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Valence-, Dipole- and Quadropole-Bound Electronically Excited States of Closed-Shell Anions Formed by Deprotonation of Cyano- and Ethynyl-Disubstituted Polycyclic Aromatic Hydrocarbons

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Citation: Strauss, M.E.; Santaloci, T.J.; Fortenberry, R.C. Valence-, Dipole- and Quadropole-Bound Electronically Excited States of Closed-Shell Anions Formed by Deprotonation of Cyano- and Ethynyl-Disubstituted Polycyclic Aromatic Hydrocarbons. *Chemistry* **2022**, *4*, 42–56. <https://doi.org/10.3390/chemistry4010004>

Academic Editors: Edwin Charles Constable, Tomas Ramirez Reina, Peter J. Rutledge and Luis R. Domingo

Received: 21 December 2021

Accepted: 18 January 2022

Published: 24 January 2022

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Abstract: Dicyano-functionalized benzene and naphthalene anion derivatives exhibit a relatively rich population of electronically excited states in stark contrast to many assumptions regarding the photophysics of anions in general. The present work has quantum chemically analyzed the potential electronically excited states of closed-shell anions created by replacing hydrogen atoms with valence-bound lone pairs in benzene and naphthalene difunctionalized with combinations of -CN and -C₂H. Dicyanobenzene anion derivatives can exhibit dipole-bound excited states as long as the cyano groups are not in *para* position to one another. This also extends to cyanoethynylbenzene anions as well as deprotonated dicyano- and cyanoethynyl naphthalene anion derivatives. Diethynyl functionalization is less consistent. While large dipole moments are created in some cases for deprotonation on the -C₂H group itself, the presence of electronically excited states beyond those that are dipole-bound is less consistent. Beyond these general trends, 2-dicyanonaphthalene-34 gives strong indication for exhibiting a quadrupole-bound excited state, and the 1-cyanoethynyl naphthalene-29 and -36 anion derivatives are shown to possess as many as two valence-bound excited states and one dipole-bound excited state. These photophysical properties may have an influence on regions where polycyclic aromatic hydrocarbons are known to exist such as in various astrochemical environments or even in combustion flames.

Keywords: dipole bound states; astrochemistry; anions; polycyclic aromatic hydrocarbons; electronically excited states; diffuse interstellar bands

1. Introduction

The myth that anions cannot possess electronically excited states is finally abating in the chemical literature [1–6]. Anions are showing a rich field of both traditional and exotic types of electronic excitations [7–11]. Granted such states are only present in a subset of anions and are not generally applicable. However, those that do exhibit electronically excited state behavior are promising to open novel areas of discovery for both applied and fundamental chemical physics. One of these fields is astrochemistry.

The first anion conclusively detected in astrophysical media was C₆H[−] [12]. This was followed shortly by C₄H[−] [13], C₈H[−] [14,15], C₃N[−] [16], C₅N[−] [17], and CN[−] [18] leading to the notion that anions are somewhat ubiquitous in the interstellar medium (ISM) [19,20]. The formation of these anions has been debated since their detection, mostly due to the fact that few astrophysicists thought that anions would be stable enough to endure the harsh conditions of the ISM, in the first place, even in molecular clouds like the Taurus Molecular Cloud (TMC-1) where so many anions have been observed [21]. While some

may form from collisional processes like CN^- , others likely form through what is called a dipole-bound state.

Such a state occurs when the excess electron is attracted to the positive end of the dipole moment in the remaining neutral molecular core [2]. While the theoretical minimum for such a state to exist is 1.625 D [22], the more practical value is some value above 2.0 D or so [23–27]. While most dipole-bound states are ground electronic states, if the anion's ground state electronic structure is purely valence in nature, the excited state may be dipole-bound.

In the case of C_6H^- , specifically, the ground $^2\Pi$ state of the neutral radical exhibits a dipole moment of greater than 4.0 D while that of the ground $^2\Sigma^+$ state C_4H radical is less than 1.0 D. In the general C_{2n}H family of radicals, the $^2\Pi$ state is strongly dipolar while the $^2\Sigma^+$ is not, as is shown by these two species. However, the $^2\Pi$ state is the excited state of C_4H lying a mere $\sim 500\text{ cm}^{-1}$ above the ground $^2\Pi$ [28,29]. Hence, the dipole-bound formation of C_4H^- begins with the $\tilde{X}^2\Sigma^+$ state of the radical. It must then undergo an electronic excitation into the more dipolar $^2\Pi$ state of the radical before the excess electron can bind. As a result, the abundance of C_4H^- is orders of magnitude less than its corresponding radical while this is inverted in the case of C_6H^- where the anion is much more abundant [30,31]. Additionally, C_2H^- has been famously undetected in the ISM, even though its radical has been known for nearly 50 years [32] and this radical is one of the most abundant molecules in some astrophysical regions [33]. The weakly dipolar $\tilde{X}^2\Sigma^+$ state in C_2H cannot access the more strongly dipolar $^2\Pi$ state as can happen in C_4H reducing the population of the C_2H^- anion below the limit of detection.

Ironically, two of the strongest dipole-inducing functional groups available for astrochemical reactions include C_2H itself and the cyano radical. While C_2H itself is weakly dipolar, its power as an electron withdrawing group enable it to produce novel anion photochemistry as part of a larger molecular system. Most notably, these two functional groups have allowed for the rotational observation of novel hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs) in the ISM for the first time. PAHs have long-been invoked as the origins for fairly ubiquitous infrared emission features [34] as well as interstellar carbon sinks where most of the non-CO/ CO_2 carbon in the universe is held [35–37]. However, conclusive evidence for their presence in the ISM has only come in the past few years through the detections of benzonitrile [38], both isomers of cyano-naphthalene [39], and indene [40]. Additionally, ethynyl cyclopropenylidene [40] and ethynyl cyclopentadiene [41] have also been observed. These PAHs and PAH-like molecules are mostly dipolar enough for radioastronomical observation due to their dipole-inducing cyano and ethynyl functional groups. While these structures certainly could possess dipole-bound states as radical anions, another interstellar spectral anomaly exists in the electronic region of the electromagnetic spectrum where the closed-shell anion forms of such molecules is more applicable.

The diffuse interstellar bands (DIBs) are a series of unattributed interstellar absorption features stretching from the ultraviolet through the visible and into the near-infrared [42–44]. They have been observed for over a century now [45–47] and only four bands of the observed thousands [48] have been linked to a molecular carrier (C_{60}^+) with any confidence [49–51]. While a few of the DIBs appear to correlate [52], most are seemingly independent of one another implying unique molecular carriers for most features. Additionally, a majority of the DIBs appear in the near-infrared with few in the ultraviolet. Both of these conditions give strong preference towards anions as potential carriers as most anions have few (typically one or two) electronically excited states, and most are longer wavelength in nature [6,53–58]. While PAHs themselves have been invoked as a possible carrier for many DIBs [59], electronic spectra of CN- and C_2H -functionalized PAH anions may be able to provide further insight into the provenience of the DIBs since PAHs functionalized in this way are now known in the ISM.

Recent work has shown that removal of a single hydrogen atom from a PAH structure creates a closed-shell carbene if an additional electron is added to the system after removal of the hydrogen atom, a deprotonation construct [60–62]. The presence of the valence

ground state allows for dipole-bound excited states and, in exceptional cases, additional valence excited states along with the potential for even quadrupole-bound or higher-multipole-bound states [3,63]. The presence of a nitrogen heteroatom in the PAH (created a so-called PANH) destabilizes the ring since the C=N bonds are more polarized than the C=C bonds and allows for more dynamic electronic structure below the electron binding energy (eBE). Cyano- and ethynyl-functionalization increases this dramatically [64,65]. Cyano-functionalization actually creates dipole-bound excited states in singly-deprotonated benzene anions in some isomers and in all cases once the number of rings in the structure is two or greater beginning with the case of naphthalene [64]. Ethynyl-functionalization is a bit less consistent, but the largest dipole moments for deprotonated PAH isomers arise when the deprotonation site is on the ethynyl hydrogen itself [65]. This also promotes valence excited states as the highest occupied molecular orbital is no longer a carbene lone-pair but shifts into the distributed π cloud.

As a result, the -CN and -C₂H additions to the PAH drastically change the electronic properties providing an opportunity to explore how these molecules relate to astronomical phenomena such as the DIBs. This present work extends such analyses into deprotonated PAH anions further by including two functional groups instead of one. This also allows for mixed functionalization in a manner similar to that done for amine anions [66]. The number of possible isomers, therefore, increases significantly than single functionalization and gives the opportunity for even more novel photochemistry with possible applications both astrochemically and terrestrially.

2. Computational Details

Benzene and naphthalene are difunctionalized with two cyano groups, two ethynyl groups, or both. The three combinations are cyano-cyano (CNCN), cyano-ethynyl (CNC₂H), and ethynyl-ethynyl (C₂HC₂H). Similar to past studies [64,66], each combination is singly deprotonated. For benzene, there are 27 deprotonated isomers and naphthalene has a total of 197 deprotonated isomers. A Python script generates the isomers with simplified molecular-input line-entry system (SMILES) strings and singly deprotonates each generated SMILES string. Each SMILES string is converted to Cartesian coordinates with the Open Babel (OBabel) computational package [67,68]. Another Python script writes the Cartesian coordinates into a Gaussian singlet, anion and doublet, radical input file. Each geometry is optimized via B3LYP/aug-cc-pVDZ within the Gaussian 16 quantum chemistry program [69] in order to find the relative energies and electrostatic properties. Furthermore, the dipole moment and quadrupole moment are computed with the optimized anion geometry as an open shell neutral radical at this same level of theory. The optimized anion geometry is used for the vertical excited state computations to report the absorption properties.

The electronically excited state computations are done with MOLPRO [70] using equation of motion coupled cluster theory at the singles and doubles level (EOM-CCSD) [71–73]. Similar to past studies [64,66,74,75], the basis set for the benzene derivatives is augmented with six s-type, six p-type, and two d-type basis functions. The naphthalene derivatives are augmented with eight s-type, six p-type, and three d-type basis functions. The difference in the basis set size is necessary since the naphthalenes are larger than the benzene molecular derivatives. The diffuse functions are localized about ghost atoms placed at the center of charge (COC). Lastly, the eBE, or the maximum amount of energy the electron in an anion can absorb, is computed with CFOUR using EOM-CCSD with an ionization potential formalism (EOMIP) with the aug-cc-pVDZ basis set. Past studies on CH₂CN[−] show that the eBE experimental value and the eBE computational value differ by less than 0.02 eV [54,56,76] providing confidence in the reported results. Additionally, previous work has established a confidence of 0.01 eV for the presence of electronic states below the eBE [64–66]. All molecular orbitals are plotted with the Gabedit software [77] with an isovalue of 0.05.

3. Results

3.1. Benzene Derivatives

3.1.1. Relative Energies and Electrostatic Properties

As with the singly-functionalized, deprotonated cyanobenzene study [64], the presence of the cyano groups elicits strong dipole moments in the dehydrogenated neutral radicals as given in Table 1. This also continues for the mixed cyanoethynylbenzenes, as well. The diethynyl structures are much more variable, again in line with previous work [65], where the largest dipole moments are created when the hydrogen is removed from the ethynyl group itself and not from the ring. Again, as shown in previous work, the relative energies between the anions and corresponding neutral radicals is largely inverted in Table 1 where the most stable closed-shell anions are often the least stable neutral radicals. The ethynyl groups destabilize the structures to a much larger degree than the cyano groups do in both the neutral and the charged species, again, as has been shown in previous work [64–66]. This present work, however, extends such interpretations to difunctionalized PAH and PAH-like systems.

Table 1. B3LYP/aug-cc-pVDZ relative energies along with the total dipole moments and largest quadrupole moment contributions of the difunctionalized benzene derivatives.

Dicyano	Anion Rel. E. (eV)	Radical Rel. E. (eV)	Dipole (D)	Quad (D-Å)
p-CNCN-1	0.073	0.029	0.87	26.69
o-CNCN-2	0.225	0.122	7.36	3.02
o-CNCN-3	0.277	0.075	6.35	4.32
m-CNCN-4	0.000	0.095	5.07	18.44
m-CNCN-5	0.077	0.042	4.15	18.05
m-CNCN-6	0.167	0.000	3.31	16.45
Cyanoethynyl				
p-CNC2H-1	0.973	0.022	5.00	9.24
p-CNC2H-2	1.048	0.018	3.94	9.24
p-CNC2H-3	0.000	0.931	2.34	32.45
o-CNC2H-4	0.210	0.697	8.68	5.14
o-CNC2H-5	1.163	0.075	4.12	10.80
o-CNC2H-6	1.136	0.028	3.56	12.51
o-CNC2H-7	1.135	0.049	4.14	8.64
o-CNC2H-8	1.085	0.078	5.06	9.71
m-CNC2H-9	0.143	0.631	5.56	21.61
m-CNC2H-10	0.982	0.091	5.00	9.88
m-CNC2H-11	1.055	0.037	3.47	11.17
m-CNC2H-12	1.068	0.000	4.05	9.92
m-CNC2H-13	0.976	0.060	5.01	9.81
Diethynyl				
p-C2HC2H-1	1.106	0.016	0.96	7.93
p-C2HC2H-2	0.000	0.474	7.42	15.45
o-C2HC2H-3	0.187	0.576	6.63	13.93
o-C2HC2H-4	1.213	0.072	1.19	8.81
o-C2HC2H-5	1.183	0.044	0.49	7.81
m-C2HC2H-6	0.112	0.565	6.61	14.37
m-C2HC2H-7	1.120	0.087	1.48	8.01
m-C2HC2H-8	1.112	0.054	0.91	7.57
m-C2HC2H-9	1.127	0.000	0.42	7.71

Visual depiction of the structures that correspond to the molecules listed in Table 1 are given in Figure 1. The removal position of the hydrogen atoms are simply numbered progressively from molecule to molecule within a class as given in the figure. The classes are named based on the functionalization present. For instance, the dicyanobenzenes are listed as *i*-CNCN-*x*, where *i* represents the positioning of the functional groups relative

to one another in typical ortho, meta, and para organic labeling and x is the position for hydrogen removal.

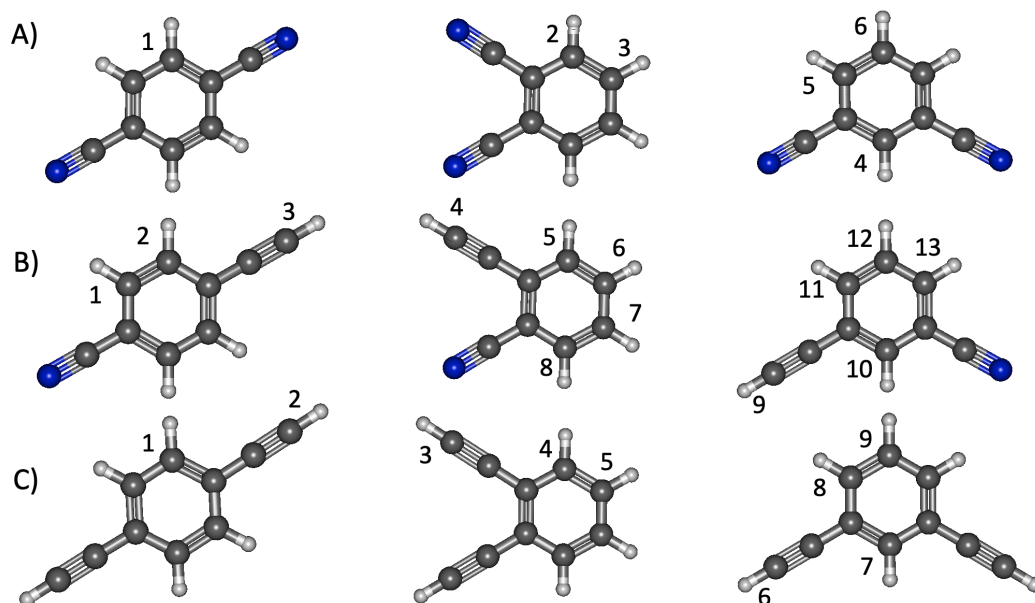


Figure 1. The optimized structure of the benzene-class molecules with numbered positions of deprotonation. (A) dicyanobenzene, (B) cyanoethynylbenzene, (C) diethynylbenzene.

The most notable exception to the above rule for the large dipole moments of the dicyanobenzene derivatives is for p-CNCN-1. While any of the four hydrogens could be removed, they are all equivalent by symmetry. Additionally, the para positioning of the CN groups effectively nullifies the dipole moment in this molecule. However, the largest contributor to the radical quadrupole moment is rather large at more than 25 D-Å. Consequently, any excited states for this molecule cannot be dipole-bound as the radical dipole moment is too small. They may be valence bound states (VBSs) or potentially quadrupole-bound states (QBSs). The minimal quadrupole moment in a corresponding neutral radical for an anion QBS to be bound is not as well established as the 2.0–2.5 D dipole moment needed for the corresponding radicals in dipole-bound states (DBSs) of molecular anions, but one can likely assume that the larger, the better [63]. For the other groups, the cyanoethynylbenzene anions all have dipole moments of greater than 3.47 D with some as large as 8.68 D from Table 1. The diethynyl structures vary from 0.42 D to 7.42 D. Again, the largest dipole moments correspond to removal of the hydrogen from one of the ethynyl groups. p-C2HC2H-1, o-C2HC2H-5, m-C2HC2H-8, and m-C2HC2H-9 all have much too small dipole moments to support excited DBSs. The largest contributors to the quadrupole moments are also relatively small, all being less than 10 D-Å.

3.1.2. Vertical Excitation Energies

In looking at Table 2 for the vertical excitation energies from the optimized anion geometries, *all* of the dicyano and cyanoethynyl benzene anion derivatives exhibit excited states. Specifically, the three *para* and *ortho* dicyano anions all exhibit $1^1B_1/1^1A''$ VBSs with excited states falling below the eBE by more than 0.5 eV. The three *meta* structures appear to produce only DBSs (the $2^1A'$ states) which are below the eBEs by less than 0.1 eV. The two *ortho* dicyano anions also possess DBSs of this same symmetry. However, the p-CNCN-1 also is exhibiting a 2^1A_1 state at 3.003 eV while the eBE is 3.005 eV. This state is within our confidence level of 0.01 eV for being able to state whether or not it is bound, but if this state is bound, it must be a QBS since the dipole moment is too small as discussed previously. The corresponding radical does exhibit a “large” quadrupole moment. Hence, this state is an excited QBS candidate, but more detailed analysis is required in order to classify this

state of p-CNCN-1 as such. No other states exist below the eBE for the dicyano benzene derivative anions in Table 2.

Table 2. EOM-CCSD/aug-cc-pVDZ+6s6p2d electronically excited states and eBEs (all in eV) of the difunctionalized benzene derivative anions.

Dicyano	Excited States				eBE (eV)
	$1^1B_1/1^1A''$	$2^1B_1/2^1A''$	$2^1A_1/2^1A'$	$3^1A_1/3^1A'$	
p-CNCN-1	2.327	3.012	3.003	3.005	3.005
o-CNCN-2	2.384	2.942	2.829	2.933	2.934
o-CNCN-3	2.442	2.863	2.779	2.855	2.855
m-CNCN-4	3.178	3.204	3.107	3.171	3.171
m-CNCN-5	2.815	3.076	3.010	3.069	3.068
m-CNCN-6	2.851	2.877	2.817	2.844	2.836
Cyanoethynyl					
p-CNC2H-1	2.393	2.596	2.585	2.589	2.587
p-CNC2H-2	2.266	2.504	2.494	2.497	2.494
p-CNC2H-3	3.801	3.827	3.817	3.699 ^a	3.825
o-CNC2H-4	3.599	3.732	3.741	3.747	3.735
o-CNC2H-5	2.361	2.436	2.405	2.429	2.427
o-CNC2H-6	2.450	2.480	2.430	2.443	2.440
o-CNC2H-7	2.450	2.479	2.426	2.443	2.441
o-CNC2H-8	2.468	2.528	2.494	2.521	2.519
m-CNC2H-9	3.666	3.759	3.732	3.766	3.759
m-CNC2H-10	2.669	2.675	2.654	2.669	2.667
m-CNC2H-11	2.576	2.605	2.561	2.569	2.563
m-CNC2H-12	2.326	2.433	2.420	2.426	2.424
m-CNC2H-13	2.669	2.697	2.649	2.662	2.661
Diethynyl					
p-C2HC2H-1	2.105	2.137	2.097	2.102	2.097
p-C2HC2H-2	3.443	3.492	3.438	3.451	3.400
o-C2HC2H-3	3.271	3.320	3.327	3.353	3.319
o-C2HC2H-4	2.046	2.078	2.038	2.041	2.038
o-C2HC2H-5	2.061	2.094	2.054	2.057	2.053
m-C2HC2H-6	3.372	3.405	3.412	3.437	3.404
m-C2HC2H-7	2.188	2.220	2.180	2.183	2.180
m-C2HC2H-8	2.179	2.212	2.172	2.176	2.172
m-C2HC2H-9	2.034	2.067	2.027	2.031	2.027

^a This is actually the 1^1B_2 state in this case.

The cyanoethynyl, difunctionalized benzene anion derivatives all exhibit at least one bound state in Table 2. All of these anions have corresponding radicals with dipole moments of more than 3.4 D meaning that all should exhibit excited DBSs [1]. While the DBSs appear within ~ 0.05 eV of the eBE, those lower than the DBS and, typically, lower than the eBE by more than 0.05 eV are excited VBSs. The orbitals involved in these processes are depicted in Figure 2 for the example of p-CNC2H-3 with its C_{2v} symmetry even though the highest bound state lies only 0.008 eV lower than the eBE in this case. Therein the hydrogen is removed from the ethynyl group producing an out-of-plane b_1 highest occupied molecular orbital (HOMO). One VBS is actually, and surprisingly, higher in energy than the DBS for this molecule but still bound at 3.817 eV and is constructed by excitation out of this HOMO into the π -space's lowest unoccupied molecular orbital (LUMO), the particle-in-box-type π^* b_1 orbital in Figure 2B. Another, VBS is present and is much lower in energy at at 3.699 eV. This 1^2B_2 state is constructed from excitation out of the HOMO-1 π orbital orthogonal to the π cloud in the ethynyl group in Figure 2A into

the same valence orbital, again shown in Figure 2B. Finally, the excited DBS at 3.801 eV excites an electron from the HOMO into the large, s -type a_1 dipole-bound orbital depicted in Figure 2C. There is some question as to whether this state may be a QBS since the dipole moment is close to the 2.0 D threshold while, at the same time, the largest contributor to the quadrupole moment is 32.45 D-Å, the largest of the set in Table 1. This may be investigated in future work. Similar excitation patterns of the VBS actually being the highest energy state are also exhibited in o-CNC2H-4, m-CNC2H-9, o-C2HC2H-3, and m-C2HC2H-6. The other mixed cyanoethynyl, difunctionalized benzene anion derivatives behave much more predictably where any possible excited VBSs are below the DBSs which are, in turn, below the eBEs.

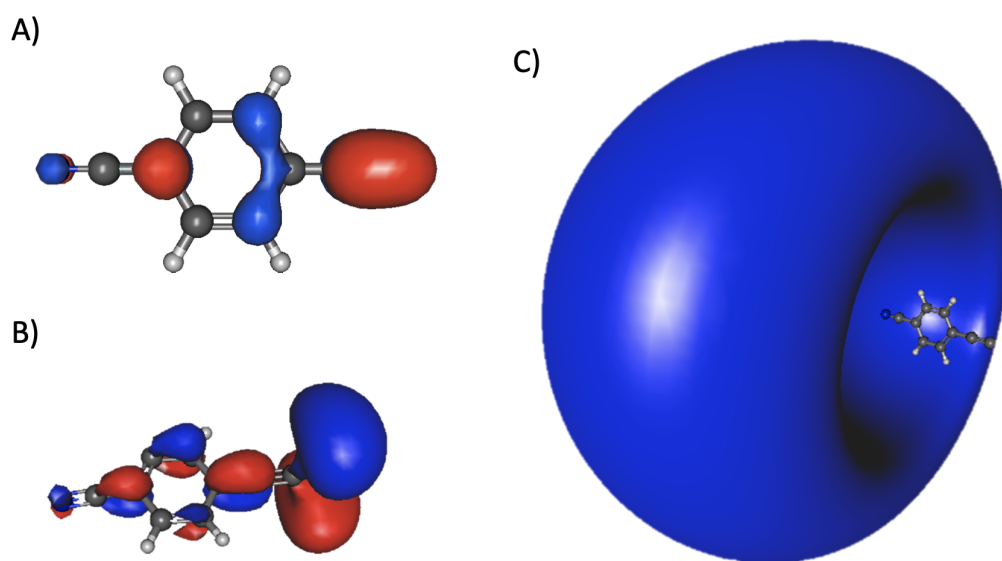


Figure 2. The electronic excited states of cyanoethynylbenzene isomer p-CNC2H-3. (A) b_1 highest occupied molecular orbital, (B) b_1 valence-bound state, (C) a_1 dipole-bound state.

The bound excited states of the diethynylbenzene anion derivatives are fewer in number. Only p-C2HC2H-2, o-C2HC2H-3, and m-C2HC2H-6, those that are deprotonated off of the ethynyl group, have dipole moments large enough to support excited DBSs. Of these three, only the latter two actually have bound states below the eBEs in Table 2, and these are the $1^1A''$ DBSs. The m-C2HC2H-7, -8, and -9 anion derivatives, though, are producing excitation energies for the $2^1A'$ states that are effectively coincident with the eBE for our computational precision. The dipole moments of the corresponding neutral radicals for these anions are too small to support excited DBSs, and these do not appear to be valence orbitals upon examination of these orbitals. Hence, these could be candidate QBSs, but the largest contributors to the quadrupole moments are less than 10 D-Å raising questions as to whether this can be the case. Again, the present methodology is not precise enough to classify these states as bound QBSs, but future work will examine these in more detail. Regardless, the previous trend of multiple excited states in cyano functionalized cyclic aromatic hydrocarbon anions and few, if any, excited states for ethynyl functionalization on such molecular systems [64,65] is maintained even extending to difunctionalization.

3.2. Dicyanonaphthalene

3.2.1. Relative Energies and Electrostatic Properties

The number of deprotonated isomers increases geometrically in moving up to two rings in naphthalene. Singly-functionalized naphthalene has two isomers: 1 and 2. These are the basis (without repeats) for the 42 deprotonated, dicyano naphthalene isomers listed in Figure 3 and Table 3. These are named based on the isomer number given in Figure 3. Lastly, the deprotonation sites in Figures 3, S1 and S2 (the last two from the

supplementary material) are not in numerical order because the Python script generates the SMILES strings for every hydrogen. However, the figures, tables, and discussion only include the unique isomers.

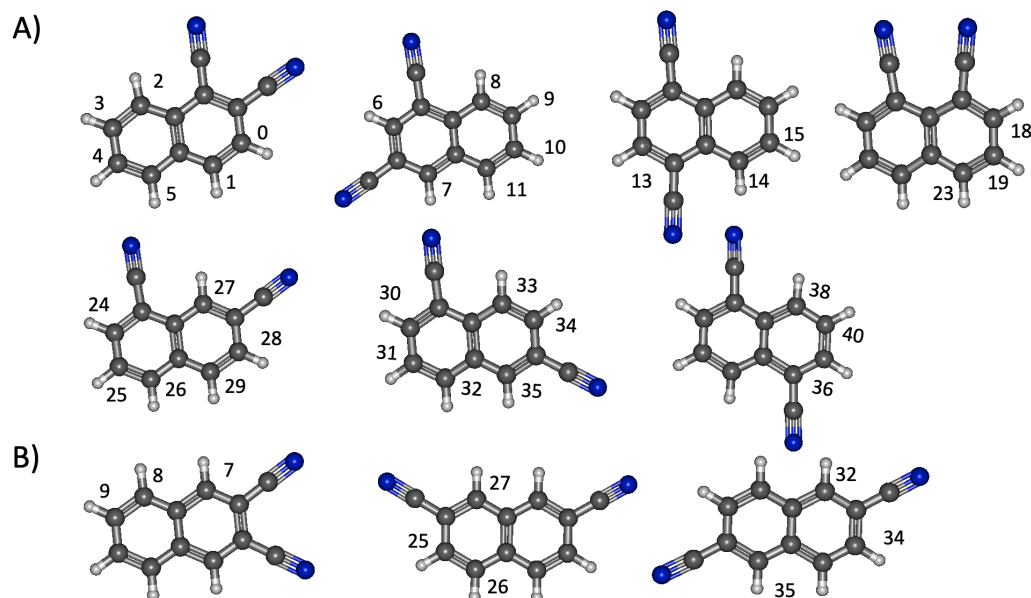


Figure 3. The optimized structure of diethylnaphthalene with numbered positions of deprotonation (A) 1-dicyanonaphthalene, (B) 2-dicyanonaphthalene.

The relative energies of the dicyanonaphthalene anion derivatives are of a slightly larger range in Table 3 compared to the benzene anions. All but eight of the 42 have dipole moments of 2.0 D or greater, and 1-dicyanonaphthalene isomer 18 has the largest dipole moment of 8.95 D. Those that exhibit dipole moments of less than 2.0 D have their cyano groups diametrically opposed to each other with the dehydrogenation site little-affecting the resulting charge balancing. However, those with the smallest dipole moments also exhibit some of the largest contributions to the quadrupole moment. For instance, 1-dicyanonaphthalene-38 has a quadrupole moment contributor of 29.02 D-Å.

3.2.2. Vertical Excitation Energies

Once more, as with the dicyanobenzene anion derivative, all of the deprotonated, dicyano naphthalene anion derivatives exhibit bound excited states, even those with dipole moments of less than 2.0 D. While most excited states are DBSs given in Table 4, clear VBSs are present for several isomers, notably 1-dicyanonaphthalene isomers 3, 9, 23, and 24 along with 2-dicyanonaphthalene isomers 8 and 9.

Those isomers with small dipole moments but large contributions to the quadrupole moment are also exhibiting bound states. Those of 1-dicyanonaphthalene isomers 14, 15, 36, 38, and 40 along with 2-dicyanonaphthalene isomers 32 and 35 are 0.006–0.002 eV below their eBEs implying that these are candidate QBSs. However, 2-dicyanonaphthalene-34 at 2.951 eV is 0.017 below the 2.968 eBE. This is larger than the precision of the method [64,65], giving the strongest evidence for the existence of an excited QBS in this study. The radical dipole moment is 0.94 D, but the largest contributor to the quadrupole moment is 26.68 D-Å, a large value as analyzed in the present set. The accepting orbital is depicted in Figure 4B. Unlike the dipole-bound orbitals, the virtual orbital involved here encapsulates the molecule as would be expected for a structure centered about the quadrupole moment. Hence, the $2^1A'$ state of 2-dicyanonaphthalene-34 is most likely an excited QBS. Additionally, this state has an oscillator strength of 0.0050 which is one of the larger intensities reported for these molecules.

Table 3. Relative energies along with the total dipole moments and largest quadrupole moment contributions of the dicyano naphthalene derivatives.

1-Dicyano	Anion Rel. E. (eV)	Radical Rel. E. (eV)	Dipole (D)	Quad(D-Å)
0	0.296	0.198	8.22	7.40
1	0.267	0.135	7.24	8.04
2	0.591	0.154	8.62	7.68
3	0.660	0.123	7.73	7.96
4	0.602	0.119	6.96	11.79
5	0.486	0.131	7.20	10.63
6	0.046	0.146	6.40	10.83
7	0.000	0.085	5.62	9.39
8	0.461	0.061	6.21	9.80
9	0.493	0.024	5.12	12.19
10	0.492	0.031	4.66	8.63
11	0.329	0.040	5.37	9.37
13	0.107	0.095	2.17	18.61
14	0.482	0.053	1.77	21.83
15	0.588	0.023	0.73	19.82
18	0.607	0.319	8.95	8.32
19	0.630	0.303	8.10	12.83
23	0.509	0.280	7.69	15.57
24	0.202	0.057	7.65	6.05
25	0.281	0.027	6.69	5.95
26	0.192	0.016	6.79	5.08
27	0.219	0.096	8.21	4.90
28	0.310	0.075	7.85	5.44
29	0.246	0.026	6.88	5.08
30	0.155	0.038	4.12	26.22
31	0.275	0.015	3.37	23.38
32	0.148	0.000	4.02	24.18
33	0.335	0.032	4.88	24.19
34	0.312	0.059	5.28	23.71
35	0.083	0.054	4.33	25.94
36	0.233	0.040	0.80	24.18
38	0.301	0.023	0.86	29.02
40	0.364	0.013	0.98	26.58
2-Dicyano				
7	0.107	0.160	8.84	7.34
8	0.370	0.116	8.61	7.90
9	0.468	0.103	7.68	11.31
25	0.156	0.044	4.15	29.30
26	0.155	0.000	3.41	27.18
27	0.000	0.048	5.08	27.82
32	0.137	0.000	0.93	25.31
34	0.176	0.046	0.94	26.68
35	0.016	0.043	0.76	27.97

Table 4. EOM-CCSD/apvdz+8s6p3d electronically excited states and electron binding energies (all in eV) of the dicyanonaphthalene derivatives.

1-Dicyano	1 ¹ A''	Excited States			eBE
		2 ¹ A''	2 ¹ A'	3 ¹ A'	
0	3.011	3.013	2.967	3.010	3.011
1	3.014	3.016	2.996	3.013	3.013
2	2.677	2.680	2.648	2.676	2.677
3	2.329	2.595	2.511	2.592	2.594
4	2.669	2.671	2.638	2.667	2.668
5	2.755	2.757	2.727	2.754	2.754
6	3.258	3.260	3.233	3.257	3.257
7	3.284	3.287	3.272	3.284	3.284
8	2.694	2.696	2.664	2.693	2.693
9	2.707	2.709	2.642	2.705	2.705
10	2.666	2.668	2.619	2.665	2.665
11	2.857	2.859	2.800	2.856	2.856
13	3.130	3.132	3.129	3.129	3.130
14	2.686	2.688	2.673	2.686	2.680
15	2.578	2.580	2.574	2.578	2.580
18	2.867	2.869	2.824	2.866	2.866
19	2.765	2.767	2.670	2.762	2.764
23	2.866	2.957	2.877	2.954	2.957
24	2.585	3.012	2.923	3.010	3.011
25	2.322	2.874	2.809	2.872	2.873
26	2.987	2.989	2.920	2.985	2.986
27	3.011	3.013	2.982	3.010	3.010
28	2.894	2.896	2.866	2.893	2.893
29	2.874	2.876	2.853	2.873	2.873
30	3.065	3.067	3.010	3.064	3.064
31	2.846	2.848	2.809	2.845	2.845
32	3.045	3.048	2.976	3.045	3.044
33	2.772	2.774	2.743	2.771	2.770
34	2.888	2.890	2.875	2.887	2.887
35	3.126	3.128	3.101	3.101	3.124
36	2.966	2.968	2.965	2.966	2.968
38	2.871	2.873	2.870	2.871	2.873
40	2.758	2.760	2.758	2.759	2.760
2-Dicyano					
7	3.138	3.140	3.109	3.109	3.137
8	2.837	2.839	2.780	2.835	2.837
9	2.742	2.744	2.643	2.737	2.741
25	3.011	3.013	2.984	3.010	3.010
26	2.896	2.898	2.881	2.895	2.895
27	3.176	3.178	3.152	3.152	3.175
32	2.937	2.939	2.935	2.937	2.938
34	2.968	2.970	2.951	2.968	2.968
35	3.134	3.136	3.132	3.132	3.135

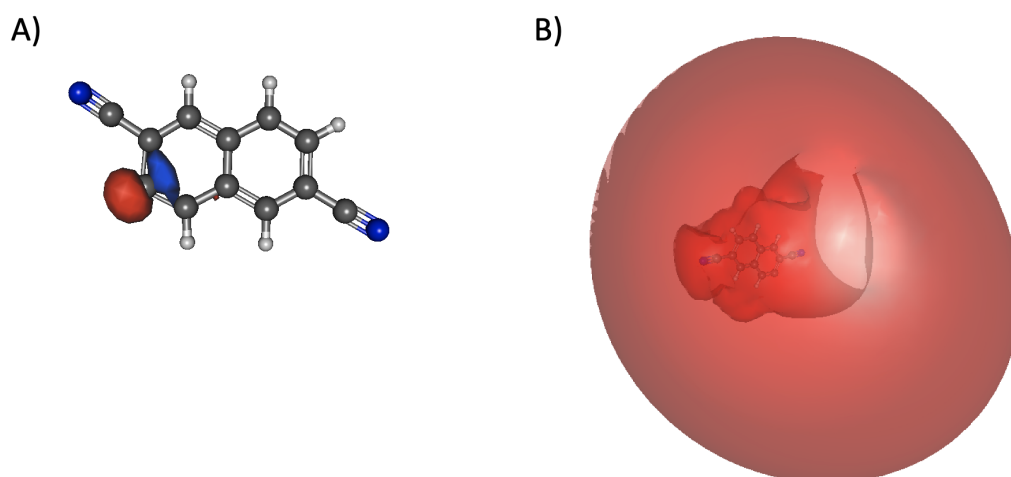


Figure 4. The orbitals for the quadrupole-bound candidate state of 2-dicyanonaphthalene-34: (A) a' HOMO & (B) a' quadrupole-bound orbital.

3.3. Cyanoethynylnaphthalene and Diethynylnaphthalene

The presence of the cyano group along with the ethynyl group is enough to stimulate dipole moments of more than 2.0 D in all of the deprotonated cyanoethynylnaphthalene isomers examined. Those where the hydrogen is removed from the ethynyl group have the largest dipole moments for this subset of molecules examined: 10.70 D and 11.14 D (Table S1). Since all of the dipole moments are large, none of the potential excited states can be claimed from the present methodology to be DBS or QBS. In contrast, the diethynyl functionalization puts the dipole moment values over a larger range from 0.12 D in 1-dethynylnaphthalene-27 all the way to the largest dipole moment computed of 15.67 D in 2-diethynylnaphthalene-32 (Table S3). The largest contributor to the quadrupole moment of the entire class of molecules examined herein is 1-dethynylnaphthalene-15 at 54.94 D-Å, but the dipole moment is a whopping 14.82 D, as well. While distinction between DBS and QBS may not be possible for this molecule specifically, such large dipole moments present the opportunity for excitations into exceptionally rare second DBSs [22]. The structures, relative energies, dipole moments, and largest contributors to the quadrupole moments for these two difunctionalized classes of deprotonated PAH derivatives are given in the supplementary material.

With regards to the electronically excited states of the cyanoethynylnaphthalene and diethynylnaphthalene anion derivatives, the results are less dramatic than the sizes of the dipole and quadrupole moments would imply. The large dipole moments stabilize the DBSs notably, such that many states are bound by more than 0.03 eV. Additionally, the shift in the structures has given rise to some anion derivatives with multiple VBSs. Most notably, 1-cyanoethynylnaphthalene-29 and -36 exhibit 1 $^1A''$ VBSs at 1.820 eV & 1.830 eV from $n \rightarrow \pi^*$ excitations, 2 $^1A'$ VBSs at 2.692 eV & 2.715 eV from $\pi \rightarrow \pi^*$ excitations, and 2 $^1A''$ DBSs at 3.389 eV & 3.418 eV from $\pi \rightarrow s$ excitations, all below their 3.480 eV & 3.487 eV eBEs, respectively. The oscillator strengths for excitation into the VBSs are also on the order of 10^{-3} or larger. However, most mixed cyanoethynylnaphthalene anion derivatives do not exhibit VBSs at all. Those diethynylnaphthalene anion derivatives whose corresponding neutral radicals have large dipole moments exhibit DBSs. However, no clear VBSs and DBSs are computed in this study. Now that the dipole and quadrupole moments are known, deeper analysis can be done to explore the photophysics of those structures with notable values.

4. Conclusions

Cyano-functionalization is the best means of inducing bound electronic excitations in PAH and PAH-like anion derivatives. Unsurprisingly, the number of excited states in an anion also increases with more functionalization, especially for cyano functionalization. Including two cyano groups extends this significantly. Ethynyl functionalization is not as consistent in producing excited states of anions, even with two such groups present. The mixed cyanoethynyl-functionalized PAH anion derivatives behave much like the dicyano anions, but this appears to be driven mostly by the cyano group.

More specifically, this work shows a likely excited QBS for 2-dicyanonaphthalene-34 since its excited state is bound and the corresponding neutral radical has a sub-2.0 D dipole moment with a greater than 25 D-Å largest contributor to the quadrupole moment. Additionally, several valence excited states are computed herein, and 1-cyanoethynylnaphthalene-29 and -36, as well as p-CNC2H-3, o-CNC2H-4, m-CNC2H-9, o-C2HC2H-3, and m-C2HC2H-6, all exhibit two excited VBSs and one DBS potentially making them the smallest PAH anions with the most excited states. The benzene class actually has some VBS transition energies in between that of the excited DBS and the eBE.

Furthermore, all of the excited states computed in this work lie between 1.820 eV and 3.817 eV corresponding to 325 nm to 681 nm. These also fit within the range of the DIBs making these difunctionalized, deprotonated PAH anion derivatives possible carriers for these features. Additionally, the absorption wavelength increases with the number of rings in the PAH structure. While the number of isomers for difunctionalized anthracene is nearly prohibitive to examine with the current methodology coupled with the length of time for the EOM-CCSD computations, the excitation energies for such a class can be assumed to be even longer than those computed here. This is also supported by previous work [64,65]. Hence, deprotonated, PAH anion derivatives can produce excited states in the range of most DIBs, and functionalization (and even difunctionalization) increases the types of molecules and excited states that could continue to contribute to the DIBs.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/chemistry4010004/s1>. The oscillator strengths for each of the EOM-CCSD/apVDZ+6s6p2d dipole-bound and EOM-CCSD/apVDZ valence excited states are available in the supplementary material. Furthermore, the relative energies, electrostatics, structures, and excitation energies of the cyanoethynyl and diethynylnaphthalene structures are also given in the supplementary material.

Author Contributions: Conceptualization, M.E.S., T.J.S. and R.C.F.; methodology, M.E.S., T.J.S. and R.C.F.; software, T.J.S.; validation, M.E.S. and T.J.S.; formal analysis, M.E.S., T.J.S. and R.C.F.; investigation, M.E.S., T.J.S. and R.C.F.; resources, R.C.F.; data curation, M.E.S. and T.J.S.; writing—original draft preparation, M.E.S., T.J.S. and R.C.F.; writing—review and editing, M.E.S., T.J.S. and R.C.F.; visualization, M.E.S., T.J.S. and R.C.F.; supervision, R.C.F.; project administration, R.C.F.; funding acquisition, R.C.F. All authors have read and agreed to the published version of the manuscript.

Funding: MES is supported by NSF REU grant CHE-1757888. TJS is supported by a Graduate Student Fellowship from the Mississippi Space Grant Consortium. RCF is supported by NASA grant NNX17AH15G, NSF grant OIA-1757220, and start-up funds provided by the College of Liberal Arts at the University of Mississippi. The Mississippi Center for Supercomputing Research, used during this research, is supported, in part, from NSF grant OIA-1757220.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available in article or supplementary material.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

ISM	Interstellar Medium
eBE	Electron Binding Energy
VBS	Valence-Bound State
DBS	Dipole-Bound State
QBS	Quadrupole-Bound State
DIBs	Diffuse Interstellar Bands

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