A computational study of the electron affinities of substituted Cope rearrangement transition states†

Paul G. Wenthold

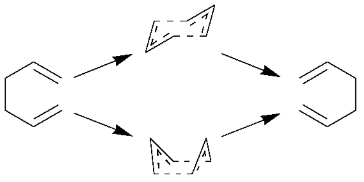
The Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA

Received (in Cambridge, UK) April 1999, Accepted 10th August 1999

The structures and properties of the negative ions of the transition states of the Cope rearrangement of hexa-1,5-diene and 2,5-dicyanohexa-1,5-diene and the negative ion of cyclohexanedione are examined at the Becke3LYP/6-31+G* level of theory. The negative ion of the hydrocarbon cyclohexane-1,4-diyl is calculated to be unstable with respect to electron detachment and with respect to ring opening. Addition of two cyano substituents results in an ion that is stable with respect to both electron detachment and with respect to ring opening, such that the Cope rearrangement has an inverted potential energy surface for the negative ion. The negative ion of cyclohexanedione is calculated to be stable with respect to ring-opening, but unstable with respect to electron detachment in the chair conformation. The ion in the boat geometry is predicted to be stable with respect to vertical electron detachment, suggesting that bicyclo[4.2.0]octa-2,5-dione will form a stable negative ion in the gas phase.

Introduction

Anyone interested in the history of physical organic chemistry is likely to be familiar with the literature on the Cope rearrangement [eqn. (1)].[1–3] The list of authors who have examined this



(1)

reaction in the nearly 60 years since it was discovered includes some of the top chemists in the field, and the elegant experimental methods one encounters illustrate the myriad of tools available for the investigation of reaction mechanisms.[4–6] Similarly, one sees the improvement of theoretical methods, beginning with semi-empirical[7,8] and small basis set self-consistent field calculations,[9,10] progressing to multireference approaches,[9,11–14] and advancing through the latest density functional theory.[15,16] Lastly, the different foci of the studies reflect the broad range of topics that are of interest to physical organic chemists, ranging from unique substituent effects[17] and variations of the Cope reactants[18,19] to engineering of potential energy surfaces.[20,21] Overall, given the extent to which the Cope rearrangement has been investigated, it is safe to conclude that the reaction constitutes an important chapter in the treatise of physical organic chemistry.

With all the interest in the Cope rearrangement in the last 60 years, it is not surprising that many of its properties are well known. For example, labeling studies in the 1970s established that the reaction pathway proceeds through a chair pathway and requires 33.3 ± 0.5 kcal mol^{-1},[6] while reaction *via* a boat pathway requires an additional 11.4 ± 2.0 kcal mol^{-1}.[22] However, the detailed electronic structures of the species involved in the reaction, especially for the chair pathway, still remain largely unsolved. Early computational studies identified two distinct singlet structures. The aromatic[16] structure is a transition state characterized by delocalized electron density and long bond-lengths between the two allylic fragments (the interallylic bond distance). The biradical structure is a stable minimum and has electron density localized on the sp^2 carbons, C^1 and C^4, and a short interallylic bond length. Recent computational results[15] find that the kinetic isotope effects for the reaction of the hydrocarbon, also measured in the 1970s,[23] are similar to those calculated for the reaction through the aromatic transition state, but not for the reaction through the biradical. This result, along with the thermochemical estimation that the heat of formation of the biradical lies 44 kcal mol^{-1} higher in energy than the hexa-1,5-diene reactant, firmly establish that the hydrocarbon undergoes a synchronous reaction[24] through an aromatic transition state.

The effect of substitution on the reaction has also been examined. The enhanced rates of the Cope rearrangement upon addition of phenyl[25,26] and cyano[27,28] substituents to the 2- and 5-positions of hexa-1,5-diene were originally interpreted as supporting a biradical for this system. However, these substituents can also stabilize the aromatic structure and therefore the rate measurements do not provide an unambiguous means for determining electronic structure.[23,29]

In principle, spectroscopy could be used to determine the electronic structures of these species. Of course, spectroscopic studies of highly reactive intermediates are not possible using conventional means. Negative ion photoelectron spectroscopy,[30] on the other hand, is a powerful tool that can be used to examine reactive organic species, including carbenes, biradicals, and transition state,[31] and could possibly be used to study intermediates and/or transition states in the Cope rearrangement. Recognizing that these studies require intense beams of negative ion precursors, Bob Squires sought to develop methods for generating these precursors of reactive intermediates in the gas phase. His insight and creativity lead to a general approach for the synthesis of these species that involved a reaction with molecular fluorine, F_2.[32] Among the negative ions generated this way were those of trimethylenemethane[33–35] and 1,2-, 1,3-, and 1,4-benzyne.[36,37] The work culminated with the measurement of the photoelectron spectra of these ions,[34,38] from which the singlet–triplet splittings and vibrational spectroscopic information for the corresponding biradicals were obtained.

---

† Optimized geometries for **1**–**6** at the Becke3LYP/6-31+G* level of theory are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/1999/2357, otherwise available from BLDSC (SUPPL. NO. 57643, pp. 13) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

Not content with only synthesizing the negative ions, Squires also sought to understand their electronic structures. In collaboration with John Nash, Squires developed a general molecular orbital description of biradical negative ions,[39] which was applied in a computational study of the benzyne negative ions. In this paper, the MO approach used by Squires is applied to the negative ions of the Cope transition states. The goal of this work is to identify those situations in which the negative ions are stable with respect to electron detachment and ring-opening, such that they could be used as precursors for negative ion photoelectron spectroscopy studies that would provide insight into the electronic structure of the Cope rearrangement transition states. These results suggest that the negative ions can be made stable by adding electron withdrawing groups at C^1 and C^4.

Computational method

All calculations were carried out at the Becke3LYP/6-31+G* level of theory using GAUSSIAN94.[40] This level of theory has been shown to give accurate electron affinities for small and medium sized molecules.[41,42] Geometries and energies were calculated for the chair and boat forms in the singlet, triplet, and ionic states. Molecules in a chair conformation were restricted to C_{2h} geometries, while those in boat conformations were restricted to C_{2v} symmetry, unless otherwise noted. Ring opened structures correspond to the closed-shell singlet in a C_{2h} geometry unless otherwise noted. Vibrational frequencies for all the ions were calculated at the optimized geometries. Relative energies are the differences in electronic energies and do not include zero-point vibrational energy corrections.

Results and discussion

In this section, the results of the calculations for three different cyclohexane-1,4-diyls are presented. For each system, the structures and energies are calculated for the singlet, triplet, and negative ion states in the chair and boat conformations. In addition, results for the ring-opened neutral and negative ion are also reported. The intermediates and transition states examined in this work are the unsubstituted and dicyanocyclohexane-1,4-diyls, and cyclohexane-1,4-dione. However, before discussing the computational results, a molecular orbital description of the electronic structure of the Cope rearrangement transition states is presented.

General considerations

The negative ions examined in this work can formally be considered to be the products of one electron reduction of the cyclohexane-1,4-diyls. Therefore, in order to understand the electronic structure of the ions, it is important to understand the electronic structure of the neutral biradicals. In this section, a molecular orbital description of the cyclohexane-1,4-diyls is provided, which can then be used as a basis for the discussion of the negative ions.

To a first approximation, the molecular orbitals for cyclohexane-1,4-diyl can be constructed from allylic orbitals as shown in Fig. 1. The electronic properties of the system most strongly depend on the $1b_u$ and $2a_g$ orbitals, which are best described as the NBMOs for the system. The $1b_u$ orbital consists of the anti-bonding combination of two bonding allyl orbitals. Occupation of this orbital gives rise to two effects. First, the electron density is evenly distributed over all the carbon atoms in this system. Second, because of the anti-bonding interaction, occupation of the $1b_u$ orbital leads to a long interallylic bond length. Therefore, this is the orbital that is responsible for the properties of the aromatic, or delocalized, transition state for the Cope rearrangement.

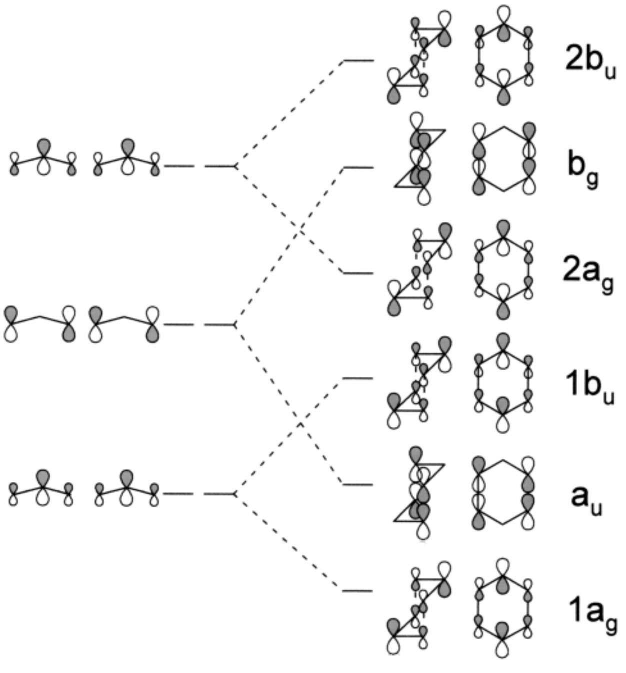


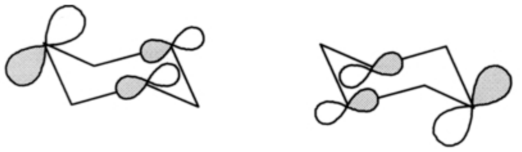
Fig. 1 Molecular orbitals for the Cope transition states created from the union of two allylic fragments.

Similarly, the biradical, or localized, intermediate of the Cope rearrangement reflects of the properties of the $2a_g$ orbital, which results from the bonding interaction of two allylic anti-bonding orbitals. The bonding interaction between the fragments results in a shorter interallylic bond distance, as has been found for that species.

If the energies of the $1b_u$ and $2a_g$ orbitals are similar, then an accurate description of the singlet requires a two-configuration wave function. The wave function for the singlet state is given by eqn. (2), where c_1 and c_2 are the CI coefficients on the $1b_u^2$ and $2a_g^2$ configurations, respectively.

$$\Psi = \frac{1}{\sqrt{c_1^2 + c_2^2}}(c_1|1b_u^2\rangle - c_2|2a_g^2\rangle)(\alpha\beta - \beta\alpha) \qquad (2)$$

If c_1 is much greater than c_2, then the $1b_u^2$ configuration dominates the wave function, and the system is best described as delocalized. If $c_1 = c_2$, then the system is an open-shell biradical, with one electron in each of the generalized valence bond (GVB) orbitals shown below.



Davidson and co-workers[14] have reported the CI coefficients for these configurations as a function of interallylic bond distance in C_6H_{10}. Near the region where the interallylic fragments are separated by 2.1 Å, which is the geometry of the delocalized system, the ratio c_2/c_1 is approximately 0.25, and the wave function is dominated by the $1b_u^2$ configuration. Near the geometry of the localized intermediate, where the interallylic bond length is ~1.7 Å, the ratio $c_2/c_1 = 0.6$, reflecting the greater diradical character for this species. The long-standing controversy regarding the nature of the Cope rearrangement transition state[23,29] results from the interplay between the CI coefficients and the transition state structure. Although it is now well established[15] that the delocalized transition state is preferred for the hydrocarbon, it is expected that substituents on the system, especially those at the 1- and 4-positions, will affect the relative energies of the $1b_u$ and $2a_g$ orbitals, and, in turn, the CI co-

Table 1 Calculated and experimental properties for singlet, triplet, and negative ion states of unsubstituted cyclohexane-1,4-diyls[a]

		interallylic bond length/Å	absolute energy/ hartrees	relative energy[b]/ kcal mol^{-1}	experimental relative energy/ kcal mol^{-1}
chair					
1s	C_{2h} ^1A_g	1.980	−234.56746	+33.4	+33.3[c]
1t	C_{2h} ^3B_u	1.551	−234.55591	+40.7	+44[d]
1$^-$	C_{2h} ^2A_g	1.629	−234.56719	+33.6	—
ring opened					
1h	C_{2h} ^1A_g		−234.62076	0.0	0.0
1h$^-$	C_{2h} ^2A_g		−234.57381	+29.5	—
boat					
2s	C_{2v} $^1A_1$	2.240	−234.55444	+41.6	+44.7[e]
2t	C_{2v} $^3B_2$	1.570	−234.54652	+46.6	+50.4[d]
2$^-$	C_2 ^2B	1.555	−234.54884	+45.1	—

[a] Calculated at the Becke3LYP/6-31+G* level of theory. [b] Relative energies do not include zero-point vibrational energy corrections. [c] Ref. 6. [d] Calculated using bond additivity; see text. [e] Ref. 22.

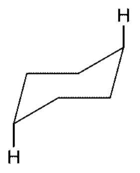
efficients. If the $2a_g$ orbital is sufficiently stabilized with respect to the $1b_u$ orbital, then the preferred structure changes from delocalized to biradical. However, the effects of substituents on the relative energies of the $1b_u$ and $2a_g$ orbitals are, for the most part, not well understood.

Occupation of these orbitals also gives rise to the other electronic states of the system. For example, the triplet biradical has one electron in each of the orbitals. As in the case of the singlet biradical, the delocalized character of the $1b_u$ cancels that of the $2a_g$ orbital, and the system is best described as a biradical with a single electron on each trivalent carbon, corresponding to cyclohexane-1,4-diyl. As described by Nash and Squires,[39] two different negative ion states are also possible. The ^2A_g state has two electrons in the $1b_u$ orbital and a singly occupied $2a_g$ orbital, while the ^2B_u state configuration is $2a_g^2 1b_u^1$. The relative energies of the two states depend on the relative energies of the orbitals involved. Davidson and co-workers[14] have reported orbital energies at different transition state geometries for the singlet state of the hydrocarbon. At all geometries examined, the $1b_u$ orbital lies lower in energy than the $2a_g$ orbital, such that the ^2A_g state will be the lower energy anion for that system.

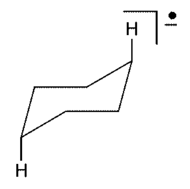
The orbitals for the C_{2v} boat conformation can be constructed in a similar manner. In this geometry, the $1b_2$ and $2a_1$ orbitals correspond to the $1b_u$ and $2a_g$ orbitals in the chair. The orbitals reduce to b and a under the C_2 symmetry of a twist-boat conformation.

Hydrocarbon

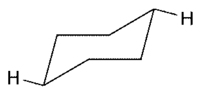
The discussion begins with the unsubstituted hydrocarbon. The calculated interallylic bond length for each species is listed in Table 1, while complete geometries and frequencies calculated at the Becke3LYP/6-31+G* level of theory are provided as supplementary data.† At this level of theory, the interallylic bond length in the singlet chair transition state, **1s**, is found to be 1.980 Å, which agrees with the values of 1.971 and 2.043 Å obtained by Wiest *et al.*[15] at the Becke3LYP/6-31G* and Becke3LYP/6-311+G* levels of theory, respectively, and 2.007 Å obtained by Jiao and Schleyer[16] at the Becke3LYP/6-311+G* level of theory. The interallylic bond lengths in the triplet and the negative ion, **1t** and **1**$^-$, respectively, are shorter than those in **1s** because these species have electrons in the a_g orbital, which prefers a shorter bond length, while the singlet does not.



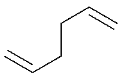
1s



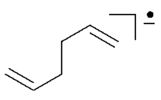
1$^-$



1t



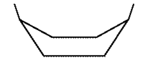
1h



1h$^-$

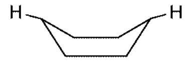
The absolute energies of **1s**, **1t**, and **1**$^-$ are shown in Table 1. This table also shows the energies of the ring-opened, C_{2h} hexa-1,5-diene, **1h**, and the C_{2h} hexa-1,5-diene negative ion, **1h**$^-$. The calculated relative energies for these species are shown in the third column of Table 1. For the cyclic geometry, the singlet state is calculated to have the lowest energy, although the energy difference between **1s** and **1**$^-$ is too small to draw any conclusions. The triplet is calculated to be *ca.* 7 kcal mol^{-1} higher in energy than **1s** and **1**$^-$. However, the lowest energy isomer for this system is hexa-1,5-diene, **1h**, which is calculated to be 33.4 kcal mol^{-1} more stable than **1s**. Moreover, although the radical anion of **1h** (**1h**$^-$) is calculated to be unstable with respect to electron detachment, it is still significantly lower in energy than **1**$^-$. Therefore, although it is possible that **1**$^-$ may be stable with respect to vertical electron detachment, it is likely to be unstable with respect to ring opening. However, vibrational analysis finds that **1**$^-$ is a minimum on the potential energy surface, such that there is a barrier for the ring opening. The ring-opened ion is also a potential energy minimum, but is unstable with respect to electron detachment.

The interallylic bond lengths of the boat forms of the singlet, triplet, and negative ion states, **2s**, **2t**, and **2**$^-$, respectively, are included in Table 1, as are the absolute and relative energies. In a C_{2v} boat conformation, the ion is found to have a single imaginary frequency, and this structure is the transition state for the interconversion of two equivalent, C_2 twist-boat structures, **2**$^-$. The C_2 ion is a stable minimum, 1.4 kcal mol^{-1} more stable than the C_{2v} triplet biradical and 3.5 kcal mol^{-1} less stable than the singlet. Therefore, the ion is predicted to be unstable with respect to vertical electron detachment to form the singlet state in addition to being unstable with respect to ring opening.



2s

2$^-$



2t

The trends in the interallylic bond lengths in the boat geometry differ slightly from those for the chair. For the chair, the bond lengths in the ion are longer than those in the triplet because the extra electron goes into the $1b_u$ orbital. This is a result of the fact that the $1b_u$ orbital is lower in energy than the $2a_g$ orbital at all interallylic bond lengths. However, in the boat the energy ordering of the $1b_2$ and $2a_1$ orbitals depends on the bond length. For long interallylic bond lengths, as in the singlet, the $1b_2$ orbital is lower in energy than the $2a_1$. For shorter bond lengths, such as those at the geometries of the ion and triplet, the $2a_1$ orbital is lower in energy than the $1b_2$. Therefore, the electronic state of the C_2 ion is ^2B, with two electrons in the a orbital and one electron in the b, and the ion prefers shorter bond lengths than in the triplet despite the fact that it is charged.

The calculated results for the unsubstituted system provide an opportunity to evaluate the reliability of the Becke3LYP approach for calculating these energies because many of the thermochemical properties are experimentally available. For example, the measured activation energies for the chair and boat pathways of the Cope rearrangement provide reasonable values for the relative energies of **1s** and **2s**. The experimental enthalpies of 33.3 ± 0.5[6] and 44.7 ± 2.0 kcal mol^{-1},[22] respectively, are in very good agreement with the computed values 33.4 and 41.6 kcal mol^{-1}, respectively. The excellent agreement for the singlet states is somewhat surprising given the qualitative MO description provided above, which suggests that a multi-reference approach should be required. However, the success of the Becke3LYP approach for the study of the Cope rearrangement has been noted previously by Wiest *et al.*[15] and by Jiao and Schleyer,[16] who obtained relative energies similar to those reported here.

The energies of the triplet states of cyclohexane-1,4-diyl can be estimated from experimental heats of formation using bond additivity methods. The enthalpy of formation can be calculated for the triplet biradical using the enthalpy of formation of cyclohexane (−29.43 kcal mol^{-1})[43] and the secondary C–H bond dissociation enthalpy of 99 kcal mol^{-1}.[43] The value obtained using this approach, 64.4 kcal mol^{-1}, is 44 kcal mol^{-1} higher in energy than that for hexa-1,5-diene (20.4 ± 0.4 kcal mol^{-1}).[43] The relative energy for the triplet calculated at the Becke3LYP/6-31+G* level of theory, 40.7 kcal mol^{-1}, is in reasonable agreement with the thermochemical estimate. The energy of the triplet state in a boat conformation should be higher than that of the chair by about the boat–chair energy difference in cyclohexane, 6.4 kcal mol^{-1}.[44] The calculated energy difference is 5.9 kcal mol^{-1}. Overall, the agreement between the calculated and experimental values listed in Table 1 is very good, indicating that the B3LYP approach gives acceptable results for these systems.

Cyano substitution

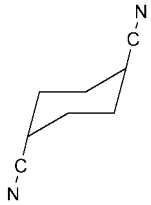
In the previous section, it was calculated that unsubstituted cyclohexane-1,4-diyl does not form a stable negative ion. The reason the ion is not stable is that the singly occupied a_g orbital is too high in energy to hold the extra electron. The energy of the a_g orbital can be decreased by adding electron withdrawing groups at the 1- and 4-positions. In this section, the effect of adding cyano substituents is examined.

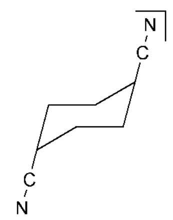
The results for the chair singlet, triplet, and negative ion states, **3s**, **3t**, and **3**$^-$, respectively, are shown in Table 2. The trend in the interallylic bond lengths for this series is similar to that found for the hydrocarbon, with the singlet bonds significantly longer than those in the triplet or anion. Again, the difference can be attributed to the properties of the b_u and a_g orbitals and the extent to which each is occupied. Compared to the unsubstituted system, the bond lengths in **3s** are significantly shortened. This effect could, in principle, result from increased contribution of the a_g^2 configuration in the two configuration wave function. Borden and co-workers have carried out CI calculations on this system and found that although the wave function is still dominated by the b_u^2 configuration[45] the a_g^2 contribution is greater than that in the hydrocarbon. This is consistent with the observation of Davidson and co-workers[14] that the CI coefficients are dependent on the interallylic bond length.

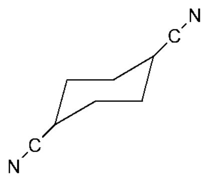
Table 2 Calculated energies for singlet, triplet, and negative ion states of dicyanocyclohexane-1,4-diyls[a]

		interallylic bond length/Å	absolute energy/ hartrees	relative energy[b]/ kcal mol^{-1}
chair				
3s	C_{2h} ^1A_g	1.756	−419.07530	+23.5[c]
3t	C_{2h} ^3B_u	1.550	−419.07866	+21.3
3$^-$	C_{2h} ^2A_g	1.598	−419.15854	−28.8
ring opened				
3h	C_{2h} ^1A_g		−419.11268	0.0
3h$^-$	C_{2h} ^2A_g		−419.13280	−12.6
boat				
4s	C_{2v} $^1A_1$	1.544[d]	−419.09724[d]	+9.7
4t	C_{2v} $^3B_2$	1.566	−419.06968	+27.0
4$^-$	C_{2v} $^2B_2$	1.550	−419.14496	−20.3

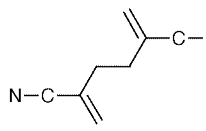
[a] Calculated at the Becke3LYP/6-31+G* level of theory. [b] Relative energies do not include zero-point vibrational energy corrections. [c] The experimental value is +23.2 kcal mol^{-1}; see ref. 28. [d] Corresponds to the bicyclic geometry. The bond length between the bridgehead carbons is 1.607 Å.

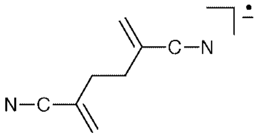

3s


3$^-$


3t

The absolute and relative energies of **3s**, **3t**, and **3**$^-$ are listed in Table 2, along with the energies for the ring opened neutral and negative ion, **3h** and **3h**$^-$, respectively. As expected, the addition of cyano substituents has significantly stabilized the negative ions. While the energy of the negative ion was similar to that of the singlet for the unsubstituted case, with cyano substituents the ion (**3**$^-$) is more stable than the singlet (**3s**) by 52.3 kcal mol^{-1}. Moreover, **3**$^-$ is also more stable than the ring-opened singlet, **3h**, and the ring-opened ion, **3h**$^-$ by 28.8 and 16.2 kcal mol^{-1}, respectively. Therefore, **3**$^-$ is calculated to be stable with respect to electron detachment and ring opening. Both **3**$^-$ and **3h**$^-$ are stable minima, as indicated by the absence of any imaginary frequencies.


3h


3h$^-$

The calculations described above predict that for the negative ion, the chair intermediate is more stable than the ring-opened species. This type of situation has been observed previously for the radical cation surfaces of hexa-1,5-diene[21] and semi-

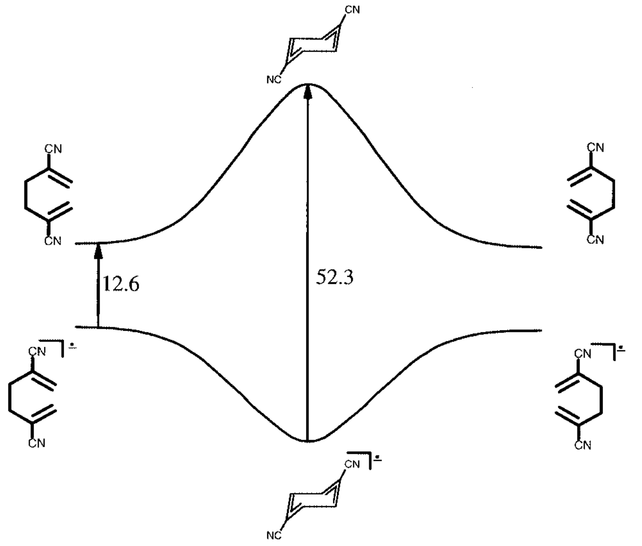
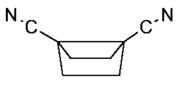


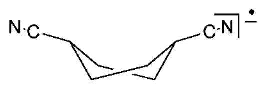
Fig. 2 Schematic potential energy surfaces for the Cope rearrangement of 2,5-dicyanohexa-1,5-diene and the corresponding negative ion. The electron affinities of the reactant and the transition state are indicated, in kcal mol^{-1}.

bullvalene,[21,46] and has been described as an "inverted potential energy surface"[21] for the Cope rearrangement. The potential energy surfaces for the Cope rearrangement of 2,5-dicyanohexa-1,5-diene and the negative ion are shown in Fig. 2. The reason for the inverted potential energy surface for the negative ion surface is that the electron affinity of the transition state (52.2 kcal mol^{-1}) is much larger than that of reactant (12.6 kcal mol^{-1}). This is analogous to the situation observed by Williams for the radical cation surface,[21] which is inverted because the ionization potential of the transition state is 63–68 kcal mol^{-1} smaller than that of the reactants.

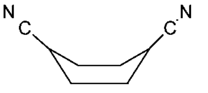
The energies and interallylic bond lengths for the boat conformations of singlet, triplet, and negative ion species, **4s**, **4t**, and **4**$^-$, respectively, are shown at the bottom of Table 2. In this conformation, the singlet, **4s**, collapses to 1,4-dicyanobicyclo-[2.2.0]hexane,[27,28] which is calculated to be only 9.7 kcal mol^{-1} higher in energy than **3h**. The C_{2v} boat negative ion is calculated to be a transition state that interconverts two equivalent C_2 forms, **4**$^-$. The C_2 twist-boat ion is more than 8 kcal mol^{-1} higher in energy than **3**$^-$, but is still stable with respect to ring opening and electron detachment. Therefore, the twist boat ion is stable with respect to electron loss and rearrangement and could be prepared as a stable species if it could be locked into that conformation.



4s



4$^-$



4t

The relative energy of the singlet dicyano transition state agrees surprisingly well with the experimental value of 23.2 kcal mol^{-1} measured by Wehrli *et al.*[27,28] for the activation energy for the Cope rearrangement of a methylated derivative. Therefore, as has been found for the unsubstituted system,[15,16] the properties of the singlet dicyano transition state are accurately calculated using a single reference method that incorporates electron correlation. Borden and co-workers have also obtained reasonable values for the activation energy of the dicyano Cope rearrangement from MP2[45] and density functional calculations.[47]

Cyclohexanedione

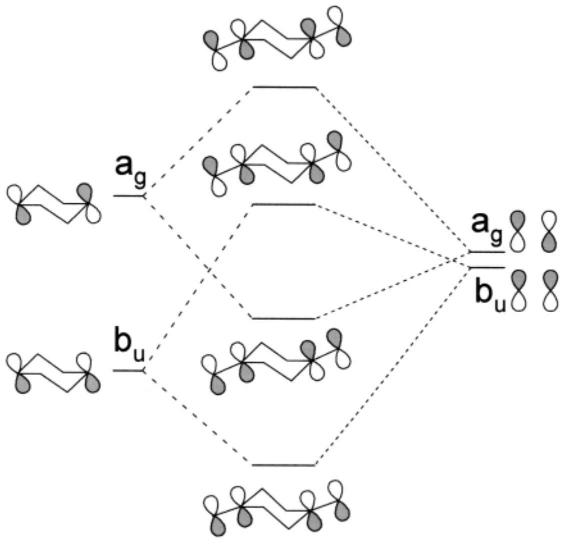
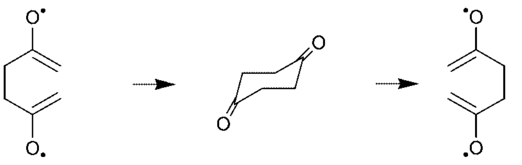


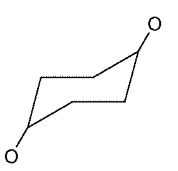
Fig. 3 Molecular orbitals created by combining the p orbitals on oxygen with the $1b_u$ and $2a_g$ orbitals in cyclohexane-1,4-diyl.

Although it is usually not recognized as such, cyclohexane-1,4-dione can be considered to be a stable intermediate for the Cope rearrangement shown in eqn. (3). In this case, an inverted potential surface for the reaction results from addition of oxygen substituents that stabilize the intermediate more than they do the reactant. The effect of the substituent on the MOs of cyclohexane-1,4-diyl is illustrated in Fig. 3. Two sets of b_u and a_g orbitals are created, corresponding to π and π* orbitals, respectively. Cyclohexanedione is a stable Cope intermediate because both the b_u and a_g orbitals are filled, while these orbitals are only half filled for the H and CN substituted transition states described above. However, although the a_g orbital is significantly more stable in cyclohexanedione than it is in **1s**, the system does not necessarily form a stable negative ion because the additional electron occupies a π* orbital. In fact, the negative ion for cyclohexanedione is a ^2B_u ion, and the singly occupied orbital is the π* b_u.

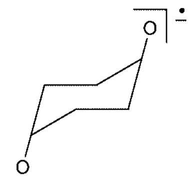


(3)

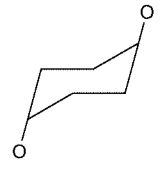
The calculated properties for the chair singlet, triplet, and negative ion states of cyclohexanedione, **5s**, **5t**, and **5**$^-$, respectively, in the chair conformation are listed in Table 3. Unlike what was found for the other systems examined in this work, the interallylic bond lengths in the singlet, **5s**, are shorter than they are in the ion and triplet. This is because the a_g orbital is doubly occupied in the singlet, while the triplet and negative ion have singly occupied b_u orbitals. Also included in Table 3 are the boat geometries, **6s**, **6t**, and **6**$^-$, respectively. As in the other systems, the energies of the $1b_2$ (b) and $2a_1$ (a) orbitals are switched at short interallylic distances. This means that the chair ion, **6**$^-$, is formed by adding an electron into



5s



5$^-$

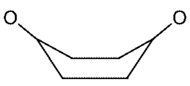


5t

Table 3 Calculated energies for singlet, triplet, and negative ion states of cyclohexanedione[a]

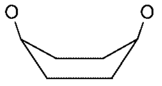
		interallylic bond length/Å	absolute energy/ hartrees	relative energy[b]/ kcal mol^{-1}
chair				
5s	C_{2h} ^1A_g	1.548	−383.91684	−70.5
5t	C_{2h} ^3B_u	1.599	−383.77454	+18.8
5$^-$	C_{2h} ^2B_u	1.612	−383.91147	−67.1
ring opened				
5h	C_2 ^3B		−383.80452	0.0
5h$^-$	C_2 ^2B		−383.89780	−58.5
boat				
6s	C_{2v} $^1A_1$	1.556	−383.90821	−65.1
6t	C_{2v} $^3B_1$	1.620	−383.76276	+26.2
6$^-$	C_2 ^2A	1.541	−383.91393	−68.7

[a] Calculated at the Becke3LYP/6-31+G* level of theory. [b] Relative energies do not include zero-point vibrational energy corrections.



6s

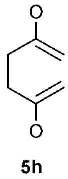
6$^-$



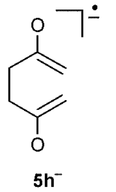
6t

the π* $2a_1$ (a) orbital. Therefore, the bond length in the ion is shorter than that in the singlet. In the C_{2v} triplet, the π* b_2 orbital is lower in energy than the π* a_1, which means that the π* b_2 orbital is occupied in that state. Therefore, the bond lengths in the triplet are longer than those in the singlet and ion.

The diene that results from ring-opening of **5s** is the biradical **5h**. For singlet **5h**, the wave function is almost purely open-shell and requires a multireference approach. Not surprisingly, attempts to calculate the geometry of the singlet using the Becke3LYP/6-31+G* method failed, and the geometry collapsed to the **5s** structure. Therefore, results for **5h** reported here correspond to the triplet state. Given that the two radical moieties are reasonably isolated in the molecule such that there is not significant interaction between them, the energies of the singlet and triplet states should not be very different. The results of TCSCF/6-31+G* calculations support this expectation, as the singlet is calculated to be lower in energy than the triplet by 140 cal mol^{-1} at this level of theory. With the Becke3LYP method, the triplet state of **5h** adopts a C_2 geometry, and the C_{2h} structure is higher in energy by 0.9 kcal mol^{-1}. The ring-opened negative ion, **5h**$^-$, also prefers a C_2 geometry that is distinct from that of **6**$^-$.

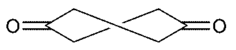


5h



5h$^-$

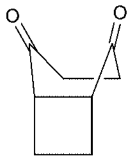
The absolute and relative energies of all the species described above are listed in Table 3. As may be expected, the singlet dione, **5s**, is the lowest energy state of the system, and is 70.5 kcal mol^{-1} more stable than the ring-opened triplet state, while the boat conformation of the dione is 5.4 kcal mol^{-1} less stable than the chair conformation. However, at this level of theory, the lowest energy conformation of cyclohexane-1,4-dione is a boat-like D_2 structure, **5s**′, which is 170 cal mol^{-1} more stable than **5s**. Allinger and Freiberg[48] predicted that **5s**′ would be similar in energy to **5s** but could not predict with confidence



5s′

which structure would be lower in energy. The present results are not sufficiently accurate to resolve this question.

The negative ion **5**$^-$ is stable with respect to ring opening by 8.6 kcal mol^{-1}, but is unstable with respect to electron detachment by 3.4 kcal mol^{-1}. Surprisingly, the twist-boat conformation of the negative ion, **6**$^-$, is 1.6 kcal mol^{-1} lower in energy than the chair, while the C_{2v} boat conformation is a transition state that is 0.1 kcal mol^{-1} higher in energy than **5**$^-$. The main result is that **6**$^-$ is lower in energy than the corresponding neutral, **6s**, although it is not lower in energy than either **5s** or **5s**′. Therefore cyclohexanedione is predicted to have a positive electron affinity near the boat geometry, which means that a molecule like bicyclo[4.2.0]octane-2,5-dione (**7**), where the system is locked into a boat conformation, should form a stable negative ion in the gas phase.



7

The triplet states of cyclohexanedione, **5t** and **6t**, are significantly higher in energy than the corresponding singlets, and, moreover, are higher in energy than the ring-opened species. Therefore, the Cope rearrangement of the triplet state does not have an inverted potential energy surface.

Conclusion

This study has involved the use of density functional theory to examine whether Cope transition states form stable negative ions. It is found that the unsubstituted hydrocarbon does not give a stable negative ion, but with cyano substituents the negative ion is the lowest energy state, stable with respect to electron loss and ring opening. The ion of the dicyano cyclohexane-1,4-diyl is stable because the singly occupied a_g orbital is stabilized by the interaction with the cyano groups. Oxygen radical substituents also stabilize the a_g orbital, but the oxygen electrons fill that orbital to give a stable intermediate, cyclohexanedione. Therefore, the negative ion of cyclohexanedione is unstable with respect to electron detachment because the extra electron occupies a π* orbital.

The results of this work suggest that negative ions of Cope reaction transition states are stable if they have substituents that stabilize the a_g orbital. Other possible substituents that would produce stable ions would be nitro, acyl, or possibly even phenyl. Studies of these ions could give direct insight into the electronic structures of the Cope transition states, and may lead to a resolution of this nearly 60 year old problem.

Acknowledgements

This research was possible because Bob Squires, my friend and mentor, taught us how to think about the electronic structures of biradicals and negative ions. His important contributions to this work, and to my life, are gratefully acknowledged. Thank you to Professor Wes Borden for sharing results of their DFT calculations prior to publication. Funding for this research was provided by the Robert A. Welch Foundation, the American Society for Mass Spectrometry, and Texas Tech University. Thanks also to the donations of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

References

1 A. C. Cope and E. M. Hardy, *J. Am. Chem. Soc.*, 1940, **62**, 441.
2 H. Levy and A. C. Cope, *J. Am. Chem. Soc.*, 1944, **66**, 1684.
3 E. G. Foster, A. C. Cope and F. Daniels, *J. Am. Chem. Soc.*, 1947, **69**, 1893.
4 W. Roth, H.-W. Lennartz, W. v. E. Doering, L. Birladeanu, C. A. Guyton and T. Kitagawa, *J. Am. Chem. Soc.*, 1990, **112**, 1722.
5 J. J. Gajewski, *Hydrocarbon Thermal Isomerizations*, Academic Press, 1981.
6 W. v. E. Doering, V. G. Toscano and G. H. Beasley, *Tetrahedron*, 1971, **27**, 5299.
7 M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.*, 1971, **93**, 7201.
8 M. J. S. Dewar, G. P. Ford, M. L. McKee, H. S. Rzepa and L. E. Wade, *J. Am. Chem. Soc.*, 1977, **99**, 5069.
9 Y. Osamura, S. Kato, K. Morokuma, D. Feller, E. R. Davidson and W. T. Borden, *J. Am. Chem. Soc.*, 1984, **106**, 3362.
10 K. N. Houk, S. M. Gustafson and K. A. Black, *J. Am. Chem. Soc.*, 1992, **114**, 8565.
11 K. Morokuma, W. T. Borden and D. A. Hrovat, *J. Am. Chem. Soc.*, 1988, **110**, 4474.
12 M. Dupuis, C. Murray and E. R. Davidson, *J. Am. Chem. Soc.*, 1991, **113**, 9756.
13 D. A. Hrovat, K. Morokuma and W. T. Borden, *J. Am. Chem. Soc.*, 1994, **116**, 1072.
14 P. M. Kozlowski, M. Dupuis and E. R. Davidson, *J. Am. Chem. Soc.*, 1995, **117**, 774.
15 O. Wiest, K. A. Black and K. N. Houk, *J. Am. Chem. Soc.*, 1994, **116**, 10336.
16 H. Jiao and P. v. R. Schleyer, *Angew. Chem.*, *Int. Ed. Eng.*, 1995, **34**, 334.
17 N. Jing and D. M. Lemal, *J. Am. Chem. Soc.*, 1993, **115**, 8481.
18 K. Black, S. Wilsey and K. N. Houk, *J. Am. Chem. Soc.*, 1998, **120**, 5622.
19 D. A. Hrovat, J. A. Duncan and W. T. Borden, *J. Am. Chem. Soc.*, 1999, **121**, 169.
20 R. Hoffman and W.-D. Stohrer, *J. Am. Chem. Soc.*, 1971, **93**, 6941.
21 F. Williams, *J. Chem. Soc.*, *Faraday Trans.*, 1994, **90**, 1681.
22 M. J. Goldstein and M. S. Benzon, *J. Am. Chem. Soc.*, 1972, **94**, 7147.
23 J. J. Gajewski and N. D. Conrad, *J. Am. Chem. Soc.*, 1979, **101**, 6693.
24 W. T. Borden, R. J. Loncharich and K. N. Houk, *Ann. Rev. Phys. Chem.*, 1988, **39**, 213.
25 M. J. S. Dewar and L. E. Wade, Jr., *J. Am. Chem. Soc.*, 1977, **99**, 4417.
26 M. J. S. Dewar and L. E. Wade, Jr., *J. Am. Chem. Soc.*, 1973, **95**, 290.
27 R. Wehrli, D. Bellus, H.-J. Hansen and H. Schmid, *Chimia*, 1976, **30**, 416.
28 R. Wehrli, H. Schmid, D. Bellus and H.-J. Hansen, *Helv. Chim. Acta*, 1977, **60**, 1325.
29 J. J. Gajewski and N. D. Conrad, *J. Am. Chem. Soc.*, 1978, **100**, 6269.
30 K. M. Ervin and W. C. Lineberger, in *Photoelectron Spectroscopy of Negative Ions*, ed. N. G. Adams and L. M. Babcock, Greenwich, 1992.
31 P. G. Wenthold and W. C. Lineberger, *Acc. Chem. Res.*, 1999, **32**, 597.
32 P. G. Wenthold, J. Hu, B. T. Hill and R. R. Squires, *Int. J. Mass. Spectrom.*, 1998, **179/180**, 173.
33 P. G. Wenthold, J. Hu and R. R. Squires, *J. Am. Chem. Soc.*, 1994, **116**, 6961.
34 P. G. Wenthold, J. Hu, R. R. Squires and W. C. Lineberger, *J. Am. Chem. Soc.*, 1996, **118**, 475.
35 P. G. Wenthold, J. Hu, R. R. Squires and W. C. Lineberger, *J. Am. Soc. Mass Spectrom.*, 1999, **10**, 800.
36 P. G. Wenthold, J. Hu and R. R. Squires, *J. Am. Chem. Soc.*, 1996, **118**, 11865.
37 P. G. Wenthold, J. Hu and R. R. Squires, *J. Mass Spectrom.*, 1998, **33**, 796.
38 P. G. Wenthold, R. R. Squires and W. C. Lineberger, *J. Am. Chem. Soc.*, 1998, **120**, 5279.
39 J. J. Nash and R. R. Squires, *J. Am. Chem. Soc.*, 1996, **118**, 11872.
40 M. J. Frisch, G. W. Trucks, H. B. Schlegal, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Kieth, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, GAUSSIAN94, Pittsburgh, PA, 1994.
41 G. S. Tschumper and H. F. Schaefer, III, *J. Chem. Phys.*, 1997, **107**, 2529.
42 J. C. Rienstra-Kirocofe, D. E. Graham and H. F. Schaefer, III, *Mol. Phys.*, 1998, **94**, 767.
43 H. Y. Afeefy, J. F. Liebman and S. E. Stein, in *Neutral Thermochemical Data*, ed. W. G. Mallard and P. J. Linstrom, Gaithersburg, MD, 20899, 1999.
44 N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 8127.
45 D. A. Hrovat, W. T. Borden, R. L. Vance, N. G. Rondan, K. N. Houk and K. Morokuma, *J. Am. Chem. Soc.*, 1990, **112**, 2018.
46 T. Bally, L. Truttman, S. Dai and F. Williams, *J. Am. Chem. Soc.*, 1995, **117**, 7916.
47 D. A. Hrovat, B. R. Beno, H. Lange, H.-Y. Yoo, K. N. Houk and W. T. Borden, *J. Am. Chem. Soc.*, 1999, submitted.
48 N. L. Allinger and L. A. Freiberg, *J. Am. Chem. Soc.*, 1961, **83**, 5028.

Paper 9/03223A