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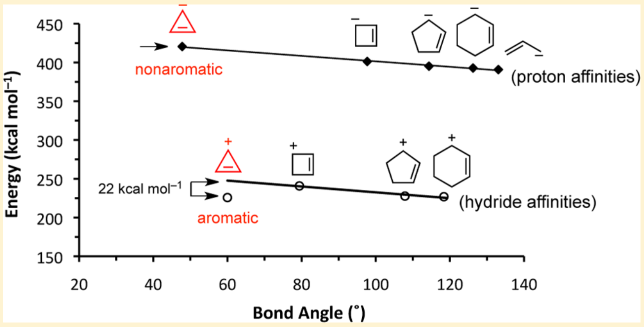
Cyclopropenyl Anion: An Energetically Nonaromatic Ion

Steven R. Kass*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States

S *Supporting Information*

ABSTRACT: A central idea in organic chemistry for the past 50 years is that cyclopropenyl anion is antiaromatic. A correlation between cycloalkene acidities and allylic bond angles reveals that energetically this is not case, cyclopropenyl anion is nonaromatic.



In 1965 Breslow coined the term antiaromaticity to describe cyclic compounds that are energetically destabilized by conjugation.[1] This concept was rapidly and widely adopted, but it is hard to define and has generated considerable controversy, largely relating to quantifying the antiaromatic destabilization energy of a given species.[2−6] Over the subsequent half-century a variety of additional definitions have been proposed, and this concept has become a well-established tenet in organic chemistry that is routinely taught in introductory chemistry courses. When it comes to the 3-cyclopropenyl anion, however, the only experimental evidence in support of this idea is kinetic and thermodynamic data that reveal it to be a very strong base (i.e., cyclopropene is an extremely weak acid at C3).[7] In this work it is shown that, on the basis of the energetic criterion of antiaromaticity and the proton affinity of 3-cyclopropenyl anion, this ion does not merit being differentiated from other allylic anions and is therefore best thought of as nonaromatic.

We recently measured the gas-phase equilibrium acidity of cyclobutene at the allylic position (i.e., C3) as part of an experimental determination of the heat of formation of cyclobutadiene.[8,9] The former result provides an opportunity to reexamine and extend Boerth and Streitwieser's 35-year-old Hartree−Fock STO-3G minimal basis set computational study that revealed that allyl anion adopts a central bond angle of 132.5°.[10] Its energy was also found to increase linearly by 8.8 kcal mol^{-1} when the C−C−C bond angle was varied from 135° down to 110°. To assess this further the gas-phase acidities ($\Delta H°_{acid}$) of cyclopentene and cyclohexene or, equivalently, the proton affinities of their conjugate bases are of interest but they are not well-established. Estimates of 394 ± 5 kcal mol^{-1} for both compounds can be obtained on the basis of their C−H bond dissociation enthalpies (BDEs)[11,12] and estimates of 5 ± 5 kcal mol^{-1} for the electron affinities (EAs) of the allyl radicals (Table 1).[13−17] This latter value is based upon the known EA of allyl radical (11.1 kcal mol^{-1})[18] and our observation of small signals for the 3-cyclopentenyl and 3-cyclohexenyl anions at subambient temperatures in a flowing afterglow device.

To obtain more accurate results would be experimentally challenging since the deprotonation of cyclopentene and cyclohexene and the fluoride-induced desilylation of their 3-trimethylsilyl derivatives lead to signal loss at room temperature.[19] Consequently, high-level G3[20] and W1[21] computations were carried out on these species using Gaussian 09[22] since these methods typically are accurate to 2 and 1 kcal mol^{-1}, respectively. The cycloalkene acidities (C_nH_{2n-2}, $n = 3-6$) and that for propene at the allylic positions are given in Table 1. As anticipated, these two independent theoretical methods give results that are in excellent accord with each other and the available experimental data. The gas-phase acidities decrease as the allylic system becomes more constrained and the ring size gets smaller. A plot of $\Delta H°_{acid}$ vs the central C−C−C bond angle is linear (Figure 1) and virtually indistinguishable for the G3 and W1 data. A least-squares fit of the of the W1 results gives $\Delta H°_{acid}$ (RH, kcal mol^{-1}) = $-0.353 \times (\text{C−C−C°}) + 436.8$, $r^2 = 0.993$ whereas the slope, intercept, and correlation coefficient (r^2) are −0.354, 436.9, and 0.976, respectively for the G3 data.

Cyclopropene is the smallest cycloalkene, and its conjugate base at C3 is considered to be a special anion that is destabilized due to the presence of 4π electrons in this fully conjugated monocyclic species. Its acidity, however, follows the same correlation as for cyclobutene, cyclopentene, cyclohexene, and propene. No additional parameter beyond the central C−C−C bond angle is needed to explain or account for the weak acidity of cyclopropene. In contrast, the hydride affinity (HA, $RH \rightarrow R^+ + H^-$ $\Delta H°_{rxn}$ = HA) of 3-cyclopropenyl cation is smaller than those for 3-cyclobutenyl, 3-cyclopentenyl, and 3-cyclohexenyl cations (Figure 2).[13−17] A three-point plot for the

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Table 1. Experimental and Computed G3 and W1 Allylic Acidities, Hydride Affinities, and C−C−C Bond Angles[a]

	ΔH°_{acid}(RH)			HA(R^+)		
	expt	calc[b]		expt[c]	calc[d]	
cmpd (RH)		G3	W1		G3	W1
propene	391.1 ± 0.3[e]	391.5	390.8	258.1 ± 0.6	258.8	258.3
	C−C−C°	133.2	133.1		117.6	118.7
c-C_6H_{10}	394 ± 5	393.3	392.8	226.9 ± 2.0	231.6	230.3
	C−C−C°	126.3	126.2		117.8	118.4
c-C_5H_8	394 ± 5[f]	393.6	395.2	228.2 ± 2.0	228.9	227.5
	C−C−C°	114.5	114.3		107.4	107.8
c-C_4H_6	400.9 ± 1.1[g]	401.2	401.2	240.8 ± 2.7	242.0	241.2
	C−C−C°	97.9	97.7		77.3	79.4
c-C_3H_4		420.8	420.5	225.8 ± 1.0	224.8	223.7
	C−C−C°	48.4	47.8		60.0	60.0

[a] All acidities and hydride affinities (HA) are at 298 K and in kcal mol^{-1}. Bond angles are in degrees. [b] Bond angles are for the allylic anions and come from the G3 and W1 computations (i.e., MP2(full)/6-31G(d) and B3LYP/cc-pVT(+d)Z geometries, respectively). [c] See ref 13. [d] Bond angles are for the allylic cations and come from the W1 calculations. [e] See ref 14. [f] Iodination BDEs are often too small by ∼3 kcal mol^{-1} (see ref 12) so this amount was added to the experimental value to obtain the estimate of the acidity. [g] See ref 8.

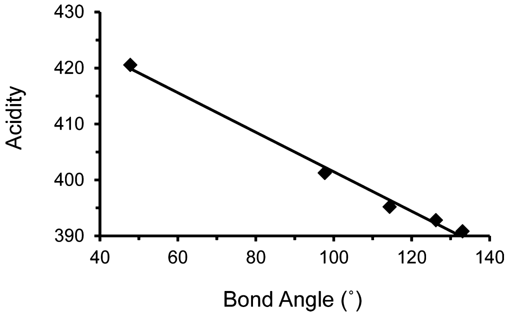

Figure 1. W1 alkene acidities vs their allylic C−C−C bond angles.

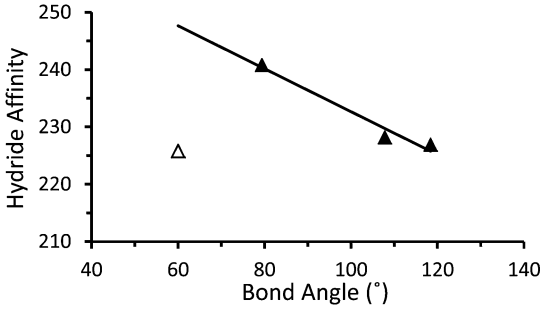

Figure 2. Experimental allylic cation hydride affinities vs their central C−C−C bond angles. The open triangle is for 3-cyclopropenyl cation.

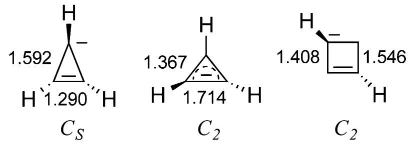

Figure 3. Computed B3LYP/cc-pVTZ(+d) structures for 3-cyclopropenyl and 3-cyclobutenyl anions. The C−H out-of-plane angles are 73.5 (C3) and 10.0° (C1 and C2) for the C_S $C_3H_3^-$ anion, 56.2° for the C_2 $C_3H_3^-$ anion and 34.3° for the C_2 $C_4H_5^-$ ion.

latter three compounds is linear (HA (R^+, kcal mol^{-1}) = $-0.379 \times$ (C−C−C°) + 270.4, $r^2 = 0.956$), but the value for 3-cyclopropenyl cation is much smaller than predicted by this correlation.[23] This is consistent with the notion that it is unusually stable (i.e., an aromatic ion).[1−3] The absence of a similar observation for 3-cyclopropenyl anion but in the opposite sense (i.e., a destabilized species) indicates that from an energetic point of view this ion is best thought of as nonaromatic.

3-Cyclopropenyl anion is predicted to be nonplanar and to adopt a C_S structure, but its C_2 form is nearly as stable (i.e., 2.0 (G3) and 2.7 (W1) kcal mol^{-1}) even though it is a pseudorotation transition structure for the interconversion of identical C_S structures (Figure 3).[24] These Jahn−Teller distortions of the D_{3h} anion, a structure which is not a stationary point on the potential energy surface (i.e., it has more than one imaginary frequency), can be viewed as minimizing the interaction of the lone pair electrons with the double bond by stabilizing one or the other of the degenerate pair of Hückel π molecular orbitals. This reduction in the antibonding interaction is also observed in 3-cyclobutenyl anion, which adopts a C_2 structure even though the B3LYP/cc-pVT(+d)Z C1−C3 distance is 2.121 Å. Both of these distortions are the result of the small central C−C−C bond angles, and allyl anion behaves similarly when C_1−C_2−C_3 is reduced. That is, B3LYP/cc-pVT(+d)Z optimizations of allyl anion in which the central C−C−C bond angle was constrained revealed that when C_1−C_2−$C_3 \leq 104°$ (or equivalently C1−C3 $\leq$ 2.238 Å) the ion adopts a C_2 structure. The angular dependence of the alkene acidities (Figure 1) is also similar to the allyl cation hydride affinities (Figure 2) even though the highest occupied molecular orbital is bonding between C1 and C3 in the latter species. These observations strongly suggest that the C1−C3 antibonding interactions in allylic anions are not the dominant reason for the geometric distortions and increased proton affinities of 3-cyclopropenyl and 3-cyclobutenyl anions.

3-Cyclopropenyl anion does not adopt a planar structure, and this is commonly attributed to its antiaromatic character. Similar distortions, however, are observed for 3-cyclobutenyl anion and constrained allyl anions (i.e., when C_1−C_2−$C_3 \leq$ 104°). One can rationalize all of this behavior by electrostatics.[25] That is, delocalization of an allylic anion with its 4π electrons over three carbon atoms in a small volume does not reduce the Coulombic repulsion sufficiently to keep the ion from distorting or displaying an increased proton affinity. In contrast, allylic cations only have 2π electrons to be distributed over the carbon framework, so that electron−electron repulsion does not play the same role in these species.

3-Cyclopropenyl anion is more basic than allyl anion and cyclopropyl anion,[26] its acyclic and saturated counterparts. This can be accounted for by the small central C−C−C bond angle and the resulting electrostatic repulsion in the constrained anion. No additional parameter is needed to account for the weak acidity of cyclopropene at the allylic position. Consequently, on the basis of the thermodynamic definition of antiaromaticity, this concept is not needed to describe the 3-cyclopropenyl anion. Magnetic criteria such as nuclear-independent chemical shifts (NICS) lead to a different conclusion,[27] but in this instance there is no energetic basis for this view. Consequently, the 3-cyclopropenyl anion is best described as nonaromatic despite 50 years to the contrary.

■ ASSOCIATED CONTENT

Supporting Information

Calculated structures, G3 and W1 energies, computational details, and the complete citation for ref 22. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*kass@umn.edu

Notes

The authors declare no competing financial interest.

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