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Aromaticity of Substituted Cyclopropenes: A Theoretical Study

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The aromaticity of several heterosubstituted cyclopropenes and corresponding protonated forms was investigated using *ab initio* calculations at the G2-MP2 level of theory, topological charge density, and NBO analysis. It was shown that according to geometric, energetic, charge density, and magnetic criteria these systems are remarkably aromatic, especially the protonated forms. It was shown that the aromatic delocalization of double bond in the cyclopropene ring can be well modeled using a three-center two-electron bond in the framework of NBO analysis proposed by Reed and Weinhold.

Introduction

Aromaticity is one of the most important concepts for the understanding of organic reactivity.¹ However, this concept has proved difficult to define and to express quantitatively.^{2,3} In recent years many reports have appeared, where new criteria based on geometry,⁴ electron structure,^{3,6} magnetic properties,⁶ IR spectra,⁷ and different energetic parameters,⁸ for establishing the aromaticity of different compounds have been proposed and also the usefulness of these different criteria has been discussed.^{2,3}

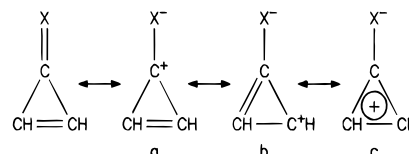
The whole concept of aromaticity has recently been reviewed in a series of interesting theoretical studies. Shaik et al. have demonstrated⁹ that the electron delocalization in several six- and three-membered rings is a by-product phenomenon. This concept is in accord with the work of Malar and Jug¹⁰ on antiaromaticity and was later confirmed by Jug et al.¹¹ To rationalize the properties of some small rings, the concept of σ -aromaticity was proposed.¹²

First suggestions about the possible aromaticity of methylenecyclopropene and cyclopropenone date back to Manatt and Roberts¹³ calculations of their delocalization energies and Breslow et al.'s¹⁴ synthesis of diphenylcyclopropenone. The stability of these systems can be thought to arise from the participation of resonance structures a, b, and c, Scheme 1, which formally contain a three-membered ring of sp^2 carbons with two π electrons.

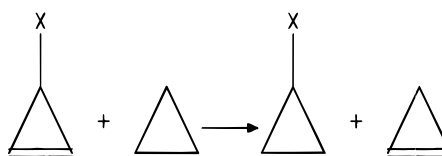
In the last 35 years extensive theoretical and experimental studies of methylenecyclopropene and cyclopropenone have been reported, but no definite conclusion has been reached concerning their aromaticity.

Cyclopropenone is usually found to be aromatic or moderately aromatic on the grounds of its thermal stability,^{14–19} low pK_b value,¹⁷ large dipole moment (4.39 D),²⁰ low C=O stretch (1640 cm^{-1}),¹⁵ large charge buildup on the O, as seen by ¹⁷O NMR spectroscopy,²¹ and the molecular geometry (elongated C=C and C=O bonds, contracted C–C bonds^{20,22}). Calculations^{18,22–26} have suggested large resonance energies, charge concentration on oxygen, and geometries similar to experimental ones. On the other hand, very small magnetic susceptibility anisotropy²⁰ suggests little aromaticity. When the electron distribution was used as the criterion for aromaticity, the results were contradictory: some authors^{24,27} suggest that cyclopropenone is not

SCHEME 1



SCHEME 2



aromatic, while others^{25,28} conclude that it possesses at least some aromatic character. Tobey¹ has argued in favor of a somewhat intermediate model.

Less work has been reported concerning the aromaticity of methylenecyclopropene. The geometry, determined by microwave spectroscopy,²⁹ indicates short C–C bond lengths and a very large dipole moment (1.90 D). Calculations^{21,22,26,29,30} suggest relatively small resonance energy. Nevertheless, methylenecyclopropene has been deemed by various authors as aromatic,^{30,31} nonaromatic,^{26,29,32} or even antiaromatic.³³

Staley and co-workers have recently reported *ab initio* and microwave spectroscopy studies of methylenecyclopropene²⁹ and cyclopropenone,²² addressing the problem of the aromaticity. They suggested three criteria for estimation of the degree of aromaticity: the amount of π -electron density at C², the length of the C–C single bond compared to that in the corresponding cyclopropane derivative, and the resonance energy. All these criteria correspond to the "classical" aromaticity as determined by Katritzky et al.² and require reference to some arbitrary model. For π -electron density and the C–C bond lengths, the comparison is made to cyclopropenium cation as aromatic reference and to the corresponding cyclopropane derivative as nonaromatic reference. Staley et al.^{22,29} and others^{18,26} have employed the isodesmic reaction (1) from Scheme 2 to approximate the resonance stabilization of cyclopropenone and methylenecyclopropene, respectively. There have been some criticisms regarding the use of this reaction,³⁴ as it does not conserve the groups as defined by Benson³⁵ and therefore contains also the energy of rehybridization. Staley et al.²⁹ found methylenecyclopropene to possess 15% aromaticity using their first two aromaticity criteria (22%, when using calculated structures) and

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TABLE 1: Selected Geometrical Parameters of Calculated Species at the MP2/6-31G* Level and Staley's Aromaticity Index (%): Bond Lengths (r) in Angstroms, Angles (a) in Degrees

	$r(\text{C}^1\text{C}^2)$	$r(\text{C}^1\text{C}^3)$	$r(\text{C}^2\text{C}^3)$	$r(\text{CX})$	$a(\text{C}^1\text{C}^2\text{C}^3)$	Staley
$\text{C}_3\text{H}_2\text{O}$	1.436	1.436	1.352	1.214	56.2	32.4
$\text{C}_3\text{H}_4\text{O}$	1.469	1.469	1.567	1.212	64.5	
$\text{C}_3\text{H}_2\text{OH}^+$	1.383	1.376	1.366	1.283	59.4	80.3
$\text{C}_3\text{H}_4\text{OH}^+$	1.435	1.426	1.571	1.261	66.6	
$\text{C}_3\text{H}_2\text{NH}$	1.446	1.431	1.340	1.274	55.5	26.3
$\text{C}_3\text{H}_4\text{NH}$	1.470	1.458	1.554	1.271	64.1	
$\text{C}_3\text{H}_2\text{NH}_2^+$	1.394	1.394	1.349	1.299	57.9	67.1
$\text{C}_3\text{H}_4\text{NH}_2^+$	1.449	1.449	1.548	1.278	64.8	
$\text{C}_3\text{H}_2\text{CH}_2$	1.445	1.445	1.326	1.330	54.6	20.4
$\text{C}_3\text{H}_4\text{CH}_2$	1.465	1.465	1.536	1.325	63.2	
$\text{C}_3\text{H}_2\text{CH}_3^+$	1.377	1.377	1.362	1.466	59.3	91.6
$\text{C}_3\text{H}_4\text{CH}_3^+$	1.389	1.389	2.327	1.503	113.8	
$\text{C}_3\text{H}_2\text{SiH}_2$	1.447	1.447	1.318	1.751	54.2	29.2
$\text{C}_3\text{H}_4\text{SiH}_2$	1.480	1.480	1.509	1.697	61.3	
$\text{C}_3\text{H}_2\text{SiH}_3^+$	1.384	1.384	1.354	1.927	58.6	
$\text{C}_3\text{H}_4\text{SiH}_3^+$	1.569	1.570	1.454	1.767	55.2	
$\text{C}_3\text{H}_2\text{PH}$	1.440	1.438	1.325	1.682	54.8	30.4
$\text{C}_3\text{H}_4\text{PH}$	1.470	1.471	1.523	1.662	62.4	
$\text{C}_3\text{H}_2\text{PH}_2^+$	1.388	1.388	1.351	1.787	58.3	80.4
$\text{C}_3\text{H}_4\text{PH}_2^+$	1.474	1.474	1.508	1.616	61.5	
$\text{C}_3\text{H}_2\text{S}$	1.427	1.427	1.339	1.615	55.9	38.8
$\text{C}_3\text{H}_4\text{S}$	1.465	1.465	1.538	1.601	63.3	
$\text{C}_3\text{H}_2\text{SH}^+$	1.391	1.390	1.350	1.666	58.1	72.2
$\text{C}_3\text{H}_4\text{SH}^+$	1.452	1.451	1.530	1.613	63.6	
C_3H_4	1.505	1.505	1.301		51.2	
C_3H_6	1.501	1.501	1.501		60.0	
C_3H_3^+	1.367	1.367	1.367		60.0	
C_3H_5^+	1.423	1.423	1.530		57.5	

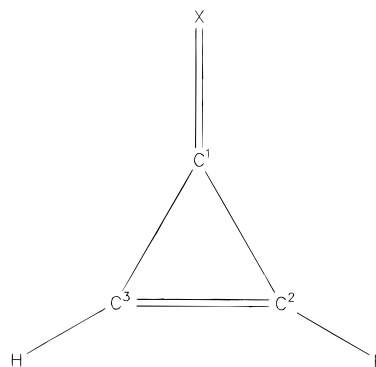
a resonance energy of 8.5 kcal/mol (at MP2/6-31G*), leading to the conclusion that methylenecyclopropene is not aromatic. On the other hand, for cyclopropenone²² they found 35% aromaticity using the electron densities and bond lengths. The resonance energy was found to be 24.1 kcal/mol, and the compound was deemed as moderately aromatic.

Bacharach and Liu³⁶ have carried out analysis of energies, geometries, and topological charge densities obtained at the HF/6-31G* level for various $\text{C}_3\text{H}_2\text{X}$ systems ($\text{X} = \text{CH}_2, \text{NH}, \text{O}, \text{SiH}_2, \text{PH}, \text{and S}$). Using the same aromaticity criteria as Staley et al.,^{22,29} they confirmed that methylenecyclopropene is non-aromatic. For both iminocyclopropene and cyclopropenone they calculated large resonance energies, large electron populations on the heteroatom, short C–C single bonds, and long C–X bonds, leading to the conclusion that both these compounds are aromatic, although the degree of aromaticity was not quantified. Similar results were also obtained for phospholenecyclopropene and cyclopropenethione, while silylenecyclopropane was found to be nonplanar due to the possible antiaromatic character of the planar form.

In the current theoretical study we have studied the aromatic stabilization of heterosubstituted cyclopropenes and their protonated forms to establish the influence of such stabilization on their proton affinities. Also, deeper insight into the aromaticity and substituent effects on aromaticity can be achieved using wider classes of substituents (charged substituents), where these effects can be more pronounced.

Methods

All calculations were performed using the Gaussian 92 program package³⁷ using the recently developed G2-MP2 computational method.³⁸ This method is claimed³⁸ to give the energies within an error of 3 kcal/mol and provide significant savings in computational time and disk storage compared to the parent G2³⁹ method.

**Figure 1.** Numbering of atoms in cyclopropylene derivatives.

As implemented in this method, all geometries were optimized at the HF/6-31G* and MP2/6-31G* levels of theory. We did not use any aid of symmetry in optimizing the molecular geometry, as several recent papers⁴⁰ have demonstrated that the use of arbitrarily imposed symmetry constraints may cause serious errors in optimized geometries.

The stabilization of species by resonance was estimated using the isodesmic reaction from Scheme 2.

The topological charge density analysis method⁴¹ was used to analyze the electron distribution in investigated species with MP2/6-31G* wave functions using Bader's AIM-PAC⁴² program package. Covalent bond orders were calculated both from charge density at the bond critical point (found using the AIM-PAC program package) according to the formula⁴¹

$$N_B = e^{6.39(\rho - 0.252)}$$

and using the program BONDER.⁴³

Magnetic susceptibilities χ and NMR chemical shifts δ were calculated using the IGLO92⁴⁴ program at MP2/6-31G* optimized geometries with the BII basis set.⁴⁴ Magnetic susceptibility anisotropies were calculated using the formula

$$\Delta\chi = \chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})$$

where χ_{zz} is out-of-plane and χ_{xx} and χ_{yy} are in-plane components of the magnetic susceptibility tensor.

Results and Discussion

1. Geometries. Main geometrical parameters of all calculated cyclopropenes, cyclopropanes, and corresponding protonated forms are presented in Table 1 (for numbering of atoms see Figure 1). In all cases, except for $\text{C}_3\text{H}_2\text{PH}_2^+$, $\text{C}_3\text{H}_2\text{SiH}_2$, and $\text{C}_3\text{H}_4\text{SiH}_3^+$, the heavy atom frameworks were planar, and molecules belonged to the D_{3d} (cyclopropane, cyclopropyl cation), C_s ($=\text{XH}$ and $=\text{XH}_3$ substituted cyclopropenes, $\text{C}_3\text{H}_2\text{-PH}_2^+$, $\text{C}_3\text{H}_2\text{SiH}_2$), or C_{2v} (other substituted cyclopropenes) symmetry groups.

The reason for nonplanarity of $\text{C}_3\text{H}_4\text{SiH}_3^+$ is the absence of a minimum on the potential energy surface corresponding to Si protonation - all optimizations led to the carbon (C^1) protonated form.

In the case of $\text{C}_3\text{H}_2\text{SiH}_2$ the lack of planarity was earlier³⁶ attributed to the possible antiaromatic character of the planar form, as silicon is less electronegative than carbon, and thus the π bond should be polarized toward the cyclopropenium ring, resembling the electron structure of cyclopropylium anion. A similar nonplanar form (see Figure 1) was found by us for $\text{C}_3\text{H}_2\text{-PH}_2^+$.

Although these nonplanar structures are unusual, they are not unprecedented. Nonplanar and nonlinear conjugated and cu-

mulene systems are known.^{47,48} Trinquier and Malrieu⁴⁸ have developed a valence bond model for double-bond formation that allows one to predict the structure of multiply bonded systems on the basis of the interacting carbene fragments. If the sum of the singlet to triplet transition energies (ΣE_{S-T}) for the two carbene fragments is less than half the $\sigma + \pi$ bond energies ($0.5E_{\sigma+\pi}$), the resulting structure will be classical. If, on the other hand, the sum of the singlet to triplet energies is larger than half the bond energies, the system will be nonclassical (i.e. nonplanar). This latter case results from the interaction of two singlet fragments, each of them tending to retain its individual character. Application of this procedure indicates that both $C_3H_2SiH_2$ and $C_3H_2PH_2^+$ should have a bent structure (as found by our calculations) and can thus both be thought of as simply the two interacting carbene fragments with no π bond. Such interpretation is also confirmed by calculated C–X bond orders (0.4 and 0.9 for $C_3H_2SiH_2$ and $C_3H_2PH_2^+$, respectively, Table 4).

It turns out that at the MP2/6-31G* level there is no minimum on the potential energy surface of $C_3H_4CH_3^+$ corresponding to a cyclic structure: all optimizations at that level of theory have led to the open-chain allyl cation. So, in later comparisons of geometries and energies of neutral and protonated methylenecyclopropane and methylenecyclopropene we have used 6-31G* results for both species.

Table 1 reveals that for all substituted cyclopropenes the C–C double bond has lengthened compared to that in cyclopropene, and as a result, the bond lengths in cyclopropene rings have been considerably equalized. Such lengthening is, however, not caused (or caused only) by the aromatizing effect of substituents, as a similar phenomenon takes place also in the case of cyclopropanes, where the distal to the substituent C–C bond is also considerably longer compared to that in cyclopropane. This fact can simply be explained in terms of sp^2 hybridization, which tends to widen the CCC angle at C¹, explaining also the long distal bond.

Staley et al.^{22,29} have used the shortening of the vicinal to the substituent C–C bonds in cyclopropenone and methylenecyclopropene compared to that in corresponding cyclopropanes as a measure of aromaticity. Normalizing this quantity by the difference in respective bond lengths in corresponding cyclopropane and cyclopropenium cation, they found that cyclopropenone and methylenecyclopropene possess 32 and 10% of the aromaticity of cyclopropyl cation. Similar aromaticity indexes calculated for all investigated compounds (at MP2/6-31G* geometries except for $C_3H_2CH_3^+$ and $C_3H_4CH_3^+$, where 6-31G* geometry was used) are presented in Table 1 and give the following aromatizing order of substituents: $CH_3^+ > PH_2^+ = OH^+ > SH^+ > NH_2^+ > S > O > PH > SiH_2 > NH > CH_2$. It is noteworthy that despite the nonplanarity of $C_3H_2SiH_2$ and $C_3H_2PH_2^+$, this aromaticity index suggests remarkably strong aromatizing effects: that of PH_2^+ is one of the strongest for investigated substituents and the effect of SiH_2 is of intermediate strength among neutral substituents. Another interesting observation is that this aromatizing order does not follow the trends in electronegativity of substituents, as one might expect that more electronegative substituents (with first row atoms) will induce more charge to themselves, making the cyclopropenyl part of the molecule more closely resemble the electronic structure of cyclopropenyl cation and thus appear more aromatic.

2. Energies. The total energies of all calculated species are presented in Table 2 as well as proton affinities of parent compounds and energies of isodesmic reaction 1. When discussing the energies of isodesmic reaction 1, one must,

TABLE 2: Calculated Total Energies (E , in au), Energies of Isodesmic Reaction 1 (ΔH , in kcal/mol), and Proton Affinities (PA, in kcal/mol) of Investigated Species; See Scheme 2

	neutral molecules		protonated species		PA
	E	$\Delta H(1)$	E	$\Delta H(1)$	
C_3H_2O	−190.335 60	−33.1	−190.649 93	−47.5	197.2
C_3H_4O	−191.551 13		−191.842 42		182.8
C_3H_2NH	−170.447 22	−25.9	−170.812 88	−39.1	229.5
C_3H_4NH	−171.674 15		−172.018 81		216.3
$C_3H_2CH_2$	−154.389 14	−20.0	−154.744 02	−62.3	222.7
$C_3H_4CH_2$	−155.625 52		−155.917 06		182.9
$C_3H_2SiH_2$	−405.387 24	−19.8	−405.720 16	−7.7	208.9
$C_3H_4SiH_2$	−406.623 88		−406.976 13		221.0
C_3H_2PH	−456.675 57	−24.4	−457.014 79	−61.3	212.9
C_3H_4PH	−457.904 90		−458.185 30		176.0
C_3H_2S	−512.929 28	−32.0	−513.259 54	−44.5	207.2
C_3H_4S	−514.146 53		−514.456 84		194.7
$C_3H_3^+$	−115.494 37				
C_3H_4	−116.357 21				
C_3H_6	−117.625 42				

however, be aware that these energies are influenced not only by the possible aromatic delocalization of π electrons but also by the differences in ring strain, σ -aromatic stabilization, and hybridization of reactants and products.³⁴ No method for quantifying the effects of the nonconservation of strain energies and σ -delocalization is available, but they are usually considered to be small.^{22,29} The energetic effect of nonconservation of hybridization can be estimated using Benson's group equivalents³⁵ to be *ca.* 8.8 kcal/mol.³⁶

The energies of isodesmic reaction 1 suggest that all investigated cyclopropenes are significantly stabilized and must thus be considered as aromatic (remember that the corresponding resonance energy in benzene is assumed to lie between 25 and 40 kcal/mol⁴⁹). The aromatizing order of substituents, obtained from energies of reaction 1, is somewhat different from that obtained from the geometries: $CH_3^+ > PH_2^+ > OH^+ > SH^+ > NH_2^+ > O > S > NH > PH > CH_2 > SiH_2$ and is more or less in accordance with the expectations based on the electronegativities of substituents. Still, the nonplanar $C_3H_2PH_2^+$ has considerable stabilization (61.3 kcal/mol) compared to corresponding cyclopropane, so that it must be one of the most aromatic among the investigated compounds. Another possible explanation of such stabilization would need an assumption of some additional stabilizing interactions in this species.

3. Electron Structure. We have employed two different methods for analyzing the electron distribution in studied molecules: Bader's atoms-in-molecules approach⁴¹ and the NBO analysis proposed by Reed and Weinhold.⁵⁰

3.1. NBO Analysis. For the problem at hand (estimating the localization–delocalization of double bonds in three-membered rings) the most appropriate approach for analysis of charge density seems to be that proposed by Reed and Weinhold,⁵⁰ as it generates the naturally localized one-center (core or lone pair) and two-center (bond) orbitals (NLMOs). The set of high-occupancy NLMOs, each taken doubly occupied, is assumed to represent the “natural Lewis structure” of the molecule. Delocalization effects appear as weak departures from this idealized localized picture. The optimal condensation of occupancy in the natural localized orbitals leads to partitioning into high- and low-occupancy orbital types. The occupancy of the latter type of orbitals (“non-Lewis occupancy”) indicates the presence of delocalization effects.

Within the NBO analysis it is also possible to allow (and even force) the use of the three-center two-electron bonds (3CB). In the case at hand it will exactly correspond to the possible cyclic delocalization of the C–C π bond in the three-membered

TABLE 3: Results of NBO Analysis: Non-Lewis Populations with and without Three-Center Two-Electron Bond (3CB)

	non-Lewis population	
	without 3CB	with 3CB
C ₃ H ₂ CH ₂	0.410	2.542
C ₃ H ₂ NH	0.496	2.092
C ₃ H ₂ O	0.591	1.709
C ₃ H ₂ PH	0.514	2.091
C ₃ H ₂ S	0.623	1.717
C ₃ H ₂ CH ₃ ⁺	1.528	0.221
C ₃ H ₂ OH ⁺	1.437	0.375
C ₃ H ₂ SiH ₃ ⁺	1.513	0.197
C ₃ H ₂ PH ₂ ⁺	1.579	0.298
C ₃ H ₂ SH ⁺	1.443	0.427
C ₃ H ₂ SiH ₂	0.562	2.488
C ₃ H ₂ NH ₂ ⁺	0.918	0.479
C ₃ H ₃ ⁺	1.450	0.117

ring. Allowing this three-center two-electron bond in cyclopropenyl cation resulted in fully occupied 100% π -character 3CB bond between carbon atoms (next to C–C single bonds) and drastically reduced the non-Lewis population (1.450 without and 0.117 with 3CB).

The results of the NBO analysis of all investigated cyclopropenes are given in Table 3. For all charged systems the 3CB was found to be present. The lone pairs of the substituents were also well localized, so that the overall non-Lewis population was low (<0.5). This indicated that the structure with 3CB is a good model for the bonding in these species, as when the formation of 3CB was not allowed, the non-Lewis population was considerably (2–7 times) higher.

To investigate the possible aromatic delocalization in neutral species, 3CB was forced by use of the keyword \$CHOOSE. It turned out that also in these cases the 3CB was readily found; it also has 100% π character and very high occupancy (>1.99). However, the lone pair(s) of substituents were in these cases largely delocalized (occupancies of corresponding NBOs were less than 1.7). The main acceptor orbital was in all cases antibonding 3CB, which was composed primarily of p orbitals from C² and C³. As a result, in all these cases an overall high non-Lewis population was observed. It can be concluded from the above analysis that in the neutral cyclopropenes studied, the ordinary structure with C²–C³ and C¹–X double bonds is preferred.

Using this non-Lewis occupation (delocalization from the strictly localized bond orbitals including the three-center two-electron bond in the cyclopropene ring) in the structures as a measure of aromaticity, we obtain the following aromatizing order of substituents: SiH₃⁺ > CH₃⁺ > PH₂⁺ > OH⁺ > SH⁺ > NH₂⁺ > O > S > PH = NH > SiH₂ > CH₂.

3.2. Bader Analysis. In Table 4 bond orders calculated from topological charge densities at bond critical points for C–C bonds⁴¹ are presented together with bond orders calculated according to Cioslowski's method.⁴³ As can be seen, both methods give very close results.

Jug has used¹¹ the "weakest link" approach to compare the aromaticity of different rings. This method rests on the assumption that the aromaticity of a cyclic system can be approximated by the lowest bond order in the ring. Application of this method gives the following aromaticity order: SiH₃⁺ > PH₂⁺ \approx CH₃⁺ > SH⁺ > OH⁺ > NH₂⁺ > S > O \approx SiH₂ \approx PH > NH > CH₂.

In Table 5 Bader's topological charges on heavy atoms are presented. This method uniquely defines the volume of any atom in a molecule, avoiding the basis set dependence and arbitrary definition of the Mulliken population. Comparison

TABLE 4: Calculated Bond Orders

	Bader bond orders			Cioslowski's bond orders			
	C ¹ C ²	C ¹ C ³	C ² C ³	C ¹ C ²	C ¹ C ³	C ² C ³	C ¹ X
C ₃ H ₂ O	1.132	1.132	1.543	1.147	1.147	1.657	1.408
C ₃ H ₄ O	1.080	1.079	0.779	0.940	0.940	0.281	1.432
C ₃ H ₂ OH ⁺	1.360	1.432	1.500	1.321	1.310	1.446	1.053
C ₃ H ₄ OH ⁺	1.156	1.216	0.786	1.083	1.078	0.931	1.193
C ₃ H ₂ NH	1.074	1.161	1.593	1.146	1.132	1.678	1.661
C ₃ H ₄ NH	1.045	1.106	0.804	1.027	1.021	0.980	1.669
C ₃ H ₂ NH ₂ ⁺	1.306	1.306	1.581	1.273	1.273	1.515	1.268
C ₃ H ₄ NH ₂ ⁺	1.108	1.108	0.831	1.046	1.046	0.956	1.402
C ₃ H ₂ CH ₂	1.078	1.078	1.654	1.109	1.109	1.740	1.853
C ₃ H ₄ CH ₂	1.045	1.045	0.842	1.038	1.038	0.997	1.861
C ₃ H ₂ CH ₃ ⁺	1.432	1.429	1.499	1.367	1.366	1.435	1.064
C ₃ H ₄ CH ₃ ⁺	1.554	1.554					
C ₃ H ₂ SiH ₂	1.060	1.060	1.703	1.146	1.146	1.706	1.203
C ₃ H ₄ SiH ₂	0.954	0.954	0.913	1.059	1.059	1.010	1.080
C ₃ H ₂ SiH ₃ ⁺	1.388	1.389	1.534	1.391	1.391	1.451	0.359
C ₃ H ₄ SiH ₃ ⁺	0.720	0.719	1.121				
C ₃ H ₂ PH	1.089	1.106	1.665	1.142	1.151	1.688	1.606
C ₃ H ₄ PH	1.010	1.014	0.875	1.046	1.052	0.994	1.578
C ₃ H ₂ PH ₂ ⁺	1.351	1.351	1.560	1.370	1.370	1.445	0.903
C ₃ H ₄ PH ₂ ⁺	0.954	0.954	0.936	1.031	1.031	0.990	1.551
C ₃ H ₂ S	1.161	1.161	1.595	1.217	1.217	1.635	1.962
C ₃ H ₄ S	1.059	1.059	0.839	1.053	1.053	0.988	2.034
C ₃ H ₂ SH ⁺	1.306	1.331	1.575	1.349	1.352	1.456	1.487
C ₃ H ₄ SH ⁺	1.054	1.070	0.876				
C ₃ H ₃ ⁺	1.477	1.477	1.477	1.399	1.406	1.407	0.881
C ₃ H ₄	0.888	0.888	1.801	1.025	1.025	1.890	0.968
C ₃ H ₅ ⁺	0.867	1.219	1.218	0.986	1.153	1.153	0.850
C ₃ H ₆	0.928	0.928	0.928	1.021	1.028	1.031	0.951

TABLE 5: Bader Charges

	C ¹	C ²	C ³	X
C ₃ H ₂ O	1.187	−0.153	−0.153	−1.175
C ₃ H ₄ O	1.051	−1.062	−1.062	−1.104
C ₃ H ₂ OH ⁺	0.854	0.015	0.040	−1.126
C ₃ H ₄ OH ⁺	0.762	−0.060	−0.035	−1.092
C ₃ H ₂ NH	0.838	−0.154	−0.132	−1.207
C ₃ H ₄ NH	0.730	−0.133	−0.113	−1.157
C ₃ H ₂ NH ₂ ⁺	0.735	−0.006	−0.006	−1.309
C ₃ H ₄ NH ₂ ⁺	0.650	−0.042	−0.042	−1.277
C ₃ H ₂ CH ₂	−0.064	−0.135	−0.135	−0.066
C ₃ H ₄ CH ₂	−0.120	−0.099	−0.099	−0.070
C ₃ H ₂ CH ₃ ⁺	0.052	0.004	0.004	−0.036
C ₃ H ₂ SiH ₂	−0.803	−0.109	−0.109	2.076
C ₃ H ₄ SiH ₂	−1.173	−0.072	−0.072	2.444
C ₃ H ₂ SiH ₃ ⁺	−0.390	−0.010	−0.010	2.805
C ₃ H ₄ SiH ₃ ⁺	−1.928	−0.053	−17.903	−0.054
C ₃ H ₂ PH	−0.701	−0.111	−0.109	1.070
C ₃ H ₄ PH	−0.932	−0.088	−0.090	1.279
C ₃ H ₂ PH ₂ ⁺	−0.452	0.004	0.004	1.688
C ₃ H ₄ PH ₂ ⁺	−1.063	−0.027	−0.028	2.184
C ₃ H ₂ S	−0.371	−0.111	−0.111	0.261
C ₃ H ₄ S	−0.573	−0.106	−0.106	0.443
C ₃ H ₂ SH	−0.366	0.013	0.021	0.642
C ₃ H ₄ SH	−0.646	−0.045	−0.040	0.058
C ₃ H ₃	0.040	0.041	0.040	0.293
C ₃ H ₄	0.015	−0.161	−0.160	0.025
C ₃ H ₅ ⁺	−0.048	−0.049	−0.056	0.215
C ₃ H ₆ ⁺	−0.100	−0.100	−0.099	0.050

of charges at C¹ and X in the investigated cyclopropanes and cyclopropenes indicates the participation of charged resonance structures in the latter cases, as in all cases in cyclopropenes the relative populations on X have increased and on C¹ decreased.

4. NMR Shifts and Susceptibilities. Molecules with cyclic conjugated π -electron systems have specific magnetic properties, different from those of other π -electron systems. These are, in particular, a stronger diamagnetic susceptibility than expected from additivity rules, a pronounced anisotropy of the susceptibility, and a deshielding of the protons attached to

TABLE 6: Calculated Magnetic Susceptibilities (χ , in ppm cgs), Components of Magnetic Susceptibility Tensor (χ_{xx} , χ_{yy} , χ_{zz} , in ppm cgs), Magnetic Susceptibility Anisotropies ($\Delta\chi$, in ppm cgs), and ^1H Chemical Shifts (δ , in ppm)

	χ	χ_{zz}	χ_{yy}	χ_{xx}	$\Delta\chi$	δ
$\text{C}_3\text{H}_2\text{CH}_2$	-37.99	-51.43	-33.52	-29.03	-20.16	8.43
$\text{C}_3\text{H}_2\text{CH}_3^+$	-33.72	-52.40	-26.58	-22.16	-28.03	10.38
$\text{C}_3\text{H}_2\text{NH}_2^+$	-33.40	-48.01	-26.20	-26.00	-21.91	9.04
$\text{C}_3\text{H}_2\text{O}$	-28.98	-42.74	-22.17	-22.03	-20.64	9.05
$\text{C}_3\text{H}_2\text{OH}^+$	-37.96	-46.02	-34.30	-33.57	-12.09	7.89
$\text{C}_3\text{H}_2\text{PH}$	-41.18	-54.99	-44.97	-23.58	-20.72	12.61
$\text{C}_3\text{H}_2\text{PH}_2^+$	-41.62	-59.73	-35.31	-29.82	-27.17	10.75
$\text{C}_3\text{H}_2\text{S}$	-44.91	-63.19	-36.09	-35.45	-27.42	9.15
$\text{C}_3\text{H}_2\text{SH}^+$	-42.80	-59.88	-35.68	-32.83	-25.63	10.28
$\text{C}_3\text{H}_2\text{SiH}_2$	-48.18	-60.36	-43.58	-40.59	-18.28	9.23
$\text{C}_3\text{H}_2\text{SiH}_3^+$	-38.64	-59.74	-31.58	-24.59	-31.66	11.07
C_3H_3^+	-20.54	-40.88	-10.37	-10.37	-30.51	10.62
C_3H_4	-31.66	-44.16	-27.87	-22.94	-18.76	7.90
$\text{C}_3\text{H}_4\text{CH}_2$	-47.04	-58.41	-41.84	-40.86	-17.06	0.40
$\text{C}_3\text{H}_4\text{CH}_3^+$	-32.61	-48.86	-26.67	-22.30	-24.38	9.31
$\text{C}_3\text{H}_4\text{NH}$	-40.84	-52.39	-38.75	-31.38	-17.33	0.55
$\text{C}_3\text{H}_4\text{NH}_2^+$	-40.30	-51.18	-37.73	-31.98	-16.33	2.15
$\text{C}_3\text{H}_4\text{OH}^+$	-35.23	-46.17	-34.99	-24.62	-16.42	2.62
$\text{C}_3\text{H}_4\text{PH}$	-53.46	-68.97	-47.33	-44.10	-23.26	0.80
$\text{C}_3\text{H}_4\text{PH}_2^+$	-53.84	-64.80	-49.24	-47.48	-16.44	2.00
$\text{C}_3\text{H}_4\text{S}$	-45.99	-68.55	-44.80	-24.63	-33.84	0.76
$\text{C}_3\text{H}_4\text{SH}^+$	-47.99	-63.14	-42.20	-38.64	-22.72	2.32
$\text{C}_3\text{H}_4\text{SiH}_2$	-59.03	-69.81	-54.06	-53.21	-16.18	0.52
$\text{C}_3\text{H}_4\text{SiH}_3^+$	-52.29	-56.36	-54.79	-45.72	-6.11	10.62
C_3H_5^+	-22.17	-42.48	-17.34	-6.68	-30.47	3.14
C_3H_6	-43.34	-50.84	-39.59	-39.59	-11.25	-0.52

the ring carbons, as compared to noncyclic conjugated π systems.

In Table 6 NMR chemical shifts for cyclopropenium ring bonded protons, magnetic susceptibilities, and susceptibility anisotropies are presented. On the basis of the ^1H chemical shifts, one can conclude that all investigated cyclopropenyl systems are aromatic, as the corresponding chemical shifts are greater than 7 ppm. However, for cyclopropene the corresponding number is also 7.9, indicating aromatic character. This phenomenon can be explained as a result of in-plane delocalization of electrons in σ bonds (σ -aromaticity).^{11,51} Thus this simple criterion, which is widely used to assess the aromaticity of different cyclic systems, cannot be used to compare the π -aromaticity of different cyclopropenes.

Schleyer has used⁵² the magnetic susceptibility anisotropy as a measure of aromaticity (the higher the anisotropy, the greater the aromaticity). However, one must take into account also the presence of other magnetically anisotropic groups, which can considerably influence the susceptibility anisotropy as can the delocalization of σ electrons in the plane of the cyclopropene ring (σ -aromaticity). Also, as shown by Benson and Flygare⁴⁵ and by Fleischer et al.,⁴⁶ the magnetic susceptibility anisotropy is not entirely due to the ring current. So, in all benzene isomers they found substantial "incremental" (i.e. not caused by ring current) anisotropy (-23 ppm cgs⁴⁶ or -26 ppm cgs⁴⁵).

Thus, on the basis of magnetic criteria, one can assume that all investigated species are to some extent aromatic, while the magnitude of the aromatizing effect of different substituents remains unknown.

Discussion

The comparison of the aromaticity criteria given above reveals that they all give quite similar ordering of investigated species. For charged (protonated) species the orders are the same except for aromaticity of $\text{C}_3\text{H}_2\text{SH}^+$ and $\text{C}_3\text{H}_2\text{OH}^+$ relative to each other; for neutral species, which are considerably less aromatic than

charged species, the differences between used criteria are more marked. However, even there the ordering is more or less the same: $\text{C}_3\text{H}_2\text{O}$ and $\text{C}_3\text{H}_2\text{S}$ are the most aromatic, $\text{C}_3\text{H}_2\text{CH}_2$ is the least aromatic, and $\text{C}_3\text{H}_2\text{NH}$ and $\text{C}_3\text{H}_2\text{PH}$ are of intermediate aromaticity, while the position of $\text{C}_3\text{H}_2\text{SiH}_2$ is not very clear. According to energetic criteria, it is the least aromatic system, while the other criteria predict intermediate aromaticity (among neutral cyclopropenes). An earlier statement of Bachrach and Liu³⁶ that this compound is nonaromatic due to the nonplanarity is questionable on the basis of our results on $\text{C}_3\text{H}_2\text{PH}_2^+$.

The most intriguing result is that all used criteria predict that $\text{C}_3\text{H}_2\text{PH}^+$ is remarkably aromatic despite the nonplanarity of the substituent and the cyclopropene ring. This raises the question whether the coplanarity of the cyclopropene ring (or, more generally, of any cyclic system) with the substituent is the prerequisite of aromaticity. On the basis of our current results, the answer seems to be negative. However, this question clearly needs further investigation, which is underway in our laboratories.

All used criteria confirm that for investigated species the protonated forms are more aromatic than neutrals. Thus, the protonation of substituted cyclopropenes should lead to the increasing basicity of these compounds relative to corresponding cyclopropanes, where the increase of aromaticity (at least π -aromaticity) is impossible. Examination of proton affinities from Table 2 reveals that this is the case: cyclopropenes are by 13–40 kcal/mol more basic than their saturated counterparts. The only exception is $\text{C}_3\text{H}_4\text{SiH}_2$, but there the protonation occurs not on the substituent but on the carbon atom. Even as the effect of aromatic stabilization is considerable (40 kcal/mol), the influence of the reaction center is more important (for example, $\text{C}_3\text{H}_2\text{NH}$ is still more basic than $\text{C}_3\text{H}_2\text{CH}_2$).

If one compares the aromaticities for neutrals and corresponding protonated forms, it is apparent that no straightforward correlation can be found: some relatively nonaromatic neutrals become upon protonation relatively aromatic ($\text{C}_3\text{H}_2\text{CH}_2$, $\text{C}_3\text{H}_2\text{PH}$) and *vice versa* ($\text{C}_3\text{H}_2\text{O}$, $\text{C}_3\text{H}_2\text{S}$), while some ($\text{C}_3\text{H}_2\text{NH}$) moderately aromatic neutrals obtain upon protonation relatively weakly aromatic character.

Conclusions

According to energetic, geometric, charge density, and magnetic criteria, all investigated heterosubstituted methylenecyclopropenes are to some extent aromatic. The use of the magnetic criterion is, however, complicated due to the very large structural changes in this series. The analysis of geometries, energies, and charge densities reveals that the protonated forms are considerably more aromatic than corresponding neutral species. It was shown that the aromatic delocalization of the double bond in the cyclopropene ring can be well modeled using a three-center two-electron bond in the framework of NBO analysis proposed by Reed and Weinhold.

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