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Can the Radical Anion of Alkyl-2-cyanoacrylates Initiate Anionic Polymerization of These Instant Adhesive Monomers?

Nicole R. Brinkmann and Henry F. Schaefer III*

Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602-2525

Cynthia T. Sanderson and Charles Kutal

Department of Chemistry, University of Georgia, Athens, Georgia 30602-2525

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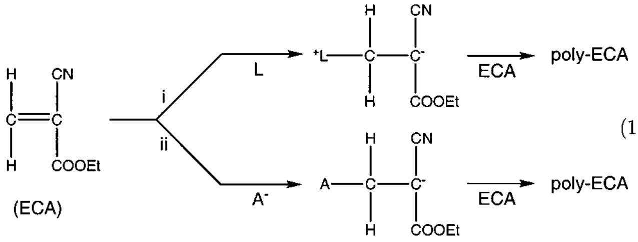
Electron affinities of methyl-2-cyanoacrylate (MCA) and ethyl-2-cyanoacrylate (ECA) were predicted using four different density functional or hybrid Hartree−Fock/density functional methods. Equilibrium structures and harmonic vibrational frequencies were computed for the neutral and anionic species of each system. Because of structural similarities to cyanoethylene and 1,1-dicyanoethylene, the results for MCA and ECA are compared to previous work at the same levels of theory on these two cyano-substituted ethylenes. Spin densities and isotropic hyperfine splitting constants (hfs) were determined for the radical anions of these four systems as a gauge of the delocalization of the unpaired electron. An experimental EA exists for 1,1-dicyanoethylene, although collisional electron transfer experiments on short-lived anions are questionable. The EAs for the four systems studied here are predicted to be 0.06 (cyanoethylene), 1.36 (1,1-dicyanoethylene), and 1.08 eV (MCA and ECA). The computed spin densities and hfs constants for these radical anions indicate that the unpaired electron is primarily localized on the C atom of the CH_2 segment of each molecule. 1,1-dicyanoethylene, MCA, and ECA each have two electron withdrawing groups, which results in appreciable resonance stabilization and a bound radical anion. The radical anions of MCA and ECA are nucleophilic and can attack the neutral monomer to initiate polymerization by a newly proposed mechanism.

I. Introduction

The adhesive properties of cyanoacrylates were discovered in an Eastman Kodak Facility in 1951.[1] While measuring the refractive index of ethyl-2-cyanoacrylate (ECA), a researcher noticed that the two prisms of the refractometer had bonded together. Within a few hours, workers had bonded a variety of available materials and knew they had an incredible new adhesive. First marketed in 1958, alkyl-2-cyanoacrylate adhesives are commonly sold today as Krazy Glue or Super Glue. Known for their quick bonding of a diverse range of substrates, these instant adhesives have been used widely in the automotive, electronics, personal care, hobby, and home repair industries.[2] Important medical applications include treating intracerebral aneurysms as an alternative to the usual surgical clipping approach,[3,4] fixing the cranial bone flap after craniotomy,[5] closing skin wounds,[6] and performing sutureless cardiac techniques.[7,8] Polycyanoacrylates have potential applications in the drug industry as colloidal drug carriers[9,10] of antibiotics, hormones, and cytostatics[11−13] and as biodegradable insulin nanocapsules.[14]

Alkyl-2-cyanoacrylates undergo polymerization by both free radical and anionic mechanisms.[2] The latter pathway has attracted the most interest owing to the ease of initiation and the rapid rates that can be achieved. This hyperreactivity of alkyl-2-cyanoacrylates toward anionic polymerization reflects the presence of the electron-withdrawing cyano and ester groups. These substituents activate the monomer to nucleophilic attack by even relatively weak Lewis bases such as amines and phosphines and by simple anions such as acetate, cyanide, and iodide.[2,15−17] Moreover, the substituents stabilize the negative charge carried by the growing polymer. As summarized in eq 1,[2,16] polymerization is initiated by Michael addition of the uncharged Lewis base (L, path i) or anion (A^-, path ii) to the carbon−carbon double bond of the monomer. The resulting zwitterion or carbanion then undergoes repeated addition of monomer units in the propagation stage. Termination of this process is difficult and is effectively accomplished only upon the addition of a strong acid.[15] Consequently, the anionic polymerization of alkyl-2-cyanoacrylates exhibits many of the features of a living polymerization process.



(1)

Light can trigger the polymerization process in systems where the active initiating species is generated in the photochemical reaction of a precursor compound, termed the photoinitiator. Photoinitiators reported to be effective for alkyl-2-cyanoacrylate polymerization include inorganic complexes such as *trans*-$Cr(NH_3)_2(NCS)_4^-$[18] and $Pt(acac)_2$ ($acac^-$ is acetylacetonate),[19] organometallic complexes such as 1,1′-dibenzoylferrocene[20] and

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* To whom correspondence should be addressed. E-mail: hfsiii@arches.uga.edu.

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TABLE 1: Optimized Parameters of Neutral $^1A_1$ 1,1-Dicyanoethylene and the $^2B_1$ 1,1-Dicyanoethylene Radical Anion[a]

parameter	species	B3LYP	B3P86	BLYP	BP86
r_1(C−H)	neutral	1.087	1.086	1.094	1.095
	anion	1.086	1.085	1.093	1.094
r_2(C_1−C_2)	neutral	1.352	1.349	1.367	1.364
	anion	1.438	1.433	1.447	1.443
r_3(C_2−C_3)	neutral	1.444	1.439	1.450	1.446
	anion	1.416	1.412	1.425	1.421
r_4(C_3−N)	neutral	1.167	1.165	1.181	1.181
	anion	1.182	1.180	1.196	1.196
θ_1(CCH)	neutral	120.6	120.5	120.6	120.6
	anion	120.2	120.2	120.2	120.2
θ_2(CCC)	neutral	121.6	121.6	121.6	121.7
	anion	121.5	121.5	121.6	121.6
θ_3(CCN)	neutral	179.5	179.5	179.7	179.7
	anion	178.0	178.1	178.0	178.0

[a] Bond lengths are in angstroms, and angles are in degrees.

TABLE 2: Optimized Parameters of Neutral $^1A'$ Cyanoethylene and the $^2A''$ Cyanoethylene Radical Anion[a]

parameter	species	B3LYP	B3P86	BLYP	BP86	expt[b]
r_1(C_1−H_1)	neutral	1.088	1.087	1.095	1.096	
	anion	1.088	1.088	1.095	1.097	
r_2(C_1−C_2)	neutral	1.345	1.342	1.358	1.356	1.3389(50)
	anion	1.427	1.423	1.436	1.433	
r_3(C_2−C_3)	neutral	1.438	1.433	1.442	1.438	1.4256(30)
	anion	1.399	1.394	1.407	1.404	
r_4(C_3−N)	neutral	1.168	1.167	1.183	1.182	1.1637(30)
	anion	1.194	1.193	1.209	1.208	
r_5(C_1−H_2)	neutral	1.088	1.087	1.096	1.096	1.0863(50)
	anion	1.089	1.088	1.096	1.097	
r_6(C_2−H_3)	neutral	1.090	1.089	1.098	1.099	1.0863(50)
	anion	1.093	1.092	1.101	1.102	
θ_1(CCH_1)	neutral	121.6	121.5	121.6	121.5	
	anion	121.5	121.5	121.6	121.5	
θ_2(CCC)	neutral	122.7	122.5	123.1	122.9	122.6
	anion	125.5	125.5	125.9	126.0	
θ_3(CCN)	neutral	178.7	178.8	178.5	178.5	
	anion	179.8	179.7	179.8	179.7	
θ_4(CCH_2)	neutral	120.4	120.4	120.4	120.4	
	anion	120.4	120.4	120.3	120.3	
θ_5(CCH_3)	neutral	121.5	121.6	121.2	121.3	121.7(5)
	anion	119.2	119.2	118.8	118.9	

[a] Bond lengths are in angstroms, and angles are in degrees. [b] Experimental values obtained by Costain and Stoicheff. See ref 43.

TABLE 3: Optimized Parameters of Neutral ^1A Methyl-2-cyanoacrylate and the ^2A Methyl-2-cyanoacrylate Radical Anion[a]

parameter	species	B3LYP	B3P86	BLYP	BP86
r_1(C_1−H_1)	neutral	1.087	1.087	1.094	1.096
	anion	1.087	1.086	1.094	1.095
r_2(C_1−C_2)	neutral	1.349	1.346	1.363	1.360
	anion	1.431	1.426	1.439	1.435
r_3(C_2−C_3)	neutral	1.442	1.437	1.448	1.443
	anion	1.425	1.419	1.432	1.427
r_4(C_3−N)	neutral	1.167	1.165	1.181	1.181
	anion	1.178	1.177	1.192	1.192
r_5(C_1−H_2)	neutral	1.086	1.086	1.093	1.095
	anion	1.085	1.084	1.092	1.093
r_6(C_2−C_4)	neutral	1.507	1.500	1.519	1.513
	anion	1.438	1.433	1.452	1.449
r_7(C_4=O_1)	neutral	1.214	1.211	1.228	1.226
	anion	1.244	1.240	1.257	1.254
r_8(C_4−O_2)	neutral	1.348	1.341	1.368	1.362
	anion	1.405	1.396	1.432	1.422
r_9(C_5−O_2)	neutral	1.444	1.434	1.464	1.453
	anion	1.419	1.410	1.436	1.428
r_{10}(C_5−H_3)	neutral	1.092	1.091	1.100	1.101
	anion	1.098	1.097	1.106	1.106
r_{11}(C_2−H_5)	neutral	1.095	1.094	1.103	1.104
	anion	1.100	1.099	1.108	1.109
r_{12}(C_5−C_6)	neutral	1.095	1.094	1.103	1.104
	anion	1.100	1.099	1.108	1.109
θ_1($C_2C_1H_1$)	neutral	121.0	121.0	121.0	120.9
	anion	120.2	120.2	120.2	120.2
θ_2($C_3C_2C_1$)	neutral	120.7	120.8	120.6	120.7
	anion	118.8	118.9	118.8	119.0
θ_3(C_2C_3N)	neutral	178.3	178.3	178.4	178.4
	anion	176.6	176.6	176.5	176.5
θ_4($C_2C_1H_2$)	neutral	120.2	120.0	120.3	120.1
	anion	120.4	120.2	120.4	120.2
θ_5($C_4C_2C_1$)	neutral	123.5	123.4	123.7	123.7
	anion	125.0	124.9	125.1	125.0
θ_6($O_2C_4C_2$)	neutral	111.9	111.8	111.6	111.5
	anion	111.9	111.8	111.5	111.4
θ_7($O_1C_4C_2$)	neutral	123.5	123.6	123.7	123.8
	anion	128.5	128.6	128.7	128.8
θ_8($C_4O_2C_5$)	neutral	115.3	114.8	114.9	114.4
	anion	114.5	114.0	114.0	113.4
θ_9($H_2C_5O_3$)	neutral	105.4	105.6	105.1	105.2
	anion	106.0	106.2	105.8	105.9
θ_{10}($O_2C_5H_4$)	neutral	110.3	110.4	110.2	110.3
	anion	111.8	111.8	111.8	111.9
θ_{11}($C_6C_5H_4$)	neutral	109.2	109.1	109.4	109.2
	anion	107.6	107.5	107.6	107.4
θ_{12}($C_6C_5H_3$)	neutral	110.8	110.7	111.0	110.9
	anion	109.8	109.8	109.9	109.9

[a] Bond lengths are in angstroms, and angles are in degrees.

$M(CO)_5L$ (M is Cr or W and L is pyridine or vinyl-substituted pyridine),[21] pyridinium[22] and phosphonium[23] salts, and leuco dyes.[24] Irradiation of these photoinitiators releases an uncharged Lewis base or an anion, which then proceeds to initiate polymerization according to the mechanism described earlier (eq 1). Recently, we obtained evidence that a new type of initiating species results from irradiating a solution of ECA containing the classic metallocene, ferrocene ($FeCp_2$, where Cp is η^5-C_5H_5).[25] The two components form a ground state donor−acceptor complex that exhibits a characteristic $FeCp_2 \rightarrow$ ECA, charge-transfer to solvent (CTTS), absorption band in the near-ultraviolet region. Irradiation into this band produces a species that initiates the anionic polymerization of ECA. Because CTTS excitation should produce the ferricenium cation and the ECA radical anion (eq 2), we propose that the latter species is responsible for initiating the polymerization process. Direct observation of $FeCp_2^+$ by electronic spectroscopy supports this proposal, but experimental evidence for the existence of the radical anion is presently lacking. Given the paucity of information about the properties of alkyl-2-cyanoacrylate radical anions, we undertook a quantum chemical investigation aimed at elucidating the important features of their structure and reactivity. Our results, in turn, can be used to judge the viability of these species as initiators for anionic polymerization.

$$\mathrm{FeCp_2} + \mathrm{ECA} \rightleftharpoons \underset{\text{complex}}{[\mathrm{FeCp_2,ECA}]} \xrightarrow{h\nu} \mathrm{FeCp_2}^+ + \mathrm{ECA}^{\bullet -} \quad (2)$$

Recent studies[26−29] have shown that density functional theory (DFT) generally can predict the electron affinity (EA) of a molecule to within 0.2 eV of the experimentally reported value. In particular, the EAs for cyanoethylene and 1,1-dicyanoethylene were predicted to be about 0.06 and 1.36 eV, respectively, using the B3LYP functional with a DZP++ basis.[30] In the present study, we compute the EAs of the two commonly used instant adhesives, methyl-2-cyanoacrylate (MCA) and ethyl-2-cyanoacrylate, as well as the energies and structures of the neutral molecules and their radical anions. Comparisons are made to the DFT results for the structurally similar cyanoethylene and 1,1-dicyanoethylene systems. The hyperfine splitting constants

TABLE 4: Optimized Parameters of Neutral ^{1}A Ethyl-2-cyanoacrylate and the ^{2}A Ethyl-2-cyanoacrylate Radical Anion[a]

parameter	species	B3LYP	B3P86	BLYP	BP86
$r_1(C_1-H_1)$	neutral	1.087	1.086	1.094	1.095
	anion	1.087	1.087	1.094	1.096
$r_2(C_1-C_2)$	neutral	1.349	1.345	1.363	1.360
	anion	1.430	1.426	1.438	1.434
$r_3(C_2-C_3)$	neutral	1.442	1.437	1.448	1.443
	anion	1.425	1.419	1.432	1.428
$r_4(C_3-N)$	neutral	1.167	1.165	1.181	1.181
	anion	1.178	1.176	1.192	1.192
$r_5(C_1-H_2)$	neutral	1.086	1.086	1.093	1.095
	anion	1.085	1.084	1.092	1.093
$r_6(C_2-C_4)$	neutral	1.508	1.501	1.520	1.514
	anion	1.437	1.432	1.452	1.448
$r_7(C_4{=}O_1)$	neutral	1.215	1.212	1.229	1.227
	anion	1.244	1.241	i.257	1.254
$r_8(C_4-O_2)$	neutral	1.346	1.340	1.366	1.360
	anion	1.406	1.397	1.434	1.424
$r_9(C_5-O_2)$	neutral	1.456	1.446	1.477	1.467
	anion	1.424	1.416	1.441	1.433
$r_{10}(C_5-H_3)$	neutral	1.095	1.094	1.102	1.103
	anion	1.100	1.010	1.108	1.109
$r_{11}(C_2-H_5)$	neutral	1.095	1.095	1.102	1.104
	anion	1.098	1.098	1.106	1.108
$r_{12}(C_5-C_6)$	neutral	1.524	1.516	1.535	1.528
	anion	1.532	1.524	1.544	1.537
$r_{13}(C_6-H_5)$	neutral	1.097	1.095	1.104	1.104
	anion	1.098	1.097	1.106	1.106
$r_{14}(C_6-H_6)$	neutral	1.095	1.094	1.102	1.103
	anion	1.096	1.095	1.103	1.104
$r_{15}(C_6-H_7)$	neutral	1.098	1.096	1.105	1.106
	anion	1.101	1.099	1.109	1.109
$\theta_1(C_2C_1H_1)$	neutral	121.0	121.0	121.0	121.0
	anion	120.2	120.2	120.2	120.2
$\theta_2(C_3C_2C_1)$	neutral	120.6	120.7	120.6	120.7
	anion	118.7	118.9	118.7	118.9
$\theta_3(C_2C_3N)$	neutral	178.3	178.3	178.4	178.4
	anion	176.6	176.6	176.5	176.5
$\theta_4(C_2C_1H_2)$	neutral	120.2	120.0	120.3	120.1
	anion	120.4	120.2	120.4	120.2
$\theta_5(C_4C_2C_1)$	neutral	123.6	123.5	123.8	123.7
	anion	125.1	125.0	125.2	125.1
$\theta_6(O_2C_4C_2)$	neutral	111.7	111.7	111.5	111.4
	anion	111.7	111.7	111.3	111.2
$\theta_7(O_1C_4C_2)$	neutral	123.1	123.1	123.8	123.3
	anion	128.3	128.3	128.4	128.4
$\theta_8(C_4O_2C_5)$	neutral	116.7	116.1	116.3	115.7
	anion	115.7	115.2	115.3	114.7
$\theta_9(H_2C_5O_3)$	neutral	104.0	104.2	103.6	103.8
	anion	105.4	105.5	105.3	105.4
$\theta_{10}(O_2C_5H_4)$	neutral	108.7	108.6	108.6	108.5
	anion	110.0	109.8	109.9	109.7
$\theta_{11}(C_6C_5H_4)$	neutral	111.3	111.3	111.4	111.4
	anion	109.7	109.6	109.6	109.6
$\theta_{12}(C_6C_5H_3)$	neutral	111.5	111.6	111.6	111.7
	anion	110.2	110.4	110.2	110.4
$\theta_{13}(C_5C_6H_5)$	neutral	111.0	110.9	111.0	111.1
	anion	110.6	110.6	110.7	110.7
$\theta_{14}(C_5C_6H_6)$	neutral	111.0	110.9	111.0	111.0
	anion	109.9	109.7	110.1	109.8
$\theta_{15}(H_6C_6H_7)$	neutral	108.2	108.2	108.2	108.1
	anion	108.6	108.7	108.6	108.6
$\theta_{16}(H_5C_6H_7)$	neutral	108.3	108.3	108.3	108.2
	anion	108.5	108.6	108.5	108.5

[a] Bond lengths are in angstroms, and angles are in degrees.

(hfs) also are computed to investigate the delocalization of the unpaired electron in the radical anions.

II. Theoretical Methods

The DFT quantum chemical computations were performed on cyanoethylene, 1,1-dicyanoethylene, methyl-2-cyanoacrylate, and ethyl-2-cyanoacrylate using the Gaussian 94 program package.[31] Four gradient-corrected functionals, denoted B3LYP, B3P86, BLYP, and BP86, were used to compute the geometries, energies, spin densities, and harmonic vibrational frequencies. Energies were converged to at least 10^{-6} hartrees in the self-consistent field procedures, although the absolute accuracy may be somewhat lower because of numerical integration procedures.

The different functionals used may be described as follows: (1) B3LYP is a hybrid Hartree−Fock and density functional theory (HF/DFT) method using Becke's three-parameter exchange functional (B3)[32] with the Lee, Yang, and Parr correlation functional (LYP).[33] (2) The B3P86 functional uses the B3 exchange functional with the 1986 correlation correction of Perdew (P86)[34] and is a HF/DFT method. (3) BLYP uses Becke's 1988 exchange functional (B)[35] and the LYP correlation functional. (4) The BP86 functional is formed from the Becke exchange functional (B) and the P86 correlation correction.

We employed a double-ζ basis set with polarization and diffuse functions, denoted DZP++. This basis was constructed from the Huzinaga−Dunning[36,37] set of contracted double-ζ Gaussian functions. Added to this was one set of p-type polarization functions for each H atom and one set of five d-type polarization functions for each C, N, and O atom [$\alpha_p(H) = 0.75$, $\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.80$, and $\alpha_d(O) = 0.85$]. To complete the DZP++ basis, the entire set of functions was augmented with one set of "even tempered"[38] s diffuse functions for each H atom and one set of "even tempered" s and p diffuse functions for each C and N atom with orbital exponents determined by the formula expressed by Lee and Schaefer[29,38] [$\alpha_s(H) = 0.04415$, $\alpha_s(C) = 0.04302$, $\alpha_p(C) = 0.03629$, $\alpha_s(N) = 0.06029$, $\alpha_p(N) = 0.05148$, $\alpha_s(O) = 0.03227$, and $\alpha_p(O) = 0.06508$]. The final contraction scheme for this basis is H(5s1p/3s1p) and C,N,O(10s6p1d/5s3p1d).

Geometries were optimized for each molecular species with each functional using analytic gradient techniques. Residual Cartesian gradients were less than 1.5×10^{-5} hartree/Bohr. Stationary points found in optimizations were confirmed as minima by computing the harmonic vibrational frequencies using analytic second derivatives with each functional.

Electron affinities were evaluated as differences in total energies between the neutral and radical anion. Classical adiabatic electron affinities were determined by

$$\mathrm{EA_{ad}} = E_{\text{(optimized neutral)}} - E_{\text{(optimized anion)}}$$

and zero-point corrected adiabatic electron affinities were determined by

$$\mathrm{EA_{zero}} = E_{\text{(zero-point corrected neutral)}} - E_{\text{(zero-point corrected anion)}}$$

Electron spin densities and hyperfine splitting constants provide a measure of the delocalization of an unpaired electron on a molecule, and thus, these quantities were computed for the radical anions investigated here. The electron spin density at a nucleus in a molecule is the unpaired-electron probability density at that nucleus.[39] For example, at a particular nucleus, $S = 1/2$ is the probability of finding one unpaired electron/cm^3 at that center. More rigorously, it is the difference between the total probability densities of all electrons with spin α and spin β at a specific nucleus.[40] However, if spin polarization effects are ignored, the α and β spins in closed shells cancel, and only the spin density of the unpaired electrons contribute.

The hyperfine structure is the splitting of the peaks in an electron spin resonance (ESR) spectrum which results from the magnetic interaction of an unpaired electron with a nucleus of

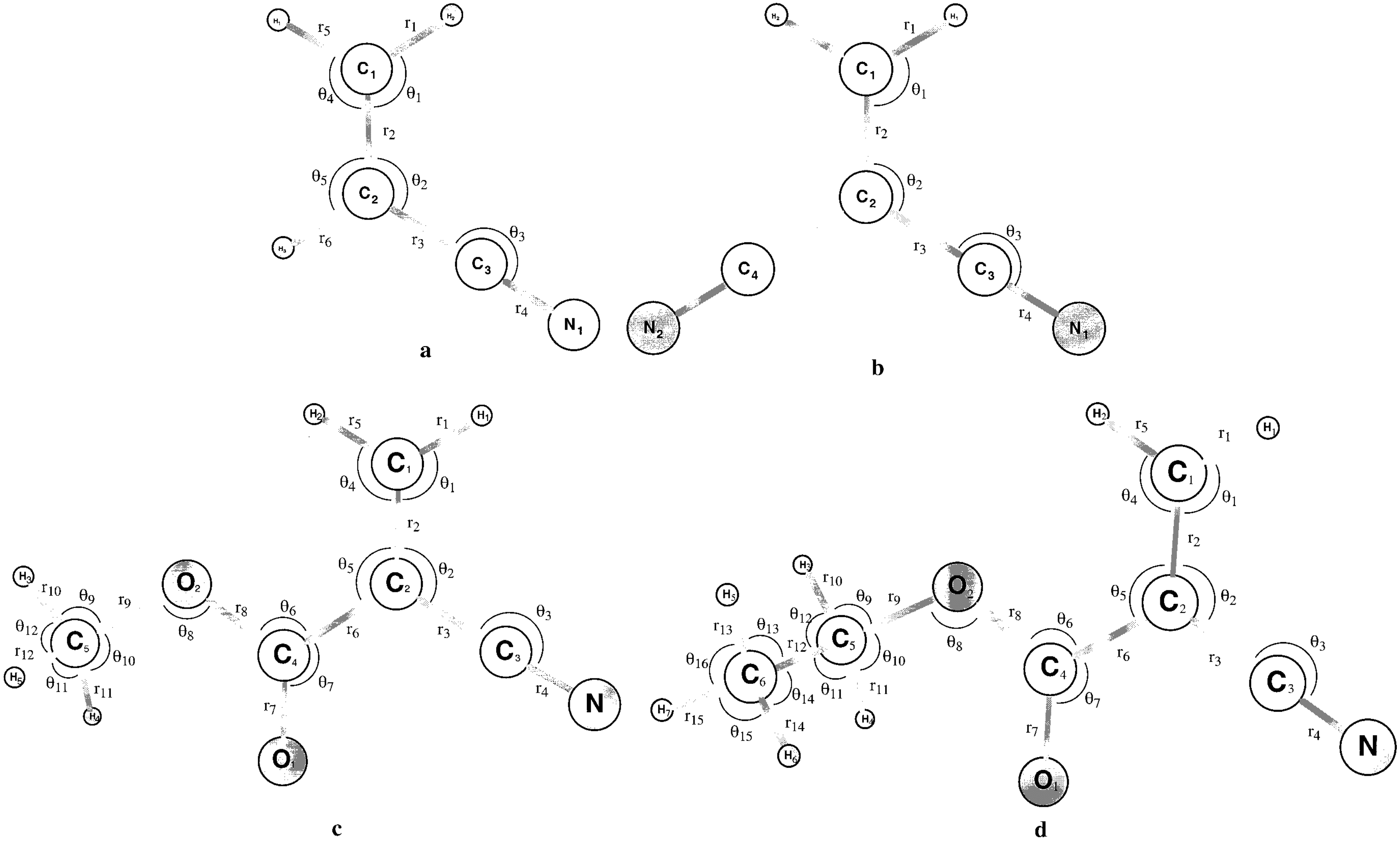


Figure 1. Structures of neutral (a) cyanoethylene, (b) 1,1-dicyanoethylene, (c) methyl-2-cyanoacrylate, and (d) ethyl-2-cyanoacrylate.

magnetic moment μ_I and nuclear spin I.[39] The isotropic hfs terms for the ^1H, ^{13}C, ^{14}N, and ^{17}O nuclei were evaluated in megahertz according to

$$A_{\mathrm{iso}} = \frac{8\pi}{3h} g_e \beta_e g_I \beta_N |\Psi_0|^2 \tag{3}$$

where h is Plank's constant, g_e is the electronic g factor, β_e is the Bohr magneton, g_I is the nuclear g factor, β_N is the nuclear magneton, and $|\Psi_0|^2$ is the unpaired electron spin density at each nucleus. Spin densities used to determine hfs constants were computed with each functional.

III. Results and Discussion

The equilibrium geometrical parameters for the neutral and anionic species of each system are given in Tables 1−4 and correspond to the definitions pictured in Figure 1. Harmonic vibrational frequencies for each structure were determined, and all frequencies are real, indicating that these structures are true minima. The experimentally reported geometrical parameters of cyanoethylene are included in Table 1, and the structures predicted by the DFT methods agree reasonably well, although direct comparisons should not be made between the vibrationally averaged structures from experiment and the equilibrium structures from theory. The spin densities of the atoms in each system were computed, and the Fermi contact terms were evaluated using these spin densities. Tables of spin densities and anisotropic hfs constants are included as Supporting Information.

With the addition of an electron to each system, there are no significant changes observed in the terminal CH_2 fragment of the molecule. However, $r_2(C_1{-}C_2)$ is longer in each radical anion by about 0.08 Å and $r_4(C_3{-}N)$ is longer by ~0.02 Å in cyanoethylene and 1,1-dicyanoethylene and about 0.01 Å longer in MCA and ECA. The distance $r_3(C_2{-}C_3)$ is shorter in the radical anions by 0.04 (cyanoethylene), 0.026 (1,1-dicyanoethylene), and 0.017 Å (MCA and (ECA). In the cyanoethylene radical anion, θ_2(CCC) is wider by almost 3° and $\theta_5(CCH_3)$ is narrower by ~2.4°. Opposite and less significant trends were observed in MCA and ECA as $\theta_2(C_3C_2C_1)$ is narrower in the radical anion by about 2° and $\theta_5(C_4C_2C_1)$ is wider by 1.5°.

In both MCA and ECA, changes in the geometrical parameters of the ester substituent are also observed upon addition of an electron. $r_6(C_2{-}C_4)$ and $r_9(C_5{-}O_2)$ are shorter in the radical anion by 0.067 (MCA) and 0.069 (ECA) and 0.026 Å (MCA) and 0.033 Å (ECA), respectively, whereas $r_7(C_4{=}O_1)$ and $r_8(C_4{-}O_2)$ are longer by 0.03 Å (MCA and ECA) and 0.06 Å (MCA and ECA). $\theta_7(O_1C_4C_2)$ is wider in both MCA and ECA by ~5°, whereas $\theta_8(C_4O_2C_5)$ exhibits minimal changes, being narrower in the radical anion by less than 1° in both systems. The methyl and ethyl segments of the ester substituent experienced only minor changes (less than 0.006 Å or 2°), if any, between the neutral and radical anion.

The computed changes in the geometrical parameters are consistent with the presence in each neutral molecule of a $C{=}C{-}(C{\equiv}N)_n$ π-conjugated system, which, upon adding an electron to a π^* orbital, undergoes partial weakening of the double and triple bonds. Reasonable Lewis structures for the resulting radical anions are shown in Figure 2. The structure containing the carbanion site, in which the negative charge is localized on C_2, should be an excellent nucleophilic attacking species for the proposed mechanism. Other resonance structures, in which the charge is delocalized onto an electronegative N or O atom of an adjacent cyano or ester group, stabilize the radical anion.

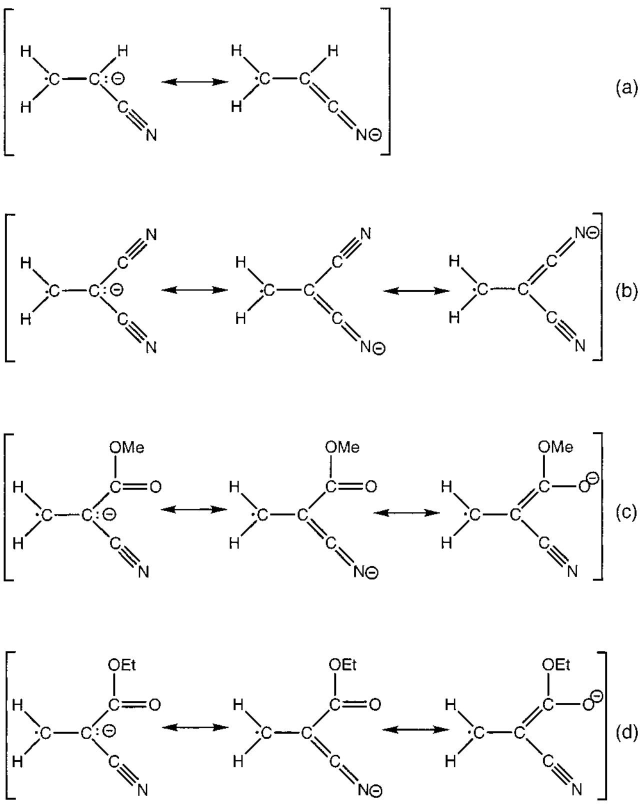


Figure 2. Proposed Lewis structures for the radical anions of (a) cyanoethylene, (b) 1,1-dicyanoethylene, (c) methyl-2-cyanoacrylate, and (d) ethyl-2-cyanoacrylate.

These proposed structures are also consistent with the computed spin densities of these systems, which indicate that the unpaired electron in each radical anion is primarily localized on C_1. Further support for these structures is provided by the computed Fermi contact terms. The positive A_{iso} values predicted for C_1 by each functional indicate that the singly occupied molecular orbital (SOMO) at this atomic center has sigma character, whereas that of C_3 in the radical anions is negative, which implies that the SOMO at this center has pi character. Both of these propositions are reflected in the resonance structures where C_1 participates only in sigma bonding, while C_3 exhibits pi bonding.

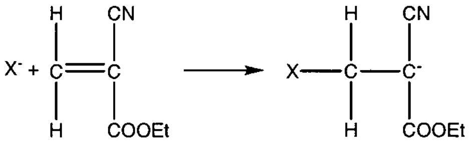
The EAs of the four systems may be found in Table 5. Zero-point vibrational corrections to the EAs are given in parentheses, and they tend to increase the predicted values, as the ZPVE of the neutral tends to be slightly greater than that of the appropriate radical anion. The negative or small positive value of the EA calculated for cyanoethylene indicates that its radical anion is essentially unbound, and in fact, the lifetime of this anion is in the picosecond/femtosecond range,[41] less than the period of the C=C stretching vibration.[41] In contrast, the large positive EA values of 1,1-dicyanoethylene, MCA, and ECA are consistent with strongly bound radical anions, a result that reflects the added resonance stabilization provided by a second electron-withdrawing substituent (Figure 2). The stability of these radical anions makes them viable species for nucleophilic attack according to the proposed mechanism and provides evidence for this new mechanism of alkyl-2-cyanoacrylate polymerization. The B3P86 method tends to overestimate energies,[42] so using the B3LYP, BLYP, and BP86 functionals the EAs of MCA and ECA are both predicted to be on the order of 1.1 eV.

TABLE 5: Adiabatic Electron Affinities of Cyanoethylene, 1,1-dicyanoethylene, Methyl-2-cyanoacrylate, and Ethyl-2-cyanoacrylate[a]

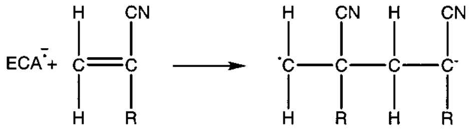
system		B3LYP	B3P86	BLYP	BP86	expt
cyanoethylene[b]	${}^1A' \leftarrow {}^2A''$	0.06	0.59	−0.02	0.17	0.01−0.02[c]
		(0.18)	(0.72)	(0.09)	(0.29)	
1,1-dicyanoethylene[d]	${}^1A_1 \leftarrow {}^2B_1$	1.36	1.92	1.23	1.45	
		(1.46)	(2.02)	(1.32)	(1.54)	
methyl-2-cyanoacrylate[e]	${}^1A \leftarrow {}^2A$	1.08	1.63	0.98	1.18	
		(1.19)	(1.74)	(1.08)	(1.28)	
ethyl-2-cyanoacrylate[f]	${}^1A \leftarrow {}^2A$	1.08	1.63	0.98	1.18	
		(1.19)	(1.74)	(1.08)	(1.28)	

[a] Zero-point corrected EAs are listed in parentheses. All energies are in eV. [b] Neutral and anion are both C_s symmetry. [c] Reference 44. [d] Neutral and anion are both C_{2v} symmetry. [e] Neutral and anion are both C_1 symmetry. [f] Neutral and anion are both C_1 symmetry.

The finding that the radical anions of MCA and ECA are both significantly bound lends support to our proposal that they are viable initiators for the anionic polymerization of the parent monomers. It is interesting to compare how initiation by these species differs from the comparable process involving a simple anion, X^-. Attack of X^- on an alkyl-2-cyanoacrylate monomer yields a single, negatively charged site that then propagates by further addition of the monomer (eq 4). In contrast, the radical anion generates two potentially reactive sites, one radical and one anionic, that become increasingly separated as polymerization proceeds (eq 5; R = COOEt). In principle, this difunctional species could initiate polymerization by both radical and anionic mechanisms, although our results show no evidence for operation of the former pathway. Alternatively, coupling of the radical sites of the two chains would yield a dianion that could undergo anionic polymerization at both ends. A study of the kinetics of polymerization and an analysis of polymer end groups are needed to test this intriguing possibility.



(4)



(5)

Conclusions

Our results for MCA and ECA test and verify the proposal that generation of the radical anions of these alkyl-2-cyanoacrylates would initiate anionic polymerization in which the radical anion acts as the attacking nucleophilic species. The computed spin densities and Fermi contact terms of cyanoethylene, 1,1-dicyanoethylene, MCA, and ECA indicate that the unpaired electron of the radical anions is primarily localized on the C of the terminal CH_2 fragment of each molecule. The radical anions of the molecules containing two electron withdrawing groups (1,1-dicyanoethylene, MCA, and ECA) provide the additional resonance stabilization necessary to result in bound anions. These stable anions, each exhibiting a carbanion resonance structure, are excellent nucleophiles for initiation of the proposed mechanism of anionic polymerization. In particular, the radical anions of MCA and ECA are both strongly bound by 1.08 eV (B3LYP).

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Supporting Information Available: Tables of spin densities and anisotropic hfs constants. This material is available free of charge via the Internet at http://pubs.acs.org.

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