

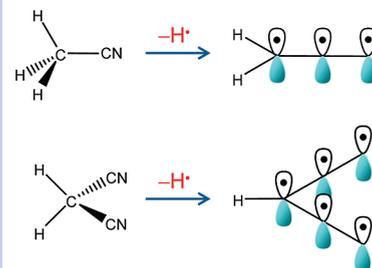
C–H Bond Dissociation Energy of Malononitrile

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ABSTRACT The C–H bond dissociation energies of closed-shell molecules decrease with increasing stability of the resulting radicals. From the electron affinity of the dicyanomethyl radical, $\bullet\text{CH}(\text{CN})_2$, $\text{EA}[\bullet\text{CH}(\text{CN})_2] = 2.88 \pm 0.01$ eV, measured by photoelectron imaging of the $\text{CH}(\text{CN})_2^-$ anion, and the acidity/electron affinity thermodynamic cycle, we obtained the C–H bond dissociation enthalpy of malononitrile, $\text{CH}_2(\text{CN})_2$, $\text{DH}_{298}[\text{H}-\text{CH}(\text{CN})_2] = 87 \pm 2$ kcal/mol. This result is compared to the corresponding value for acetonitrile, $\text{DH}_{298}(\text{H}-\text{CH}_2\text{CN}) = 93 \pm 2$ kcal/mol, determined from a similar measurement of $\text{EA}(\bullet\text{CH}_2\text{CN}) = 1.53 \pm 0.01$ eV. The relative weakness of the C–H bonds in malononitrile and acetonitrile, compared to most closed-shell neutral organic molecules, is attributed to π -resonance stabilization of the unpaired electrons in $\bullet\text{CH}(\text{CN})_2$ and $\bullet\text{CH}_2\text{CN}$.

SECTION Kinetics, Spectroscopy



Resonance stabilized radicals

Due to its large electronegativity, the CN group is often regarded as a pseudohalogen. However, halogens are π -donors, while the CN group is not and acts more like an aryl group in an extended π system. This critical distinction is revealed in the C–H bond energies of the corresponding substituted methanes.¹

We report the gas-phase C–H bond dissociation energy of malononitrile, $\text{CH}_2(\text{CN})_2$, determined from the electron affinity of the corresponding dicyanomethyl radical, $\bullet\text{CH}(\text{CN})_2$. The results are discussed in comparison with the corresponding properties of methane (CH_4), acetonitrile (CH_3CN), and cyanoform, $\text{CH}(\text{CN})_3$. This CN-substituted series is in turn compared to halogenated methanes, such as CH_nF_m ($n + m = 4$). We find a clear contrast in how the C–H bond energies are affected by the π -donating halogens compared to the resonance stabilization offered by the CN group.

The 355 nm photoelectron image and the corresponding spectrum for $\text{CH}(\text{CN})_2^-$ are shown in Figure 1a. For comparison, the photoelectron image and the corresponding spectrum of CH_2CN^- , measured at 532 nm, are displayed in Figure 1b. In both cases, the photoelectron angular distributions peak in the direction perpendicular to the laser polarization axis, characteristic of detachment from carbon 2p type orbitals.^{2,3}

For $\text{CH}(\text{CN})_2^-$, we observe a single, remarkably narrow band at an electron binding energy of $\text{eBE} = 2.88 \pm 0.01$ eV, which corresponds to the electron affinity (EA) of $\bullet\text{CH}(\text{CN})_2$. Calculations⁴ at the B3LYP/aug-cc-pVDZ level of theory predict an EA of 2.92 eV, in good agreement with the experimental value.

The CH_2CN^- spectrum shows a short vibrational progression with a sharp origin, corresponding to an electron affinity of 1.53 ± 0.01 eV. This spectrum is in good agreement with a previous study of CH_2CN^- , which yielded an EA of 1.543 ± 0.014 .⁵ The most intense spectral peak in Figure 1b is the transition origin, while all other bands (spaced by ~ 700 cm^{-1})

correspond to the excitation of the umbrella mode of $\bullet\text{CH}_2\text{CN}$.⁵ Our B3LYP/6-311++G(3df,3pd) calculations⁴ on $\bullet\text{CH}_2\text{CN}$ predict an umbrella mode frequency of 684 cm^{-1} and electron affinity of 1.57 eV, in good agreement with the experimental data.

The comparison of the $\text{CH}(\text{CN})_2^-$ and CH_2CN^- photoelectron spectra in Figure 1 highlights the absence of a discernible vibrational progression in the $\text{CH}(\text{CN})_2^-$ case. This observation suggests that the $\text{CH}(\text{CN})_2^-$ anion and the $\bullet\text{CH}(\text{CN})_2$ neutral must have very similar geometries. To support this conclusion, we optimized the geometries of $\text{CH}(\text{CN})_2^-$ and $\bullet\text{CH}(\text{CN})_2$ at the B3LYP/aug-cc-pVDZ level of theory.⁴ The resulting structures are shown in Figure 2. Both $\text{CH}(\text{CN})_2^-$ and $\bullet\text{CH}(\text{CN})_2$ are predicted to have planar structures of C_{2v} symmetry, with a 1A_1 electronic state for the anion and a 2B_1 ground state for the neutral radical. The anion and neutral structures are indeed essentially identical at this level of theory, with the most noticeable difference being in the CCC bond angle, which is predicted to decrease by 1.2° upon electron detachment.

In contrast, CH_2CN^- is known to be nonplanar (C_s symmetry), while the corresponding neutral radical has a planar structure.⁵ This geometry difference is responsible for the vibrational progression in the photoelectron spectrum of CH_2CN^- seen in Figure 1b. The striking difference between the planar geometry of $\text{CH}(\text{CN})_2^-$ and the nonplanar structure of CH_2CN^- is attributed to decreased electron density on the central carbon atom in the presence of two CN groups. The Mulliken analysis of $\text{CH}(\text{CN})_2^-$ in Figure 2 indicates a large positive charge on the central carbon, which favors a planar geometry. A similar calculation for CH_2CN^- shows a negative

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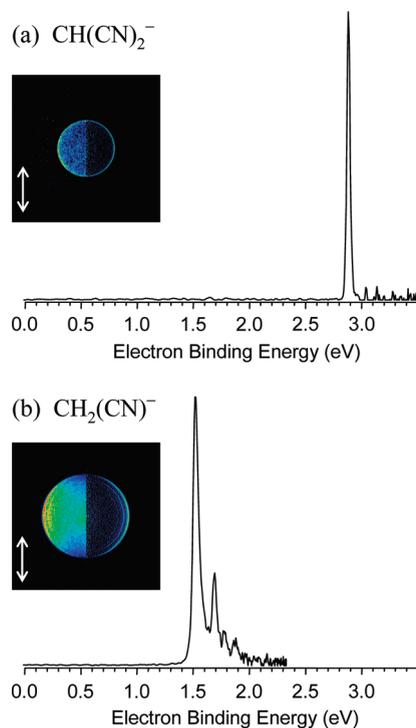


Figure 1. Photoelectron images and corresponding spectra of (a) $\text{CH}(\text{CN})_2^-$, measured at 355 nm, and (b) $\text{CH}_2(\text{CN})^-$, measured at 532 nm. The composite images show the raw (left side) and reconstructed data (right). The double arrows indicate the laser polarization direction.

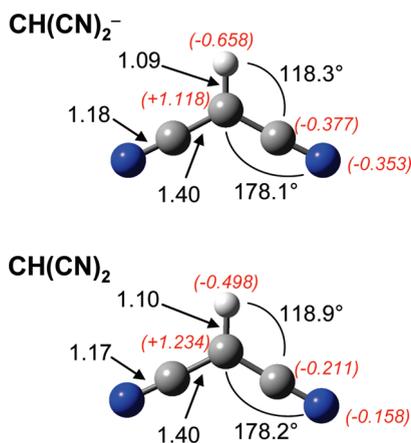


Figure 2. Geometries of $\text{CH}(\text{CN})_2^-$ and $\text{CH}(\text{CN})_2$ optimized at the B3LYP/aug-cc-pVDZ level of theory. Both structures are planar and belong to the C_{2v} symmetry point group. Bond lengths are in Angstroms. Values in parentheses are Mulliken charges.

Mulliken charge (-0.536) on the central carbon. To put the relationship between geometry and charges in perspective, the carbon in CH_3^+ is positively charged and the ion is planar, while in CH_3^- , the carbon is negatively charged and the anion is nonplanar. While these arguments are not new,⁶ this subtle result highlights inductive effects typically associated with the pseudohalogen (electronegative) nature of the CN group, which is electron-withdrawing in the σ system.

The experimental electron affinity of $\bullet\text{CH}(\text{CN})_2$ allows us to calculate the C–H bond enthalpy (DH_{298}) of malononitrile using the general acidity/electron affinity cycle¹

$$\text{DH}_{298}(\text{R-H}) = \Delta_{\text{acid}}H_{298}(\text{RH}) + \text{EA}(\text{R}^\bullet) - \text{IE}(\text{H}) + [\text{thermal correction}] \quad (1)$$

In this equation, $\Delta_{\text{acid}}H_{298}(\text{RH})$ is the gas-phase acidity of a closed-shell molecule, $\text{EA}(\text{R}^\bullet)$ is the electron affinity of the corresponding radical, and $\text{IE}(\text{H}) = 315.1$ kcal/mol is the ionization energy of atomic hydrogen.⁷ The small thermal correction is a set of heat capacity integrals from 0 to 298 K, corresponding to RH, R^- , H, and H^+ . This correction is usually smaller than 0.3 kcal/mol and is hence absorbed by larger experimental uncertainties.⁸ Neglecting the [thermal correction] term in eq 1 and using the known acidity of malononitrile, $\Delta_{\text{acid}}H_{298}[\text{CH}_2(\text{CN})_2] = 335.8 \pm 2.1$ kcal/mol,⁹ and the experimental EA of dicyanomethyl radical, $\text{EA}[\bullet\text{CH}(\text{CN})_2] = 2.88 \pm 0.01$ eV, we find the C–H bond dissociation energy of malononitrile to be $\text{DH}_{298}[\text{H-CH}(\text{CN})_2] = 87 \pm 2$ kcal/mol. A similar calculation for acetonitrile, with $\Delta_{\text{acid}}H_{298}(\text{CH}_3\text{CN}) = 372.9 \pm 2.1$ kcal/mol (from ref 10) and $\text{EA}[\bullet\text{CH}_2\text{CN}] = 1.53 \pm 0.01$ eV (as determined here), gives $\text{DH}_{298}(\text{H-CH}_2\text{CN}) = 93 \pm 2$ kcal/mol. This result is within the uncertainty of the previously reported value, 94.2 ± 2.0 kcal/mol.⁵

The so determined bond dissociation energy of malononitrile, 87 ± 2 kcal/mol, is small compared to typical C–H bond energies of neutral closed-shell organic molecules. In general, bond energies reflect the stability of the corresponding radicals; smaller DH_{298} values translate into greater radical stability. As a reference, the bond dissociation energy of methane, $\text{DH}_{298}(\text{H-CH}_3) = 104.9 \pm 0.4$ kcal/mol,¹ is significantly larger than the corresponding values for acetonitrile and malononitrile. In the methyl radical, the unpaired electron is localized on the carbon atom and receives no additional stabilization. For comparison, the bond energies of molecules producing “stable” radicals, such as toluene, $\text{DH}_{298}(\text{H-CH}_2\text{C}_6\text{H}_5) = 89.8 \pm 0.6$ kcal/mol, and propene, $\text{DH}_{298}(\text{H-CH}_2\text{CHCH}_2) = 88.8 \pm 0.4$ kcal/mol, are similar to those of acetonitrile and malononitrile.¹ Compared to that of methane, the lower $\text{DH}_{298}(\text{H-CH}_2\text{CN})$ of acetonitrile reflects stabilization of the unpaired electron in the cyanomethyl radical through π resonance with the CN group. In the dicyanomethyl radical, the additional CN group further stabilizes the unpaired electron via increased resonance interaction, resulting in the even lower C–H bond dissociation energy of the parent molecule, malononitrile.

Although the CN group is often regarded as a pseudohalogen, radical stabilization in $\bullet\text{CH}_2\text{CN}$ and $\bullet\text{CH}(\text{CN})_2$ is not due to electron-withdrawing properties of CN, which it shares with atomic halogens, but is manifested in the π system. Similar halogenated methanes are not resonance-stabilized as halogens act as π -donors. For the case of $\text{H-CH}_n\text{F}_m$ ($n + m = 3$), we find $\text{DH}_{298}(\text{H-CH}_2\text{F}) = 100 \pm 6$ kcal/mol, $\text{DH}_{298}(\text{H-CHF}_2) = 102 \pm 5$ kcal/mol, and $\text{DH}_{298}(\text{H-CF}_3) = 104 \pm 2$ kcal/mol,¹¹ thus, the bond energies increase with sequential halogen substitution.

While the DH_{298} difference between CH_4 and CH_3CN is about 14 kcal/mol, the difference between CH_3CN and $\text{CH}_2(\text{CN})_2$

is about 6 kcal/mol, indicating a moderate increase in resonance stabilization with the addition of the second CN group. On the basis of this trend, we hypothesize that cyanoform, $\text{CH}(\text{CN})_3$, should have an even smaller C–H bond dissociation energy because of additional resonance stabilization in the resulting radical, $\cdot\text{C}(\text{CN})_3$. While difficult to isolate,^{12,13} $\text{CH}(\text{CN})_3$ may have one of the weakest C–H bonds for a closed-shell neutral organic molecule.

Finally, we calculate the heats of formation of the $\cdot\text{CH}_2\text{CN}$ and $\cdot\text{CH}(\text{CN})_2$ radicals¹

$$\Delta_f H_{298}(\text{R}\cdot) = \text{DH}_{298}(\text{RH}) + \Delta_f H_{298}(\text{RH}) - \Delta_f H_{298}(\text{H}) \quad (2)$$

Using $\Delta_f H_{298}(\text{H}) = 52.103 \pm 0.003$ kcal/mol,¹⁴ $\Delta_f H_{298}[\text{CH}_2(\text{CN})_2] = 63.64 \pm 0.24$ kcal/mol,¹⁵ and the C–H bond dissociation energy of malononitrile determined here, we find $\Delta_f H_{298}[\cdot\text{CH}(\text{CN})_2] = 99 \pm 2$ kcal/mol. For comparison, using $\Delta_f H_{298}(\text{CH}_3\text{CN}) = 17.70 \pm 0.09$ kcal/mol¹⁶ and our value of $\text{DH}_{298}(\text{H}-\text{CH}_2\text{CN})$, we find $\Delta_f H_{298}(\cdot\text{CH}_2\text{CN}) = 59 \pm 2$ kcal/mol, in good agreement with the previous studies, which yielded 59.7 ± 2.0 ⁵ and 58.5 ± 2.2 kcal/mol.¹⁷

In summary, the electron affinity of the dicyanomethyl radical, $\text{EA} = 2.88 \pm 0.01$ eV, was measured by photoelectron imaging of the $\text{CH}(\text{CN})_2^-$ anion. This result was used to obtain the C–H bond dissociation energy of malononitrile, $\text{DH}_{298}[\text{H}-\text{CH}(\text{CN})_2] = 87 \pm 2$ kcal/mol, and the heat of formation of the resulting radical, $\Delta_f H_{298}[\cdot\text{CH}(\text{CN})_2] = 99 \pm 2$ kcal/mol. The C–H bond dissociation energy of malononitrile is smaller than that of most closed-shell neutral organic molecules, including methane and acetonitrile. The bond weakness is attributed to resonance stabilization of the unpaired electron in $\cdot\text{CH}(\text{CN})_2$.

EXPERIMENTAL METHODS

The electron affinities of $\cdot\text{CH}(\text{CN})_2$ and $\cdot\text{CH}_2\text{CN}$ were measured using a previously described negative ion¹⁸ velocity map¹⁹ photoelectron imaging²⁰ spectrometer.²¹ The $\text{CH}(\text{CN})_2^-$ and CH_2CN^- ions were generated by the proton-abstraction reaction of O^- with malononitrile or acetonitrile, respectively. Mass-selected anions were photodetached using the third (355 nm) or second (532 nm) harmonic of a Nd:YAG (yttrium aluminum garnet) laser with pulse energies of 10–20 mJ and an 8 ns pulse width. Photoelectron images were analyzed following published procedures.²² The photoelectron spectra were calibrated using the known electron affinity of O^- .²³

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