

A case study of antiaromaticity: carbomethoxy cyclopropenyl anion

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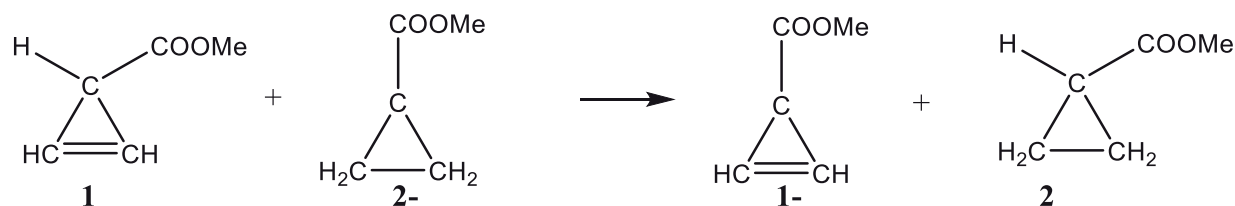
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Abstract: The simplest ideas of antiaromaticity refer to regular monocyclic systems and the eigenfunctions of the Hückel Hamiltonian for $4n$ π electrons in such systems. The antiaromaticity is expressed in the energy penalty for such idealized systems relative to the Hückel energy for $2n$ noninteracting π pairs. Observed systems seldom achieve the regular planar geometry assumed in this picture, owing to their ability to ease the antiaromaticity penalty by departures from the regular geometry and also by export of the $4n$ π electrons' charge to substituents. In this report we estimate numerical values for the stabilization derived from such departures from the structure and the charge distribution of the idealized antiaromatic cyclopropenyl anion for a specific case, 3-dehydro-3-methyl carboxylate cyclopropenyl anion **1**(⁻) using the thermochemical scheme CBSQB3 supplemented by CCSD(T) calculations. According to the isodesmic reaction, the anion **1**(⁻) is destabilized by about 10–15 kcal/mol relative to the saturated 3-dehydro-3-methylcarboxylate cyclopropyl anion **2**(⁻). We propose that the anion relieves a portion of the antiaromatic destabilization by (a) pyramidalization of one carbon of the ring, and (b) export of negative charge into the ester substituent. Both of these responses are expressed in the equilibrium structure of the anion. In the course of the study we estimate the acidity of several related anions and the enthalpy of formation of their neutral conjugate acids, and describe the interconversion of **1** to the dehydrotrifulvalene anion **3**(⁻) by reaction with CO_2 .



Key words: Antiaromaticity, monocyclic system, cyclopropenyl anion, isodesmic reaction, homoisodesmic reaction, triafulvenone, cycloheptatrienyl anion, CBSQB3, CCSD(T)

1. Introduction

Aromaticity is an organizing principle in chemical theory that is associated with a number of interrelated properties of molecules.^{1,2} These properties generally depart from what might be expected from compounds composed of localized pair bonds, that is, distinct bond lengths characteristic of single, double, and triple connections; simple additive representations of molecular properties including enthalpy and magnetic susceptibility; and reactivity and spectra attributable to the behavior of local features (functional groups and chromophores). The notion of aromaticity is rooted in the study of conjugated unsaturated monocyclic planar hydrocarbons, but

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the idea has been generalized to include three-dimensional systems, molecules with atoms other than H and C (both main-group and metals), and rings with nominally saturated centers. It is closely associated with another idea, that of delocalization, which has subtleties of its own.³

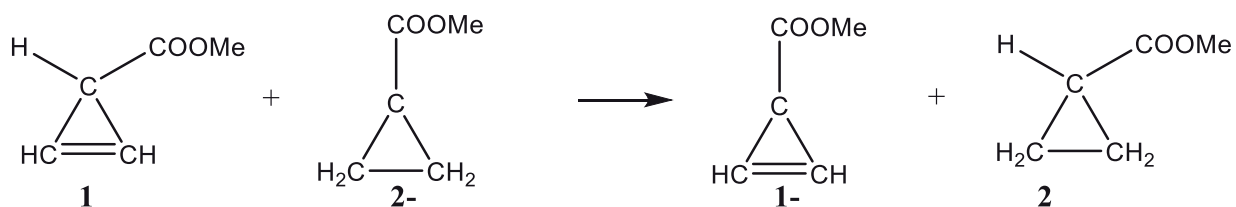
One task of chemical theory is to express useful intuitive notions in quantitative and measurable (or at least computable) ways. Even the most careful efforts to make the concept of aromaticity rigorous in such senses have not been unambiguously successful. The most immediate energetic criteria (enthalpies of formation or hydrogenation) require choice of a reference system. Definition of energies for “homoisodesmic” reactions⁴ helps to isolate the strain energy (itself elusive of definition^{5,6}) from the stabilization energy associated with delocalization, called the resonance energy (RE).⁷

Measures of bond length uniformity define an index called the harmonic oscillator model of aromaticity (HOMA) and the expression of delocalization provided by the chemical shielding tensor provides a basis for the nucleus independent chemical shift (NICS) criterion for aromaticity and its counterpart antiaromaticity, first systematically discussed by Breslow.^{8,9} A study of the mutual correlation of RE, HOMA, and NICS indices in a series of systems for which strain was not a complicating issue suggested that while these quantities were all successful in sorting molecules into the categories aromatic, nonaromatic, and antiaromatic, they showed little mutual correlation within those categories.¹⁰

The notion of aromaticity was deepened by the work of Shaik et al.¹¹ Rather than attributing aromaticity to a tendency toward delocalization in the π system, these investigators showed by valence-bond modeling that π systems favor localization into two-center bonds, while the sigma systems drive bond-length equivalence. It seems that once the sigma system forces a ring into the proper geometry the π system is then capable of delocalization and its consequence, the stabilization called aromaticity. Much later Pierrefixe and Bickelhaupt were able to explain this behavior in the LCAO-MO context.¹²

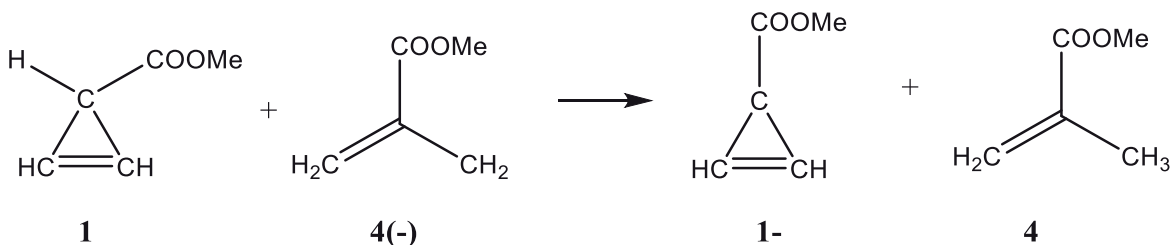
Antiaromaticity would seem to be the opposite face of aromaticity, but the possibilities for molecules to evade energy penalties cloud the discussion.¹³ Rings obeying the Hückel $4n+2$ criterion for delocalization and aromaticity are planar with uniform bond lengths, but $4n$ rings that would be classed as antiaromatic can adopt lower symmetry structures (cyclooctatetraene buckles; cyclobutadiene assumes a rectangular shape) or maintain symmetry only in excited singlet or triplet states.^{14,15} Even cyclopropenyl anion assumes a geometry (C_s -symmetric with a strongly pyramidalized anionic carbon center) that minimizes interaction between the C=C π bond and the carbanionic lone pair according to the analysis by Glukhovtsev et al.¹⁶ In principle (and in modeling¹⁷) electron-withdrawing substituents can further reduce destabilization of $4n$ electron systems, as recognized already by Breslow.^{8,9} Isolation of the antiaromatic portion of destabilization of a $4n$ electron system can be further complicated by the (likewise nonobservable) change in strain energy.¹⁸ Thus the resultant destabilization for an existing $4n$ electron system can be generally smaller than the stabilization enjoyed by a $4n+2$ electron system. To characterize antiaromaticity we will rely on the time-honored device of referring to idealized systems. This is familiar from molecular mechanics, which takes a strain-free system with electrostatic interactions as the zero-energy reference point; group additivity methods, which take noninteracting fragments as the reference point; the Hückel model, which begins with identical interactions between adjacent π centers; and the hierarchy of isodesmic reactions, which incorporate a zeroth order assumption that similar fragments have like energy in various molecules, a “transferability” assumption. In this case, we choose as a reference planar species for which the destabilization from π interactions is fully expressed. Then we can see clearly how real systems evade this destabilizing influence.

Thermochemical data bearing on antiaromaticity can only be recovered from experimental data, which of necessity refer to molecules at their equilibrium geometries. In such cases rings can be nonplanar and the $4n$ electrons need not be confined to the ring. The antiaromatic penalty relative to the ideal ring system is thus minimized and obscured. In this work we will recover the full antiaromatic penalty for the carboxylate-substituted cyclopropenyl anion **1**(⁻) studied experimentally by Sachs and Kass.¹⁹ They describe the gas phase reaction shown in Reaction 1 below.



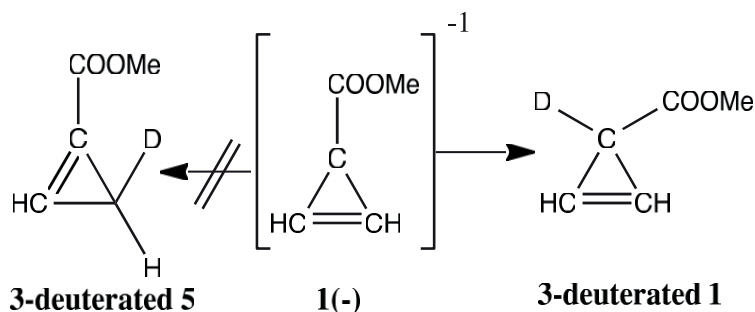
Reaction 1. Isodesmic reaction for production of antiaromatic anion **1**(⁻) from saturated anion **2**(⁻).

Here species **1** and **2**(⁻) form **1**(⁻) and **2**, intended to capture the destabilization associated with the four π electrons confined to the cyclopropenyl anion ring. Their assumption seems to be that the difference in sigma strain between **1** and **2** is comparable to the difference in strain between **1**(⁻) and **2**(⁻). Then the change in strain for the reaction is minor, and the energy of the reaction can be attributed to the π system. Sachs and Kass¹⁹ also describe the reaction in the scheme Reaction 2, which bears on the destabilization of the cyclopropenyl anion; this reaction employs methyl methacrylate **4** and its conjugate base **4**(⁻), each of which has much less strain energy than the corresponding small ring species.



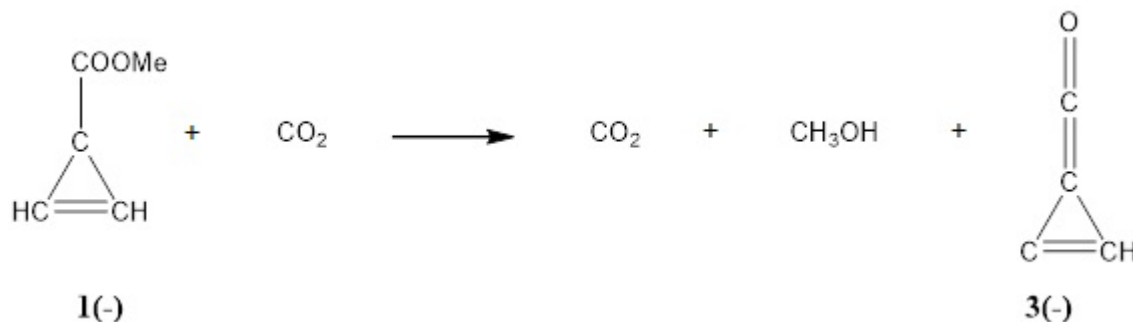
Reaction 2. Alternative production of **1**(⁻) from **1** and unstrained **4**(⁻).

Sachs and Kass¹⁹ studied deuterium exchange for species **1** and found that protonation produced species 3-deutero-3-methylcarboxylatecyclopropene (3-deuterated **1**) rather than 3-deutero-1-methyl cyclopropenecarboxylate (3-deuterated **5**), as shown in Reaction 3 below. This suggests the anionic charge is located on the site of ester substitution.



Reaction 3. Preferred site of protonation of **1** is at the site of methylcarboxylate substitution.

Sachs and Kass¹⁹ studied the reaction of anion **1**(-) with CO₂ and concluded that the dehydrotriafulvalene anion **3**(-) was the dominant product, as shown in Reaction 4.



Reaction 4. Production of 3-dehydrotriafulvalene from cyclopropenyl methylcarboxylate.

They recommended consideration of a “symmetric cyclic anhydride intermediate” that accommodates their observation that 15%–20% of the isotopic label in ¹³CO₂ was incorporated in the dehydrotriafulvalene anion product **3**(-).

By computations of enthalpy changes for Reactions 1 and 2, we will provide independent estimates of the thermodynamic properties of cyclopropenyl and cyclopropyl anions. We will also evaluate the relative enthalpies of the alternative products of protonation shown in Reaction 3. With these results and comparative studies on cyanosubstituted derivatives we can describe the twofold response (by geometric distortion and charge export) of the anion 3-dehydro-3-cyclopropenyl methyl carboxylate **1**(-) to the stress derived from the presence of four π electrons in its three-membered ring. Finally we will sketch the reaction profile for Reaction 4, following a mechanistic suggestion by Sachs and Kass.¹⁹

2. Results and discussion

2.1. Computational methods

We use the CBSQB3²⁰ scheme for thermochemical calculations, as implemented in Gaussian software.²¹ This method includes a geometry optimization and verification of its character (be it an energy minimum, a saddle point, or a maximum in two or more dimensions). The sequence of basis sets used in the extrapolation, which include diffuse members, allows a reasonable treatment of anions, as attested by the accuracy of electron affinity values observed for this method.^{22–24}

We compare the CBSQB3 results to structures and energy values obtained by CCSD(T)/cc-pVTZ//MP2/cc-pVTZ calculations, with zero-point vibrational energies and thermal corrections evaluated in MP2/cc-pVTZ. To estimate the impact of diffuse functions on the energetics, we also conduct CCSD(T)/aug-cc-pVTZ single-point calculations for the structures defined by MP2/cc-pVTZ optimization.

2.2. Structures

Structures, energies, and selected internal coordinates for species participating in Reactions 1 and 2 are collected in Figure 1. (Reaction 4 is discussed separately, below.)

The neutral structures shown in Figure 1 are unsurprising: cyclopropenyl methylcarboxylate (**1**) and cyclopropyl methoxycarboxylate (**2**) are both C_s-symmetric with the ester fragment lying in a plane that bisects

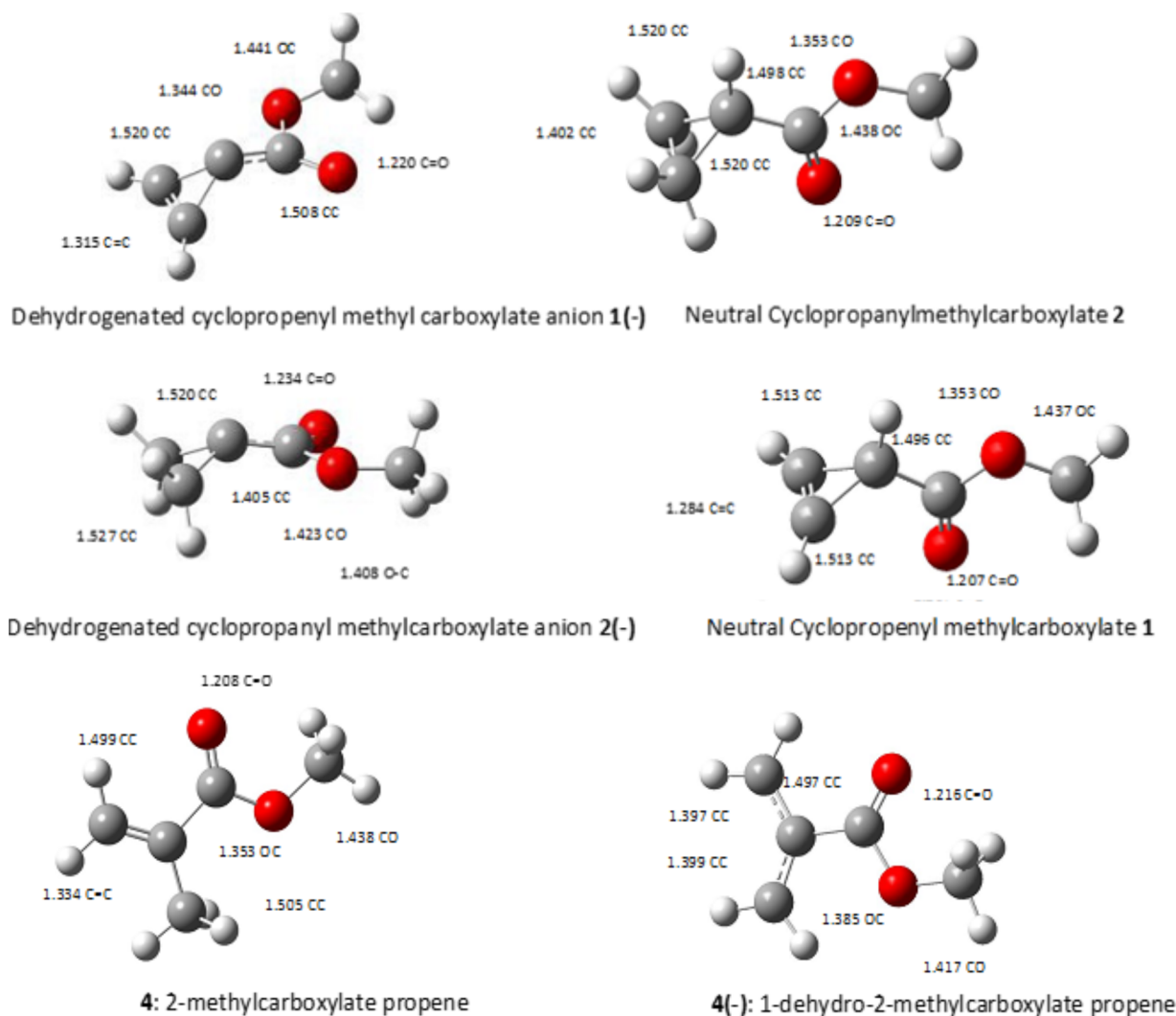


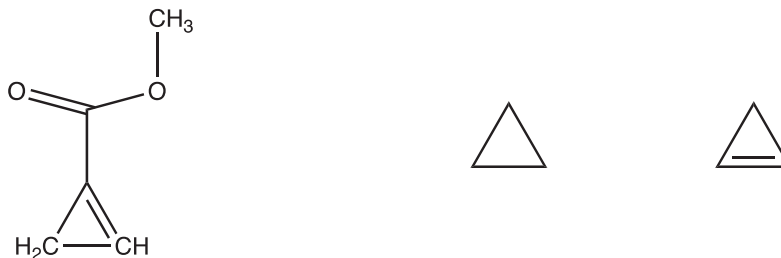
Figure 1. Structures of species taking part in Reaction 1. The bond lengths are in Ångströms.

the three-carbon ring. The O=C–O–Me fragment assumes the *cis* conformation and the carbonyl is *syn* to the 3-membered ring. Removing the proton at the 3 (ester-substituted) position leaves the pyramidal anions dehydro cyclopropenyl methylcarboxylate **1(-)** and dehydro cyclopropyl methoxycarboxylate **2(-)**. Upon deprotonation, the ester fragment rotates, breaking C_s symmetry so that the lone pair formerly confined to the ring can be delocalized toward the carbonyl π^* local MO. Accordingly the C=O bond length increases in the cyclopropyl system, from 1.212 to 1.234 Å. Open chain analogues to **1** and **1(-)**, 2-propenyl methylcarboxylate **4**, and dehydro 2-propenyl methylcarboxylate **4(-)** are also shown in Figure 1. We describe the acidity and proton affinity of these species below.

2.3. Acidities and proton affinities

The gas phase basicity and proton affinity (PA) of a molecule M are both defined in terms of the hypothetical reaction $M + H(+) \rightarrow MH(+)$. The gas phase basicity is the negative of the Gibbs energy associated with this reaction, while the proton affinity is the negative of the corresponding enthalpy change.²⁵ Sachs and Kass¹⁹ bracketed the acidity of **1** from experimental data, arriving at an estimate of 391 ± 4 kcal/mol, and estimated

the acidity of the saturated analogue **2** as 377 ± 4 kcal/mol. The thermochemical scheme CBSQB3 produces free energy changes agreeing closely with these estimates, as shown in Table 1. We also include related structures **5**, **6**, and **7**, shown below.



Species **5**: cyclopropenyl-1-methylcarboxylate

6

7

Table 1. Thermodynamic parameters for reactions of species in Reactions 1–3 (kcal/mol).

Species	Bracketed	CBSQB3	CBSQB3	MP2/TZ	CCSD(T)/TZ ^b	CCSD(T)/ATZ ^c
	acidity ^a	acidity	PA	PA	PA	PA
1: 1(-)	391 ± 4	390	395	399	400	394
2: 2(-)	377 ± 4	379	376	385	388	383
3: 3(-)	343 ± 3	349	352	356	358	352
4: 4(-)	NA	378	383	386	390	
5: 5(-)		358	363			
6: 6(-)		406	412			
7: 7(-)		414	419			

^aExperimentally derived values from Sachs and Kass¹⁹, ^bcc-pVTZ basis, ^caug-cc-pVTZ. Acidity is obtained as the difference between computed G functions plus the TΔS corrected estimated by use of the Sackur–Tetrode entropy for H⁺.

This enhances our confidence in the accuracy of CBSQB3 thermochemistry. We include estimates of acidity for species **3(-)** and **5(-)**. Comparison may be made with the substantially larger acidities and proton affinities of cyclopropane **6** and cyclopropene **7**; the effect of substitution is substantial. We obtained alternative proton affinities by computing MP2/cc-pVTZ structures, zero point energies, and thermal corrections. Retaining the MP2 ZPEs and thermal corrections and using the MP2 geometries, we conducted single-point calculations with the CCSD(T)/cc-pVTZ and CCSD(T)/aug-cc-pVTZ models. The resulting estimates of proton affinities, as shown in Table 1, are close to the CBSQB3 values. The augmented basis set improves enthalpies of protonation by about 5 kcal/mol.

2.4. Reaction energies

Enthalpy changes for Reactions 1–3 are collected in Table 2. The estimate for ΔH for Reaction 1 of 14 ± 6 kcal/mol derived from acidity bracketing agrees closely with the CBSQB3 estimate of ΔH, and the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ and CCSD(T)/cc-pVTZ//OLYP/cc-pVTZ values of ΔE (electronic) with ZPE and thermal corrections are consistent with the thermochemical estimates. Our calculations overall put the enthalpy

change for the reaction in the range 12 to 16 kcal/mol. Estimates for Reaction 2 are a bit smaller than the value 14 kcal/mol adopted by Sachs and Kass.¹⁹

Table 2. Thermodynamic parameters for Reactions 1–3 (kcal/mol).

	CBSQB3 ^a	MP2 ^b	CCSD(T)//MP2 ^b	Sachs and Kass ^c
$\Delta H(\text{RX1})$	12	14	12	14 ± 6
$\Delta H(\text{RX2})$	12	13	10	14 est.
$\Delta H(1-5)^d$	-3.9	-6.5	-5.5	NA

^aEnthalpy changes, ^bvalues are electronic energy differences computed with the cc-pVTZ basis set, ^cSachs and Kass,¹⁹

^denthalpy difference for the process Species 5 to Species 1.

Protonation of anion **1**(-) produces neutral species **1** rather than the alternative species **5**, as shown in Reaction 3. The protonation occurs at the site with the substituent methyl carboxylate. CBSQB3 enthalpy values cited in Table 2 show that **5** is about 4–6 kcal/mol less stable than **1**. The equilibrium ratio of concentrations of **5** to the concentration of **1** should be the Boltzmann factor, $\exp(-4000/RT)$ or about 1 part per thousand.

2.5. Enthalpies of formation by atomization

One straightforward way to estimate gas phase enthalpies for formation of a species is to calculate its energy of atomization. Then with experimental values of enthalpies of formation of atoms, one can infer the enthalpy of formation of the molecule in question. Using CBSQB3 values and the experimental data quoted in Table 3 we obtain the values appearing in Table 4.

Table 3. Experimental enthalpies of formation (kJ/mol: 298 K).

Species	Cyclopropane	Cyclopropene	Methyl acetate	Methane	Ketene
$\Delta H(\text{formation})$	53.3 ± 0.6	277 ± 3	-410^a	-74.6 ± 0.3	49.6 ± 0.9^c
Species	Propylene	Formaldehyde	Ethylene	Acetonitrile	
$\Delta H(\text{formation})$	20.4 ± 1	-109.0 ± 1.8^b	52.5 ± 0.5	74.0 ± 0.4	

^ano error reported in the NIST webbook;²⁶ alternative estimate from enthalpy of formation of liquid and enthalpy of vaporization produces -413 ± 2 kJ/mol. ^bExperimental values from da Silva et al.²⁷ and Ruscic et al.²⁸ ^ccited value is from NIST; CBSQB3 yields -51.1 kJ/mol

For comparison, we quote values obtained by the group additivity method of Benson^{29,30} as extended by Verevkin et al.³¹ and Cohen.³² Results for species **4** can be compared with the experimental values appearing in the NIST database.²⁶ Two such values are reported in the NIST webbook²⁶ for methyl methacrylate, -348.7 kJ/mol and -342.3 kJ/mol. The CBSQB3 result for methyl methacrylate, -347.2 kJ/mol, is consistent with experimental values. Notice that cyclopropene is a weaker acid at the allylic position than cyclopropane by 7 kJ/mol (PA values are 419 and 412, respectively). CN substitution shifts that difference to 10 kJ/mol (PA values are 386 and 376 kcal/mol, respectively) and ester substitution increases the difference to 19 kJ/mol (PA values are 395 and 376, respectively).

Table 4. Enthalpies of formation (neutrals) by CBSQB3 atomization, isodesmic reactions, and group additivity, all in kJ/mol; proton affinities in kcal/mol for consistency with literature usage.

Neutrals (HB)	$\Delta H(f)$ Atom'n	$\Delta H(f)$ Isodesmic	$\Delta H(f)$ GAM	PA ^a
2-Methylcarboxyl-cyclopropene (MCE) 1	-89	-89	-79	395
Methylcarboxyl-cyclopropane (MCA) 2	-319	-312	-319	376
Trifulvalene (TFV) 3	360	347 ^b ; 364 ^c	354	352
Methyl methacrylate (MMA) 4	-347	-344	-336	383
Cyclopropane (CPA, 6)	53		51	412
Cyclopropene (CPE, 7)	286		280	419
Cyano-CPA (CA, 8)	191	185	159	376
3-Cyano-CPE (CE, 9)	419	405	406 ^d	386

^aPA= H(HB)-H(B-), ^bfrom Reaction 5d, ^cfrom Reaction 5e, ^dGAM (group additivity method) calculations rely on data from Hess et al.,³³ Winkelhofer et al.,³⁴ and Li et al.³⁵ The group additivity method (GAM) calculation for trifulvalene uses a ring strain contribution of 225 kJ/mol from Benson et al.,^{29,30} and the group value for Cd-H(Cd)(Cd) from Verevkin et al.³¹ and introduces a value for Cd=(CO) to reproduce the gas phase enthalpy of formation of ketene according to $\Delta H_f(\text{ketene}) = \text{Cd}=(\text{CO}) + \text{H}_2\text{Cd}-\text{Cd}$, the latter term already known.^{29,30} ^eC-H(C_d)₂(CN) is not available; we used C-H(C_d)₂(CN) where C_d is an sp² carbon and C is an sp³ carbon.

2.6. Enthalpies of formation by isodesmics

We can estimate the enthalpies of formation of neutral species in the gas phase according to the CBSQB3 enthalpies for the reactions shown in the schemes Reactions 5a-5d.

The necessary experimental data associated with structures of Reaction 5 appear in Table 3. Values are from the NIST webbook,²⁶ except as noted.

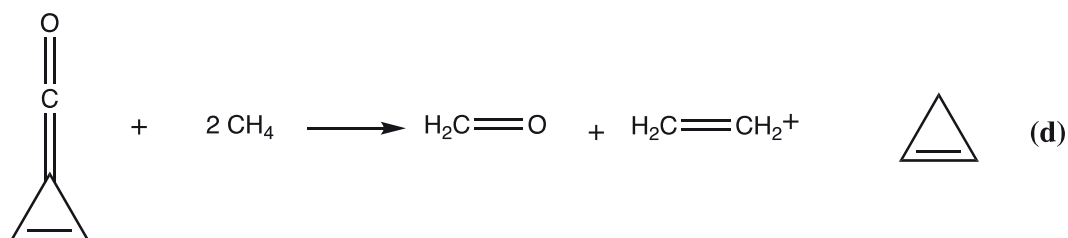
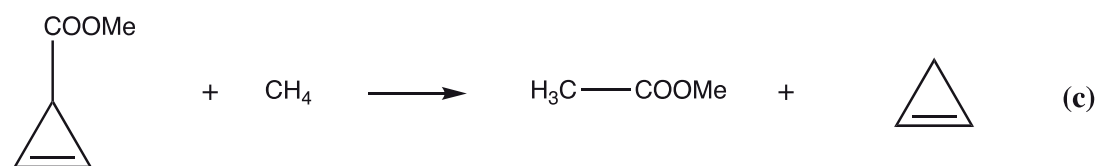
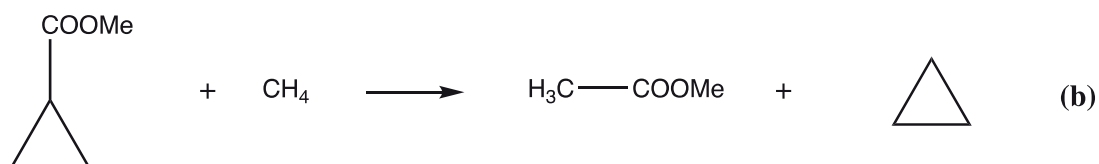
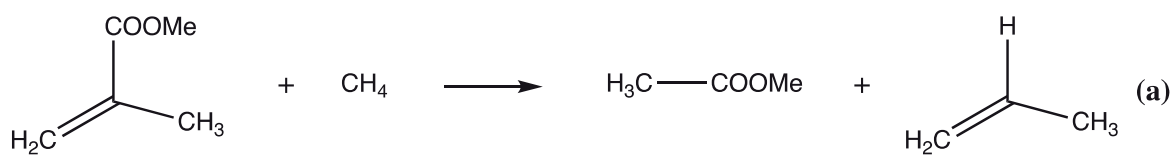
Values inferred for the species at issue are listed in Table 4: enthalpies for the anions can then be obtained from the proton affinities already in hand. Values derived from isodesmic reactions are largely consistent with the estimates from atomization energies. Merrill and Kass¹⁷ compute values of proton affinities for cyclopropenyl anion ranging from 412 to 422 kcal/mol and for cyanocyclopropenyl anion ranging from 379 to 388 kcal/mol. The differences have a narrower range, from 33.5 to 34.7 kcal/mol.

2.7. Destabilization arising from antiaromaticity

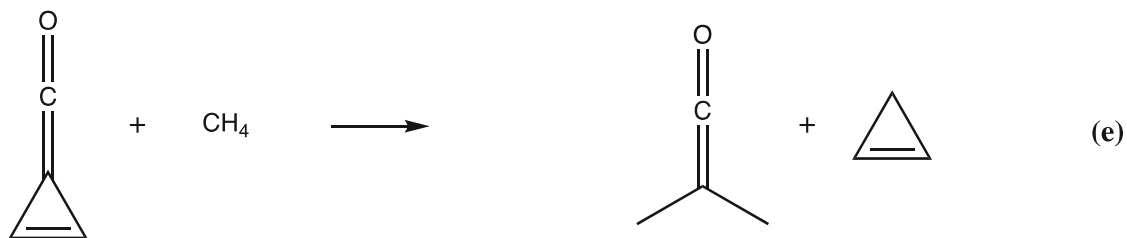
As we showed above, the detailed structures of these species show that (a) the conjugate base **2** anion is strongly pyramidalized at the substituted site; (b) the bond lengths of the three-membered ring are far from uniform in length; and (c) a substantial portion of the charge is exported from the three-membered ring to the ester substituent.

All these departures from the ideal structure with an equilateral ring and overall planarity are ways to reduce the destabilizing effect associated with antiaromaticity. We will illustrate these points by calculations on the parent cyclopropene and cyclopropane rings and their conjugate bases, as well as these rings with the electron-withdrawing cyano substituent.

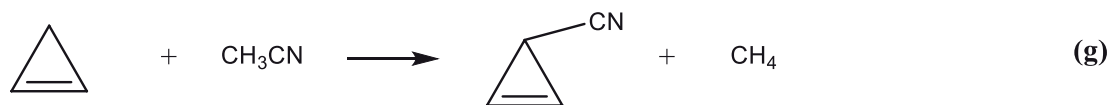
These and similar systems have attracted the attention of many investigators.^{15,17,33-47} Among the confirmed results are (i) the experimental elusiveness of the cyclopropenyl anion and (ii) the nonplanar structure of the ion.



An alternative isodesmic reaction for triafulvenone is 5e:

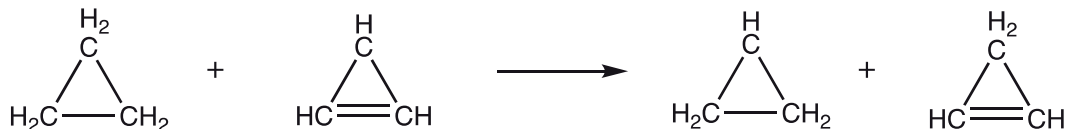


The cyano-substituted cyclopropane and cyclopropene can be obtained from the reactions 5 f and g



Reaction 5. Schemes a–d represent the isodesmic formation reactions of sample substituted species; scheme 5e is an alternative isodesmic reaction for triafulvenone; schemes 5f and 5g are the formation reactions for the cyano-substituted cyclopropane and cyclopropene, respectively.

If we are to develop an estimate of the destabilization associated with the four electron cyclic systems we must somehow isolate the effects of geometric distortion and charge transfer from the total reaction energy. We address this task first by considering the parent ring in Reaction 6.

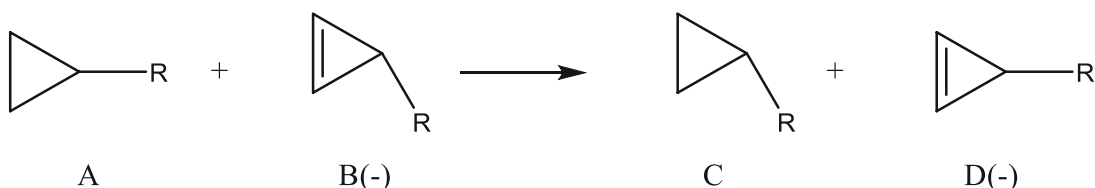


Reaction 6. Isodesmic reaction for production of cyclopropenyl anion.

Glukhovtsev et al.¹⁶ used G2 thermochemistry to evaluate the enthalpy change for this reaction, reporting $\Delta H = +4.1$ kcal/mol. Our value from CBSQB3 is 7.0 kcal/mol for the geometry-optimized cyclopropenyl anion. By this measure the cyclopropyl anion is energetically preferred to the cyclopropenyl anion. Forcing D_{3h} symmetry on the cyclopropenyl anion incurs an enthalpy penalty of 30.5 kcal/mol; the net 37.5 kcal/mol enthalpy change suggests that the relative stability of the cyclopropenyl anion is entirely due to the opportunity to pyramidalize an anionic center. The destabilization is substantially larger than the G2 enthalpy value of destabilization of cyclobutadiene upon forcing D_{4h} symmetry, 30.8 kcal/mol.¹⁶

Of course the high-symmetry forms of the cyclobutadiene and cyclopropenyl anion are not even local minima and would not have a meaningful lifetime. The symmetric forms are serving as reference structures in which the π interaction is most pronounced, for better (in the aromatic $4n+2$ case) or worse (in the $4n$ antiaromatic case). Following the well-established practice of using hypothetical systems as references we use these ideal structures to estimate the limiting value of antiaromatic destabilization. One may well object that the energy difference between a D_{3h} cyclopropenyl anion and the equilibrium C_s pyramidal form must include a change in strain energy as a carbon environment changes from trigonal planar to a pyramidal form. We can address this issue by defining an isodesmic reaction shown in the scheme Reaction 7 in which the strain energy is largely canceled.

Here a planarized cyclopropyl anion (A) and a pyramidal cyclopropenyl anion (B) are transformed to a pyramidal cyclopropyl anion (C) and a planar cyclopropenyl anion (D).

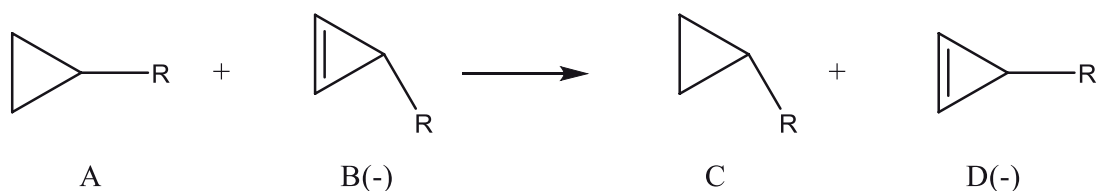


Reaction 7. An isodesmic reaction for which ring strain tends to be canceled.

For the parent ($R=H$, with the planarized anion forced to D_{3h} symmetry) the CBSQB3 enthalpy of the reaction is 19.4 kcal/mol (Table 5). This is an estimate of the total antiaromaticity penalty for planarizing the cyclopropenyl anion, roughly independent of the change in strain energy. The strain energy portion of the total 37.5 kcal/mol cost for planarization and symmetrization, ca. 17 kcal/mol, is similar in magnitude to the π -antiaromaticity penalty (that is, the difference between the total energy penalty and the change in strain energy, ca. 20 kcal/mol).¹

Reaction 8 is the analogy to Reaction 6, illustrating the impact of a single CN substituent. The CBSQB3 enthalpy change for Reaction 8 is 9.5 kcal/mol.¹

¹ The analogous exercise for the cycloheptatrienyl anion systems with eight π electrons in the reference system and the planar



Reaction 8. The isodesmic reaction analogous to Reaction 6, with CN substitution.

Planarization of cyano-substituted cyclopropenyl anion **9(-)** requires 17 kcal/mol and so the total cost for production of planar **9(-)** through Reaction 8 and planarization becomes 26 kcal/mol. The antiaromaticity penalty obtained by the isodesmic Reaction 7 with R = CN is 9.7 kcal/mol, and the inferred strain energy change would be about 17 kcal/mol. For the methylcarboxylate substitution the CBSQB3 enthalpy change for Reaction 7 becomes 14 kcal/mol. For anion **1(-)** the penalty for planarization is only 1.1 kcal/mol and so the total cost of producing planar **1(-)** is reduced to about 15 kcal/mol. The antiaromaticity penalty according to Reaction 7 with R = -COOMe is only 1.0 kcal/mol and so in this case the strain energy attending planarization is about 14 kcal/mol.

Table 5. Energetics of Reaction 7 (kcal/mol).

Enthalpy	Planar cyclopropyl A	Pyramidal cyclopropenyl B	Pyramidal cyclopropyl C	Planar cyclopropenyl D	$\Delta H(\text{RX})$
R=H	-116.947173	-115.711771	-116.971725	-115.65638	19.4
R=CN	-209.139626	-207.888433	-209.151332	-207.861190	9.7
R=COOMe	-344.592458	-343.325325	-344.592592	-343.323547	1.0
Gibbs energy	Planar cyclopropyl A	Pyramidal cyclopropenyl B	Pyramidal cyclopropyl C	Planar cyclopropenyl D	$\Delta G(\text{RX})$
R=H	-116.974834	-115.741493	-117.000292	-115.683730	20.3
R=CN	-209.171145	-207.921913	-209.184424	-207.893360	9.6
R=COOMe	-344.630457	-343.366668	-344.633884	-343.362747	0.31

The decline in planarization penalty and the decrease in the barrier to planarization upon substitution by an electron-withdrawing agent can be understood as a consequence of enhanced export of the ring charge in the planar form. The banishment of charge from the ring relieves the antiaromaticity penalty. This behavior is also seen in methylcarboxyl substituted cyclopropenyl anion. The graphs of local ionization potential (Figure 2) show that labile charge (in red, situated at the 3-carbon of the cyclopropenyl ring) is delocalized by substituents. A balance is struck between stabilization by charge export and by pyramidalization, since the export is more complete in the planarized form. The reddest regions representing the most easily removed charge are localized on the ring in the pyramidalized form, relocated to the substituent in the planarized form.

We notice that the pyramidalization angle increases (in our convention, it is 180 for the planar form) and the system becomes more nearly planar as the amount of charge exported from the ring increases. The Weinhold natural atomic charges^{48,49} reported in Gaussian 09 are recorded in Table 6. For the acyl cyclopropenyl anion, export is nearly complete; the cyano substituent is less effective than the ester.

anion forced to D_{7h} symmetry yields 1 kcal/mol. Planarization of $C_7H_7(-)$ requires only 2 kcal/mol if the ring is allowed to assume distinct bond lengths, but a total of 10.5 kcal/mol if equal bond lengths are enforced. Of this total essentially all is strain energy.

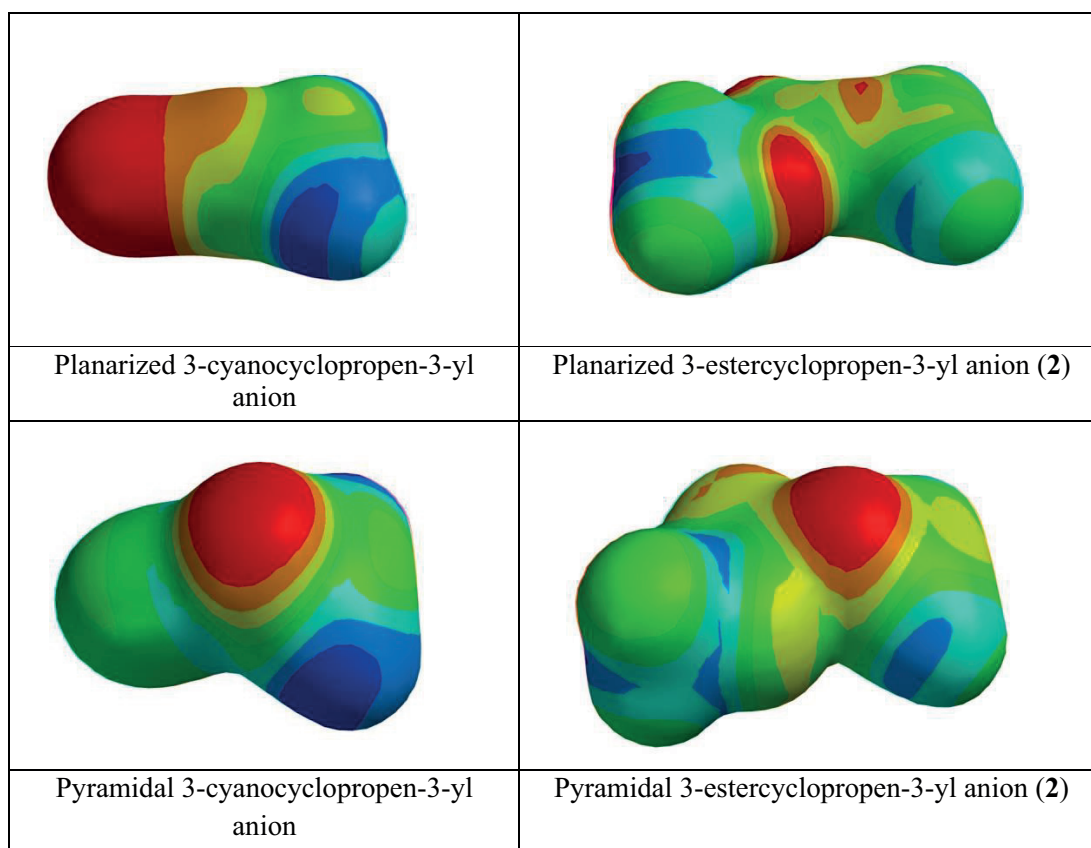


Figure 2. Local ionization potential for pyramidal and planarized cyclopropenyl anions.

Table 6. Export of charge from cyclopropenyl to substituents.

	Ring charge	Apex charge	Pyramidalization angle
CP	-1.00	-0.58	96.1
CN-CP	-0.63	-0.07	102.6
Ester-CP	-0.31	+0.04	116.1
Acyl-CP	-0.06	0.53	120.9

A reasonable correlation ($R^2 = 0.970$) is observed between pyramidalization angle and ring charge (Figure 3), suggesting that pyramidalization is a response to the presence of charge in the ring, stabilizing the system by reducing its antiaromatic character.

2.8. A remark on electrostatics

Kass has presented an analysis of the acidity of cyclic alkenes C_3H_4 , C_4H_6 , C_5H_8 , and C_6H_{10} .⁵⁰ These values correlate well with CC^*C bond angles, C^* being the site of deprotonation. Kass remarks that one need not appeal to antiaromaticity to explain the monotonic increase in the energy necessary to remove a proton as the allylic angle CC^*C decreases; the increase in electrostatic repulsion with confinement rationalizes the trend. We see from the analysis above that strain energy and the antiaromatic penalty and then of course their sum, the total destabilization, are all correlated, which explains the relation between CCC angle and acidity

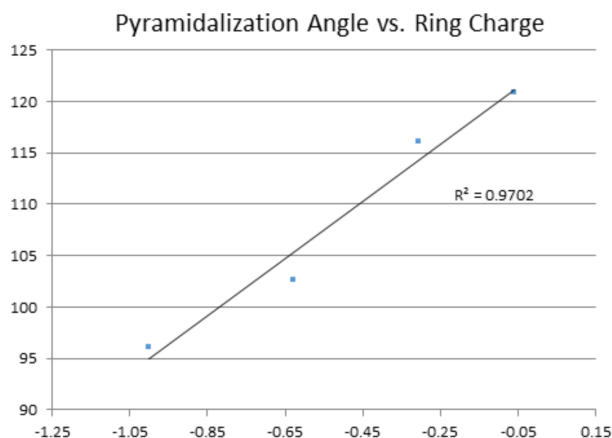


Figure 3. Correlation between ring charge and equilibrium pyramidalization angle.

Kass observes. The appeal to electrostatic repulsion alone is problematic in view of the requirement to satisfy the virial theorem, which relates kinetic and (the total) potential energy.^{51–54} For present purposes we focus on the total energies attending the geometric response as the anion is formed. In the case of cyclobutene, deprotonation produces a nearly planar C_2 -symmetric anion with a CC^*C angle of about 98° . Forcing the anionic system into planarity requires less than 2 kcal/mol. In contrast, deprotonating cyclopropene produces a strongly pyramidalized anionic center with a CC^*C angle of 48° . As noted above, planarizing the system and forcing the CC^*C angle to 60° costs ca. 30 kcal/mol. The geometric distortion returns the acidity to the correlation line established by larger cycloalkene rings. We would say again that the geometric distortion has minimized the antiaromaticity penalty, and that distortion permits the observed correlation of acidity and CC^*C bond angles.

2.9. Exploration of the mechanism for production of species **3(-)** from species **1(-)**

Reaction 4 in which anionic species **1(-)** reacts with carbon dioxide to produce anion **3(-)** was reported by Sachs and Kass,¹⁹ who speculated on a possible mechanism. The enthalpies and Gibbs energies for some important structures are collected in Table 7. The species **I(-)** represents the anionic form of the species **I**.

The reaction pathway leading to the production of anhydride and methanol from the reaction of species **I** and CO_2 is shown in Figures 4–6. Note that the anion **I** is identical with species **1(-)** of Reaction 1. The CO_2 adduct **II** in Figure 4b seems to form by a barrierless process of the reaction of species **I** with CO_2 . The transition state **III** by which the anionic anhydride **IV** is formed and CH_3OH is expelled is represented in Figure 4c. The equilibrium structure **IV** of the anionic anhydride and H-bonded methanol is shown in Figure 4d.

Figure 5 depicts the reaction steps for the breakup of the symmetric anhydride. The structure for the product of the proton transfer reaction is shown in Figure 5b. The transition state for the anhydride breakup is depicted in Figure 5c. The resulting structure after complete breakup of the anhydride is shown in Figure 5d.

The reaction steps for the formation of the butatrieneone **10(-)**, methanol, and CO_2 as final products are shown in Figure 6. The transition state species **VI** of extrusion of CO_2 is depicted in Figure 6a. The result of the reaction step in which species **XIII** anion **3(-)** is produced and methanol and CO_2 are lost is

Table 7. Enthalpies and Gibbs energies and energy differences relative to product XI.

Code	Description	H	G	Enthalpy	Gibbs E
I	Species 1(-) + CO ₂	-531.69207	-531.755554	33.5	45.3
II	CO ₂ adduct	-531.77420	-531.821751	-18.0	3.8
III	TS to anhydride	-531.725305	-531.771923	12.7	35.1
IV	H transfer complete	-531.739465	-531.79299	3.8	21.8
V-TS	TS anhydride breakup	-531.711558	-531.764558	21.3	39.7
VI	Breakup complete	-531.739461	-531.792935	3.8	21.9
VII	TS for CO ₂ loss	-531.69466	-531.75164	31.9	47.8
VIII	CO ₂ loss complete	-531.701	-531.763447	27.9	40.4
IX	Species 3(-) isolated	-531.6692	-531.75439	47.9	46.1
X-TS	TS for 3(-) to 10(-)	-531.63605	-531.72113	68.7	66.9
XI	Product 10(-)	-531.74548	-531.82781	0	0

represented in Figure 6b. The transition state for the transformation of the dehydrotriafulvalene anion product **3**(-) to butatrieneone anion **10**(-) is shown as Figure 6c. Figure 6d represents the end of the reaction step where butatrieneone **10**(-) is formed along with methanol and CO₂. Internal coordinates and further thermochemical data for some of the selected species discussed above are listed in Tables A1 and A2 in the appendix.

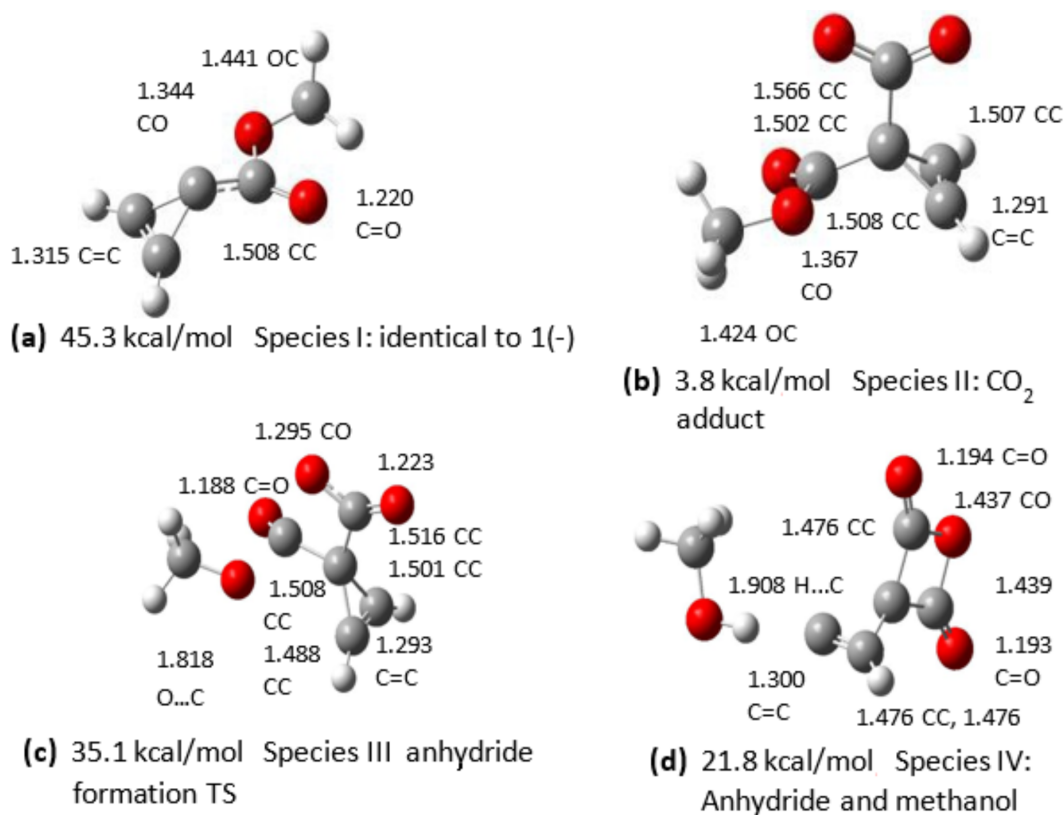


Figure 4. Landmarks for transformation I-IV. The bond lengths are in Ångströms. Relative Gibbs energies of the species are given below the structures.

We found that the adduct shown in Figure 4b was formed with no enthalpic barrier, and the CO₂ adduct **II** occupies a deep minimum in the energy surface. ΔH for the CO₂ addition to **1(-)** is -51 kcal/mol, while ΔG is -41 kcal/mol, which can be calculated from the data in Table A2 in the appendix. This helps explain why a species with the mass of the CO₂ adduct is found among the reaction products. Formation of the cyclic anhydride intermediate can precede or be accompanied by deprotonation of the cyclopropenyl ring, which is accomplished by the methoxy anion expelled as the cyclic anhydride is formed.

No low-energy transition state (TS) is found in the CBSQB3 trace of the methoxide expulsion and proton transfer producing methanol as the anhydride ring closes (arriving at species **V**), though lower levels of theory suggest the presence of a small energy barrier. The anhydride can open along with the former three-membered ring, to form species **VI**.

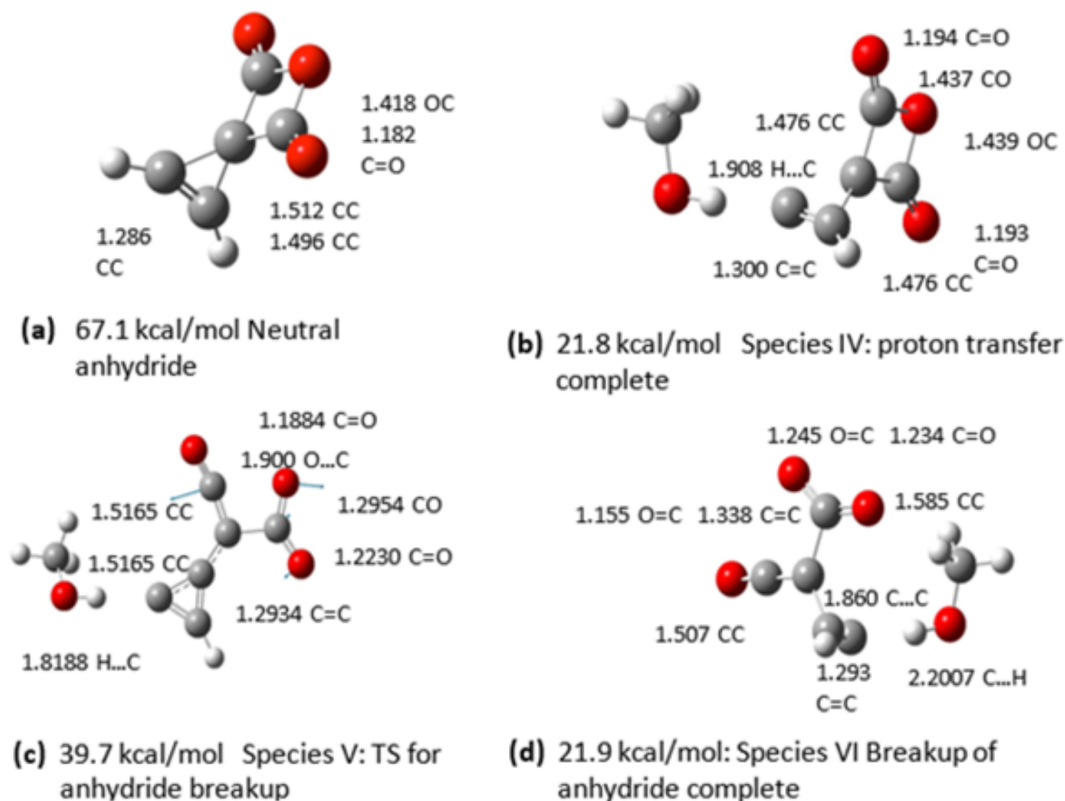


Figure 5. Deprotonation and breakup of the symmetric anhydride. The bond lengths are in Ångstroms. Relative Gibbs energies of the species are given below the structures.

Then CO₂ and methanol can be expelled, leaving the deprotonated dehydrotrifulvalene **3(-)**, shown here as species **X**. For the production of isolated CO₂, methanol, and **3(-)** according to Reaction 4 ΔH (RX) = +14.7 kcal/mol by CBSQB3, while ΔG (RX) in that model is very small, only +1 kcal/mol. The corresponding values in G4 are 15.4 and 3.2 kcal/mol, while the CBS-APNO method yields values of 16.1 and 3.4 kcal/mol for ΔH (RX) and ΔG (RX), respectively. These methods all have a mean error in ΔH_f and ΔG_f of less than 2 kcal/mol for species in the G2/97 database. CBS-APNO has a mean unsigned error of about 0.7 kcal/mol and a maximum error of 1.5 kcal/mol for that data set.

Assuming comparable reliability for species **1(-)** and **3(-)** these very consistent values suggest that Reaction 4 is endothermic and not spontaneous. It is not beyond the bounds of possibility that the error in ΔG

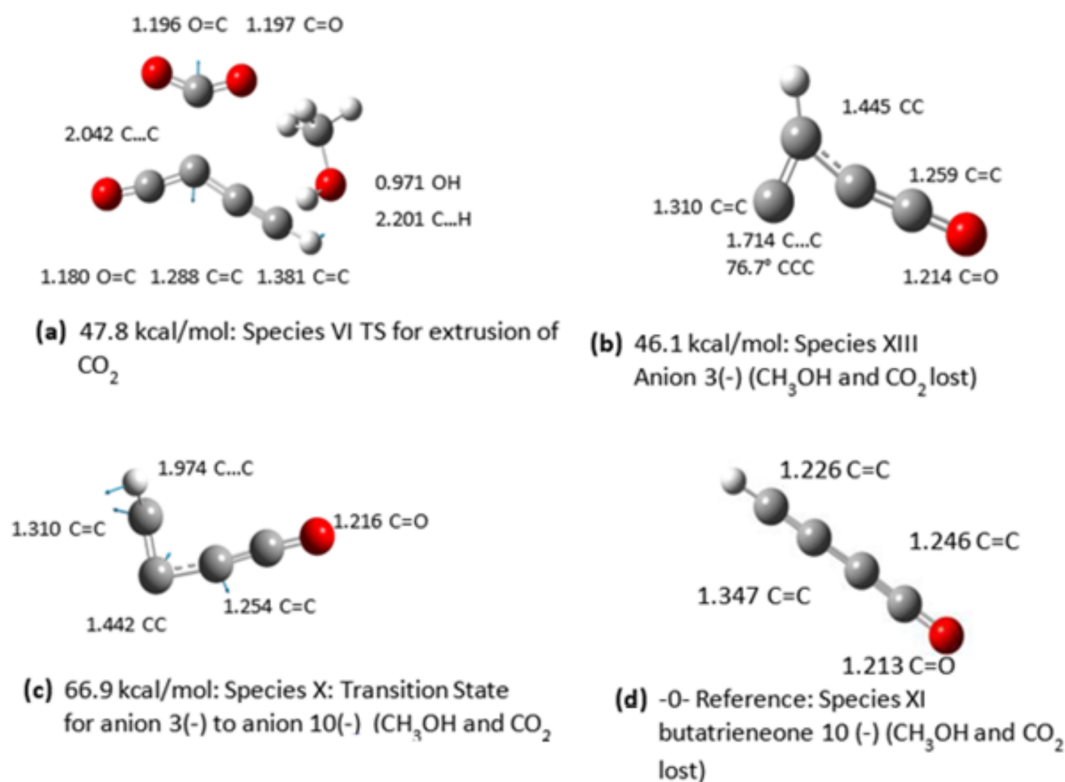


Figure 6. Landmarks for transformation IX–XII. The bond lengths are in Ångströms. Relative Gibbs energies of the species are given below the structures.

(RX) for this specific reaction is large enough that the prediction of nonspontaneity is ambiguous. We should, however, consider that an alternative product is formed. A referee, whom we thank, suggests that the open chain diyne species HCCCCO anion **10**(-) may be formed rather than **3**(-). We find that CBSQB3, G4, and CBS-APNO are consistent in their estimates of ΔH and ΔG for the overall reaction producing the diyneone **10**(-), CO_2 , and methanol from **1**(-) and CO_2 to be near -31 and -42 kcal/mol, respectively. However it is necessary to surmount a barrier of ca. 20 kcal/mol to produce the quasilinear product. Whether the linear form is in fact produced in the gas phase must depend in part on the rate of collisional deactivation—efficient cooling would favor the product dehydro triafulvalene species **3**(-) over the diyneone product species **10**(-).

3. Conclusion

Our simplest ideas of aromaticity begin with the n π electrons on regular monocyclic $(\text{CH})_n$ systems. The π energy as modeled in Hückel theory for a “benzene” six-electron six-center system is 8β . Adding two electrons reduces the π energy to 6β . A three-center two-electron “cyclopropenyl cation” system has energy 4β while the corresponding anion has energy 2β . In general, stabilization is found for this model of cyclic systems with $4k+2$ electrons (aromaticity); in contrast cyclic systems with $4k$ electrons show no such stabilization (antiaromaticity). We call this deficit the antiaromaticity penalty. Here we study 4-electron variants of cyclopropyl anion. By isodesmic reactions we estimate the energy changes attending two kinds of response to the antiaromaticity penalty. The penalty can be reduced in two ways: (i) geometric distortions of the ring (bond length changes and ring buckling) and (ii) charge export from the ring. The prototype cyclopropenyl anion pyramidalizes so

to reduce coupling among the four electrons. They become a localized lone pair and a π bonding pair.

A strong electron-withdrawing substituent on a planar three-center four-electron system can remove a pair of electrons from the π -antiaromatic set. CBSQB3 and supplementary CCSD(T)/cc-pVTZ//MP2/cc-pVTZ calculations establish a correlation between ring charge and pyramidalization angle at minimum-energy structures. In real systems a balance is struck between the charge export (which is easiest near planarity) and pyramidalization. By analysis of isodesmic reactions we can make independent estimations of the strain and π -antiaromaticity components of the total energy required for planarization.

These calculations permit evaluation of enthalpies of formation for $-\text{CN}$ and $-\text{COOMe}$ substituted cyclopropenyl anions and also the dehydro triafulvenone anion produced by the reaction of $-\text{COOMe}$ substituted cyclopropenyl anion with CO_2 .

In the course of this study we also estimated enthalpies of formation of several three-carbon ring compounds including the $-\text{CN}$ and $-\text{COOMe}$ substituted cyclopropenyl anions. We elucidated how the dehydro triafulvenone anion may be produced by reaction of $-\text{COOMe}$ substituted cyclopropenyl anion with CO_2 . Our analysis supports the proposal that a symmetric anhydride is an important intermediate in that reaction.

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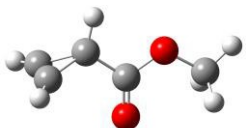
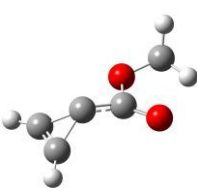
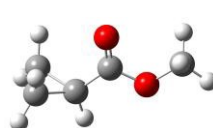

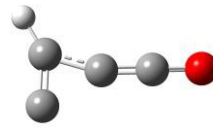
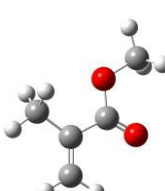

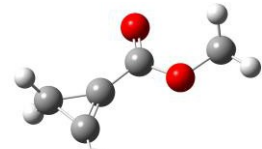
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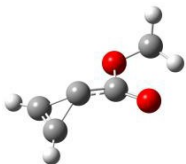
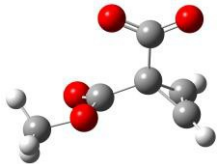
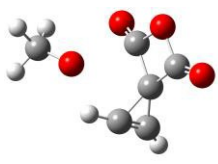
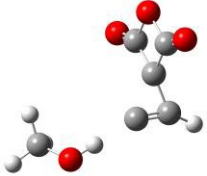
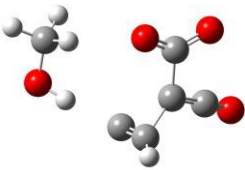
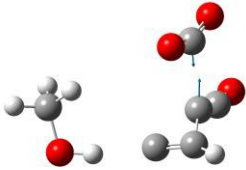
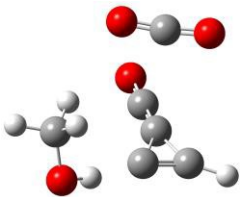
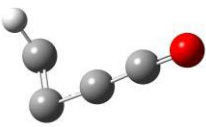

Appendix: Internal coordinates for several key species

Table A1. Molecular diagrams, CBSQB3 enthalpies (Hartrees), and internal coordinates for species participating in Reactions 1 and 2.

								
Species 1 H = -343.954584		Species 1 anion -343.325325		Species 2 -345.203329		Species 2 anion -344.592592		
								
Species 3(-) anion H = -227.765036		Species 4 -345.213975		Species 4(-) anion -344.603924		Species 5 -343.948297		
Species	C1-C2	C1-C3	C2-C3	C1-Cc	Cc=O	Cc-O	O-Cm	$\tau(\text{C1-C3-Cc=O})$
1(-)	1.315	1.520	1.520	1.508	1.220	1.344	1.441	88.5
1	1.293	1.509	1.509	1.489	1.212	1.350	1.433	104.4
2(-)	1.527	1.479	1.489	1.405	1.234	1.423	1.408	117.7
2	1.492	1.520	1.520	1.484	1.209	1.351	1.438	105.2
3(-)	1.317	1.713	1.445	1.259	1.214	-	-	180.0
4	-	1.339	1.506	1.510	1.210	1.363	1.436	114.5
4(-)	-	1.397	1.395	1.488	1.220	1.379	1.416	180.0
5	1.295	1.502	1.512	1.462	1.207	1.350	1.439	180.0

Cc is the carbon of the carbonyl (C=O) group; Cm is the carbon of the methoxy (-OCH₃) group. Energies in Hartrees, distances in Ångstroms, and angles in degrees

Table A2. Landmarks on Reaction 4 pathway: CBSQB3 thermochemistry.

		
A: Species 1 anion (with separate CO ₂)	B: CO ₂ adduct to 1 anion	C: TS for proton transfer, production of D
H = -531.69207 G = -531.75554	H = -531.774200 G = -531.821751	H = -531.698365 G = -531.745147
		
D: Proton transfer complete	E: TS for anhydride breakup	F: TS for CO ₂ extrusion; Production of G
H = -531.739465 G = -531.792990	H = -531.711558 G = -531.764558	H = -531.69466 G = -531.75164
		
G: Product 3(-) + CO ₂ + CH ₃ OH	H: TS for 3(-) to 10(-) + CO ₂ + CH ₃ OH	I: Product 10(-) + CO ₂ + CH ₃ OH
H = -531.66920 G = -531.75439	H = -531.63605 G = -531.72113	H = -531.74548 G = -531.82781