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A Fresh Look at Aromatic Dianions

Thomas Sommerfeld*

Contribution from Theoretische Chemie, Universität Heidelberg Im Neuenheimer Feld 229,
69120 Heidelberg, Germany

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Abstract: Isolated dianions of cyclooctatetraene and cyclobutadiene are, despite their aromatic character, unstable with respect to electron loss. Here we present the first ab initio study of the autodetachment lifetimes of several “aromatic” dianions. In particular, we investigate whether aromatic π systems are associated with an enhanced stability with respect to electron loss and whether cross-conjugated (Y-aromatic) hydrocarbon dianions possess longer lifetimes than their linear-conjugated isomers. Moreover, our results are compared with bound state calculations for these metastable dianions, allowing us to analyze the validity of the latter approach. All considered, hydrocarbon dianions are found to possess surprisingly short autodetachment lifetimes on the order of a few femtoseconds, and therefore only electron scattering techniques seem to be capable of observing these species in the gas phase. The trends of the computed energies and lifetimes are best understood in terms of the mutual Coulomb repulsion of the extra charges. Small gas phase dianions can only be stable if the excess electrons can localize at least at two subgroups of high local electron affinity. Adding both extra electrons into *one* delocalized π system leads to a very unstable species, and thus especially those structures associated with pronounced aromaticity are found to show high energies and short lifetimes.

1. Introduction

The notion of aromaticity has captured the imagination of chemists ever since it was introduced by Kekule and Erlenmeyer in the 1860s.[1,2] A number of recent reviews is collected in the May 2001 issue of *Chemical Reviews*. As discussed in these review articles, aromaticity is a nonreductive term that cannot be defined uniquely. Yet if we restrict our attention for the moment to simple monocyclic hydrocarbons, aromaticity is usually associated with an enhanced stability of species obeying Hückel’s $(4n + 2)$ rule that implies a closed-shell π system. In this context, the main focus is on the electron count that “determines” the charge of the system, and, indeed, the most frequently presented examples for aromatic species include benzene, the cyclopentadiene anion, the cycloheptatriene cation, and the cyclooctatetraene dianion. On the other hand, it is well established that multiply charged systems behave quite differently from neutral and singly charged species[3,4] related to the dominating role of Coulomb repulsion in the former. For example, most small dianions known from solids or solution have been found to be unstable in the gas phase,[5] and only a very small number of dianions consisting of up to 10 atoms has so far been observed by mass spectrometry.

Clearly, from a Hückel rule point of view, one would expect the cyclooctatetraene (COT) dianion to be quite stable, whereas from a doubly charged species viewpoint, one would expect the opposite. These opposing views give rise to a number of questions. It is, in fact, known that the prominent aromatic dianions of COT and cyclobutadiene (CBD) are, as isolated species, unstable with respect to electron loss, but does the aromatic character translate into a long lifetime? Regardless of aromatic stability, how long does a species such as COT live, and with what kind of experiments would it be possible to observe the isolated dianion? Other questions pertain to theoretical considerations based on standard quantum chemistry computations for aromatic dianions. It is well known that results of bound state methods applied to unbound systems can be useful guidelines, but do the established pictures change if the energies of the metastable species are computed more reliably? For instance, the notion of Y-aromaticity has been debated in terms of the relative energies of the trimethylenemethane (TMM) and the butadienediyl (BD) dianions, but the computed energy difference is too small to be conclusive.[6]

In this article we will study the energies and lifetimes of the metastable dianions of COT, CBD, and its linear conjugated isomer (BDY), as well as the TMM and the BD dianions (see Chart 1). To the best of our knowledge, this is the first time electron autodetachment from aromatic dianions is explicitly studied. The paper is organized as follows. Section 2 is a brief introduction into the theoretical description of electronically metastable dianions. The computation of autodetachment lifetimes and the relation with results from bound state calculations are discussed in section 3. Numerical results for the cyclic systems CBD and COT as well as a linear-conjugated $C_4H_4^{2-}$

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* To whom correspondence should be addressed. E-mail: Thomas.Sommerfeld@urz.uni-heidelberg.de.

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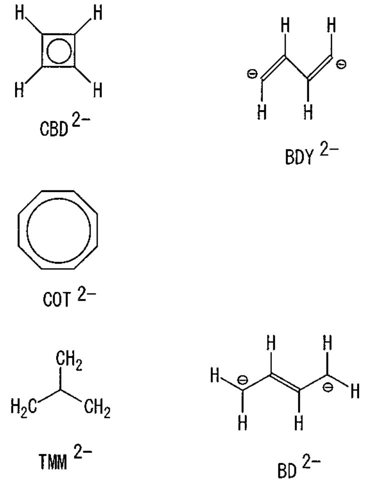
Chart 1



isomer will be presented in section 4. Section 5 deals with different TMM and BD conformers that are related to the controversial concept of Y-aromaticity. Section 6 constitutes a summary of our conclusions.

2. Metastable Dianions

Electronic states which lie energetically above the ground state of the associated $N - 1$ electron system can decay by autodetachment and are referred to as resonance or temporary states. Over the last 10 years it has been established that almost all small dianions known from solid and solution chemistry belong to this class.[3,5] In other words, most small dianions, such as CO_3^{2-}, SO_4^{2-}, and all dianions mentioned in the Introduction, are unstable with respect to electron loss and possess only short lifetimes in the gas phase.[7−9]

Theoretically, a resonance state can be characterized by a complex Siegert energy[10,11]

$$E_{\mathrm{res}} = E_{\mathrm{r}} - i\frac{\Gamma}{2} \tag{1}$$

where E_r is the resonance energy or position and Γ is the resonance width, which is related to the associated lifetime $\tau = \hbar/\Gamma$. There are many different ways to compute the resonance parameters E_r and Γ, for example, the stabilization,[12] the complex-scaling,[13,14] and the complex absorbing potential (CAP)[15,16] methods are well known. Here we use the CAP approach that is particular attractive for autodetaching *molecular* species, since it can easily be combined with existing electron structure codes, and electron correlation effects can be included in a straightforward manner.[17] This method has been termed CAP/CI,[17] and more methodological details will be given in the next section.

Having emphasized the metastability of the investigated dianions, let us consider what happens if one ignores the possible electron loss and treats a dianion as if it were stable. Applying a standard bound state method in conjunction with a finite (Gaussian) basis set is effectively equivalent to putting the system into a box, and we will refer to this approach as basis set confinement (BSC). Unbound electrons cannot escape, and the obtained energies can be loosely related to the energy needed to add one extra electron to the anion within the spatial confinement defined by the basis set. Thus, in BSC type calculations, the sought metastable state will mix with the states describing the discretized continuum; one then obtains in general a mixed solution. A wave function resembling the bound part of a metastable state can nevertheless be obtained if the box is made small (i.e., the basis set is made compact), such that the lowest pseudo-continuum state is much higher in energy than the metastable state and the mixing can be neglected. Results obtained in this way are of course only rough guidelines, since the computed properties, in particular the energy, will depend dramatically on the employed basis set. Moreover, one faces the dilemma that diffuse functions are needed to describe the extended electron density of anionic systems, but they increase the probability that the computed state has significant pseudo-continuum character.

The shortcomings of the BSC approach can be overcome in two ways. On one hand, the isolated dianion can, as described above, be treated as the metastable species it actually is. On the other hand, a stabilizing environment (solvent molecules or counterions) can be introduced, and then the electronically stable compound system can be studied with standard bound state methods. The counterion approach has been applied to some of the systems studied in this paper,[6,18−20] but has in the present context the decisive drawback that is notoriously difficult to unravel aromatic stabilization from the interaction with the counterions. In this article, we are interested in the intrinsic stability of the isolated dianionic species and are therefore using the former approach.

A convenient bridge between the Siegert energies obtained from our CAP calculations and the BSC energies computed with compact basis sets can be built using the Feshbach/Fano theory.[21−23] In this theory, a resonance state is described as a discrete state that is embedded in and interacts with a continuum.[24] The discrete state is represented by a square-integrable ($\mathscr{L}^2$) wave function with a sharp energy E_d. Owing to the interaction with the continuum, the discrete state acquires a width Γ, that is, a finite lifetime, and its energy is shifted by Δ. Let us emphasize that we do not use the corresponding Feshbach projector techniques to compute the resonance parameters E_r and Γ. Nevertheless, this way of thinking about resonances provides a straightforward connection between the CAP and BSC calculations.[9] The BSC wave function and energy of a dianion can be understood as the discrete state and its energy E_d, respectively, since using a compact basis set effectively

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Table 1. Energies and Lifetimes of the Investigated Dianions[a]

			E_d (hartree)	Re(E_{res}) (hartree)	E_r (eV)	Δ (eV)	τ (fs)
$C_4H_4^{2-}$	CDB^{2-}	D_{4h}	−153.3185	−153.3761	7.3	1.57	0.7
	CDB^{2-}	C_2	−153.3414	−153.3915	5.9	1.36	1.6
	BDY^{2-}	C_{2h}	−153.4399	−153.4764	3.8	1.00	26
$C_8H_8^{2-}$	COT^{2-}	D_{8h}	−307.3457	−307.3773	5.3	0.86	6.0
$C_4H_6^{2-}$	TMM^{2-}	D_{3h}	−154.6090	−154.6532	5.7	1.20	2.0
	TMM^{2-}	C_s	−154.6171	−154.6556	5.4	1.05	3.3
	BD^{2-}	C_{2h}	−154.5785	−154.6246	6.9	1.25	0.7
	BD^{2-}	C_2	−154.6041	−154.6440	5.5	1.08	2.1

[a] E_d is the BSC energy at the SCF level that can be identified with the discrete level of Feshbach/Fano theory. Re(E_{res}) is the real part of the Siegert energy on an absolute scale, i.e., the "total energy" of the resonance. The resonance position E_r is identical to Re(E_{res}), but the associated anionic decay product defines the origin of the energy scale. Δ is the level shift of the discrete state due to its decay, and τ is the corresponding lifetime.

prevents the coupling with the continuum. Adding diffuse functions to the compact basis set and performing a CAP calculation then yields the shifted energy E_r and the associated width Γ, and the level shift can be computed as $\Delta = E_r - E_d$.

Finally, we need to make a brief comment on the "resonance position". The real part of the computed Siegert energy E_r is the "total energy" of the resonance (the separated electrons and nuclei define the energy origin), and this value is needed to compare, for example, two isomers or conformers of a metastable dianion. Yet one usually associates the resonance position with the energy of the metastable state above its decay products, that is, with the energy above the target in an electron scattering or transmission experiment. Thus, for a temporary dianion, the position E_r is understood as the energy above the ground state of the *associated* monoanion at the same geometry. Normally, no confusion should arise from using these different energy scales; in Table 1, E_r on the absolute scale is labeled Re(E_{res}).

3. Computational Details

The CAP/CI method and its application to dianions have been described in depth in refs 9 and 25, and in this section we only briefly report the technical details of the present calculations.

A suitable wave function for a metastable dianion can be constructed starting from a BSC self-consistent field (SCF) calculation using a compact basis set and projecting the compact molecular orbitals (MO) onto an extended basis. As a compact basis set, we have used Dunning's standard double-ζ basis set[26] augmented with one d-type polarization function, and the SCF calculations have been performed with the MOLCAS4 package of programs.[27] In the second step, the BSC MOs are projected onto an extended basis set that consists of the compact basis and a (1s6p)/[1s5p] set of diffuse functions on the carbon atoms ($\alpha_s = 0.0765$; even scaled p-exponents between 0.0716 and 0.00683; the lowest eigenvalue of the overlap matrix of these six p-type functions was discarded). Using the projected MOs, we construct a configuration interaction (CI) wave function for the resonance taking into account the closed-shell configuration describing the resonance within the BSC approach and all possible single excitations within the extended basis set. Loosely speaking, the single excitations into the diffuse orbitals describe the decay into the continuum in the ensuing CAP/CI calculation, and the excitations into compact orbitals account for relaxation effects of the possibly too compact BSC wave function.[9]

In a CAP calculation, an absorbing potential $-iW$ is added to the physical Hamiltonian H, and one works with a parametrized non-Hermitian complex-symmetric Hamilton operator

$$H(\eta) = H - i\eta W \tag{2}$$

where W is typically a real "soft" boxlike potential in the dissociation coordinate R, for example, R^2 or R^4, and η is a strength parameter. The specific CAP form is the box-CAP suggested in ref 28, where the CAP box size has been set to the maximum component of the respective nuclear coordinates plus 2.5 bohr in each Cartesian direction. To compute the matrix representations of H and W in our CI basis, the MR-CI program[29] developed at the University of Bonn has been used. The CAP Hamiltonian $H(\eta)$ is then diagonalized repeatedly for different CAP strengths η using standard numerical routines from the LAPACK or ARPACK[30] libraries. Resonance states can be identified from the η-trajectories of their complex energies that stay close to the real axis and show stabilization cusps.[16] In contrast, η-trajectories belonging to pseudo-continuum states accelerate quickly into the complex plane. Large diffuse basis sets are needed to obtain a satisfying stabilization behavior, and with our basis set we could clearly identify the investigated resonance states at all considered geometries.

To compute the resonance position E_r of a metastable dianion, the energy of the associated monoanion is needed. At the employed level of theory for the resonance states, there are basically two choices for the computation of the energy of the anionic target. On one hand, the anion ground state can be approximated at a frozen-orbital level by the corresponding one-hole configuration, or, on the other hand, a separate CI singles calculation for the anion based on the projected MOs can be performed.[9] Neither of the two approaches seems to be perfectly balanced.[9,25] Here we report E_r values based on the latter choice.

4. Cyclobutadiene and Cyclooctatetraene Dianions

In this section, we investigate the two cyclic dianions CBD and COT. The geometrical structures of both species have been investigated repeatedly using BSC-type approaches (see, e.g., refs 18−20, 31, 32), but autodetachment has so far not been taken into account. The BSC studies reveal that the two species behave quite differently. COT has the expected planar D_{8h} geometry and evidently exhibits an aromatic character.[31,32] In contrast, only the counterion stabilized CBD dianion shows a D_{4h} geometry, whereas the isolated CBD dianion is found to possess a highly distorted nonplanar C_2 symmetrical structure with one very long carbon−carbon bond.[19]

In view of these findings, we commence this section with the rather "unproblematic" COT dianion to establish a point of reference. At the BSC/SCF level of theory, the COT dianion shows a D_{8h} symmetrical geometry, and with our compact basis set a carbon−carbon bond length of 1.412 Å is obtained in satisfying agreement with ref 31. We find a closed-shell $^1A_{1g}$ electronic ground state, but the positive energy of the e_{2u} HOMO ($\epsilon(e_{2u}) = 4.2$ eV) shows that COT is electronically unstable. Taking account of the possible electron ejection from the e_{2u} orbital and performing a CAP/CI calculation yield a resonance position of 5.3 eV above the $^2E_{2u}$ state of the associated anion and an autodetachment lifetime of $\tau = 6$ fs (Table 1). Thus, isolated COT is indeed highly unstable with respect to electron loss, and its lifetime is very short, in particular in comparison

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with other small temporary dianions. For example, the tetratomic dianions C_4^{2-} and CO_3^{2-} show lifetimes of 260 and 6500 fs,[9] several orders of magnitude longer than COT. We will come back to the very short lifetimes of cyclic dianions at the end of this section.

Let us now turn to the CBD dianion. We have considered two conformers of this system: the D_{4h} constraint conformer, that corresponds to a higher order saddle point at the BSC/SCF level, and the C_2 symmetrical conformer, that represents the minimal energy structure of CBD within the BSC approach.[19] The geometries obtained with our compact basis set are in good agreement with ref 19. Both conformers exhibit closed-shell electronic ground states, but high positive orbital energies reveal that the CBD dianion is very unstable with respect to electron loss at both geometries. By performing CAP/CI calculations for the D_{4h} and the C_2 symmetrical conformers, we find resonance positions of 7.3 and 5.9 eV above the corresponding anions, and the associated lifetimes are extremely short: 0.7 and 1.6 fs, respectively (Table 1). Thus, from a lifetime point of view, the nonplanar conformer is more stable than the planar squarelike system, and both conformers are substantially less stable than the COT dianion.

Regarding the qualitative stability order of the two $C_4H_4^{2-}$ conformers, the findings at the BSC level are substantiated by the resonance positions and by the respective lifetimes, but, from a quantitative point of view, there are significant differences. The energy difference between the D_{4h} and the C_2 conformations is decreased from 0.70 eV (67 kJ/mol) at the BSC/SCF level to 0.53 eV (51 kJ/mol) at the CAP/CI level. We will see similar tendencies for TMM and BD in the next section, and the same effect has been observed for C_2^{2-} and C_4^{2-} in refs 9 and 25. These trends are manifestations of a less obvious shortcoming of the BSC approach. Loosely speaking, within the BSC approach the highest occupied MOs from which electrons can autodetach are not correctly described, and, if these orbitals are bonding or antibonding in character, the computed geometrical parameters will be incorrect. In other words, for a molecular system, energies E_d, E_r, and their difference Δ will depend on the nuclear coordinates, and the minima of E_d and E_r will in general be different. Specifically, for the two dianionic CBD conformers, the level shift Δ is larger for the planar conformer, and thus the BSC approach effectively overestimates the energy gain associated with the distortions from planarity. We conclude that a geometry optimization at the CAP/CI level would yield a structure with less pyramidalized carbon atoms, but, unfortunately, geometry optimization at the CAP/CI level is so far limited to systems with only one or two geometrical parameters owing to the costly complex stabilization procedure.

In addition to the two cyclic CBD conformers, we have investigated the linear-conjugated $C_4H_4^{2-}$ isomer BDY, that is, doubly deprotonated butadiene (Chart 1). In the present context, this isomer arises from breaking the long carbon−carbon bond of the cyclic C_2 conformer and letting the species relax to a minimum energy structure. It is interesting to note that in going from the planar D_{4h} conformer of CBD via the nonplanar C_2 conformation to the planar BDY dianion, one starts with six π electrons, but ends up with a “four π” system. The BDY dianion exhibits a C_{2h} symmetrical geometry and a ^1A_g electronic ground state. At the BSC/SCF level, BDY is 2.7 eV (258 kJ/mol) lower in energy than is its cyclic C_2 isomer and represents most probably the global minimum on the $C_4H_4^{2-}$ BSC potential energy surface. The two short terminal (1.36 Å) and the long central (1.51 Å) carbon−carbon bonds reflect that only the two bonding π orbitals are occupied, and the excess electrons reside formally within the lone-pair-like orbitals at the terminal carbon atoms. As expected, these orbitals show high positive energies (2.2 and 1.2 eV for the $7a_g$ and $6b_u$ orbitals corresponding to the “plus” and “minus” lone-pair combinations), but, surprisingly, the second π-like orbital ($1b_g$) is even higher in energy ($\epsilon(1b_g) = 2.6$ eV), and thus at the BSC/SCF level BDY possesses three occupied orbitals with positive energies.

By treating BDY as a metastable species and allowing detachment from these orbitals, we find a resonance position of 3.8 eV and a lifetime of 26 fs. The BDY dianion is therefore not only energetically more stable than is its cyclic isomer but shows an increased lifetime by more than 1 order of magnitude. It is interesting to analyze the detachment rates from the three unbound orbitals which can, due to their different symmetries, be easily distinguished.[25] The partial b_g, a_g, and b_u widths contribute roughly 20, 60, and 20% to the total width, and thus electron detachment from the lower lying lone-pair-like $7a_g$ and $6b_u$ orbitals is 4 times more probable than detachment from the higher lying π-like $1b_g$ orbital. We note that the energetic ordering of the electronic states of the anion as predicted from the dianion’s orbital energies is maintained in separate CI singles calculation of the anionic states: the ground state has ^2B_g symmetry, and the first and second excited states are ^2A_g and ^2B_u.

The BDY $C_4H_4^{2-}$ isomer may not seem to be a particular useful partner for comparison in the context of aromaticity, but it is very instructive in the context of doubly charged species. From both the resonance position and the lifetime criteria, it is evident that BDY is far more stable than its cyclic isomer and considerably more stable than the much larger *aromatic* COT dianion. These findings clearly reflect what has been established for other doubly charged species[3,33,34] and, in particular, for dianionic carbon clusters.[35,36] The key issue concerning the stability of isolated dianions is electron accommodating groups showing a high local electron affinity. All small dianions that have been observed or predicted to possess a long lifetime in the gas phase have at least *two* electron accommodating units. Depending on the structural properties and variabilities of the different systems, there is then a tradeoff between compact forms possessing many electron affine substructures and chainlike forms showing only two electron accommodating groups but maximizing their distance. In contrast, distribution (delocalization) of both excess charges over *one* cyclic or cagelike structure leads to a very unstable species.[36]

From our results for CBD and COT, we arrive at the following conclusions. In contrast to neutral and singly charged systems where certain cyclic structures show an enhanced stability associated with their aromatic character, cyclic structures of *doubly* charged anions are strongly destabilized. Essentially, the structural and energetic characteristics of isolated

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dianions are dominated by the strong Coulomb repulsion of the extra electrons, and, therefore, in particular those structures that are typically associated with aromatic stabilization will be highly unstable with respect to electron loss and show only short lifetimes. In solution, this repulsion is greatly attenuated, and aromatic stabilization can play a crucial role. Yet, from an analysis of the energies of gas-phase dianions it will be very difficult, if not impossible, to separate any effects of aromaticity from the huge Coulomb background.

5. Trimethylenemethane and Butadiene Dianions

The question of whether cross-conjugated (Y-delocalized) systems are more stable than their linear-conjugated analogues has now been discussed for nearly 30 years, but it is still a matter of controversy. In 1972 Gund considered the "peculiar chemical stability" of several Y-delocalized species, including the guanidinium cation ($C(NH_2)_3^+$), the TMM dianion, and the carbonate dianion (CO_3^{2-}), and introduced the notion of "Y-aromaticity" to characterize these species.[37] Many of the subsequent investigations focused on TMM, perhaps because it is the closest analogue of the CBD dianion (see refs 38 and 39 and references therein for recent studies and[40] for a thorough review of earlier work).

Let us at this point separate question A "Do Y-delocalized species exhibit a *certain stability*?" from question B "Should this stability, provided it exists, be called Y-aromaticity?" The answer to question A depends dramatically on defining with respect to what "stability" is measured. In some reference systems, TMM does indeed possess a special stability, whereas in others it does not. Examples for different frames of reference are the rotational barriers of the methylene groups[40] and the conjugative stabilization[39] of TMM. In other studies, "stability" has been defined by comparison with the associated linear-conjugated dianion, and total energies, heats of formation (see ref 6 and references therein), and the possibility of charge alternation[41] were considered. Moreover, the first and second proton affinities of different Y-delocalized dianions have served as stability measures.[42]

Most of the studies mentioned above rely heavily on BSC computations for the metastable TMM dianion and possibly other unstable dianionic systems. The noteworthy exception is ref 6 where counterions were added, and electronically stable species were compared with each other. In the following paragraphs we study the *temporary* dianions of TMM and its linear-conjugated isomer BD and compare the metastable systems. Moreover, the lifetimes of the cross- and linear-conjugated dianions are relevant for comparison with the cyclic dianions considered in the previous section.

Let us begin with a brief review of the findings from BSC computations. Extensive investigations of the isolated TMM and BD at the SCF and different correlated levels of theory, but within the BSC approach, have been described in ref 6. Both systems show closed-shell electronic ground states, and in their planar D_{3h} and C_{2h} symmetrical conformations (cf. Chart 1) both species possess six π electrons. Yet, similar to CBD, TMM and BD possess pyramidalized methylene groups and nonplanar C_s and C_2 minimal energy structures, respectively. It is worth noting that TMM exhibits a relatively small deviation from planarity and that the associated energy difference between its planar and nonplanar conformation is much smaller than those of BD or CBD. From a total energy point of view TMM and BD are very close with correlation favoring BD and counterions favoring TMM.[6] From these BSC energies no definitive conclusion regarding a special stabilization or Y-aromaticity could be reached.

Because the relevant energy differences from the BSC computations are small, the level shift due to the coupling to the continuum can be decisive. We will consider four $C_4H_6^{2-}$ structures: the D_{3h} and C_s conformers of TMM as well as the C_{2h} and C_2 BD conformers. As a first step, we have recomputed the equilibrium geometries of these four species employing our compact basis set, and the obtained geometrical parameters are, as expected, in good agreement with the findings from earlier studies. From the BSC calculations it is obvious that all four systems are electronically very unstable. For both conformer pairs the three occupied π or π-like orbitals are considerably higher in energy than the σ framework orbitals, and even the lowest π(-like) orbital is only weakly bound ($\epsilon \approx -0.2$ eV). The other two occupied π/π-like orbitals show high positive orbital energies. As a second step, CAP/CI calculations were performed, and our results for the resonance energies and autodetachment lifetimes of the two isomers are collected in Table 1. Clearly, both dianionic systems TMM and BD are very short-lived. The lifetimes of the different conformers fall into a range between 1 and 3 fs, that is, between CBD and COT. TMM is predicted to be more stable and to show a longer autodetachment lifetime than BD, but the differences are not very pronounced.

Before we analyze the energy and lifetime differences between TMM and BD in more detail, let us consider the effect of the pyramidalizing distortions. For both conformer pairs the energy difference between the planar and nonplanar forms is reduced in going from BSC computations to the resonance energies at the CAP/CI level. For BD, pyramidalization has a noticeable impact, and the relaxation energy is reduced from 0.7 eV (67 kJ/mol) at the BSC/SCF to 0.53 eV (51 kJ/mol) at the CAP/CI level, similar to CBD. For TMM, the respective energy differences are much smaller, 0.22 eV (21 kJ/mol) and 0.07 eV (6.3 kJ/mol). Thus, as discussed for CDB, the deviations from planarity are overestimated at the BSC/SCF level, and at the CAP/CI level we expect equilibrium structures with less pyramidalized carbon atoms.

Regarding the relative energy of TMM and BD, the picture obtained from the BSC calculations is not greatly changed by including the coupling to the continuum, since the level shifts of the respective planar and nonplanar isomers are surprisingly similar (Table 1). Comparing the planar species, the TMM dianion shows a lower energy and a longer lifetime than does BD and is clearly more stable. Yet since TMM profits much less from a pyramidalizing distortion than does BD, the energy and lifetime differences are notably reduced in going to the nonplanar conformers. TMM is still the more stable system, but the differences are small, and electron correlation effects could easily reverse the picture. We note that in BSC type computations dynamic correlation effects have been found to

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favor BD;[6] however, in these calculations diffuse basis sets have been used that put a question mark on the obtained correlation energies.[43]

Having established that both TMM and BD are very short-lived dianions, and in view of the closeness of the two $C_4H_6^{2-}$ isomers in energy, what can be concluded regarding the notion of Y-aromaticity? We are comparing two highly unstable species whose properties are primarily determined by the large Coulomb repulsion of the extra charges, and therefore any stabilizing "aromatic" effect will be overruled by the necessity of charge separation. By investigating CBD and COT we have seen that even cyclic, clearly aromatic, dianions are short-lived and dominated by Coulomb repulsion. Thus, results for isolated dianions can tell us only very little, if anything, about closed-shell π system/low total energy correlations. (Note that the same is true for counterion stabilized systems.) Even the facts that the methylene groups of the TMM dianion do pyramidalize only very little and that the energy and lifetime differences between the planar and nonplanar TMM conformers are small are no indication of a favorable Y-delocalization. Instead, these trends can be explained by the nonbonding character of the TMM HOMO in contrast to BD where the two highest occupied π orbitals are bonding and antibonding, respectively. To study Y-aromaticity as such, we suggest neutral or singly charged species, since in isolated dianionic (and dicationic) systems aromaticity will be hidden under the long shadow of Coulomb repulsion.

6. Summary and Conclusions

We have investigated five small hydrocarbon dianions, a cyclic and a chainlike $C_4H_4^{2-}$ isomer, the COT dianion, and a branched and a chainlike $C_4H_6^{2-}$ isomer. Aromatic species are usually associated with a "special stability", for example, the ionization potential of benzene is 9.3 eV, whereas that of cyclohexene is 8.9 eV. Yet despite their aromatic character, the investigated dianionic aromatics are unstable with respect to electron loss and show surprisingly short autodetachment lifetimes of only a few fs, 3 orders of magnitude shorter than the lifetime of the carbonate dianion. Among the studied dianions BDY is clearly the most stable species showing the smallest electron detachment energy as well as the longest lifetime of $\tau = 26$ fs. The lifetimes of the other examined dianions are considerably shorter; even the COT dianion lives only 6 fs despite consisting of twice as many atoms. We conclude that experimental studies of isolated "aromatic" dianions are only possible using electron scattering or transmission techniques.

Our findings are best rationalized within the pictures established for electronically stable dianions. The properties of small dianions are dominated by the large Coulomb repulsion of their two excess charges, and at least two groups of high electron affinity that allow the localization of the two extra electrons are needed to form a "stable" system.[35,33] In view of this requirements, it is not surprising that adding two electrons to *one* delocalized π system leads to a very unstable species, since the extra electrons cannot be separated from each other. Indeed, the tendency of the very small systems CBD, BD, and, to a somewhat lesser extend, TMM to distort from planarity can be understood in terms of enhanced electron localization and separation.

Clearly, from a doubly charged ion viewpoint, putting two excess electrons into one delocalized π system, aromatic or not, will lead to a very unstable species. Consequently, for cyclic hydrocarbon and related dianions, aromaticity in the sense of possessing one delocalized π system will correlate *negatively* with stability in the sense of showing a long autodetachment lifetime. The notion that aromaticity is related to a "special stability" is thus limited to isolated neutral or singly charged species and can only be applied to doubly charged systems in a meaningful way if these are embedded in a stabilizing environment.

Finally, let us briefly comment on the BSC results obtained from bound state calculations employing compact basis sets. In particular for closed-shell dianions, BSC computations represent a useful guideline, but it is very dangerous to base quantitative conclusions on BSC results. The shortcomings of the BSC approach are best understood in terms of the Feshbach/Fano theory of resonances, where the BSC wave function defines the discrete state that will be shifted in energy and aquires a width if the coupling with the continuum is taken into account. Geometric parameters obtained from BSC computations will therefore only be meaningful if the level shift is virtually independent of the nuclear coordinates. This seems to be the case if the orbitals from which electrons can autodetach are nonbonding in character (e.g., CO_3^{2-}).[9] In contrast, BSC energy differences will in general be at best a rough guess, since the level shifts of two different systems will only be equal by chance. With increasing experience of metastable states, it may be possible to systematically set up compact basis sets that minimize these problems and can then be used to study larger species.

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