

Remarkable electron accepting properties of the simplest benzenoid cyanocarbons: hexacyanobenzene, octacyanonaphthalene and decacyanoanthracene

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The optimised structures, electron affinities, and vibrational frequencies of the simplest benzenoid cyanocarbons, namely hexacyanobenzene $C_6(CN)_6$, octacyanonaphthalene $C_{10}(CN)_8$, and decacyanoanthracene $C_{14}(CN)_{10}$, have been studied using carefully calibrated density functional methods (*Chem. Rev.*, 2002, 102, 231–282); the predicted adiabatic electron affinities are 3.53 eV for $C_6(CN)_6$, 4.35 eV for $C_{10}(CN)_8$ and 5.02 eV for $C_{14}(CN)_{10}$, which are significantly larger than those of the analogous benzenoid fluorocarbons as well as tetracyanoethane and tetracyanoquinodimethane.

The electron affinities (EAs) of polycyclic aromatic hydrocarbons (PAHs) are known to increase as the number of aromatic rings is increased. Thus benzene has a negative EA, naphthalene has an EA near zero, and anthracene exhibits a positive EA.¹ Theoretical studies^{2,3} have shown that halogen substitution in these three benzenoids increases the EA enough for polyhalogenated benzenes and naphthalenes to exhibit definitively positive EAs. The resulting effective electron acceptor properties of these polyhalogenated derivatives have generated much recent attention.^{4–10}

Cyanocarbons are related to the parent hydrocarbons by replacement of all or most of the hydrogen atoms with cyano (nitrile) groups. An important property of olefinic cyanocarbons arising from the electron-withdrawing cyano substituents is their facile reduction to stable radical anions.^{11,12} For example, tetracyanoethylene can readily be reduced to its radical anion using reducing agents as weak as iodide and even cyanide.¹³ The paramagnetism of the stable resulting tetracyanoethylene radical anion has been used by Miller and co-workers¹⁴ to synthesize bulk ferromagnetic organic materials containing tetracyanoethylene and metallocene units. In contrast, the parent ethylene molecule will not bind an electron.

The high stability of benzenoid aromatic compounds makes benzenoid cyanocarbons of potential interest as electron acceptors in novel magnetic materials. At the present time hexacyanobenzene, $C_6(CN)_6$, is the only known benzenoid cyanocarbon.¹⁵ In order to evaluate the electron acceptor properties of the simplest benzenoid cyanocarbons, namely hexacyanobenzene $C_6(CN)_6$, octacyanonaphthalene $C_{10}(CN)_8$, and decacyanoanthracene

$C_{14}(CN)_{10}$, we have predicted their electron affinities (EAs) using density functional theory (DFT) methods. In this context, DFT has proven to be an effective means of computing EAs. Thus in 2002, Rienstra-Kiracofe *et al.*¹⁶ conducted a statistical analysis on the agreement of several DFT functionals and experimental values on a set of 91 molecules for which reliable experimental EAs were known. The B3LYP functional^{17,18} was found to give an average absolute error of only 0.14 eV and in 71% of the cases the theoretical EA lay above the experimental value. Discussions concerning the validity of DFT in describing the negative ions can be found elsewhere.^{19,20}

Total energies, equilibrium geometries, harmonic vibrational frequencies and zero-point vibrational energies (ZPVE) were determined for each molecule considered in this study. The geometries were all optimised using analytic gradients to satisfy tight convergence criteria. All quantities referred to hereafter are defined by the following formulae:

$$EA_{ad} = E_{\text{optimised neutral}} - E_{\text{optimised anion}}$$

$$EA_{\text{vert}} = E_{\text{optimised neutral}} - E_{\text{anion at optimised neutral geometry}}$$

$$VDE = E_{\text{neutral at optimised anion geometry}} - E_{\text{optimised anion}}$$

where VDE is the vertical detachment energy. The computations were carried out within the GAUSSIAN 03,²¹ NWCHEM 4.7^{22,23} and Q-CHEM 2.1²⁴ program packages. The hybrid functional B3LYP²⁵ was utilised as the exchange–correlation density functional.^{22,23} This method encapsulates the Lee, Yang, and Parr (LYP)¹⁸ correlation and Becke's¹⁷ three-parameter HF–DFT hybrid functional.

The basis set used throughout this study is identical to that mentioned earlier and allows for comparison with previous DFT studies.¹⁶ The DZP basis set comprised the standard Huzinaga–Dunning^{26,27} DZ basis, augmented with one set of five *d* polarisation functions for each C and N atom. To complete the DZP++ basis, a set of even-tempered *s* and *p* diffuse functions was added to each atom, according to the recipe of Lee and Schaefer.²⁸

The equilibrium geometry of the neutral $C_6(CN)_6$ in its $^1A_{1g}$ ground state has D_{6h} symmetry, while the anion undergoes an in-plane Jahn–Teller distortion to a 2A_u electronic ground state with D_{2h} symmetry. For the neutral species, the optimised C–C bond lengths (Fig. 1) are 1.415 Å in the ring and 1.434 Å external to the ring, with predicted C≡N bond lengths of 1.166 Å. These theoretical distances differ from the experimental crystal

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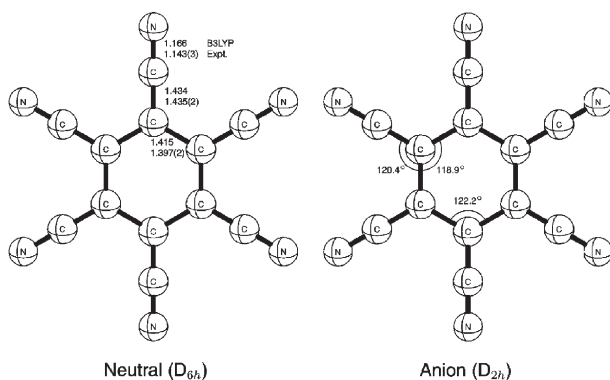


Fig. 1 Geometrical structures of percyanobenzene and its radical anion. Bond distances are in Å.

structure²⁹ by less than 0.02 Å in all three cases. For the anion, the ring C–C bond distances are 1.412 and 1.461 Å while the external C–C and C≡N bond lengths differ from those in the neutral species by less than 0.005 Å. Note that the neutral to anion progression gives rise to a bond alternation of 0.049 Å.

Neutral $C_{10}(CN)_8$ and its radical anion have the same qualitative D_{2h} geometrical conformation (Fig. 2). The naphthalene C–C bond distances exhibit perturbations no larger than 0.014 Å (see the central C–C bond) upon the addition of an electron to the neutral molecule. The slightly increased anion bond distances may be attributed to the last electron occupying an antibonding orbital, delocalized around the rings. The bond angles of the anion differ by no more than 0.5° (central exterior C–C–C angle) from those of the neutral.

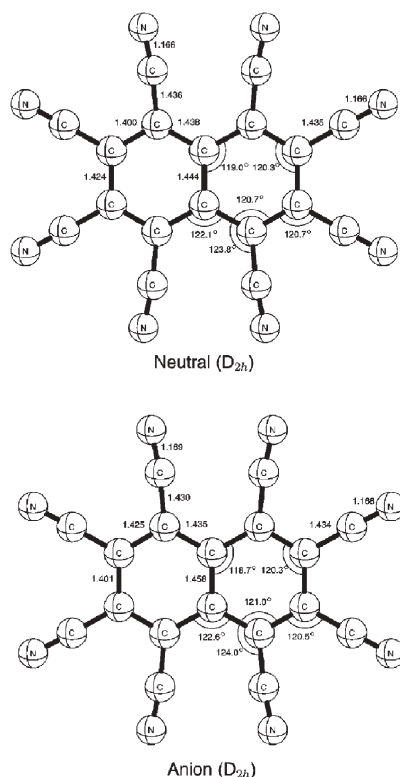


Fig. 2 Geometrical structures of percyanonaphthalene and its radical anion. Bond distances are in Å.

The $C_{14}(CN)_{10}$ species was studied in both C_{2h} and C_{2v} symmetry. The C_{2v} neutral and anion were found to be 1.40 and 1.36 kcal mol^{−1} respectively lower in energy than the C_{2h} neutral and anionic species, respectively. The orientation of the two central CN groups provides the main difference between the two systems. The C_{2v} structure (Fig. 3) incorporates these two CN groups in a *cis*-conformation, whereas in the C_{2h} structure (not shown) the two groups are necessarily oriented in a *trans*-conformation. For the neutral systems, the bond distances change by no more than 0.004 Å between the C_{2v} and C_{2h} structures, with differences of less than 0.7° (central interior C–C–C angle) observed for the bond angles. Upon addition of an electron to the C_{2v} neutral, the bond distances change by less than 0.019 Å (Fig. 3). Interestingly, the anion shows less bond alternation (0.018 Å in the outer ring) than the neutral (0.049 Å in the outer ring). From neutral to anion, the bond angles change by less than 0.5°.

Hexacyanobenzene will bind an electron with a positive EA_{ad} of 3.53 eV, which increases to 3.64 eV accounting for ZPVE. Given that the non-substituted parent systems display an increasing propensity to bind an electron with increasing ring size, the EA of $C_{10}(CN)_8$ is expected to be larger than that of $C_6(CN)_6$, while that of $C_{14}(CN)_{10}$ should be higher still. Indeed, it is observed that these trends propagate into the percyano substituted systems; the ZPVE corrected EA_{ad} of percyanonaphthalene is 4.38 eV. The EA_{ad} determined for the C_{2v} and C_{2h} structures of $C_{14}(CN)_{10}$ are 5.05 and 5.06 eV, respectively, with ZPVE included.

Compared with the analogous benzenoid fluorocarbons, the EA_{ad} of $C_6(CN)_6$ (3.53 eV) is much larger than that for C_6F_6 (0.69 eV). Similar differences in electron affinities (Table 1) also hold for the corresponding naphthalene and anthracene derivatives, indicating that benzenoid cyanocarbons have a much

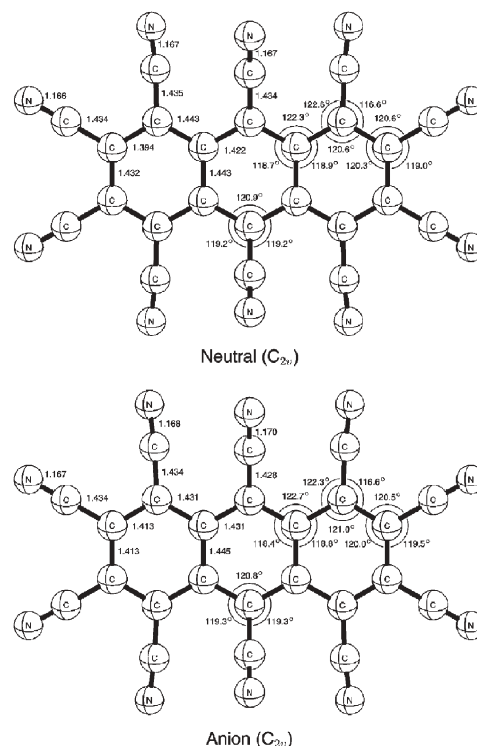


Fig. 3 Geometrical structures of percyanoanthracene (C_{2v}) and its radical anion. Bond distances are in Å.

Table 1 Predicted electron attachment/detachment energies (in eV), with zero-point vibrationally corrected values in parentheses

	C ₆ (CN) ₆	C ₁₀ (CN) ₈	C ₁₄ (CN) ₁₀ (C _{2v})
EA _{ad}	3.53 (3.64)	4.35 (4.38)	5.02 (5.05)
EA _{vert}	3.42	4.28	4.95
VDE	3.64	4.42	5.09
Analogous fluorocarbon ^a	0.69	1.02	1.84

^a These are the EA_{ad} values of the perfluoro analogues included for comparison.³

stronger tendency to bind an additional electron than the corresponding benzenoid fluorocarbons. Furthermore, the EA of C₆(CN)₆ is significantly greater than that found experimentally for tetracyanoethylene (2.3 ± 0.3 eV)³⁰ or tetracyanoquinodimethane (2.8 ± 0.3 eV),³¹ which are well known to form stable radical anion salts.^{11,12}

Our computations suggest the use of benzenoid cyanocarbons as effective electron acceptors to introduce the corresponding radical anions into novel stable magnetic materials. Thus the synthesis of the C₆(CN)₆[−] radical anion would be of great interest. Such a synthesis should be achievable by reduction of C₆(CN)₆ with a one-electron reductant such as cobaltocene in an unreactive non-polar organic solvent, which could lead to the precipitation of a stable radical anion salt such as [Cp₂Co][C₆(CN)₆]. Furthermore, the high EAs computed for C₁₀(CN)₈ and C₁₄(CN)₁₀ may relate to the fact that they have never been synthesized; successful syntheses of such strong oxidants must necessarily avoid any reagents or solvents with potential reducing properties including dimethylformamide used in several syntheses of C₆(CN)₆.

It is pertinent to compare these benzenoid cyanocarbons with buckminsterfullerene, which has extensive chemistry based on its electron affinity of 2.65 ± 0.05 eV.³² Clearly, cyanocarbons are even more interesting in this respect.

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