β -Cyanoethyl anion is a marginally stable E1_{cb} intermediate which can readily expel cyanide to form ethylene (eq 14a). This



transformation is exothermic, -8 ± 5 kcal/mol, and is well reproduced at every level of theory that was examined (Table 4) by comparing the relative energies of **1** α and **1** β (eq 14c) and using the experimentally derived value for $\Delta H_{\text{elim}}(\alpha)$ (-8.6 ± 3 kcal/mol).^{34,45} A direct calculation of the elimination (eq 14a) provides poor results not only because of the 6.4 kcal/mol

discrepancy in the proton affinity of **1** β but also because cyanide is not well described at the G2+ level (e.g., $\text{EA}(\text{CN}^\bullet) = 4.03$ eV (G2+) and 3.74 ± 0.13 eV (experiment)).⁴⁶ The elimination barrier (ΔH^\ddagger) is computed to be 5.7 kcal/mol at our best level of theory, and this value accounts for the difficulty in generating **1** β ; elimination is facile but not so facile as to preclude the formation of **1** β . In this regard, it is worth noting that anions with electron binding energies of approximately 6 kcal/mol or more can be readily generated in helium at 298 K in the reaction region of a flowing afterglow device whereas species with smaller electron affinities cannot.⁴⁷

A few specific comments about the density functional calculations carried out in this work are warranted. First, the DFT structures are in good accord with one another and their ab initio MP2/6-31+G(d) counterparts. Not surprisingly, the biggest differences are found in the elimination transition structures (**ITS**). Both B-VWN5 and B-LYP have shorter $\text{C}_\alpha\text{--CN}$ and longer $\text{C}_\alpha\text{--C}_\beta$ bond lengths (0.03–0.06 and 0.02–0.03 Å, respectively) than the Becke3-LYP and MP2 structures, indicating that the former methods lead to an earlier and looser transition state.⁴⁸ This is consistent with the fact that the imaginary frequencies corresponding to the reaction coordinate for the B-VWN5 and B-LYP eliminations are about 70 cm^{-1} smaller than for the MP2 or Becke3-LYP structures. Second, Becke3-LYP gives the best overall energetic data. In particular, the average unsigned error relative to the G2+ energies is only 1.7 kcal/mol,⁴⁹ and all of the values are within 2.3 kcal/mol except for the proton affinity of **1** α . This quantity is too small by 4.5 and 3.2 ± 2.1 kcal/mol relative to the G2+ and the experimental results, respectively. Third, the B-VWN5 results are the poorest of the three with an average error of 4.3 kcal/mol, but this method does appear to give the most reliable proton affinities. Fourth, the $\langle S^2 \rangle$ values for the DFT wavefunctions are appreciably smaller (less spin contamination) than their conventional ab initio counterparts, and the electron affinities are accurately reproduced by both functionals which make use of a nonlocal correction to the correlation functional. Finally, all of the DFT methods predict elimination barriers (ΔH^\ddagger) which are smaller than those at the G2+ level, although the Becke3-LYP value is only 1.6 kcal/mol lower than the G2+ result. The consistent underestimation of barrier heights by density functional calculations appears to be a general shortcoming and has been noted previously.^{50,51}

Conclusions

The fluoride-induced desilylation of 3-(trimethylsilyl)propionitrile leads predominantly to the formation of cyanide. A small but significant amount (5%) of β -cyanoethyl anion (**1** β)

(42) Smith, B. J.; Pople, J. A.; Curtiss, L. A.; Radom, L. *Aust. J. Chem.* **1992**, *45*, 285.

(43) The B-LYP and Becke3-LYP results are less sensitive to this problem. For example, $\text{HA}(\alpha$ or $\beta)$ increases by 0.6 (B-LYP) and 5.0 (Becke3-LYP) kcal/mol when the exact energy for hydride is used.

(44) If one uses the calculated β -acidity of ethyl cyanide and experimental heats of formation for all of the other quantities, then the following results (in kcal/mol) for $\text{HA}(\beta)$ are obtained: 34.7 (G2+), 35.8 (G2+(MP2)), 36.5 (MP2/aug-cc-pVTZ), 34.0 (MP2/6-31+G(d)), 34.2 (MP2/6-31+G(d)//HF/6-31+G(d)), 36.8 (Becke3-LYP), 41.0 (B-LYP), and 34.2 (B-VWN5).

(45) The following heats of formation ($\Delta H_f^\circ_{298}$), in kcal/mol, were used: 19.6 (N_2O), 44.0 ($\text{CH}_2=\text{CHCN}$), 21.7 (**1** α), 38 (**1** β), and 0 (HN_2O^-). All of these energies, with the exception of $\Delta H_f^\circ_{298}(\text{HN}_2\text{O}^-)$, are available or can be derived using the data given in ref 34 and our experimental measurement for the proton affinity of **1** β . The missing quantity was obtained by averaging the temperature-corrected (298 K) G2+ results for the following two transformations: (1) $\text{HN}_2\text{O}^- \rightarrow \text{H}^- + \text{N}_2\text{O}$ and (2) $\text{1}\alpha + \text{N}_2\text{O} \rightarrow \text{HN}_2\text{O}^- + \text{CH}_2=\text{CHCN}$. Note, $\text{G2}+(\text{N}_2\text{O}) = -184.43698$, $\text{G2}+(\text{HN}_2\text{O}^-) = -185.04717$, and the temperature corrections are as follows: 2.68 (N_2O), 2.54 (HN_2O^-), 2.30 (**1** α), 1.84 ($\text{CH}_2=\text{CHCN}$).

(46) The electron affinity is 4.18 and 3.97 eV at the G2+(MP2) and G2 levels, respectively. Additional calculations reveal that CN^- is too stable at the G2 (G2+) level. This problem has recently been addressed; see: Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1995**, *103*, 4192.

(47) Dahlke, G. D.; Kass, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 5566.

(48) The further developed transition structures are also closer to planarity (i.e., they are flatter).

(49) In calculating the average error, the DFT hydride affinities with the calculated energies for H^- were used (i.e., the parenthetical values in Table 4). The direct calculation of $\Delta H^\circ_{\text{elim}}(\text{1}\beta)$ (eq 14a and the values not in parentheses in Table 4) was also used in this comparison. In any case, it is clear that the agreement between B3-LYP, G2+, and the experimental data is good.

(50) Merrill, G. N.; Kass, S. R. Unpublished results.

(51) (a) Gronert, S.; Merrill, G. N.; Kass, S. R. *J. Org. Chem.* **1995**, *60*, 488. (b) Latajka, Z.; Bouteiller, Y.; Scheiner, S. *Chem. Phys. Lett.* **1995**, *234*, 159. (c) Johnson, B. G.; Gonzales, C. A.; Gill, P. M. W.; Pople, J. A. *Chem. Phys. Lett.* **1994**, *221*, 100. (d) Fan, L.; Ziegler, T. *J. Am. Chem. Soc.* **1992**, *114*, 10890.

also is produced, and this latter ion is a stable E1cb intermediate. Some of the reactions and thermodynamic properties of 1β were explored experimentally and computationally, and an extremely large (29 ± 6 kcal/mol) β -substituent effect was noted. Preliminary analysis of this system suggests that the stabilization is principally due to resonance and field effects. Given these results, it should be possible to generate additional β -substituted alkyl anions ($^-\text{CH}_2\text{CH}_2\text{X}$) in the gas phase, and probably even more remotely substituted carbanions (e.g., $^-\text{CH}_2\text{CH}_2\text{CH}_2\text{X}$). Work along these lines is currently in progress and will be reported in due course.

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administered by the American Chemical Society, and the Minnesota Supercomputer Institute is gratefully acknowledged.

Supporting Information Available: Calculated structures (xyz coordinates) and energies for all of the computed species in this work (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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