

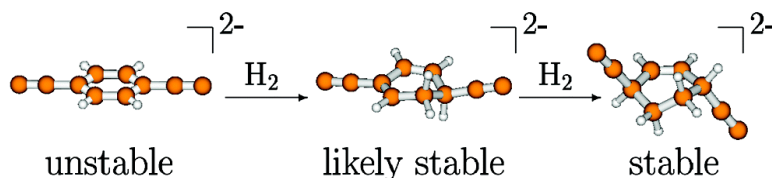
Article

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Influence of Delocalization on the Stability of Dianions: Study of a Systematic Series of Dianions with Growing Electronic Localization

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Abstract: The electronic stability of a dianion is influenced by the degree of delocalization of its electrons, but it is generally not possible to separate this influence from other effects. Here, we investigate by theoretical means the sequence of dianions consisting of phen-1,4-ylenebis(ethynide) and seven of its derivatives obtained by hydrogenating the benzene core in several steps. These dianions are structurally similar and mainly differ by the degree of delocalization of their electrons. We present geometries and electron detachment energies computed at a correlated level of theory. The results point to a classification of the eight dianions in three distinct groups of electronic stability. We are able to explain this grouping by a simple resonance structure picture, which demonstrates why the dianions with more delocalized electrons are less stable.

1. Introduction

Delocalization by conjugation, above all the special case of aromaticity, has been known for its stabilizing effect for many decades in organic chemistry (see, e.g., the classical works by Wheland¹ and Pauling²). Only recently have new theoretical investigations shown that delocalization also can have a destabilizing effect: This happens when the system is doubly or higher negatively charged.^{3,4} Because of the delocalization, the two (or more) extra electrons cannot separate efficiently, resulting in a strong Coulomb repulsion. The destabilization of the molecule can be large enough to give rise to the autodetachment of an electron if the system is isolated in the gas phase, that is, not stabilized by its environment like counterions or solvent. In the resulting monoanion, the strong Coulomb repulsion is, of course, absent.

The instability of doubly and higher charged anions is a general phenomenon and quite obviously not restricted to delocalized systems. This was demonstrated both theoretically and experimentally for many systems over the past decade; for example, such common and well-known dianions as CO_3^{2-} ,^{5,6} SO_3^{2-} ,⁷ and SO_4^{2-} ,⁷⁻⁹ and also quite large systems like the *closo*-hexaboronate dianion $\text{B}_6\text{H}_6^{2-}$,^{10,11} succinate

$[\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2]^{2-}$,³ and even C_{60}^{2-} ¹²⁻¹⁴ are all unstable in the gas phase and spontaneously emit an electron. Note that, despite their instability, multiply charged anions can have quite long lifetimes in the gas phase, for example, about 1 ms for C_{60}^{2-} .¹⁵ This is due to the existence of a repulsive Coulomb barrier in doubly or higher charged anions (see, e.g., refs 16–20).

One of the goals of both theory and experiment is to find the smallest dianion which is still stable in the gas phase. The smallest dianion found by theoretical calculations until today is the alkali halide LiF_3^{2-} ,^{6,21,22} while the smallest species found by experimental means possesses five atoms, for example, BeC_4^{2-} .²³ During these investigations, many other interesting stable dianions were also found. The interested reader is referred to reviews on the subject.^{17,24-27} We mention here only some examples for which theory and experiment stimulated each other. First, the measurement of the photoelectron spectra of hexahalogenometalates MX_6^{2-} (M = Re, Os, Ir, Pt; X = Cl, Br)²⁸ has stimulated the theoretical investigation of PtX_6^{2-} (X = F, Cl, Br).²⁹ In the calculations, an unusual ordering of the

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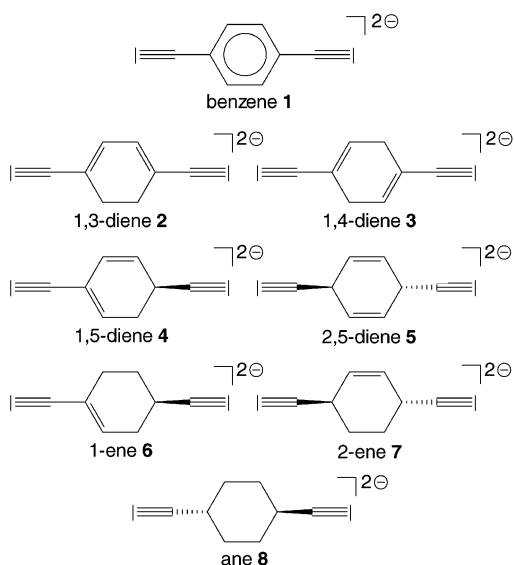


Figure 1. Lewis structures of (hydrogenated) phen-1,4-ylenbis(ethynide)s **1–8**. The numbers and acronyms given below the formulas will be used throughout the text to identify the respective dianions.

molecular orbitals and the respective monoanionic states has been found which has led to a partial reassignment of their peaks in the measured spectra.²⁹ Another example is the theoretical prediction of stable earth alkali halides EX_4^{2-} ($E = \text{Be, Mg, Ca}$; $X = \text{F, Cl}$)^{30,31} which was later confirmed by the experimental observation of BeF_4^{2-} and MgF_4^{2-} .³² Finally, one of the most recent publications in the field of dianions is a combined experimental and theoretical work on dianionic oxygen–carbon clusters with the general formula OC_n^{2-} .³³

The scope of this paper is to study in detail the influence of delocalization of the electrons on the electronic stability of dianions. We demonstrate this influence by studying a systematic series of dianions with growing electron localization. This series is constructed by gradually saturating the benzene core of the dianionic skeleton $[\text{C}_2-\text{C}_6\text{H}_4-\text{C}_2]^{2-}$. This choice was motivated by our investigation of wheel-like cyclic carbon cluster dianions such as $(\text{CC}_2)_6^{2-}$ and their aromaticity.³⁴ The series of doubly negatively charged molecules investigated in this paper provides a very convenient example for tuning the degree of delocalization by only minor variations of the molecule, that is, by partial or total hydrogenation of the benzene core. Starting from the “parent” system phen-1,4-ylenbis(ethynide) **1**, one specifically obtains four possible isomers by adding two hydrogen atoms to carbon atoms of the ring (dienes **2–5**), two possible isomers when four hydrogen atoms are added (enes **6–7**), and finally the totally ring-hydrogenated ane **8**. The Lewis structures of these compounds are shown in Figure 1. Note that, for the dianions for which cis–trans isomeric forms are possible, we restricted ourselves to the trans-isomers. These are expected to be more stable than the corresponding cis-isomers due to the larger distance between the most likely charge-bearing groups.

Because the two extra electrons can be more and more localized on opposite sides of the molecule, we expect from a naive point of view the electronic stability to increase with increasing hydrogenation, that is, from **1** to **2–5**, **6–7** to **8**. In this paper, we present theoretical calculations on a correlated level of theory to check this hypothesis and to provide a complete picture of the intricate influence of delocalization on the electronic stability of dianions. First, we outline the computational details in section 2. In section 3, optimized geometries of the molecules and their respective electron detachment energies are given, followed by a discussion of the correlation between structural features and stability with respect to electron autodetachment in section 4. Finally, section 5 completes the paper with a summary and demonstrates the conclusions which can be drawn from our results.

2. Computational Methods

All calculations were done within the framework of the Gaussian 98³⁵ ab initio package of programs. We employed a Cartesian Gaussian-type double- ζ basis set, which represents a contraction of Huzinaga’s primitive sets.³⁶ Additionally, the set was augmented with a set of d-type polarization functions on the carbon atoms and of p-type polarization functions on the hydrogen atoms. This basis set is referred to as DZP³⁷ and proved to be sufficiently accurate to investigate electronic stability in several previous theoretical studies of dianions.^{11,34,38} For most of the calculations, further diffuse functions were added to account for the diffuse nature of the charge distribution which is typically found in multiply charged anions. These diffuse functions are especially necessary to make a meaningful prediction of the stability of a dianion if it lies at the edge of electronic stability.¹¹ A set of p-type functions with an exponent of 0.034000 was placed on the carbon atoms, and an s-type function with an exponent of 0.048273 was placed on each hydrogen atom. This set will be denoted as DZPD in the following. Apart from making reliable stability predictions, this basis set is also expected to yield quite accurate geometric parameters.

To find the respective minima on the potential energy surfaces of compounds **1–8**, we performed geometry optimizations starting from sensible guesses of their structures. We first employed the self-consistent field (SCF) restricted Hartree–Fock (RHF) technique, which corresponds to an independent particle picture. For completeness, the geometries of the respective monoanions have also been determined, using the restricted open-shell Hartree–Fock (ROHF) technique as implemented in Gaussian 98. The geometries of the dianions obtained at the SCF level of theory were further refined using the correlated method Møller–Plesset perturbation theory of second order (MP2). By searching the harmonic vibrational frequencies for imaginary ones, we tested whether the stationary points found on the potential energy surfaces of the dianions represent minima or mere saddle points.

After having established the equilibrium geometries, we were in the position to investigate the electronic stability of the dianionic organic compounds at these geometries. We used direct as well as indirect

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methods to check for the stability with respect to electron emission. The simplest approach to determine the binding energy of the excess electron, equivalent to the electron detachment energy (EDE), is to employ Koopmans' theorem (KT).³⁹ It relates the EDE to the negative of the orbital energy of a RHF calculation. Yet this method gives only a first guess. To include electron correlation and orbital relaxation effects, we used the far more accurate outer-valence Green's function (OVGF) approach.^{40,41} In addition, indirect methods have been used to determine the EDE. This is done by calculating the difference of the total energies of the monoanion and the dianion; thus, they are referred to as Δ -methods. For most of the dianions, we have employed two different levels of theory, leading to Δ SCF- and Δ MP2-values. In case the former two values were inconclusive in establishing electronic stability, we also calculated Δ CCSD-values (coupled clusters including singles and doubles). To determine the MP2 and CCSD energies of the monoanions, we used the restricted open-shell MP2 (ROMP2) and the unrestricted open-shell CCSD (UCCSD) techniques, both as implemented in Gaussian 98.

Apart from the difference between direct and indirect methods for obtaining the EDE, one can further distinguish so-called vertical and adiabatic EDEs, abbreviated with the subscripts "v" and "a" in the following. Vertical EDEs are obtained by taking the difference of the total energies of the dianion and the monoanion at the optimized geometry of the dianion, whereas for adiabatic values the energies at the separately optimized geometries of the dianion and the monoanion are used. Note that a positive value of the EDE corresponds to a stable dianion with respect to electron autodetachment, in the sense that energy has to be applied to detach an electron.

Apart from electron autodetachment, another possibility to spatially separate the excess charges of a multiply charged anion is the fragmentation of the molecular framework into two or more pieces. For the compounds 1–8, it is not necessary to check this stabilizing pathway. This is due to the fact that there are only strong covalent bonds in organic molecules and therefore high barriers would have to be overcome to break the molecule apart.^{42,43} We also remind that all harmonic vibrational frequencies have been found to be real.

3. Geometries and Energetics

According to our calculations, all investigated dianions possess closed-shell 1A ground states. Geometry optimizations at both the SCF and the MP2 levels of theory always yielded structures of the expected point group for the dianions 1–8. These structures are shown in Figure 2 for illustration. For example, the totally delocalized benzene dianion 1 is planar and thus belongs to the point group D_{2h} , whereas the ane dianion 8 prefers a chair-type structure of C_{2h} symmetry. The calculated structures all represent minima on the respective potential energy surfaces of dianions 1–8 because the analysis of the harmonic vibrational frequencies always gave only real frequencies. Table 1 summarizes the calculated point groups for the dianions. The geometries of the corresponding monoanions have also been computed at the SCF level of theory. Note that except for 2,5-diene 5, where the symmetry is lowered from C_{2h} in the dianion to C_2 in the monoanion, the symmetry of the monoanion remains the same as for the respective dianion.

For all optimized geometries, the simple Lewis picture seems to be accurate enough to predict approximate bond lengths. Selected carbon–carbon bond lengths obtained at the MP2 level

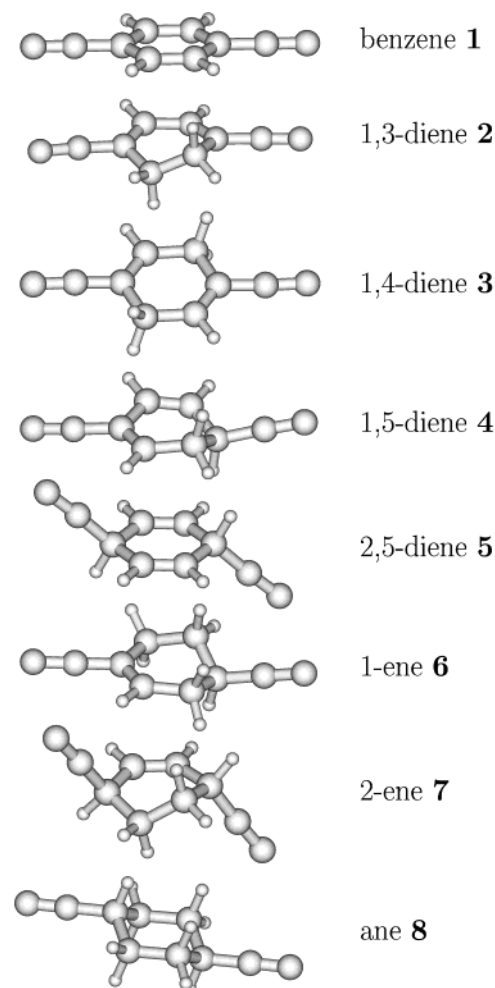


Figure 2. Structures of the (hydrogenated) phen-1,4-ynlenbis(ethynide)s 1–8 generated with the MOLDEN program.⁵⁵ Large spheres represent carbon atoms, and small spheres represent hydrogen atoms. Note that the corresponding monoanions possess the same point group for all compounds excluding 2,5-diene 5 and their geometries are similar to those of the respective dianions, except for 2-ene 7 (see text).

Table 1. Geometries of the Dianions 1–8 Optimized with the DZPD Basis Set at the MP2 Level of Theory^a

	point group	d_{C_2}	d_{C_2-ring}	"size"
benzene 1	(D_{2h})	(127.6)	(144.1)	(824.6)
1,3-diene 2	(C_2)	(127.9)	(143.1)	(828.1)
1,4-diene 3	C_{2h}	127.7	144.2	825.4
1,5-diene 4	C_1	127.3/127.7	148.2/144.0	821.7
2,5-diene 5	C_{2h}	127.4	149.1	794.8
1-ene 6	C_1	127.3/127.7	148.2/144.1	827.9
2-ene 7	C_2	127.4	148.9	757.4
ane 8	C_{2h}	127.3	148.2	828.2

^a Note that compounds 1 and 2 are unstable with respect to electron autodetachment. This is why their geometries have to be regarded with caution and are given in parentheses. d_{C_2} is the bond length within the ethynide groups, and d_{C_2-ring} is the length of the bond connecting them to the ring. There are two values given for compounds 4 and 6 because their two ethynide groups are inequivalent. The "size" of the molecule is defined as its greatest extension, that is, the distance between the two outermost carbon atoms. Distances are in picometers.

of theory are given in Table 1. Note that the values for compound 1 and 2 are in parentheses because these two are unstable with respect to electron autodetachment as discussed below, but the computational methods used are in principle only suitable for bound molecular systems.

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Several points can be clearly deduced from the data in Table 1: First, within the ethynide groups, the carbon atoms have a distance of 127–128 pm for all dianions. These bonds are elongated as compared to the typical textbook value for triple bonds of 120 pm (see, e.g., ref 44). This elongation can be explained by the strong Coulomb repulsion between the two carbon atoms, because the negative charges are mainly localized on them. This explanation is confirmed by the fact that the distance between these two carbon atoms decreases to 123.2 pm in doubly protonated **1**, that is, neutral HC₂–C₆H₄–C₂H.

Another interesting fact to note is that the bond lengths of the ethynide groups vary only slightly in the two cases where conjugation with the π -system of the ring is possible or not. In the compounds in which conjugation is possible (**1–4**, **6**), the bond lengths of the ethynide groups are 127.6–127.9 pm, whereas in the others, lengths of 127.3–127.4 pm are found. For the bonds connecting the ethynide groups with the ring – single bonds in the Lewis picture – the differences are somewhat larger, but nevertheless small. For this distance, values of 143.1–144.2 pm in the conjugated case as compared to 148.2–149.1 pm in the other case are found. The latter results resemble the textbook value of 154 pm for single bonds.⁴⁴ Note that compounds **4** and **6** are special cases in which both kinds of conjugated and nonconjugated ethynide groups are present. The small differences discussed above indicate that the π -electrons of the ethynide groups are not largely delocalized over the π -system of the ring in those compounds for which this is possible at all. Nevertheless, delocalization is definitely present and greatly affects the properties of the dianions as will be seen below.

Regarding the bond lengths within the ring, isolated double bonds according to the Lewis picture are always found to be shorter (135.3–135.4 pm) than conjugated double bonds (136.0–142.1 pm). The converse holds for single bonds: isolated are always longer (150.8–154.5 pm) than conjugated (142.1–148.4). These results go well with the usual trends observed in organic compounds and thus confirm the reliability of the employed methods.

We now proceed to the energetics which constitute the main point of this paper. Our results on the EDEs are collected in Table 2. A first guess about the stability of the (hydrogenated) phen-1,4-ylenbis(ethynide)s can be obtained by employing KT. For all dianions except for **1** and **2**, positive EDEs of 0.67–1.29 eV are found. These are large enough to make a further investigation of these compounds worthwhile. A rule of thumb is that the KT value of the EDE should be at least about 0.5–1.0 eV to expect the dianion to be stable with respect to electron emission, as KT tends to overestimate the EDE by about this amount.^{38,45} The values –0.03 and –0.29 eV found for benzene **1** and 1,3-diene **2**, respectively, make clear that they are unstable dianions. For completeness, we also calculated KT values with the DZP basis set for these two compounds. For unstable anions, EDEs computed via bound state methods should be handled with care. The values obtained may provide a useful estimate of the energy of the metastable anion if computed with compact basis sets without diffuse functions. Using a compact basis set is equivalent to putting the system into a small box. Thus, the

Table 2. Electron Detachment Energies (EDEs) of the Dianions **1–8** Given in eV (1 eV = 96.5 kJ/mol)^a

	KT DZPD/DZP	Δ SCF _v	Δ SCF _a	Δ MP2 _v	Δ CCSD _v	OVGF
benzene 1	(–0.027/ –0.369)	(–0.715)	(–0.993)	(–0.297)		(–0.360)
1,3-diene 2	(–0.285/ –0.626)	(–1.086)	(–1.479)	(–0.624)		(–0.709)
1,4-diene 3	0.691	0.050	–0.092	0.162	0.284	0.109
1,5-diene 4	0.667	–0.572	–0.722	0.630	0.165	0.140
2,5-diene 5	1.285	0.512	0.323	0.548		0.548
1-ene 6	0.763	–0.598	–0.746	0.619	0.182	0.195
2-ene 7	1.099	0.299	–0.080	0.355		0.342
ane 8	1.217	0.406	0.315	0.686		0.515

^a All EDEs were calculated with the DZPD basis set, and for **1** and **2** the value for KT was also calculated with the DZP basis set (see text). Note that compounds **1** and **2** are unstable with respect to electron autodetachment. This is why their EDEs have to be regarded with caution and are given in parentheses. The KT and Δ SCF values were computed at the SCF optimized geometries (for the definition of the subscripts “v” and “a”, see text). The Δ MP2, Δ CCSD, and OVGF values were calculated at the MP2 optimized geometries of the dianions.

lowest pseudocontinuum state lies much higher in energy than the metastable state under investigation, and the mixing between the two can be neglected. This fact has been pointed out numerous times in the literature, see, for example, refs 4 and 46.

The EDE results with the DZP basis set employing KT are –0.37 eV for benzene **1** as compared to –0.63 eV for 1,3-diene **2**. We conclude that 1,3-diene **2** is the most unstable compound of all compounds studied here, followed by benzene **1**. Note that this conclusion applies to the energies of the dianions **1–8**. However, from another point of view, one may define the stability of a metastable dianion with respect to its lifetime. Yet, the calculation of lifetimes requires very advanced and elaborate techniques (see, e.g., ref 4 and references therein) and is beyond the scope of this paper. Although the values for **1** and **2** obtained at a higher level of theory have to be regarded with caution because of the reasons outlined above, they nevertheless confirm the conclusion that 1,3-diene **2** is the most unstable dianion and that **1** is unstable too (see Table 2).

The dianions **3–8** have been predicted to be electronically stable on the KT level of theory above, but further calculations on higher levels of theory are needed to decide on this issue. For an overview, all calculated values are summarized in Table 2. Let us first inspect the Δ SCF_v values. According to these, dianions **3**, **5**, **7**, and **8** have EDEs of 0.05, 0.51, 0.30, and 0.41 eV, respectively, and can be expected to be stable. These EDEs are seen to decrease by 0.6–0.8 eV as compared to the results obtained using KT. Such a trend is well-known^{38,45} and stems from the fact that Δ SCF takes orbital relaxation in the monoanion into account. Dianions **4** and **6** demonstrate this nicely: In contrast to all of the other dianions and in accord with the lack of symmetry, their highest molecular orbital (HOMO) is centered on only one side of the molecule. We show the HOMOs of 1,3-diene **3** and 1-ene **6** in Figure 3 to illustrate this. If an electron is removed from the relatively localized HOMO in **4** or **6**, the resulting orbital relaxation is much larger than that encountered for species where the HOMO is delocalized over both sides of the molecule. Consequently, the impact of Δ SCF_v on the EDEs is also larger for **4** and **6** than for the

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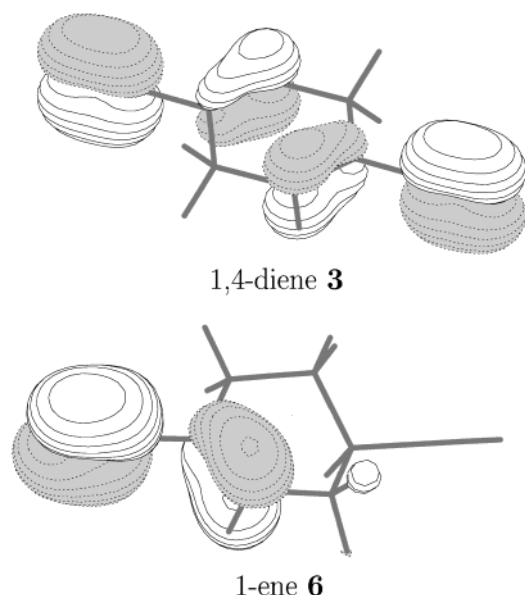


Figure 3. Highest occupied molecular orbitals (HOMOs) of 1,3-diene **3** and 1-ene **6** obtained with the DZPD basis set (see text). Note that in **3** the HOMO is delocalized over both ethynide groups, whereas in **6** it is centered on one side. The plots were generated with the MOLDEN program.⁵⁵

other compounds. The difference between the EDEs obtained via KT and ΔSCF_v is 1.2–1.4 eV for **4** and **6** as compared to 0.6–0.8 eV for the others.

If, in addition to the relaxation of the orbitals, the same is also allowed for the geometry, that is, the energy of the monoanion is evaluated at its separately optimized geometry, one obtains so-called adiabatic ΔSCF_a values. These EDEs are of course even smaller than the ΔSCF_v values. For the stable dianions studied here, the difference between vertical and adiabatic values is small and amounts to 0.15–0.19 eV. An exception is the dianion 2-ene **7** with a difference of nearly 0.4 eV between ΔSCF_v and ΔSCF_a . This can be explained by the fact that in the monoanion corresponding to **7** there are large geometry changes as compared to **7**. The ethynide groups in the dianion are bent away from the double bond in the ring, whereas they are bent toward it in the monoanion. Additionally, the angle between these groups and the plane of the ring decreases greatly. A possible explanation for these changes in geometry is that by this means the dihedral angle between the hydrogen atoms at ring carbon atoms 1 and 4 (these to which the ethynide groups are connected) and the hydrogen atoms of the adjacent CH_2 groups increases from 38.5° in the dianion to 48.6° in the monoanion, thus reducing the steric repulsion. The same steric repulsion is also present in the monoanion corresponding to ane **8**, but in that case the bending of the ethynide groups toward one side of the ring would release no strain because of its mirror symmetry.

Inclusion of electron correlation by employing the MP2 level of theory changes the EDEs again. Comparing ΔMP2_v with ΔSCF_v values shows that the EDEs increase by about 0.05–0.3 eV for dianions **3**, **5**, **7**, and **8**. The general trend that EDEs obtained with ΔMP2_v are larger than those obtained with ΔSCF_v is explained by the fact that a dianion with N electrons gains more from correlation than its corresponding monoanion, in which only $N - 1$ electrons are present and can be correlated. The impact of electron correlation on the two dianions without any symmetry, **4** and **6**, is much more substantial. Here, the

difference between the ΔMP2_v and ΔSCF_v values is about 1.2 eV. Large changes were also seen above for the differences between KT and ΔSCF_v for these two compounds, which could be readily explained by the greater orbital relaxation in that case. Here, the large differences hint at the possibility that MP2 is not capable of describing these two dianions correctly (there are known problems with Møller–Plesset perturbation theory, see, e.g., ref 47). We therefore decided to additionally calculate EDEs on the ΔCCSD_v and the OVGf (see below) levels of theory for dianions **4** and **6**. The results confirmed our suspicion that MP2 has severely overestimated their stability. For dianion 1,5-diene **4**, a ΔCCSD_v value of 0.17 eV was found, as compared to -0.57 eV for ΔSCF_v and 0.63 eV for ΔMP2_v . The corresponding EDEs for dianion 1-ene **6** are in the same order 0.18, -0.60 , and 0.62 eV.

By calculating the ΔCCSD_v value also for the unproblematic case 1,4-diene **3**, we were able to validate the reliability of the method because its EDE of 0.28 eV obtained with CCSD fell well in line with its other calculated EDEs; for example, its ΔMP2_v value is 0.16 eV. Because the other EDEs calculated for dianion **3** fluctuate around zero, this ΔCCSD_v value also helps to clarify its electronic stability.

The OVGf method provides EDEs directly. These were calculated at the geometry of the dianion which was obtained by optimization at the MP2 level of theory. The OVGf values can be expected to be reliable because correlation and relaxation in the dianion and the monoanion are treated consistently within this method. For most dianions investigated here, the calculated EDEs do not change greatly as compared to the EDEs obtained by ΔMP2_v . The difference amounts to at most 0.17 eV (see Table 2) for **3**, **5**, **7**, and **8**, but once again dianions **4** and **6** are exceptions. Their OVGf values of 0.14 and 0.20 eV differ by almost 0.5 eV as compared to the EDEs obtained via ΔMP2_v , but correspond well to their respective ΔCCSD_v EDEs (see above and Table 2). This observation further confirms the reliability of CCSD as compared to MP2 for these two compounds.

4. Discussion

According to the results summarized in Table 2, one can arrange the (hydrogenated) phen-1,4-ylenbis(ethynide)s into three groups. The first includes **1** and **2** which were found to be unstable. A second group consists of 1,4-diene **3**, 1,5-diene **4**, and 1-ene **6**. For these dianions, the results were not fully conclusive, although it is very likely that they are stable compounds. 2,5-Diene **5**, 2-ene **7**, and ane **8** form the last group. These three dianions are clearly stable with respect to electron autodetachment, as was indicated by only positive calculated vertical EDEs throughout.

Before we start to discuss the reasons for the occurrence of three distinct groups of stability, we first like to mention that even if dianions **3**, **4**, and **6** possessed a slightly negative EDE in reality, they still would be expected to be very long-lived, that is, metastable, dianions. It is quite possible that their lifetime would exceed 10^{-5} s in that case, making their observation in a time-of-flight mass spectrometer possible. This long lifetime is due to the so-called repulsive Coulomb barrier (RCB) occurring in all multiply charged anions. The RCB is equivalent

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to the barrier which an electron would experience in approaching the corresponding anion with one electron less. It emerges from the combination of the short-range Coulomb attraction of the nuclei and the long-range Coulomb repulsion of the other electrons and effectively hinders the emission of one of the excess electrons (for an extensive discussion of this phenomenon, see ref 20 and references therein; for several experimental observations of the RCB, see, e.g., refs 17 and 48).

It is immediately clear from the present data on the size of dianions **1–8** (see Table 1) that the simple picture of two localized charges at opposite sites of the molecule does not explain at all the observed pattern. The Coulomb repulsion for two negative charges separated by 757.4 pm (the smallest size) amounts to 1.90 eV; for 828.2 pm (the largest size) one obtains 1.74 eV. One would thus expect at most differences of 0.16 eV in the EDEs, in contrast to the observed differences of over 1 eV. Additionally, there is no apparent correlation between stability and distance; for example, 1,3-diene **2** is most unstable, although its outermost carbon atoms are nearly furthest apart of all investigated dianions. The only possible exceptions are the dianions 2,5-diene **5** and 2-ene **7**. These compounds are very similar electronically (see below), but nevertheless the EDE of **7** is about 0.2 eV less than the EDE of **5** at the OVGf level of theory. In this case, the much smaller extension of 757 pm in 2-ene **7** as compared to 795 pm in 2,5-diene **5** could explain about one-half of the difference between the EDEs in the picture of localized charges.

Rather than elongation of the whole molecular structure, other changes in geometry could be the main factor which determines electronic stability. We were able to rule this out by a simple computational check: We took the optimized geometry of benzene **1**, added two hydrogen atoms in positions 3 and 6 to formally obtain the 1,4-diene **3**, and optimized only the positions of the hydrogen atoms while maintaining the carbon skeleton. With the DZPD basis set, we obtained an EDE of 0.46 eV at the level of KT for this partially optimized 1,4-diene. The gain in stability of 0.49 eV as compared to **1** is nearly 70% of the difference between the EDEs of **1** and **3**, leaving only about 30% of the stabilization to changes in the overall geometry of the carbon skeleton.

After steric explanations are ruled out, the only remaining possibility is that the stabilizing effect is of electronic nature. We found that drawing the possible resonance structures of the dianions **1–8** sheds considerable light on the problem. Resonance structures with two negative charges on the ring were excluded because of the strong Coulomb repulsion and the fact that both outermost carbon atoms would only have an electron sextet around them in this case.

As an example, the resonance structures of 1,3-diene **2** are shown in Figure 4. As can be clearly seen, for four out of five resonance structures, one of the negative charges is located at a ring carbon atom and thus much nearer to the other negative charge than in the central resonance structure in the drawing. In two of them, the second charge is even located at the carbon atom to which the other ethynide group is connected. This illustrates nicely why dianion 1,3-diene **2** is highly unstable with respect to electron emission. The situation is hardly better for the second member of the group of unstable dianions which is

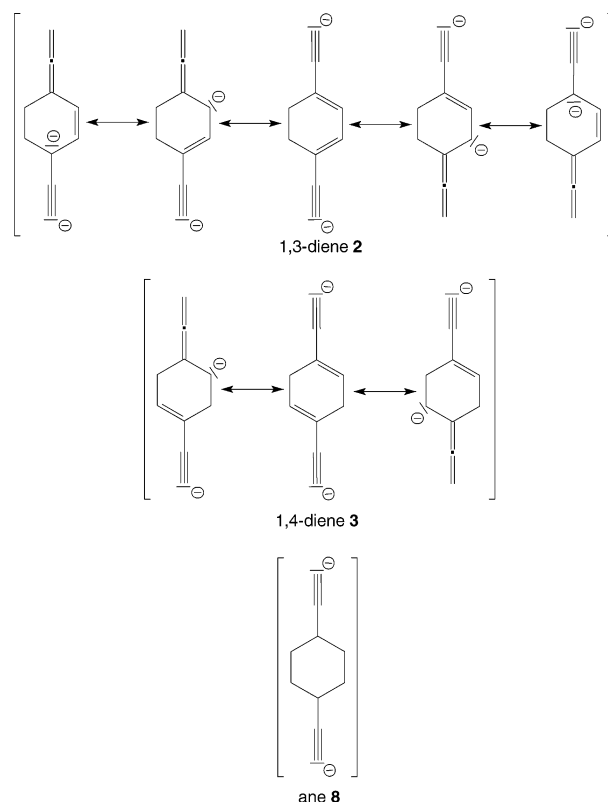


Figure 4. Possible resonance structures for 1,3-diene **2**, 1,4-diene **3**, and ane **8**, excluding those with two negative charges at ring carbon atoms. Note that for 1,3-diene **2**, four out of five resonance structures possess one of the negative charges at a ring carbon atom, whereas for 1,4-diene **3** this is only the case for two out of three. For ane **8**, no resonance structures with negative charges at ring carbon atoms can be drawn.

benzene **1**. There are six out of eight resonance structures of **1** for which the second charge is located at a ring carbon atom; in two of them, the charge resides at the carbon atom to which the second ethynide group is connected.

Such “close encounters” of the charges are not possible in the three possible resonance structures of 1,4-diene **3** also shown in Figure 4. Yet, nevertheless, in two of them the second charge is located at a ring carbon atom, thus destabilizing the dianion. For 1,5-diene **4** and 1-ene **6**, there are only two resonance structures, and in one of them one of the charges is located at a ring carbon atom. This explains nicely why these three dianions form the second group which consists of the likely stable compounds.

The resonance structure picture finally explains the third group of stable dianions **5**, **7**, and **8**. For all of these, only *one* resonance structure can be drawn, and this is exactly the one with the charges located furthest apart from each other at the two outermost carbon atoms (see Figure 4). This picture may be not complete, and there are further factors which would have to be included to explain the stabilities of the investigated dianions entirely. Yet, the resonance structure picture is simple, easy to understand, and after all accounts well for the observed trends.

One last point remains to be investigated. After one electron is removed, the resulting monoanion does not suffer any more from the strong Coulomb repulsion between the two excess charges. It should thus benefit from delocalization now. Exactly this is observed: As shown in Table 3, the respective monoanion

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Table 3. Relative Energetic Stability of the Monoanions Corresponding to the Dianions 1–8^a

	dienes	enes
1,3-diene 2	0.0	
1,4-diene 3	1.456	
1,5-diene 4	1.124	
2,5-diene 5	2.577	
1-ene 6		0.0
2-ene 7		1.193

^a The results were calculated with the DZPD basis set at the SCF level of theory. All energies are given in eV (1 eV = 96.5 kJ/mol), and the energy of the lowest lying monoanion is set to 0.0 eV.

in which most delocalization is possible lies lowest in energy. Note that only a comparison between the energies of dianions with the same number of hydrogens makes sense. The stability of the monoanionic dienes is almost reversed as compared to the stability of the corresponding dianions with respect to electron autodetachment. The monoanion of 1,3-diene **3** is most stable, whereas the monoanion of 2,5-diene **5** is the least stable and lies about 2.6 eV higher in energy. The same holds for the enes: the monoanion of 2-ene **7** is 1.2 eV less stable than the monoanion of 1-ene **6**. These energy differences were obtained at the SCF level of theory, but we do not expect that including correlation would change the results much. Please note that a very similar conclusion was drawn by Skurski et al.³ in their investigation of butyrdioate [O₂C–C₂–CO₂]²⁻. They found that in the dianion the two carboxylate groups are orthogonal to each other, whereas the corresponding monoanion is planar and delocalizes the extra charge over the whole molecular structure.

Note that we also performed preliminary calculations on (hydrogenated) benzene-1,4-diolates and (hydrogenated) benzene-1,4-dicarboxylates which can be obtained by substituting the ethynide groups of dianions 1–8 by O⁻ or CO₂⁻ groups, respectively. The results suggested that *all* of the diolates are unstable and *all* of the dicarboxylates are stable. The latter is confirmed by two recent publications, one by Wang et al.⁴⁹ who experimentally and theoretically found all three benzenedicarboxylates (ortho, meta, and para ≡ 1, 4) to be stable dianions. Enlow and Ortiz later confirmed this theoretically and also calculated the properties of the fluorinated benzenedicarboxylates.⁵⁰ By choosing the (hydrogenated) phen-1,4-ylenbis(ethynides) 1–8 for our investigation, we were able to demonstrate the whole spectrum between the two extremes of stable and unstable dianions.

5. Summary and Conclusion

In this paper, we investigated phen-1,4-ylenbis(ethynide) **1** together with its partially hydrogenated derivatives **2–8**. Their geometries were optimized with *ab initio* methods and were found to match well with the Lewis structures which can be drawn for them. From the differences in the bond lengths between dianions where conjugation of the ethynide groups with the ring is possible and those where this is not the case, it was concluded that conjugation between the ethynide groups and the ring is small, but nevertheless clearly present.

All calculated EDEs pointed to a classification of dianions 1–8 into three groups: the first consisting of clearly unstable phen-1,4-ylenbis(ethynide) **1** and *cyclo*-hexa-1,3-diene-1,4-

diylbis(ethynide) **2**, the second includes 1,4-diene **3**, 1,5-diene **4**, and 1-ene **6**, which are at the borderline of stability, and the third group contains the clearly stable 2,5-diene **5**, 2-ene **7**, and ene **8**. We were able to demonstrate that most of the differences between their EDEs were *not* related to geometrical differences but in fact could be nicely explained purely electronically. A simple picture using resonance structures provided a possibility for successfully accounting for the occurrence of three different stability classes.

This study demonstrated that a first guess predicting the stability to increase from **1** to **8** is clearly insufficient. According to our results, we suggest that the simple picture of charges localized on opposite sites of a doubly charged anion also is overly simplistic and only applies to some special cases. If one wants to decide whether a given dianion is stable with respect to autodetachment, accurate *ab initio* calculations still seem to be necessary for many individual cases. Over the past decade, some rules of thumb for predicting the stability of a dianion were established; for example, dianions with a positively charged center surrounded by negative ligands as in the so-called “ionic model” are often stable.^{6,42,51} Yet, the interaction of two or more excess charges in an extended molecule in which delocalization is possible remains a delicate problem to be solved. We think that our current paper has made a significant contribution to the solution of this problem.

To close, we return to the opening of the paper. There it was stated that delocalization can destabilize a dianion. This point can now be clarified using our computational results. As is seen in our calculations of the total energies of the monoanions corresponding to **2–7**, delocalization stabilizes these singly charged molecules. Note that the total energies of the stable dianions also decrease slightly with increasing delocalization, but the effect is far less pronounced than that for the monoanions and arises to at most a 0.7 eV difference in energy. It follows that one must carefully distinguish between the thermodynamic stability of the molecular structure, which is positively influenced by delocalization, and the overall thermodynamic stability including electronic stability. We demonstrate that the Coulomb repulsion between two (or more) delocalized excess negative charges can easily overcompensate the stability gained by delocalization. Thus, it is not possible to speak of stability by delocalization in general; it is essential to consider *both* kinds of effects in multiply charged anions.

To our knowledge, only the doubly protonated form of dianion **1**, that is, phen-1,4-ylenbisethyne, has been synthesized until now.^{52,53} Yet, the synthesis of the other (protonated) dianions and their deprotonation should be a practicable task. Their stability could then be checked, for example, by electrospray ionization combined with a time-of-flight mass spectrometer.⁵⁴ Thus, in principle, an experimental verification of our theoretical predictions seems to be possible.

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