

Is Antiaromaticity Absolute?

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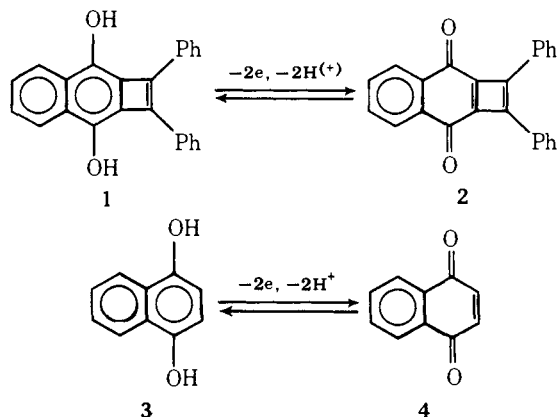
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Abstract: The concept of antiaromaticity as applied to $4n-\pi$ electron monocyclic conjugated systems is examined and two subtypes distinguished. Relative antiaromaticity is the term which describes cyclic systems which are less stable than acyclic conjugated analogues. Absolute antiaromaticity refers to cyclic systems which are less stable than even nonconjugated models (e.g., ethylene). The extensive experimental evidence for absolute antiaromaticity (particularly for cyclobutadiene and cyclopropenide) is critically examined and judged inconclusive in view of the existence of alternate, plausible rationalizations. Theoretical analysis also challenges the reality of absolute antiaromaticity, at least in the monocyclic series. Relative antiaromaticity is affirmed, but only for the three smallest monocyclic systems (the two mentioned above plus cyclopentadienylum).

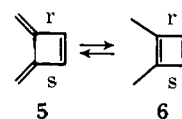
Previous to 1965, nonaromatic cyclic conjugated systems had sometimes been termed "pseudoaromatic". Included in this category, of course, were molecules having monocyclic systems of $4n-\pi$ electrons. In 1965 Breslow concluded that certain $4n$ monocycles are actually "antiaromatic", these including at least cyclopropenide (C_3^-) and 1,3-cyclobutadiene (C_4), as well as possibly cyclopentadienylum (C_5^+).¹ The term "antiaromatic" denoted and emphasized *destabilizing cyclic conjugation*. Two reference systems were considered for more explicitly defining the cyclic conjugation energy. When the reference system is an acyclic conjugated analogue (e.g., 1,3-butadiene for 1,3-cyclobutadiene), the π electron energy difference represents a relative conjugation energy. Alternatively, the reference system can be an unconjugated one (e.g., two ethylene π units for cyclobutadiene), thereby giving an absolute conjugation energy. Based upon an array of experimental evidence and encouraged by the fact that certain types of MO calculation lead to predictions of negative absolute conjugation energies for C_3^- and C_4 , Breslow was impelled to the conclusion that both of these latter are antiaromatic, not only in the relative, but even in the absolute sense. If this conclusion is accepted, a new and basic concept has emerged. The present paper presents a critical evaluation of the key aspects of the proof of absolute antiaromaticity.

Experimental Proof

Cyclobutadiene. The classic experiment for characterizing the antiaromaticity of a cyclobutadienoid system, devised and executed by the Breslow group, involves measuring the energy change (as $E_{1/2}$) associated with the transformation of a structure having little cyclobutadienoid character to one having much more and comparing this with the corresponding energy change ($E_{1/2}'$) for an analogous model reaction wherein cyclobutadiene character is absent in both reactant and product.² The two-electron oxidation $1 \rightleftharpoons 2$, e.g., has $E_{1/2} = 0.163$ V compared to the $E_{1/2}'$ value of -0.113 V for $3 \rightleftharpoons 4$. The $\Delta E_{1/2}$

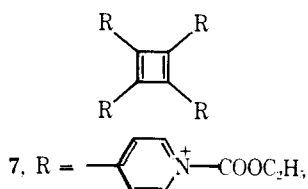


for $1 \rightleftharpoons 2$ relative to $3 \rightleftharpoons 4$ is thus 0.27 V (12.4 kcal). This was construed as an approximate quantitative measure of the absolute antiaromaticity of **2**. The approach has obvious merit in that troublesome variables such as angle and torsional strain, hybridization effects, and even substituent effects should be quite small. Fundamentally, however, $\Delta E_{1/2}$ reflects the difference in "cyclic" conjugation effects between **1** and **2**. Breslow's assignment of 12.4 kcal to antiaromaticity in **2** therefore assumes negligible cyclic conjugation effects in **1**. Indeed, in principle, it might be at least equally reasonable to assign the cyclobutadienoid conjugation energy of **2** a negligibly small or even a modest positive value and to attribute 12.4 kcal (or more) to cyclic conjugation in **1**. Assuming that $\Delta E_{1/2}$ reflects fairly accurately the difference in cyclic conjugation effects between **1** and **2**, the basic question of the allocation of the 12.4 kcal as between cyclic conjugation in **1** and **2** must be objectively confronted. To analyze the problem further it may be helpful to consider the schematic prototype reaction $5 \rightleftharpoons 6$ and to inquire about the magnitude of the cyclic conjugation

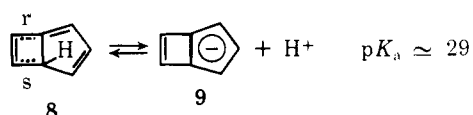


effect in **5** occasioned by attaching the left-hand cis-diene moiety to the right-hand olefinic unit through conjugative interactions r and s. Breslow evidently viewed these π interactions as negligibly stabilizing, inferring that linear polyenes have little apparent resonance energy. Although it is, of course, true that heats of formation of linear polyenes are remarkably additive, Dewar found the apparent polyene "single bond" energy to be 11 kcal greater than that of the pure sp^2-sp^2 single bond, to have significant π character, and to be shorter than the pure sp^2-sp^2 σ bond (1.512 Å).³ The correct inference would appear to be that the amount of π bonding in polyene "single bonds" is essentially invariant to introduction of other C=C conjugating units. The position that linear polyenes have no (or negligibly small) conjugation energies would seem to have little merit or current support. What, then, is the (at least approximate) value of the relevant (r,s) conjugation energy in **5** or in **1**? The observation that linear conjugation energies are highly independent of structural details suggests the assumption that the conjugative interactions at r and s are mutually independent and individually well approximated by a typical linear polyene conjugation energy. Dewar's semiempirical value for this interaction (11 kcal) would yield a total r,s conjugation energy of 22 kcal. In such an event the r,s (cyclobutadienoid) conjugation energy in **2** emerges as positive (9.6 kcal). Purely experimental values of the polyene stabilization energy are varied and usually somewhat lower than the above value. The lower limit appears to be 3.1 kcal, a number based on relative heats of hydrogenation of 1,3-butadiene and

propylene. This value is undoubtedly too low, since propylene appears to have at least some π hyperconjugation stabilization. With ethylene as a reference, instead of propylene, the polyene stabilization energy is 8.5 kcal, in better accord with the semiempirical value. In any event, the value (6.2 kcal) which would yield a null conjugation energy for **2** appears well within reason. Indeed, the data are compatible with even a small *positive* cyclobutadienoid conjugation energy in this molecule. More recently, Hunig, in an electrochemical experiment analogous to Breslow's, has derived the value 11.8 kcal for the absolute antiaromaticity of another cyclobutadienoid system (**7**).⁴ This value agrees extraordinarily well with Breslow's but is subject to the same interpretive ambiguity.

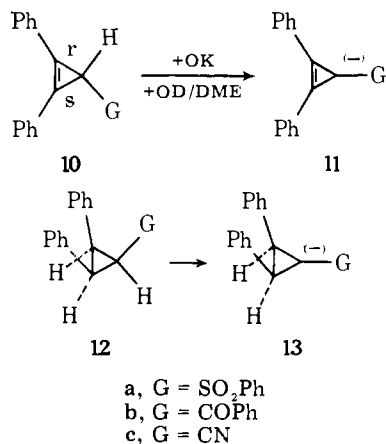


Breslow has also attributed absolute antiaromaticity to the cyclobutadienoid moiety of **9**, based upon the observation that the pK_a of **8** is ca. 11 units (15 kcal) larger than that of cyclo-



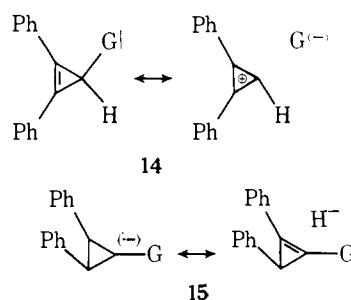
pentadiene.⁵ It was, of course, conceded that some part of this amount undoubtedly arises from increased strain in **9** relative to **8**. Stabilizing conjugative (r) and hyperconjugative (s) interactions in **8** were evidently neglected. The former interaction, according to the preceding discussion, could provide as much as 11 kcal of acid-weakening effect. As will be noted in a subsequent discussion, the hyperconjugative interaction might well provide 2.7 kcal of stabilization. These two factors, in conjunction with the strain factor mentioned by Breslow, could easily account for the reduced acidity of **8** without invoking antiaromaticity in **9**.

Cyclopropenide. In order to probe antiaromaticity in the cyclopropenide series, Breslow's group first investigated the kinetic acidities of various cyclopropenyl compounds (**10a-c**) in relation to the correspondingly substituted cyclopropanes (**12a-c**).⁶ The relative kinetic acidities for G = phenylsulfonyl,



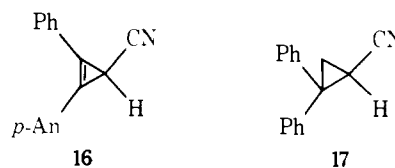
benzoyl, and cyano, measured by relative H/D exchange rates in potassium *tert*-butoxide/*tert*-butyl alcohol-*O-d*, are 10^3 , 6×10^3 , and 10^4 , respectively, the cyclopropane being more acidic in each case. These factors translate into energies of 4, 5, and 5.5 kcal, respectively. In the enolates (**11**, **13**, G = benzoyl) the anionic carbon is presumably trigonally hybridized. Deprotonation should thus engender increased angle

strain in both the cyclopropene (**10**) and the cyclopropane (**12**), but somewhat more in the former. This factor was considered, but a simple calculation suggested that it could account for no more than 3.5 kcal of the ΔpK_a . It was also recognized that four eclipsing interactions were relieved upon enolization in the cyclopropane series and two created in the cyclopropene series. These torsional effects also contribute positively to ΔpK_a , potentially as much as 6 kcal. It was argued, however, that, since 1,4-H- -H distances are longer in cyclopropane than, e.g., in ethane, eclipsing effects should be smaller than in ethane. On the balance it was concluded that absolute antiaromaticity was the best explanation of the results. The possible contributions of angle strain and torsional effects, as discussed above, weaken the argument in the case of the ketone, but Breslow pointed out that these factors should not be relevant in the sulfone, in which the anionic carbon is presumably pyramidal in both the cyclopropenide (**11**) and cyclopropide (**13**) ions.⁷ A potentially significant factor, however, is again conspicuous by its absence from Breslow's analysis, viz., hyperconjugative stabilization in the reactant cyclopropene (see r and s in **10**). Typically, of course, alkyl substitutions stabilize alkene π bonds by ca. 2.7 kcal/alkyl group. Conceding the possibility that some part of this stabilization could be the result of differential hybridization effects, it is nevertheless evident that **10** is stabilized to some extent by two hyperconjugative links and that this stabilization could be as much as 5.4 kcal. This is, per se, more than the 4.0 kcal effect revealed by the kinetic acidities. Indeed, resonance of the type illustrated in structure **14** might stabilize the cyclopropene series still further in relation to the cyclopropanes. Nor should anionic hyperconjugation in the cyclopropide ion (**15**) be neglected.



It appears that effects more conventional and well established than antiaromaticity are capable of accounting for these results.

Subsequently, Breslow and Douek contributed the observation that cyclopropene **16** undergoes H/D exchanges in +O⁻/+OD only 4.0 times faster than racemization, whereas Walborsky's 2,2-diphenylcyclopropanecarbonitrile (**17**) has



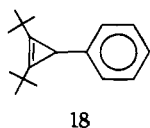
$k_c/k_r = 77$.⁸ It was concluded that the antiaromatic interaction between the carbanion center and the double bond center displaces charge onto the cyano group, thereby flattening the anion more than in the cyclopropide case. One can heartily agree with the essence of this interpretation except that the term antiaromatic is gratuitous, i.e., is by no means an essential part of the explanation. The conjugative interaction between the cyano group and the carbanion center is more powerful in the cyclopropenide case fundamentally because the carbanion HOMO is of relatively high energy and thus interacts more effectively with the cyano group LUMO. That the HOMO of a cyclopropenide system is higher in energy than that of a

Table I. Absolute Antiaromaticities of 4n- π Electron Monocyclic Systems^a

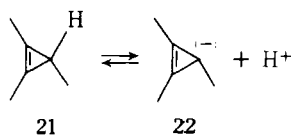
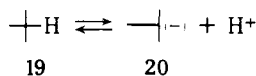
| calcn | C ₃ ⁻ | C ₄ | C ₅ ⁺ | C ₆ (Möbius) | C ₇ ⁻ | C ₈ |
|---------------------------|-----------------------------|----------------|-----------------------------|-------------------------|-----------------------------|----------------|
| HMO | 0 | 0 | 1.24 | 0.92 | 2.11 | 1.24 |
| EHMO ^b | -78.4 | -25.3 | 26.5 | 0.0 | 35.3 | 23.0 |
| CNDO ^c | 0.6 | 0.03 | 149 | | 214 | 162. |
| PPP-SCF | 0 | 0 | | | | |
| PPP/CI ^{d,f} | 14.0 | 12.4 | 91.4 | | | |
| Hubbard/CI ^{e,f} | 22.5 | 24.7 | 106.6 | 73.5 | 141.6 | 162.2 |

^a In kcal/mol (except for the HMO results) for regular polygonal geometries. ^b Using standard EHMO parameters ($\alpha = -11.4$ eV; $\beta = 1.75\alpha S$; $S = 0.25$). ^c The procedure involved zeroing appropriate π electron β 's to simulate the fully localized model (e.g., $\beta_{1,4}$ and $\beta_{2,3}$ in C₄). A common C-H bond length of 1.089 was assumed. The optimized C-C lengths of 1.420 for C₃⁻ and C₄, 1.41 for C₅, and 1.39 for C₇⁻ and C₈ were used. ^d Resonance integrals computed using an exponential form. Parameter values due to Karplus et al.²⁸ Repulsion integrals computed using Ohno's formula.²⁹ Geometries identical to those in footnote c used. ^e $\beta = 3.0$ eV, $I = 6.0$ eV.³⁰ ^f Localized models simulated by zeroing appropriate β_{ij} 's, i.e., for C₃⁻, $\beta_{13} = \beta_{23} = 0$, and for C₄, $\beta_{14} = \beta_{23} = \beta_{13} = \beta_{24} = 0$. Full Π configuration employed in both the Hubbard and PPP calculations.

simple carbanion is undoubtedly, irrespective of the presence or absence of antiaromaticity in the ion. A similar comment applies to the cyclopropenyl radical **18** which has been described as antiaromatic on the basis of the large amount of spin delocalized onto the phenyl ring.⁹



In a brilliant series of papers, culminated by the estimation of the pK_a of isobutane by an electrochemical cycle, Breslow compared the equilibrium acidity of 1,2,3-trimethylcyclopropene (**21**) with that of isobutane.¹⁰⁻¹² The latter ($pK_a = 71$)

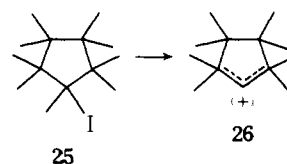
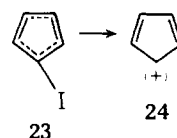


is actually more acidic than the former ($pK_a = 74$). The ΔpK_a corresponds to a free-energy difference of 4 kcal (about the same as in the case of sulfone **10**). Breslow pointed out that this is all the more impressive because in the cyclopropene, the C-H bond should have been acidified by increased s character at carbon and by the inductive effect of the two vinyl carbons. Further, since the cyclopropenide ion **22** should be pyramidal, I strain was thought not to be a factor.

Hyperconjugative reactant stabilization was once more omitted from consideration even though this factor alone could potentially accommodate the results. As noted in the previous discussion, this factor could contribute as much as 5.4 kcal of stabilization to **21**. It should also be noted that Breslow's contention that Baeyer strain effects are absent in $19 \rightleftharpoons 20$ requires not merely that the anionic center in **20** be pyramidal, but that it be at least as pyramidal as in **19** (no rehybridization in the direction of trigonality). Moreover, any flattening in the *tert*-butyl anion should tend to relieve steric repulsions between methyl groups ("B strain"). These would both contribute to positive ΔpK_a 's, as would anionic hyperconjugation in the *tert*-butyl anion.

Other 4n Monocycles. Breslow and Mazur estimated the pK_{R+} of cyclopentadienylium (C₅⁺) at -40 °C and construed this ion as antiaromatic.¹³ Relative antiaromaticity, however, is implicit here, since the only comparison was with the allyl cation. Solvolysis (assisted by Ag⁺) of 5-iodocyclopentadiene (**23**) has been shown to be at least 10⁵ slower than that of cyclopentyl iodide (**25**).¹⁴ The effect has been attributed to conjugative destabilization (absolute antiaromaticity) in the

C₅⁺ system (**24**). Alternatively, it could be argued that the ionization **23** \rightarrow **24** simply attenuates the diene conjugative interaction and the two hyperconjugative interactions in **23**, while the ionization **25** \rightarrow **26** engenders two strong hyperconjugative interactions with the cationic center. Inductive destabilization of **24** relative to **26** could also be involved.



Apparently no serious attempts have been made to characterize C₇⁻ or C₈ as antiaromatic, although they are occasionally referred to as such. Breslow, in his earliest statement on antiaromaticity, made it clear that not all 4n monocycles were necessarily antiaromatic. The stability of C₇⁻ forthwith rules out absolute antiaromaticity as a possibility for this ion. Indeed, even relative antiaromaticity appears questionable. No substantial experimental data are available which illuminate the question of antiaromaticity in planar C₈. The higher annulenes, on the basis of their relatively short "single bond" lengths, are certainly not absolutely antiaromatic, but the question of relative antiaromaticity is unresolved.

Conclusion. The results of even these ingenious experiments are disappointingly ambiguous. In order to perceive absolute antiaromaticity one must ignore or deny the importance of certain rather well-regarded forms of conjugation and/or hyperconjugation. Reasonable estimates of these latter effects are at least consistent with small positive or null conjugative stabilizations in C₃⁻ and C₄. It is also pertinent that the quantities designated by Breslow as antiaromaticities do not conform in two salient respects to the profile anticipated for such a phenomenon. As Breslow has said, the antiaromaticities of stabilized cyclopropenides such as **11a-c** should be but a fraction of that of the parent ion, yet measured "antiaromaticities" of **11a-c** and **22** are negligibly different. Even more surprising is the fact that, although C₃⁻ should be the most antiaromatic cycle of all (refer to next section, Table I), the designated antiaromaticities of the cyclobutadienoid systems (12 kcal) greatly exceed the values found for C₃⁻. On the other hand, both of these observations are predictable if reactant conjugation/hyperconjugation is the dominant factor underlying the experimentally measured effects.

Theoretical. Theoretical treatments of cyclobutadiene are numerous, frequently of high quality, and in excellent accord:

a rectangular singlet is predicted to be the ground state.¹⁵⁻¹⁹ Chemical trapping experiments confirm this,²⁰ although matrix IR studies have appeared to favor a square geometry.^{21,22} The question of absolute antiaromaticity can be explored with either or both types of structure, and indeed both are considered in some sections of this discussion. However, it appears to be a generally accepted and well-founded premise that if antiaromaticity exists in either structure it exists in both, although the magnitude of the effect should be greatest in the square structure. Similar comments apply to equilateral vs. isocles cyclopropenide. Any theoretical discussion of antiaromaticity ultimately hinges on the theoretical model used to simulate the hypothetical localized state. In the simpler π electron treatments suitable localized references (ethylene, e.g.) are easily found, but when σ electrons are included the modeling problem becomes a more subtle and challenging one. Therefore, even such relatively sophisticated calculations as are now available for C_3^- and C_4 do not perforce immediately resolve all questions concerning antiaromaticity. As is the case in the experimental realm, progress toward resolution of the problem is contingent upon evolving a consensus localized model. The following discussion is intended to reflect the apparent present status of antiaromaticity within the context of various theoretical calculations, beginning with the simplest (HMO).

As is well known, HMO theory with zero overlap ($S = 0$) generates zero conjugation energies for C_3^- and C_4 relative to one and two ethylene π units, respectively. Larger monocycles including C_5^+ , Mobius C_6 , C_7^- , and C_8 have positive (absolute) conjugation energies (Table I). On the other hand, the simple HMO method including overlap appears to support antiaromaticity. The following discussion, however, reveals that even this prediction is not without some ambiguity. The orbital energies in this case have the form $\epsilon_i = (\alpha + m_i\beta)/(1 + m_iS)$ and the ratio β/α is critical in determining even the sign of the conjugation energy. The "theoretical" value, derived from the relationship $\beta = \alpha S$, is $\beta/\alpha = S$. This selection, in fact, yields $\Delta E = 0$ for C_3^- and C_4 , the same as when overlap is neglected. Unfortunately, as is well known, the extended Huckel method fails to work with this parameter selection, yielding no bonding at all, even for ethylene. The pragmatic selection $\beta/\alpha = 1.75S$ is usually made, and this does yield negative ΔE 's for both C_3^- and C_4 , but still not for C_5^+ or other larger monocycles (Table I, EHMO).

Negative conjugation energies are not found at all in semiempirical SCF-MO calculations such as Pariser-Parr-Pople, CNDO, and MINDO (Table I). It should be noted here that the negative conjugation energy calculated by Dewar and de Llano for benzocyclobutadiene is of the relative kind. For this broad class of calculations, which are more sophisticated than the HMO or extended Huckel type in that electron repulsions are accounted for within the self-consistent field framework, the only internally consistent procedure is to select $S = 0$. This is a consequence of the fact that such calculations must neglect the myriad of relatively small repulsion integrals involving overlap clouds (zero differential overlap assumption) and, having assumed differential overlap to be zero (no overlap clouds), the overlap integral cannot consistently be given a nonzero value. The worrisome possibility that negative conjugation energies can only be foretold by properly including the overlap integral therefore arises. It may be pertinent to recall, however, that Parr has argued that for systems (like delocalized and hypothetically localized square cyclobutadiene) in which the form of the MO's is determined by symmetry, the neglect of S in semiempirical limited CI treatments should occasion no error whatever: the semiempirically evaluated integrals may simply be regarded as between Lowdin orthogonalized orbitals, for which S is indeed zero.²³ This, of course, also applies to full configuration interaction regardless

of symmetry. If this be accepted, then C_3^- and C_4 are not only absolutely antiaromatic, but they both possess modest positive conjugation energies as a result of configuration interaction, which is more stabilizing in open shell C_3^- and C_4 than in the closed shell reference π units (Table I, PPP/CI, Hubbard/CI).

Ab initio SCF/MO calculations potentially provide a basis for exploring further the S effect as a possible basis for absolute antiaromaticity. The procedure for modeling the hypothetical localized model, of course, becomes considerably more difficult and somewhat arbitrary. Clark has reported a calculation of C_3^- in which the localized model was said to be a cyclopropenide ion having a doubly occupied "symmetry orbital" at the carbanion carbon.²⁴ A negative conjugation energy of 146 kcal was found. The abbreviated nature of the description provided will not justify detailed evaluation of this model. Minimum basis set ab initio SCF-MO calculations appear invariably to generate negative bond orders for the "single" bonds of C_3^- and C_4 , as in extended Huckel theory. Clark's result thus appears to be at least qualitatively valid for a single configuration calculation. The balance of the counterpoised S and CI effects in a calculation which includes both is not yet certain, but a number of considerations suggest the negation of the S effect in a full CI treatment, in accord with Parr's theorem. The relevant effect of including S in an MO calculation on, e.g., square C_4 , is to generate negative bond orders between C_1-C_4 and C_2-C_3 (**27**). Such a configuration is indeed "superlocalized" or antiaromatic, having negative density in the overlap regions of the "single" bonds. Mixing this configuration with the degenerate one having positive overlap density in the C_1-C_4 and C_2-C_3 overlap regions (**28**) gives the symmetric, open-shell



singlet and considerable stabilization. The negative overlap densities are wholly removed. One might say that, in its qualitative effect, the neglect of S in a single configuration calculation is analogous to including some CI. These arguments suggest that superlocalized or antiaromatic states are not found in calculations which include all possible CI.

The replacement of negative by positive overlap density occasioned by CI, besides providing stabilization, should tend to shorten the "single bond". The optimum SCF-MO "single bond" length in the most recent calculation on rectangular C_4 is 1.605 Å, and CI shortens this to 1.57 Å.¹⁵ Even though the latter is still an unusually long carbon/carbon bond, it is not necessary to invoke antiaromaticity to rationalize it, especially since bond lengths are obviously not determined by π electronic effects alone. In particular, cyclobutane itself has a rather long bond, a circumstance which has been interpreted in terms of repulsive 1,3 carbon/carbon σ interactions.²⁵ Such effects should be even greater in C_4 and would presumably tend to enlarge the rectangle at the single bonds in order to increase the 1,3 distance. The 1,3 effects could also contribute substantially to the high reactivity of C_4 .

A nonempirical π electron SCF-MO-CI calculation of the Goeppert-Mayer-Sklar type²⁶ and a complete VB calculation²⁷ on cyclobutadiene have also been interpreted as suggesting a small (positive) conjugation energy for this molecule. The models utilized in these calculations, however, appear not to be carefully defined in the present context.

Finally, one notes that in no theoretical treatment is there any hint of support for absolute aromaticity in monocycles larger than C_4 (Table I). In fact, Table I reveals that PPP- or Hubbard-type calculations, including full CI, suggest that, while C_5^+ is antiaromatic in the relative sense, that none of Mobius C_6 , C_7^- , or C_8 are antiaromatic even in this limited sense.

Theoretical Conclusions. If antiaromaticity is absolute, its domain must be the limited one of C_3^- and C_4 (in the monocyclic series). Even here the support is tenuous, at best. The present preponderance of evidence suggests that C_3^- and C_4 , in fact, have small positive cyclic conjugation energies. This same evidence suggests that C_3^- , C_4 , and C_5^+ are antiaromatic in the relative sense, but that Mobius C_6 , C_7^- , C_8 and all other $4n$ monocycles are possibly not antiaromatic even in this limited sense.

Conclusions

The concept of antiaromaticity articulated by Breslow is an original and highly significant one, and well worth our critical attention. The brilliant experimental sallies of the Breslow group validate beyond reasonable doubt the relative antiaromaticity of C_3^- , C_4 , and probably C_5^+ . The attempt to demonstrate absolute antiaromaticity may well be one of the most difficult experimental proofs ever undertaken in chemistry. The upshot of the present paper is that the latter extreme form of antiaromaticity is demanded neither by experiment nor theory. Indeed, the weight of the evidence of both kinds would appear to negate the proposal of absolute antiaromaticity, even for C_3^- and C_4 . Nevertheless it is evident that the conjugation energies of these latter species are unusually small.

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Theoretical ab Initio SCF Investigation of the Photochemical Behavior of Three-Membered Rings. 2. Azirine¹

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Abstract: Ab initio SCF CI methods have been used to calculate the different potential energy curves corresponding to the ground and low-lying states of the azirine system when various reaction paths are simulated. On one hand, the ring openings, either by CN or CC bond rupture, are examined. On the other hand, the different fragmentation processes into a cyanide molecule HCN and a methylene entity CH_2 are studied. The two-step processes (the CH_2 departure following the ring opening) are compared to the direct simultaneous two-bond scission. These theoretical results afford a rationale for the understanding of the experimental facts and confirm that the preferential photochemical path is the ring opening via the CC bond rupture while the thermal one is the ring opening via CN bond rupture. The substituent influence, as shown, can reverse this order.

For 10 years a constant interest has been devoted to the derivatives of the three-membered heterocyclic ring 1-azirine **1**. The high energy strain locked in this structure renders it particularly suitable to be a precursor for easy fragmentation and further reactions. These compounds are indeed useful intermediates in the synthesis of larger heterocyclic rings.³ The most frequently occurring reaction is the photochemical ring cleavage resulting in a rupture of the CC bond to yield reactive nitrile ylides.⁴ These 1,3-dipolar species can be trapped by a variety of dipolarophiles to form five-membered rings⁵ or can also undergo photochemical (but not thermal) reclosure, regenerating the starting molecule.⁶

Other reactive processes are also documented, depending on the reaction conditions or on the cycle substituents. For example, the thermal reaction of 1-azirine derivatives can in-

volve both a CN⁷ and a CC cleavage,⁸ according to the location of the aromatic substituents on carbon 2 or 3. In all cases, the intermediate formed can lead in a second step to the formation of a carbenic species plus a nitrile molecule.^{8,9} At any rate, the products obtained by thermal cleavage are different from those resulting from a photochemical process.

It was therefore interesting to get theoretical information about all these reaction paths and to try a rationalization of the main tendencies governing this complex reactive pattern.

In this perspective we have simulated by calculation the chart of Figure 1. Path a, CN bond rupture, and path b, CC bond rupture, correspond to the primary ring openings, and lead respectively to the formation of the intermediates **2** and **3**. These two can, in a second step, cleave into a carbenic