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**Observation of the Dipole- and Quadrupole-Bound Anions of
1,4-Dicyanocyclohexane**

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Observation of the Dipole- and Quadrupole-Bound Anions of 1,4-Dicyanocyclohexane

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Abstract

Quadrupole-bound anions are negative ions in which their excess electrons are loosely bound by long-range electron-quadrupole attractions. Experimental evidence for quadrupole-bound anions has been scarce; until now, only *trans*-succinonitrile had been experimentally confirmed to form a quadrupole-bound anion. In this study, we present experimental evidence for a new quadrupole-bound anion. Our combined Rydberg electron transfer/anion photoelectron spectroscopy study demonstrates that the *ee* conformer of 1,4-dicyanocyclohexane (DCCH) supports a quadrupole-bound anion state, and that the *cis*-DCCH conformer forms a dipole-bound anion state. The electron binding energies of the quadrupole- and dipole-bound anions are measured as 18 and 115 meV, respectively, both of which are in excellent agreement with theoretical calculations by Sommerfeld.

Introduction

Negative ions can be formed due to electron capture by long-range, electrostatic forces, in which the excess electrons reside in diffuse non-valence orbitals. The component potentials associated with these electrostatic forces can be expressed through the multipole expansion for a given charge distribution, e.g., dipole, quadrupole, and octupole moments. Whereas this representation is strictly valid only at a distance, in cases where there is no valence electron binding, and where all but one of the electrostatic moments are null, it is customary to attribute that non-zero moment as the primary attractive interaction responsible for the binding of the excess electron. The formation of such weakly-bound states is thought to be the initial step in certain electron attachment processes, thus these are also referred as “doorway” states.¹⁻¹¹ The best studied category of weakly-bound anions are dipole-bound anions, i.e., anions whose excess electrons are weakly tethered by the dipolar fields of the anions’ neutral counterparts.¹²⁻²⁴

The next higher term in the multipole expansion is the quadrupole moment. Unlike dipole-bound anions, the evidence for quadrupole-bound anions, where their excess electrons are bound by the long-range

charge-quadrupole attraction, has been scarce. Quadrupole-bound anions were first predicted theoretically in 1979.²⁵ Early experimental studies on quadrupole-bound anions were conflicting: the anions of carbon disulfide, formamide, and para-dinitrobenzene were investigated by Rydberg electron transfer and suggested to be quadrupole-bound anions, but the lack of theoretical support rendered them less convincing;²⁶⁻²⁹ the small cluster anions of magnesium oxide were investigated by photoelectron spectroscopy and interpreted as quadrupole-bound anions, but their high electron binding energies and rather localized orbitals made them more characteristic of conventional valence-bound anions.³⁰ It was not until 2004 that Schermann, Bowen, and Compton presented the first convincing evidence of quadrupole-bound anions by combining results from two different, but complimentary experimental techniques: the dipole-bound anion state of the *gauche*-succinonitrile conformer was revealed by anion photoelectron spectroscopy, and the quadrupole-bound anion state of the *trans*-succinonitrile conformer was revealed by Rydberg electron transfer.³¹ While each of these techniques revealed one type of a multipole-bound anion, they were each unable to discern the other type. This led us to revisit this earlier study using the unique combination of Rydberg electron transfer and negative ion photoelectron spectroscopy. In that study, the anion photoelectron spectra of succinonitrile anions, which were formed via Rydberg electron transfer, exhibited distinctive features for both dipole- and quadrupole-bound anions in the same photoelectron spectrum, providing direct spectroscopic confirmation for the presence of both multipole-bound states in the same molecule and in a single experiment.³²

Additional progress in the study of quadrupole-bound anions has included the development of computational models,³³⁻³⁶ theoretical prediction of several stable quadrupole-bound anions,³⁷ and the discovery of excited-state, quadrupole-bound states in a valence-bound anion.³⁸ Despite these advances, however, the *trans*-succinonitrile anion remained the only experimentally-confirmed example of a ground-state, quadrupole-bound anion. The search for quadrupole-bound anions is intrinsically challenging because (i) their weakly-bound nature requires specialized experimental techniques for making and analyzing them; (ii) unlike dipole-bound anions, whose electron binding energies are proportionally correlated to the magnitude of the neutrals' dipole moments, there is no clear correlation between the magnitude of the molecular quadrupole moment and the electron binding energy of the quadrupole-bound anion;³⁷ thus, the prediction of stable quadrupole-bound anions relies heavily on high-level *ab initio* calculations; (iii) if the molecule can sustain both quadrupole-bound and valence-bound states, the nascent quadrupole-bound state may quickly decay into the more stable valence-bound state, hiding the incipient quadrupole-bound anion state from view.³⁸

Recently, several neutral molecules have been theoretically predicted by Sommerfeld to form quadrupole-bound anions.³⁷ Among these, the 1,4-dicyanocyclohexane (DCCH) molecule was seen as a

promising candidate for the experimental interrogation for two reasons. While its conformers were predicted to support both dipole- and quadrupole-bound anionic states, it was not predicted to form a valence state. In addition, its laboratory synthesis was deemed to be more tractable than other candidates. In the present work, the parent anions of DCCH were formed by Rydberg electron transfer and interrogated by velocity mapping imaging, anion photoelectron spectroscopy. The resulting anion photoelectron spectra exhibited distinctive spectral features for both dipole- and quadrupole-bound anions, whose electron binding energies were measured as 115 meV and 18 meV, respectively. These values are in excellent agreement with theoretical calculations. Thermodynamic analysis rationalized the relative quantity of the two types of anions.

Experimental Methods

Synthesis of 1,4-Dicyanocyclohexane This compound can be prepared according to a known literature procedure.^{39,40} It was obtained as a mixture of *cis*- and *trans*- conformations, which appeared as an off-white solid; m.p. 54-55 °C. Characterization data: ¹H NMR (400 MHz, CDCl₃) δ 2.77-2.72 (2H, m), 2.10-1.97 (4H, m), 1.89-1.75 (4H, m); ¹³C NMR (400 MHz, CDCl₃) δ 120.9, 120.8, 26.3, 26.2, 26.1, 26.0; $\nu_{\max}/\text{cm}^{-1}$ 2238 (CN, strong).

Anion Photoelectron Spectroscopy Our Rydberg electron transfer/anion photoelectron spectroscopy apparatus has been described previously.^{23,24,32,41} Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. This technique is governed by the energy-conserving relationship, $h\nu = \text{EKE} + \text{EBE}$, where $h\nu$, EKE, and EBE are the photon energy, the electron kinetic energy, and the electron binding (transition) energy, respectively. Electron kinetic energies were measured using a velocity-map imaging (VMI) spectrometer. Mass-selected anions were crossed with 1064 nm, linearly polarized photons in an electric field. The resultant photodetached electrons were accelerated along the axis of the ion beam toward a position-sensitive detector coupled to a CCD camera. The two-dimensional image formed from the sum of the electrons was reconstructed into a portion of the three-dimensional distribution via the BASEX method.⁴² Photoelectron spectra are calibrated against the well-known spectrum of NO⁻.⁴³

DCCH anions were generated by our Rydberg electron transfer (RET) source. Neutral DCCH molecules were vaporized in a pulsed valve, which was heated to 140 °C, and then supersonically expanded with 10 psi of helium gas. DCCH anions, DCCH⁻, were formed when neutral DCCH molecules collided with a thermally-expanded beam of potassium atoms, which had been excited to specific Rydberg states in two steps using two dye lasers. One dye laser pumped the potassium atoms to the ²P_{3/2} state with 766.7 nm light, while the other was tuned to reach specific *nd* Rydberg levels, where *n* is the principal quantum

number. In this study, Rydberg levels from $n = 13d$ to $18d$ were selected. Upon electron transfer and subsequent ion-pair separation, the resulting anions, DCCH^- , were extracted into a time-of-flight mass spectrometer. There, they were mass-selected before having their excess electrons photodetached and energy-analyzed by velocity-map imaging spectroscopy.

Calculations The electron affinities of DCCH had been accurately calculated by Sommerfeld in an earlier contribution.³⁷ The calculations conducted during the present work serve to explain the relative amounts of dipole- versus quadrupole-bound DCCH anions that were formed. The second-order Møller-Plesset perturbation theory calculations were performed with the ORCA computational chemistry software package.⁴⁴ All calculations were carried out with the resolution of identity (RI) and the RIJCOSX approximation.⁴⁵ The cc-pVTZ basis set⁴⁶ was used throughout our calculations in conjunction with the auxiliary basis sets def2/J⁴⁷ and cc-pVTZ/C⁴⁸. Frequency calculations were performed to verify the optimized structures and transition states.

Results and Discussions

Figure 1a shows the structures of the three DCCH conformers. In *cis*-DCCH, one CN group is at the equatorial(*e*) site, and the other one is at the axial(*a*) position. The *trans*-DCCH can have two conformers, which are labeled as *aa*-DCCH and *ee*-DCCH, depending on the positions of the CN groups. Since the sample was synthesized as a mixture of *trans*- and *cis*-conformations, all three conformers were present. Also provided in Figure 1a are calculated dipole and quadrupole moments of these conformers as well as their vertical electron affinity (VEA) values.³⁷ Calculations show that the *aa*-DCCH molecule is unable to form a weakly-bound anion; the *ee*-DCCH, which has a vanishing dipole moment but a significant quadrupole moment, can form a quadrupole-bound anion with a VEA of 19 meV; the *cis*-DCCH, which has a large dipole moment, can form a dipole-bound anion with a VEA of 108 meV.

Figure 1b presents a representative mass spectrum of molecular and cluster anions of DCCH made via Rydberg electron transfer (RET). Cluster anions of the dimer and trimer of DCCH are observed, demonstrating the capability of RET to make not only molecular, but also cluster anions. A mass peak corresponding to CN^- physisorbed (solvated) by three DCCH molecules is also observed. The CN^- anion results from the dissociative electron attachment to DCCH clusters. While it would be interesting to investigate the nature of electron binding to DCCH clusters, i.e., quadrupole-binding, dipole-binding or a synergy of quadrupole- and dipole-binding, the focus of the present study is on identifying the weakly-bound states of the DCCH parent molecular anion, DCCH^- .

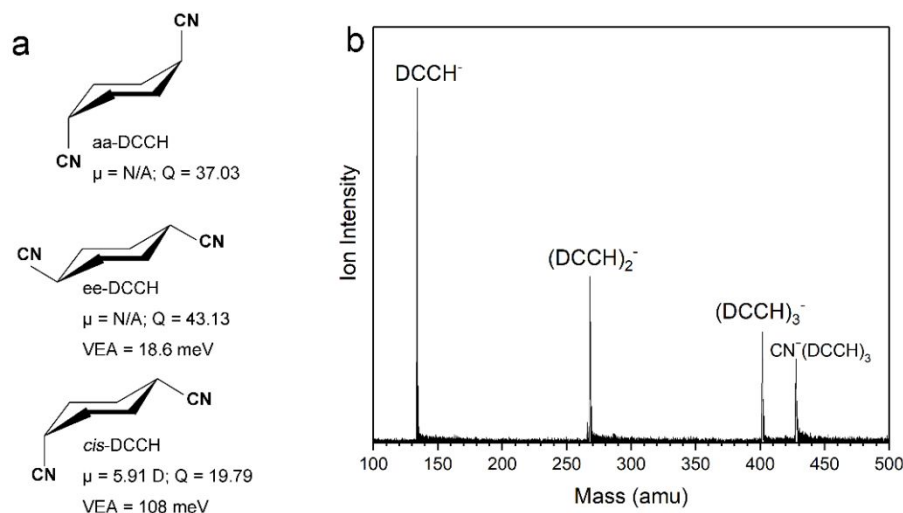


Figure 1. (a) Structures of the *trans*- and *cis*- isomers of 1,4-dicyanocyclohexane (DCCH), along with their electronic properties. The unit of the quadrupole moment, Q , is the atomic unit ea_0^2 . (b) Mass spectrum of molecular and cluster anions of DCCH made by Rydberg electron transfer.

Figure 2 presents the anion photoelectron spectra of DCCH anions made at different Rydberg n levels. Spectra collected at $n = 13d, 14d$, and $18d$ Rydberg levels are dominated by a single sharp peak at a low electron binding energy (EBE). For spectra obtained at $n = 15d, 16d$ and $17d$, an additional sharp, yet weaker peak appears on the lower EBE side of the principal peak. These sharp peaks at low EBE in photoelectron spectra are the signature of weakly-bound anions. In RET, the electron attachment to diffuse electron states occurs via resonance charge transfer, and thus maximal electron transfer efficiency occurs at different Rydberg levels, when electrons are attached to different multipole environments. Therefore, the appearance of the lower EBE feature at only $n = 15d-17d$ suggests that it is associated with a different multipole field environment than is the higher EBE feature. The lower EBE peak is centered at 18 meV, with a full width at half-maximum (fwhm) of ~ 37 meV. The higher EBE peak is centered at 115 meV, with a fwhm of ~ 35 meV. These peaks are due to the photodetachment transitions between the anions and their corresponding neutral molecules. Therefore, the vertical detachment energy (VDE) values of these two peaks are 18 and 115 meV, respectively. When anion photoelectron spectra are dominated by single sharp peaks, it strongly suggests a close similarity between the structures of the anion and its neutral counterpart. In such cases of structural similarity, the anion's VDE value will be almost identical to that of its corresponding neutral's adiabatic electron affinity (EA) and to its VEA value. By comparing our experimentally-determined VDE values with VEA values from previous calculations³⁷, we assigned the feature at 18 meV to be the signature of the quadrupole-bound anion of *ee*-DCCH, and the feature at 115 meV to be the signature of the dipole-bound anion of *cis*-DCCH.

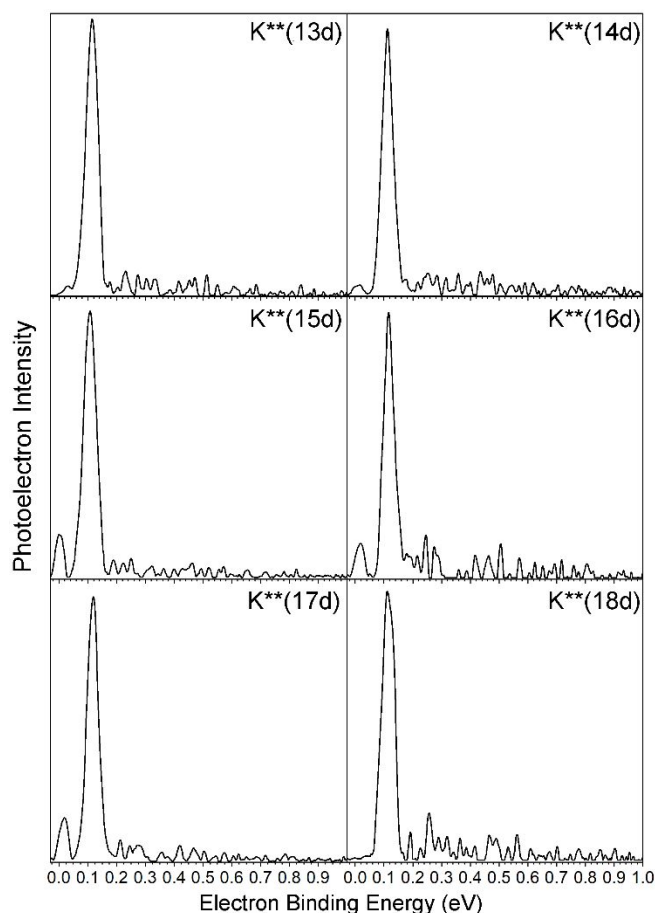


Figure 2. Anion photoelectron spectra of dipole- and quadrupole-bound DCCH anions, DCCH⁻, made at different Rydberg levels ($n = 13d-18d$).

Figure 3 presents a representative photoelectron image of dipole- and quadrupole-bound DCCH anions, which were formed at the $n = 17d$ Rydberg level. The inner brighter ring corresponds to the dipole-bound anion state, while the outer weaker intensity ring corresponds to the quadrupole-bound anion state. Both dipole- and quadrupole-bound anion states show significant anisotropy. The anisotropy parameters, β , of the photodetached dipole-bound electrons are calculated to be between 1.8-2.0. For the photodetached quadrupole-bound electrons their β values are calculated to be 1.4-1.6. Since both the dipole- and quadrupole-bound states can be viewed as spatially diffuse s -character orbitals, the matter wave of photodetached electrons should have p character and a sizeable β value close to 2.⁴⁹ The experimental β value associated with the photodetached dipole-bound electrons is consistent with this number. While the β value associated with the photodetached quadrupole-bound electrons is less than expected, it may only be because the intensity of photodetached quadrupole-bound electrons was too low to yield an accurate evaluation of β .

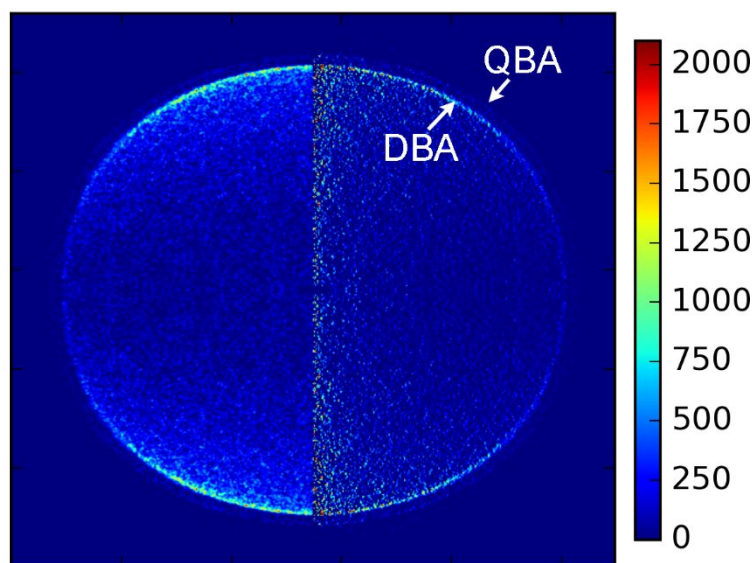


Figure 3. Photoelectron image of DCCH anions collected at the $n = 17d$ Rydberg level.

The feature from quadrupole-bound anions is only weakly seen in the photoelectron spectrum and the velocity map image of DCCH anions (Figure 3), suggesting that only a small portion of the DCCH anions are quadrupole-bound. We explain this with a quantum mechanical and thermodynamic analysis, the results of which are summarized in Table 1 and Figure 4. Calculations at the RI-MP2/cc-pvtz level of theory reveal that the *aa*-DCCH, which is unable to bind an excess electron, is the most stable conformer. The *cis*-DCCH, which forms dipole-bound anions, is 5.1 kJ/mol higher in energy, while *ee*-DCCH, which forms quadrupole-bound anions, is the least stable conformer, at 9.3 kJ/mol above *aa*-DCCH. As shown in Figure 4, quantum calculations show barriers of 0.56 and 0.63 eV for the interconversion from *ee* to *aa* and from *aa* to *ee*, respectively. Such interconversions constantly occur at room temperature when DCCH is in the solid state. In the molecular beam, however, due to the low temperature achieved by supersonic expansion and the lack of external energy input, these barriers are high enough to quench interconversion. Therefore, we estimate the composition of DCCH conformers in the molecular beam to be similar to that in the DCCH vapor before expansion, i.e., in the heated pulse valve. A thermodynamic analysis shows that at an elevated pulse valve temperature (140°C), nearly 80% of the DCCH exists as the *aa* conformer. Therefore, most of the DCCH in the molecular beam will not form anions. The neutral candidate for the dipole-bound anion, *cis*-DCCH, makes up 17.3% of the DCCH in the beam, while the neutral candidate for the quadrupole-bound anion, *ee*-DCCH, makes up only 5.1%. Therefore, only a small portion of DCCH neutral molecules in the beam can form quadrupole-bound anions. This is the main reason for the weak intensity of the quadrupole-bound feature compared to the dipole-bound feature in the photoelectron spectra. While increasing the pulse valve temperature favors the conversion to *ee*-DCCH, temperatures higher than 140°C were found to cause the sample to decompose.

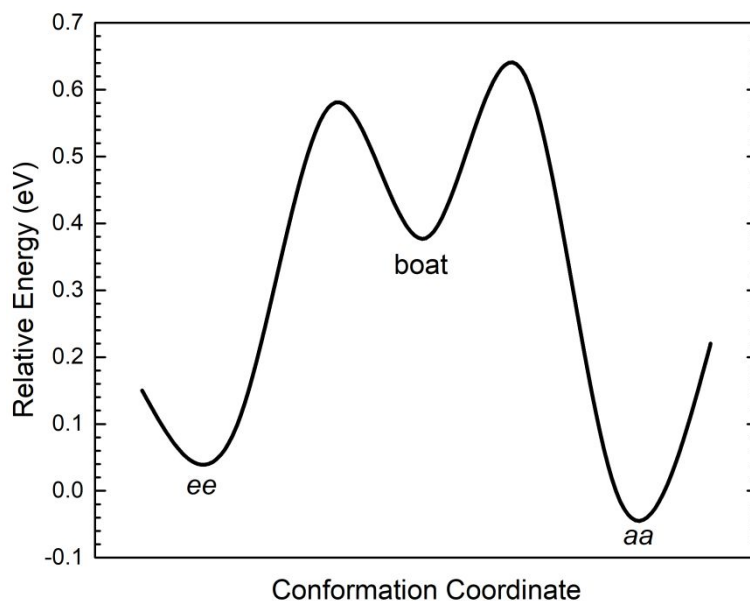


Figure 4. Potential energy surface for neutral *trans*-DCCH along the conformation coordinate connecting the *ee*- and the *aa*-conformers.

Table 1. Relative energies, E_{rel} , of the three DCCH conformers and their relative percentages, P , at room and experimental temperatures.

	E_{rel} (kJ/mol)	$P_{25^{\circ}\text{C}}$ (%)	$P_{140^{\circ}\text{C}}$ (%)	Anion Type
<i>aa</i> -DCCH	0	85.1	77.6	Electron not bound
<i>cis</i> -DCCH	5.1	10.9	17.3	Dipole-bound
<i>ee</i> -DCCH	9.3	2.0	5.1	Quadrupole-bound

Summary

In this contribution, we present experimental evidence for a new, ground state, quadrupole-bound anion obtained in a combined Rydberg electron transfer-anion photoelectron spectroscopic study. The sharp peaks in the photoelectron spectra and the highly anisotropic rings in photoelectron imaging reveal the dipole- and quadrupole-bound anion states of DCCH^- . The quadrupole- and dipole-bound electron affinities are measured as 18 and 115 meV, respectively, these being in excellent agreement with previous theoretical calculations.³⁷ The discovery of this new quadrupole-bound anion extends the knowledge base about quadrupole-bound anions and provides an experimental benchmark for additional theoretical modelling.

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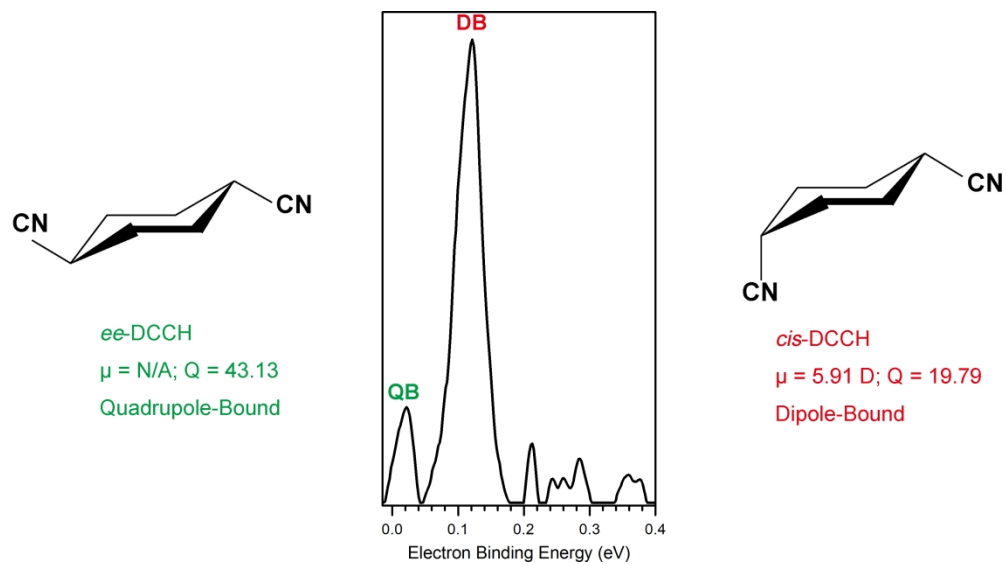
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