

**Table II.** CNDO/S Calculated Values (eV) of the Energies Associated with the Highest Occupied Molecular Orbitals (with Their Symmetries) for a Chair Form (Experimental Structure<sup>21</sup>) and for a Twist Form of *S*-Tetrathiane

Chair form ( $C_{2h}$ )	Twist form ( $D_2$ )
9.33 ( $a_g$ )	9.38 ( $b_2$ )
9.39 ( $b_g$ )	10.00 ( $b_1$ )
9.74 ( $a_u$ )	10.19 ( $a$ )
12.37 ( $b_u$ )	10.84 ( $b_3$ )

thiane (B) prefer respectively the twist and chair conformations. It is interesting to note that these two compounds present the same preferential structure in solution<sup>2</sup> (A: 70% twist form; B: 80% chair form at  $-15^\circ\text{C}$  in  $\text{CS}_2$ ) as in the crystal for compound A.<sup>3</sup> This is not the case for the 3,3:6,6-bis(pentamethylene) derivative (C) which exists in a chair conformation in the vapor phase as well as in the crystal<sup>21</sup> but prefers the twist form in solution (20% chair form at  $-15^\circ\text{C}$  in  $\text{CS}_2$ ).

### Experimental Section

In this study, we have used a Perkin-Elmer PS<sub>18</sub> photoelectron spectrometer with a flowing helium discharge lamp source (He(I), 584 Å). The resolution was at about 20 meV. The spectra were calibrated with <sup>2</sup>P<sub>1/2</sub> and <sup>2</sup>P<sub>3/2</sub> doublet of xenon (12.127 and 13.427 eV) and argon (15.755 and 15.943 eV).

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## Relationship between Orbital Ionization Energies and Molecular Properties. Proton Affinities and Photoelectron Spectra of Nitriles

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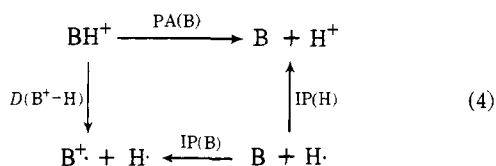
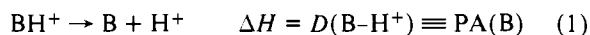
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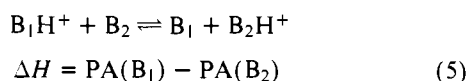
**Abstract:** Proton affinities are determined for a series of nitriles using ion cyclotron resonance techniques. Photoelectron spectra of nitriles are also obtained. In previously examined series of bases, linear relationships have been established between proton affinities and adiabatic first ionization potentials which correspond to removal of an electron from a lone pair localized at the site of protonation. Nitrile proton affinities are found to be linearly related not to the first CN  $\pi$  ionization potentials but rather to the adiabatic N lone pair  $\sigma$  ionization potentials at higher energy. This relationship provides a useful chemical means for the assignment of bands in photoelectron spectra; specific examples are considered and assigned. A linear relationship is also found between nitrile (RCN) and primary amine (RNH<sub>2</sub>) proton affinities for a range of substituents R. The results are discussed in terms of the intrinsic factors affecting molecular basicity.

Recent developments in techniques for the study of ion-molecule reactions have made it possible to quantify base strengths relative to a variety of cationic reference acids in the gas phase.<sup>2-13</sup> While Li<sup>+</sup>, K<sup>+</sup>, NO<sup>+</sup>, and other species are now also being studied,<sup>11-13</sup> the most widely studied reference acid has been the proton.<sup>2-10</sup> Proton affinity, PA(B),

is defined for a base B as the heterolytic bond dissociation energy for removing a proton from the conjugate acid BH<sup>+</sup>, eq 1. The homolytic bond dissociation energy  $D(\text{B}^+-\text{H})$  defined by eq 2 is related to PA(B) and the adiabatic ionization potentials IP(H) and IP(B), eq 3, by the thermochemical cycle 4.



Determination of equilibrium constants for proton transfer between two bases, reaction 5, using ion cyclotron resonance (ICR) techniques<sup>2-9</sup> or high-pressure mass spectroscopy<sup>10</sup>



yields accurate ( $\pm 0.2$  kcal/mol in most instances) relative free energies of protonation. Temperature dependence is observed to be slight, confirming the expectation that  $\Delta S$  for reaction 5 is small and can be accounted for by changes in symmetry numbers.<sup>10</sup> A relative scale of  $\text{PA}(\text{B})$  has been established by examining reaction 5 for a large number of organic and inorganic bases and calibrated by reference to a variety of species for which absolute values of  $\text{PA}(\text{B})$  may be derived from appearance potential measurements.<sup>9</sup>

The systematic variation of molecular properties related to basicity in series of primary, secondary, and tertiary amines,<sup>2-4,10</sup> substituted pyridines,<sup>5,14</sup> and the methyl phosphines<sup>6</sup> has been examined. In particular it has been demonstrated that for homologous series, for example the primary amines, molecular ionization potentials  $\text{IP}(\text{B})$  and homolytic bond dissociation energies  $D(\text{B}^{\cdot+}-\text{H})$  are linear functions of  $\text{PA}(\text{B})$ .<sup>3,4</sup> Stabilization of the conjugate acid  $\text{BH}^+$  or radical cation  $\text{B}^{\cdot+}$  by resonance interactions or hyperconjugation may lead to important exceptions.<sup>4,7</sup>

In the amine and phosphine series examined to date, the lone pair orbital involved in bond formation to the proton in process 1 corresponds to the lowest ionization potential of the molecule.<sup>4,6</sup> The present work uses ICR techniques and photoelectron spectroscopy (PES) to examine a series, the nitriles, in which this is not the case, the CN  $\pi$  orbital having the lowest ionization potential.

## Experimental Section



ICR instrumentation and techniques used in these studies have been previously described in detail.<sup>6,15,16</sup> Photoelectron spectra were obtained using an instrument built at Caltech employing a 127° electrostatic analyzer. Spectra were calibrated using the <sup>2</sup>P<sub>3/2</sub> and <sup>2</sup>P<sub>1/2</sub> lines of an internal argon standard. The spectrometer is occasionally checked with other species such as Xe and CH<sub>3</sub>I, and ionization potentials relative to the argon standard are reproduced to within  $\pm 0.01$  eV of the accepted values. The capillary discharge lamp was operated at 2 Torr of helium for He(I) spectra and at 0.1 Torr for He(II) spectra. Both the ICR and PES experiments were conducted at room temperature. Chemicals were used as obtained from readily available commercial sources except for degassing at liquid nitrogen temperature.

## Results and Discussion

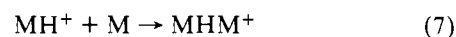
The gas phase ion chemistry of HCN, MeCN, and various alkyl nitriles has been previously investigated in detail using ICR.<sup>17-19</sup> Electron impact at energies just above the first ionization potential in these systems produces parent ion which reacts to give protonated parent, for example reaction 6. Dimer formation, reaction 7, while significant at



Table I. Reaction Mixtures Studied and Derived  $\text{PA}(\text{RCN})$  Values<sup>a</sup>

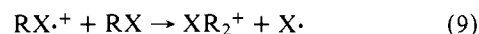
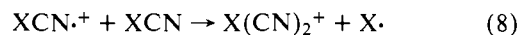
RCN	Ref base	$\text{PA}(\text{B})^b$	$\delta_R \Delta G^\circ c$	$\text{PA}(\text{RCN})^d$
<i>c</i> -C <sub>3</sub> H <sub>5</sub> CN	HCO <sub>2</sub> - <i>n</i> -Bu	193.4	0.67 $\pm$ 0.2	194.1
<i>i</i> -PrCN	HCO <sub>2</sub> Et	192.1	0.95 $\pm$ 0.2	193.1
<i>n</i> -BuCN	HCO <sub>2</sub> Et	192.1	0.71 $\pm$ 0.2	192.8
<i>n</i> -PrCN	HCO <sub>2</sub> Et	192.1	0.71 $\pm$ 0.2	192.3
<i>n</i> -PrCN	Me <sub>2</sub> O	191.4	0.84 $\pm$ 0.2	192.2
<i>n</i> -PrCN	EtCN	191.0	1.18 $\pm$ 0.2	192.2
EtCN	<i>n</i> -PrCN	192.3	-1.18 $\pm$ 0.2	191.1
EtCN	HCO <sub>2</sub> Et	192.1	-1.08 $\pm$ 0.2	191.0
EtCN	<i>i</i> -PrCHO	191.6	-0.22 $\pm$ 0.2	191.4
EtCN	Me <sub>2</sub> O	191.4	-0.27 $\pm$ 0.2	191.1
EtCN		189.8	0.88 $\pm$ 0.2	190.9
EtCN	EtCHO	189.0	1.88 $\pm$ 0.2	190.9
CH <sub>2</sub> =CHCN		189.8	-1.20 $\pm$ 0.2	188.8
CH <sub>2</sub> =CHCN	EtCHO	189.0	-0.20 $\pm$ 0.2	188.8
CH <sub>2</sub> =CHCN	MeCN	188.0	0.76 $\pm$ 0.2	188.8
ClCH <sub>2</sub> CH <sub>2</sub> CN	MeCN	188.0	-0.87 $\pm$ 0.2	187.1
BrCN	AsH <sub>3</sub>	182.0	0.3 $\pm$ 0.5	181.5
BrCN	HCO <sub>2</sub> H	181.5	-0.3 $\pm$ 0.7	180.8
BrCN	F <sub>2</sub> CHCH <sub>2</sub> OH	179.0	>1.5 $\pm$ 0.5	>180.5
ClCN	F <sub>2</sub> CHCH <sub>2</sub> OH	179.0	-0.5 $\pm$ 0.5	178.5
ClCN	HCHO	176.0	>1.5 $\pm$ 0.5	177.9

<sup>a</sup> All data in kcal/mol. <sup>b</sup> Proton affinities of the reference bases from ref 9; all data are relative to  $\text{PA}(\text{NH}_3) = 202.3 \pm 2.0$  kcal/mol. Relative to NH<sub>3</sub>, reported values are estimated to be accurate to  $\pm 1$  kcal/mol, with higher accuracy for smaller differences. <sup>c</sup> Free-energy differences for reaction 5 derived from ICR determinations of the equilibrium constant for proton transfer from the reference base to RCN. <sup>d</sup> Derived from the data of columns 3 and 4 and corrected for changes in  $\Delta S$  calculated from symmetry number changes for reaction 5.



higher pressures ( $> 3 \times 10^{-5}$  Torr) was slow at the pressures which were typically used to study reaction 5 (about  $3 \times 10^{-6}$  Torr). No other reactions of the protonated parent ions were observed. Proton transfer in mixtures of nitriles with various bases was found to be fast so that equilibrium constants for reaction 5 could be readily measured. Rate constants for exothermic proton transfers were typically  $10^{-9}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

The ion chemistry of the cyanogen halides has not previously been elucidated and deserves special mention. In cyanogen chloride and bromide, the parent ions  $\text{XCN}^{\cdot+}$  were the predominant ions observed in the 70 eV mass spectrum and react with their respective neutrals to give  $\text{X}(\text{CN})_2^+$ , reaction 8, X = Cl and Br. Similar processes have been observed in the ion chemistry of alkyl halides where, for X = Br and I, formation of dialkyl halonium ions  $\text{XR}_2^+$  occurs directly by reaction 9.<sup>20</sup> Double resonance investigation of the halogen isotopic contributions to the  $\text{X}(\text{CN})_2^+$  prod-



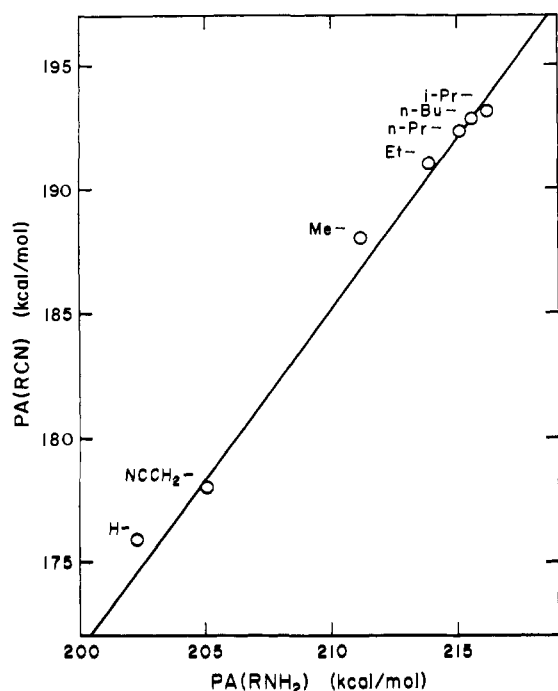
uct<sup>20</sup> indicate nearly equal contributions from the ionic and neutral reactants. In studies of the proton transfer reactions of these cyanogen halides in mixtures with other bases, a third gas such as methane was sometimes added to increase the abundance of protonated species.

Mixtures which were examined by ICR for the present work and derived PA values are given in Table I. Proton affinities which appear in Tables I and II for HCN, CH<sub>2</sub>(CN)<sub>2</sub>, Cl<sub>3</sub>CCN, ClCH<sub>2</sub>CN, MeCN, and various reference molecules were available from studies of a large number of organic and inorganic bases, details of which will be published separately.<sup>9</sup>

**Table II.** Nitrile Proton Affinities, Adiabatic Ionization Potentials, and Homolytic Bond Dissociation Energies<sup>a</sup>

RCN	PA <sup>b</sup>	$\pi$ IP	$\sigma$ IP	$\sigma D(B^+ - H)^c$
HCN	175.9	313.9 <sup>d</sup>	322.8 <sup>d</sup>	185.2
CH <sub>2</sub> (CN) <sub>2</sub>	178.0	292.4 <sup>e</sup>	309.2 <sup>e</sup>	173.7 <sup>e</sup>
			313.4 <sup>e</sup>	177.8 <sup>e</sup>
ClCN	178.5	285.0 <sup>f</sup>	318.2 <sup>f</sup>	183.2
Cl <sub>2</sub> CCN	178.7		320.1 <sup>g</sup>	185.2
BrCN	181.2	273.7 <sup>f</sup>	312.7 <sup>f</sup>	180.3
ClCH <sub>2</sub> CN	181.9	297.5 <sup>g,h</sup>	313.4 <sup>g,h</sup>	181.7
ClCH <sub>2</sub> CH <sub>2</sub> CN	187.1	282.5 <sup>h</sup>	305.3 <sup>h</sup>	178.8
MeCN	188.0	281.3 <sup>i</sup>	303.0 <sup>i</sup>	177.4
CH <sub>2</sub> =CHCN	188.8	285.0 <sup>g</sup>	300.7 <sup>g</sup>	175.9
EtCN	191.0	273.3 <sup>g,h</sup>	296.3 <sup>g,h</sup>	173.8

<sup>a</sup> All data in kcal/mol. <sup>b</sup> Data from Table I and ref 9. <sup>c</sup> Calculated using eq 3 and the N lone pair  $\sigma$  ionization potential. <sup>d</sup> References 26 and 22. <sup>e</sup> Reference 31, both  $n^+$  and  $n^-$  values are given. <sup>f</sup> References 23 and 30. <sup>g</sup> Reference 23. <sup>h</sup> Present work. <sup>i</sup> Present work and ref 22 and 23.

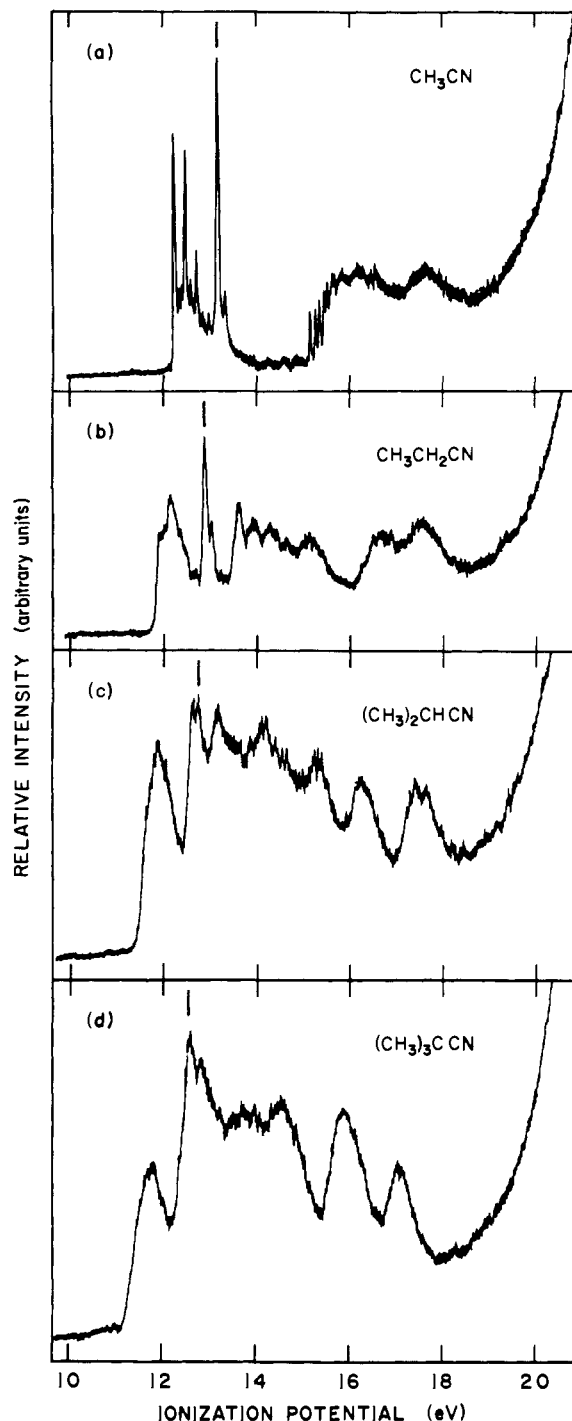


**Figure 1.** Proton affinities of nitriles, RCN, vs. proton affinities of primary amines, RNH<sub>2</sub>. The data for NCCH<sub>2</sub>NH<sub>2</sub> are from ref 9; the remaining amine data are from ref 4.

The proton affinity results reflect changes in polarizability and inductive effects with the substituent group R. Comparison of proton affinities in the nitrile and primary amine series, Figure 1, reveals that the magnitude of these effects is linearly related in the two series but larger for the nitriles.<sup>21</sup> A least-squares fit to the data is given by eq 10 with all quantities in kcal/mol.<sup>21</sup>

$$PA(RCN) = 1.3153PA(RNH_2) - 90.68 \quad (10)$$

The photoelectron spectra of several alkyl nitriles are shown in Figure 2. Assignment of the low-lying bands in the photoelectron spectra of nitriles has been the subject of several experimental and theoretical papers.<sup>22-31</sup> In MeCN, Figure 2a, the CN  $\pi$  band is clearly separated from the N lone pair  $\sigma$  band allowing this spectrum to be confidently assigned, Table II.<sup>22-24</sup> The photoelectron spectra of EtCN, Figure 2b, and CH<sub>2</sub>=CHCN (not shown) have been similarly assigned except that CH<sub>2</sub>=CHCN has an additional band at 10.91 eV which is associated with ionization of the C=C  $\pi$  bonding electrons.<sup>23,24</sup> For HCN the CN  $\pi$  and N



**Figure 2.** He(I) photoelectron spectra of (a) CH<sub>3</sub>CN, (b) CH<sub>3</sub>CH<sub>2</sub>CN, (c) (CH<sub>3</sub>)<sub>2</sub>CHCN, and (d) (CH<sub>3</sub>)<sub>3</sub>CCN. Adiabatic N lone pair  $\sigma$  ionization potentials predicted by eq 11 are indicated by the vertical line above each spectrum.

lone pair  $\sigma$  bands are closer in energy but several detailed analyses have resulted in a convincing assignment.<sup>22,24-29</sup> While the N lone pair ionization has been unambiguously assigned in ClCN and BrCN, interaction of the CN  $\pi$  orbitals with the halogen  $\pi$  lone pair orbitals is substantial, resulting in two bands which may be associated with ionization of the CN  $\pi$  electrons.<sup>23,30</sup> The lower of these are given in Table II; the upper bands are at 15.13 and 14.19 eV in ClCN and BrCN, respectively.<sup>23</sup> The spectrum of CH<sub>2</sub>(CN)<sub>2</sub>, which is complicated by interaction of the two equivalent CN groups, has been analyzed by Stafast and Bock.<sup>31</sup> Lake and Thompson obtained the photoelectron

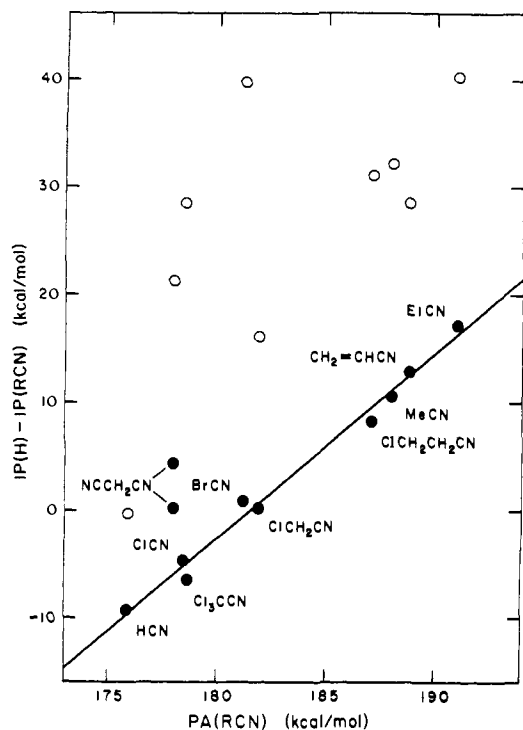


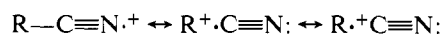
Figure 3. The quantity  $IP(H) - IP(RCN)$  vs.  $PA(RCN)$  for adiabatic (○) CN  $\pi$  and (●) N lone pair  $\sigma$  ionization potentials for nitriles.

spectra of  $ClCH_2CN$  and  $Cl_3CCN$  but did not assign the observed bands.<sup>23</sup> Data for the nitrile CN  $\pi$  and N lone pair  $\sigma$  adiabatic ionization potentials and  $PA(RCN)$  results are summarized in Table II along with  $\sigma D(B^+ - H)$  values calculated using the N lone pair ionization potentials.<sup>32</sup>

In accordance with eq 3, it is of interest to consider the variation of the quantity  $IP(H) - IP(RCN)$  with  $PA(RCN)$ , Figure 3. It is apparent that CN  $\pi$  ionization potentials are poorly correlated with  $PA(RCN)$  values; for N lone pair  $\sigma$  ionization potentials, however, the data fall closely about a straight line. A least-squares fit to these data, excluding the points for  $CH_2(CN)_2$  which are discussed below, is given by eq 11 with all quantities in kcal/mol. It is reasonable that the N lone pair  $\sigma$  ionization poten-

$$IP(H) - \sigma IP(RCN) = 1.7270PA(RCN) - 313.54 \quad (11)$$

tial but not the CN  $\pi$  ionization potential should be related to  $PA(RCN)$ . Stabilization of the protonated species is effected by charge redistribution in the R-C-N-H  $\sigma$  system. Similarly in the  $\sigma$  state of the radical cation, charge stabilization results from electron redistribution in the R-C-N  $\sigma$  system. The presence of the radical site in the latter case allows for greater charge redistribution by electron donation into the partially filled orbital and accounts for the larger effect of changes in R on ionization potential as compared to proton affinity, eq 11 and Figure 3. It has been suggested that decreasing  $D(B^+ - H)$  in the amine series  $Me_nNH_{3-n}$ ,  $n = 0-3$ , can be attributed to the effects of  $\pi$  hyperconjugation;<sup>4</sup> the present series evidences the effects of  $\sigma$  hyperconjugation



which are also reflected in the dependence of  $\sigma D(B^+ - H)$  on  $PA(RCN)$ , Table II. In the  $\pi$  state of the radical cation, charge stabilization is affected by different factors. Most important is the interaction of the CN  $\pi$  orbitals with orbitals of  $\pi$  symmetry in R.

The two data points in Figure 3 for the ionization potentials of the  $n^+$  and  $n^-$  combinations of the nitrogen lone

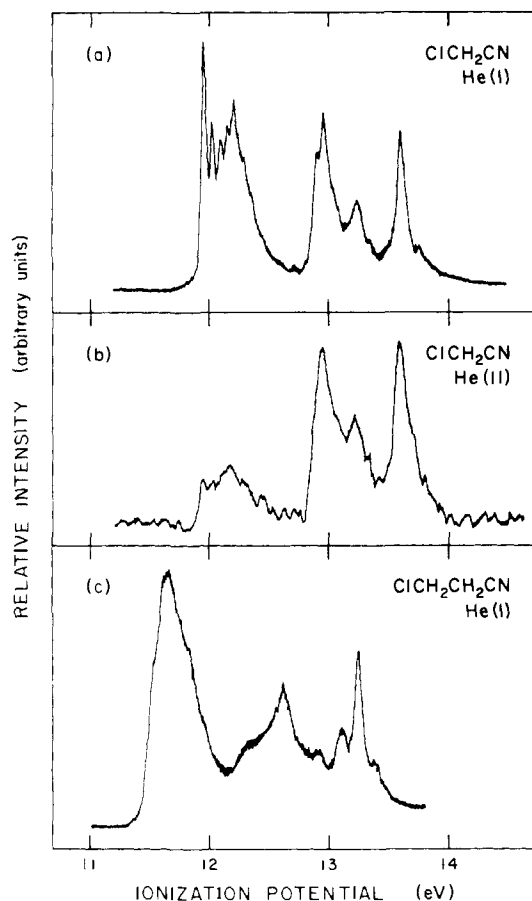


Figure 4. (a) He(I) photoelectron spectrum of  $ClCH_2CH$ , (b) He(II) photoelectron spectrum of  $ClCH_2CN$ , and (c) He(I) photoelectron spectrum of  $ClCH_2CH_2CN$ .

pairs of  $CH_2(CN)_2$  are clearly an exception to the relationship between  $\sigma IP(RCN)$  and  $PA(RCN)$  described by eq 11. Previous studies of molecules containing equivalent lone pairs<sup>7</sup> lead to the expectation that this may result from resonance stabilization of the radical cation arising from lone pair interactions. Thru space interactions should be slight since the two nitrogen atoms are separated by about 4 Å.<sup>33</sup> The analysis by Stafast and Bock<sup>31</sup> suggests that both  $n^+$  and  $n^-$  orbital energies should be destabilized by thru bond interactions. This is consistent with the present result in which both of the observed ionization potentials are lower than the ionization potential predicted by eq 11. Resonance stabilization of the radical cation, calculated by comparing the  $n^+$  (lower) ionization potential with the ionization potential predicted by  $PA(CH_2(CN)_2) = 178.0$  kcal/mol and eq 11, amounts to 10.4 kcal/mol, reducing the homolytic bond dissociation energy  $\sigma D(B^+ - H)$  for  $NCCH_2CNH^+$  from an expected 184.1 to 173.7 kcal/mol.

The relationship between N lone pair  $\sigma$  ionization potentials and nitrile proton affinities described by eq 11 provides a useful means for assigning photoelectron spectra. The first three bands in the photoelectron spectrum of  $ClCH_2CN$  are shown in Figure 4a.<sup>34</sup>  $PA(ClCH_2CN) = 181.9$  kcal/mol and eq 11 predict  $\sigma IP(ClCH_2CN) = 13.57$  eV, identifying the strong sharp peak at this energy as the N lone pair ionization. The first band at 11.95 eV may be assigned to the Cl lone pair ionization by noting its reduced intensity in the He(II) spectrum of  $ClCH_2CN$ , Figure 4b; second-row lone pairs are relatively weaker as compared to first-row  $\pi$  and  $\sigma$  bands in He(II) spectra.<sup>35</sup> The middle band at 12.90 eV in the  $ClCH_2CN$  spectrum can then be assigned to the CN  $\pi$  ionization. The peak at 13.17 eV in

this band, a spacing of  $2200\text{ cm}^{-1}$ , results from excitation of the  $\text{C}\equiv\text{N}$  stretching vibration. Assignment of the  $\text{ClCH}_2\text{CH}_2\text{CN}$  spectrum, Figure 4c, is similar to that of  $\text{ClCH}_2\text{CN}$ , all peaks being shifted to lower ionization potential by about  $0.4\text{ eV}$ .<sup>36</sup>

Equation 11 may also be usefully applied to the analysis of spectra which are less well resolved. The photoelectron spectra of a series of alkyl nitriles  $\text{RCN}$  in which methyl is substituted for hydrogen in  $\text{CH}_3\text{CN}$  appear in Figure 2. As  $R$  increases in size, the decreasing ionization potential of the  $\text{C}-\text{C}$  and  $\text{C}-\text{H}$   $\sigma$  bands obscures the region of the  $\text{N}$  lone pair, the position of which as predicted by eq 11 is indicated in Figure 2.<sup>37</sup> Similarly, eq 11 and  $\text{PA}(\text{c}-\text{C}_3\text{H}_5\text{CN}) = 194.1\text{ kcal/mol}$  predict  $\sigma\text{IP}(\text{c}-\text{C}_3\text{H}_5\text{CN}) = 12.66\text{ eV}$  which can be usefully applied in a detailed analysis of the cyclopropyl cyanide spectrum.<sup>38</sup> While relationships of the type given by eq 11 provide useful chemical means for assigning spectra, physical methods such as angular dependent photoelectron spectroscopy<sup>39</sup> might also be usefully applied to further resolve and identify structure in spectra where several bands overlap.

In conclusion, the nitrile results have provided new examples of linear relationships among properties related to molecular basicity. The slope and intercept of such relationships depend on the nature of the basic site, whether charge is localized in orbitals of  $\pi$  or  $\sigma$  symmetry, and whether the system is closed or open shell. The results to date indicate that the magnitude of substituent effects is proportional in all series, and suggest that a single set of substituent constants might be developed. As additional examples are found, it will be of interest to see whether this proportionality is maintained. The results also point out that caution must be exercised in developing relationships between ionization potentials and molecular properties such as base strength: the correct ionization potential must be chosen and molecules in which the presence of equivalent lone pairs leads to resonance stabilization of the radical cation should be regarded as potential exceptions.

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