

STRUCTURE, TOPOLOGICAL ELECTRON DENSITY ANALYSIS AND AROMATICITY OF 4-HETEROSUBSTITUTED METHYLENECYCLOPROPENES: $X=\overline{CCH=CH}$ $X=CH_2, NH, O, SiH_2, PH$ and S

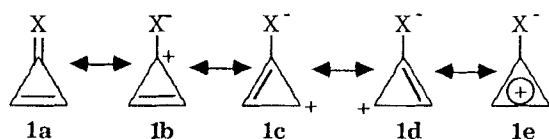
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The structures of a series of heterosubstituted methylenecyclopropenes and methylenecyclopropanes were optimized at the HF/6-31G* level. All methylenecyclopropenes are planar except for the silicon analogue, which is bent at both C-3 and Si. The planar silicon structure is a transition state. The relative aromaticity of these compounds were evaluated using the C-1—C-3 bond length, the integrated charge on C-3 and the heteroatom, and delocalization energy. Second-row systems have slightly larger delocalization energies than their first-row counterparts, owing to their larger polarizability. Using these criteria, methylenecyclopropene and the silicon analogue are not aromatic and the N, O, P and S analogues are moderately aromatic. The planar silicon analogue is antiaromatic and bends from planarity to reduce this antiaromaticity.

INTRODUCTION

Interest in the aromaticity of methylenecyclopropene and cyclopropenone date back to Manatt and Roberts' calculation¹ of their delocalization energies and Breslow *et al.*'s synthesis² of diphenylcyclopropenone. The stability of these systems can be thought to arise from the participation of resonance structures (**1b-e**) which formally contain three-membered rings having two π -electrons.

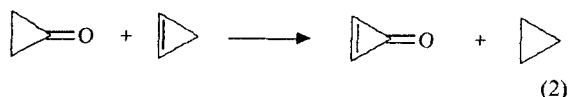


Extensive experimental and theoretical studies of the properties of methylenecyclopropene and cyclopropenone have been reported, but no absolute decision has been reached concerning the aromaticity of these compounds. Experimental evidence supporting the aromaticity of cyclopropenone include the thermal stability of the molecule and its derivatives,²⁻⁵ the large dipole moment of 4.39 D,⁶ the low C=O stretch of 1640 cm^{-1} ,³ large charge build up on O as seen in ¹⁷O NMR spectra⁷ and the molecular geometry having elongated C=O and C=C bonds and contracted C—C bonds.^{6,8} Calculations⁸⁻¹⁵ have suggested large

resonance energies, charge build-up on oxygen and geometries very similar to the experimental structure. On the other hand, the very small magnetic susceptibility anisotropy⁶ suggests little aromaticity and Tobey¹⁶ has described the dipole moment, NMR and UV spectra of cyclopropanones without resorting to aromaticity.

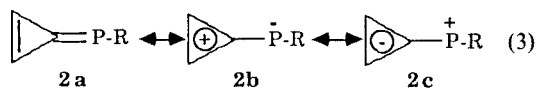
Less work has been reported concerning the aromaticity of methylenecyclopropene. The microwave structure indicates a short C—C bond length and a very large dipole moment of 1.90 D.¹⁷ Calculations suggest relatively small resonance energies.^{8,15-18} Nevertheless, methylenecyclopropene has been deemed by various researchers as aromatic,^{8,15-18} nonaromatic^{8,15} or antiaromatic.²⁰

Staley and co-workers have recently reported in-depth *ab initio* studies of methylenecyclopropene¹⁷ and cyclopropenone,⁸ addressing the problem of their aromaticity. They defined three criteria that can be used to estimate the extent of aromaticity: the amount of π -electron density at C-2, the length of the C—C single bond and the resonance energy (*RE*). These correspond with the 'classical' definitions of aromaticity as determined by Katritzky *et al.*²¹ All three of these require reference to some arbitrary model. For comparison of the π -electron density and the C—C distance, reference is made to cyclopropenyl cation. Other possibilities could include, for example, cyclopropenone and cyclopropene. Staley and co-workers^{8,17} and others^{14,15} have



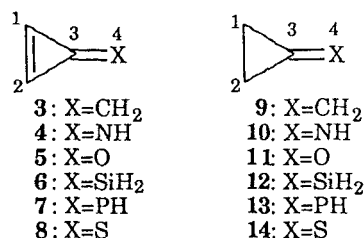
employed reactions (1) and (2) to approximate the resonance energy of methylenecyclopropene and cyclopropenone, respectively. We have previously detailed some inherent errors in the appropriateness of these reactions,²² and it is best to refer to the energies of these reactions as the delocalization energy (*DE*). Since aromaticity is defined only with reference to some arbitrary standard, a definitive answer to the extent of aromaticity in these compounds is precluded. Nevertheless, with judicious selection of reference systems, qualitative estimates are possible. Staley *et al.*⁸ found methylenecyclopropene to possess 15 per cent aromaticity using their first two criteria (22 per cent aromaticity using calculated structures) and a *DE* of 8.5 kcal mol⁻¹ (at MP2/6-31G*), leading to the conclusion that it is not aromatic. On the other hand, for cyclopropenone they found⁸ 35 per cent aromaticity using the electron density and bond length criteria and a *DE* of 24.1 kcal mol⁻¹, indicating 'moderate "aromaticity"'.

Markl and Raab²³ recently synthesized a variety of stable, substituted phosphafulvenes. They suggested that 4-phosphamethylenecyclopropene may be stable owing to the participation of charged resonance structures **2a** and **b** [equation (3)]. We have been interested in the structure and electron density distribution of organophosphorus compounds, with emphasis on strained systems.²⁴⁻²⁶ Our previous calculations indicated that phosphorus carries a large positive charge,²⁴ suggesting that the traditional charged resonance structures would not contribute, and that 4-phosphamethylenecyclopropene might, in fact, be antiaromatic (see **2c**). We therefore undertook a theoretical study of a series of 4-heterosubstituted methylenecyclopropenes **3-8** in order to determine and compare the structures and electron density distributions in these systems. Using Staley *et al.*'s⁸ criteria, we examined the relative aromaticity of these systems.



COMPUTATIONAL METHODS

All *ab initio* calculations were performed using GAUSSIAN-86.²⁷ The geometries of the unsaturated 4-heterosubstituted methylenecyclopropenes **3-8** and the partially saturated 4-heterosubstituted methylenecyclopropanes **9-14** were completely optimized at the



HF/SCF level using the 3-21G and 6-31G* basis sets.²⁷

All compounds were optimized invoking *C*_{2v} symmetry, except for **4**, **7**, **10** and **13**, which have *C*_s symmetry. The nature of all structures was determined by analytical frequency analysis for the HF/3-21G geometries. The *C*_{2v} geometry of **6** (shown in Figure 1 as **6p**) was found to be a transition structure (one imaginary frequency at both HF/3-21G//HF/3-21G and HF/6-31G*//HF/6-31G*) and was reoptimized under *C*_s symmetry, with the mirror plane bisecting the C=C bond. This geometry proved to be a local minimum with both basis sets. All other structures proved to be local minima. The analytical frequencies of **7**, **12** and **13** were also examined at the HF/6-31G* level and confirmed to be local minima.

We used the topological electron density method^{28,29} to evaluate atomic charges. The topological method uniquely defines the volume of any atom in a molecule,²⁹ avoiding the basis set dependence and arbitrary definition of Mulliken populations. Gradient paths trace out the path of ∇ρ and follow the direction of increasing electron density. The union of all gradient paths that terminate at a nucleus defines the volume of that atom. The PROAIM program³⁰ integrates the density within the atomic basin and can be used to determine atomic charge.

RESULTS

Geometries

The optimized structures at HF/6-31G* of **3-14** with pertinent geometric data are drawn in Figure 1. The HF/6-31G* energies of these compounds are listed in Table 1. We shall now discuss the individual geometries of these compounds.

Compounds **3**, **5**, **9**, and **11**

The structures of these molecules have been determined using microwave spectroscopy. A number of theoretical studies at various levels have been reported. Staley and co-workers' calculated structures^{8,17} at MP2/6-31G* (the highest level yet reported) are in excellent agreement with the experimental geometries. Staley and co-workers discussed these structures in great detail and

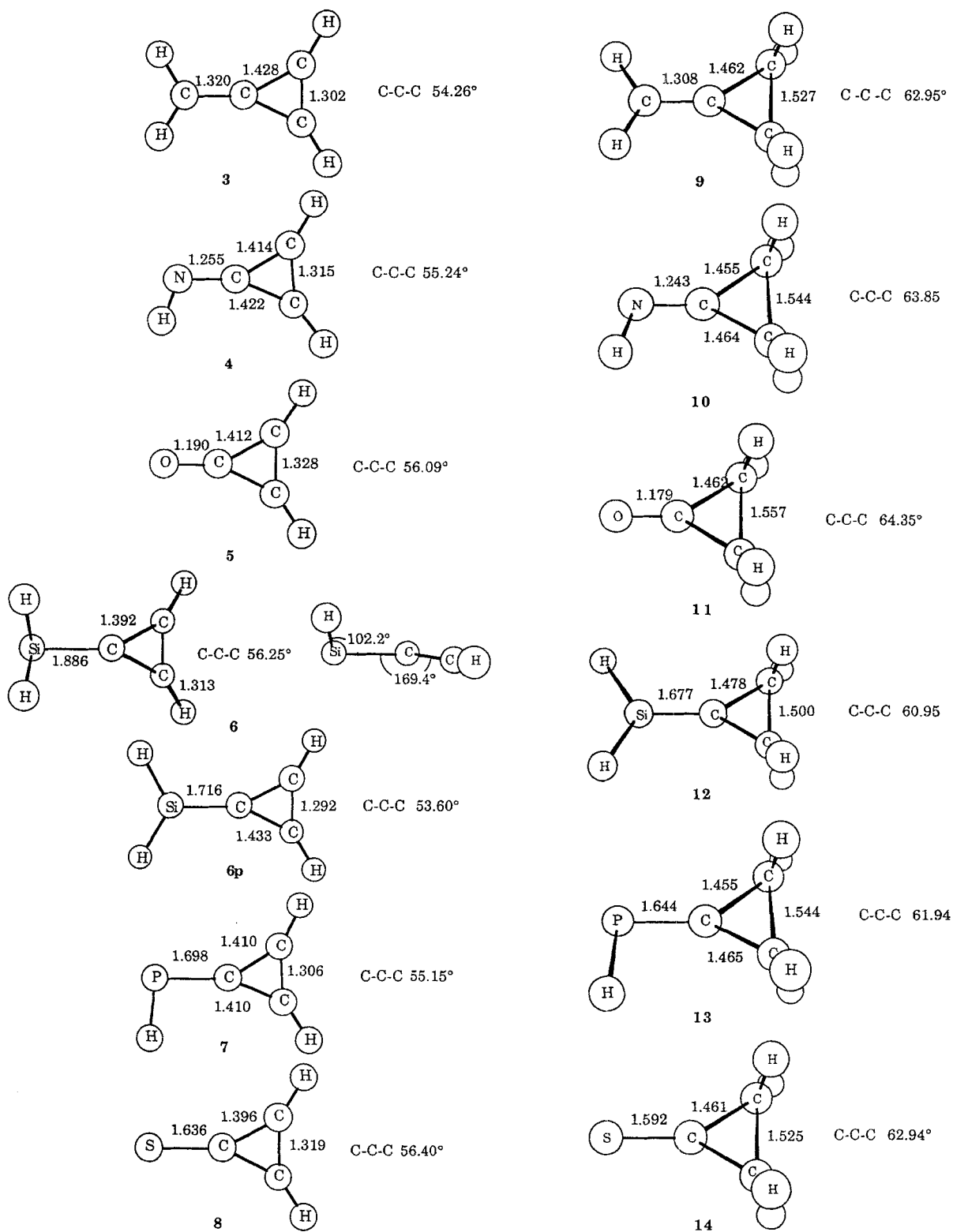


Figure 1. Optimized HF/6-31G*//HF/6-31G* geometries of 3-14. All distances are in Å and all angles are in degrees. The C-C-C angle specified is for the internal angle C-1-C-3-C-2

Table 1. HF/6-31G* energies

Compound	$E(\text{au})$	Compound	$E(\text{au})$
3	-153.669 772	10	-170.885 890
4	-169.679 864	11	-190.726 169
5	-189.533 978	12	-405.897 441
6	-404.689 314	13	-457.148 909
6p	-404.678 044	14	-513.370 198
7	-455.946 140	17	-115.823 048
8	-512.183 242	18	-117.058 865
9	-154.887 345		

they need not be repeated here. We report the HF/6-31G* geometries for comparison with the remaining compounds in the series. These geometries differ only slightly from the MP2 structures.

Compounds 4 and 10

The structures of these two compounds have been optimized at the HF/3-21G level¹⁵ and differ minimally from the HF/6-31G* structures reported here. The 6-31G* energy of **10** has been reported but without the geometry.³¹ The two molecules belong to the C_s point group and were confirmed to be local minima by frequency analysis. The C=N bond length in **4** is 0.012 Å longer than that in **10** and the C-C lengths are about 0.04 Å shorter in the former.

Compounds 6 and 12

No previous *ab initio* or experimental structures for **12** have been reported. The optimized structure belongs, as expected, to the C_{2v} point group. The C=Si distance of 1.677 Å is typical. Compared with its first-row analogue **9**, the cyclopropane ring of **12** is less distorted by the presence of the exocyclic double bond. The internal bond angle in **12** is close to 60° and the C-1-C-3 distance is only 0.022 Å shorter than the C-1-C-2 distance. In **9**, the internal angle at C-2 is nearly 63° to accommodate this sp^2 center and the opposite bond (C-1-C-2) is 0.065 Å longer than the C-1-C-3 distance.

Shriver *et al.*³² optimized the planar structure of **6** (hereafter referred to as **6p**) at both HF/3-21G and HF/6-31G*, imposing C_{2v} symmetry. We repeated their calculations and characterized these structures using analytical frequencies. This C_{2v} structure was found to have one imaginary frequency with both basis sets. The planar structure is thus a transition state and not a local minimum. We then reduced the symmetry to C_s , with the symmetry plane bisecting the C=C bond. Frequency analysis for the resulting 3-21G and 6-31G* structures indicated that both are local minima. The C_s

structure is 7.07 kcal mol⁻¹ lower in energy than the C_{2v} structure at 6-31G*.

The HF/6-31G* geometry of **6**, shown in two perpendicular orientations in Figure 1, is certainly unorthodox. The H-Si-H plane is bent 77.8° out-of-plane and the cyclopropene group is bent 10.6° out-of-plane in the opposite direction. The Si-C distance of 1.886 Å is very long, indicating little double-bond character. No major distortions of the cyclopropene ring are apparent.

Although the C_s structure is unusual, it is not unprecedented. Non-planar and non-linear conjugated and cumulene systems are known.³³⁻³⁶ For example, silaketene is bent at both the silicon and carbon atoms.³⁶ Carter and Goddard³⁷ examined the energetic consequences of the formation of double bonds in a classical (i.e. planar and/or linear) versus nonclassical (i.e. bent) configuration using interacting carbene fragments. The geometric consequences were outlined by Trinquier and Malrieu.³⁶ They developed a valence bond model for double-bond formation that leads to a simple test to predict the structure of multiple bonded systems based on the interacting carbene fragments. If the sum of the singlet to triplet transition energies ($\Sigma E_{S \rightarrow T}$) 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. This latter case results from the interaction of two singlet fragments and each tends to retain its individual character. In fact, evidence presented below will indicate that **6** may be thought of as simply the interaction of the two carbene fragments with no π bond.

We can apply Trinquier and Malrieu's criteria³⁶ to **6** and **12**. The interacting fragments in **6** are silylene (:SiH₂) and cyclopropenyl carbene (**15**), with $E_{S \rightarrow T}$ of 19 and 55 kcal mol⁻¹, respectively.³⁸ Since $0.5E_{\sigma+\pi}$ for the formation of the Si=C bond is ca 54 kcal mol⁻¹,³⁶ $\Sigma E_{S \rightarrow T}$ is greater than $0.5E_{\sigma+\pi}$, predicting a bent structure. The interacting fragments in **12** are :SiH₂ and cyclopropanyl carbene (**16**), with $E_{S \rightarrow T}$ of 19 and 9 kcal mol⁻¹, respectively.³⁸ Since this sum is less than 54 kcal mol⁻¹ from half the bond energies, the prediction is that **12** will have a classical, planar structure. Both predictions are confirmed by our calculations.

Compounds 7 and 13

No previous reports on either **7** or **13** appear in the literature. The optimized C_s HF/6-31G* geometries are shown in Figure 1.

To apply the test of Trinquier and Malrieu³⁶ we need only the values of $E_{S \rightarrow T}$ for PH, **15** and **16**, which are -28.8, 55 and 9 kcal mol⁻¹, respectively.³⁸ This gives

$\Sigma E_{S \rightarrow T}$ values of 26 kcal mol⁻¹ for **7** and -20 kcal mol⁻¹ for **13**. Any reasonable estimate³⁸ of $0.5E_{\sigma+\pi}$ will certainly be larger than these values, predicting classical planar structures for both **7** and **13**. Frequency analysis at 3-21G and 6-31G* indicates that the planar structure is a local minimum for both **7** and **13**.

The P=C bond length in **13** is 1.644 Å, typical for a phosphalkene. On the other hand, the P=C distance in **7** is 1.698 Å, about 0.05 Å longer than typical P=C bonds. The geometry of the cyclopropane ring of **13** is extremely similar to that in **10**, its nitrogen analogue. Similarly, the cyclopropene ring of **7** is very similar to the ring in **4**.

Compounds **8** and **14**

The structure of cyclopropanethione **14** has been obtained at the STO-3G level.⁴⁰ The 6-31G* structure differs from the STO-3G structure in the standard ways, having slightly longer C=S and C-C bonds. As expected, the molecule is planar. The cyclopropane ring is very similar to the ring in **11**.

Only semi-empirical calculations of **8** have been published. The MINDO/3⁴¹ structure predicts longer C=C and C-C bonds and a shorter C=S bond than our 6-31G* structure exhibits, but these differences are each less than 0.04 Å. The molecule is predicted to be planar, both by Trinquier and Malrieu's³⁶ method and by our calculations. The cyclopropene rings of **8** and **5** have similar bond distances and interior angles.

Population analysis

Integrated electron populations for all heavy-atom centers in **3-14** are listed in Table 2. Integrated densities

Table 2. Integrated populations (in e) at HF/6-31G*

Compound	$N(X)$	$N(C-3)$	$N(C-1)$
3	5.72	6.30	6.12
4	8.45	4.89	6.74, 6.68
5	9.39	4.55	6.15
6	12.29	6.35	6.10
7	13.91	6.63	6.09, 6.09
8	15.83	6.31	6.09
9	5.93	6.21	6.00
10	8.40	5.06	6.04, 6.01
11	9.32	4.77	6.06
12	11.30	7.33	5.97
13	13.53	7.06	5.98, 5.98
14	15.53	6.69	5.99
17		6.01	
18		5.86 ^a	6.14 ^b

^aMethylene carbon.

^bCH=C.

tend to indicate a greater ionic character than the more traditional Mulliken populations.⁴² Nevertheless, integrated populations do reflect the actual spatial distribution of the density and correspond directly to an observable.

To interpret the integrated density in the three-membered rings, we integrated the charge on the carbon atoms in cyclopropane **17** and cyclopropene **18**. The population of C in cyclopropane is 6.01 e. The methylene C in cyclopropene carries 5.86 e and C-1 carries 6.14 e. Except for **4**, the integrated populations (N) at C-1 and C-2 of the unsaturated compounds are virtually indistinguishable from $N(C-1)$ in cyclopropene. The populations at C-1 and C-2 in **9-14** are identical with the population on C in cyclopropane.

We discuss the comparison of the atomic populations of the unsaturated compounds (**3-8**) with their saturated analogues (**9-14**) in the next section. We can make some comparisons of the populations on the heteroatoms from the limited reports in the literature. Bachrach and Streitwieser⁴² reported integrated populations on oxygen in a variety of carbonyl compounds. These calculations were at the HF/3-21G*//HF/3-21G* level, but integrated populations are relatively insensitive to basis sets. They report $N(O)$ ranging from 9.26 e to 9.35 e. The O population in cyclopropanone is 9.32 e, which lies in the standard range, whereas that in cyclopropenone is 9.39 e, just larger than the reported range. The larger population in cyclopropenone is consistent with the participation of charged resonance structures.

The integrated populations of N in CH₂=NH and CH₃CH=NH at HF/6-31G* are 8.39 e and 8.42 e, respectively.²⁵ The N populations in **4** and **10** are 8.45 e and 8.40 e, very similar to the charges in the simple imines. The N population is slightly larger in **4** than in the other examples, consistent with charged resonance structure participation.

The integrated populations on silicon and carbon in silene are 11.26 e and 7.32 e, respectively. These values are nearly identical with the populations on Si and C in **12**. However, the Si and C populations in **6** are different; silicon carries an additional full electron and carbon carries one less electron. This charge distribution is consistent with the participation of charged resonance structures in **6**; however, it should be recalled that **6** is non-planar. We have also integrated the charge distribution in the planar form, **6p**: $N(Si) = 11.60$ e and $N(C) = 6.98$ e. Silicon carries fewer electrons in the planar form than in the bent ground-state conformation.

The range of P integrated populations for five simple phosphalkenes is between 13.42 e and 13.60 e, the highest value being the P population in (CH₃)₂C=PH.²⁵ The P population in **13** of 13.53 e lies in the middle of this range. However, the P population in **7** is 13.91 e, significantly above this range. In fact,

it is larger than any P population yet reported. This large P population is consistent with negative charge build-up on the 4-position, as indicated by the charged resonance structures.

Finally, the integrated populations on sulfur and carbon in thiaformaldehyde are 15.48 e and 6.67 e, respectively. The populations of S and C in **14** are nearly identical with the values of thiaformaldehyde. The S population in **8** is 0.30 e larger than in **14**, suggesting that charged resonance structures do participate.

DISCUSSION

The results given in the previous section can provide insight into the degree of participation of the charged resonance structures that lead to aromaticity. Staley *et al.*⁸ used the C-1-C-3 bond distance (in comparison with the C-C distance in cyclopropenyl cation), the π -density at C-3 and the resonance energy as criteria for estimating the aromaticity of **3** and **5**. We shall use these descriptors together with the C-3=X distance and integrated charges to evaluate the nature of **3-8**.

The C-3=X bond length in **3-8** and their unsaturated analogues **9-14** are given in Figure 1. Participation of the charged resonance structures would dictate a longer C-3=X distance in the methylenecyclopropenes than in the methylenecyclopropanes, and this is true for all the systems examined. However, Staley and co-workers^{8,17} cautioned that the C=X distance is dependent on other factors than just aromaticity, particularly the hybridization at C-3 and in-plane resonance.

If the methylenecyclopropenes are aromatic, the C-1-C-3 distance should contract relative to a standard C-C single bond length. Staley *et al.*⁸ framed this contraction in terms of how much the distance has approached the C-C distance in the cyclopropenyl cation, an aromatic system. Staley *et al.* defined the '% aromaticity' as the ratio of the difference in the C-C length in methylenecyclopropane and methylenecyclopropane over the difference in the C-C length in methylenecyclopropane and cyclopropenyl cation. The values of the '% aromaticity' for **3-8** are listed in Table 3. According to this criterion, all the substituted methylenecyclopropenes are aromatic. The degree of aromaticity is predicted to increase across the period and down each row of the Periodic Table.

Table 3. '% Aromaticity' using C-C bond lengths

Compound	'% Aromaticity'	Compound	'% Aromaticity'
3	30	6p	34 ^a
4	37	7	47
5	42	8	55

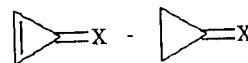
^aThe value increases to 63 per cent if **6** is used.

All previous analyses of the charge distribution in **3** and **5** have utilized Mulliken populations.^{8-15,17} Mulliken populations are extremely basis set dependent and reflect only the electrons in arbitrarily defined atomic orbitals and not the spatial distribution of the electron density. Instead, we have opted to use the topological method to obtain integrated charges about the atoms. This method requires no recourse to arbitrary definitions of orbitals since the total density is integrated within a basin defined by the total density.

Staley *et al.*⁸ used the π -density as a criterion for aromaticity in **3** and **4**. For non-planar molecules, such as **6**, separation of σ - and π -orbitals is not unique. Even in planar molecules, occupation of the atomic p-orbitals that belong to the π -system do not reflect the spatial distribution of the electrons that 'belong' to an atom, but rather only the arbitrary size of the p-orbitals, their occupation and the fact that they happen to be centered on a particular atom. We report here only the total integrated charge on the heavy atoms to avoid the need for any arbitrary definitions. These charges will necessarily reflect both σ and π effects. This is advantageous given the recent work of Shaik *et al.*⁴³ which suggests that the σ -system is responsible for the geometric symmetry (one indicator of aromaticity) of benzene. Qualitative trends and comparisons of these charges do lead to some insight into the aromaticity in **3-8**.

Table 4 gives the difference in the integrated charge on the heteroatom and C-3 in various substituted methylenecyclopropenes in comparison with their methylenecyclopropane analogue. Since all the methylenecyclopropanes have charge distributions at C-3 and the heteroatom similar to their simple double-bond analogues, the comparison with the methylenecyclopropenes will reflect the changes due solely to the increased unsaturation. The charge differences result from three major effects: π -conjugation (acyclic delocalization), σ -redistribution and aromaticity (π -delocalization in rings). It is not possible to separate these effects in an unambiguous or non-arbitrary fashion. Nevertheless, if the charged resonance structures participate, it is

Table 4. Comparisons of integrated populations



X	$\Delta N(X)$	$\Delta N(C-3)$
CH ₂	-0.21	0.09
NH	0.05	-0.17
O	0.07	-0.22
SiH ^a	0.30	-0.35
PH	0.38	-0.43
S	0.30	-0.38

^aThe values cited were obtained using **6p**. The values using **6** are $\Delta N(X) = 0.99$ and $\Delta N(C-3) = -0.98$.

reasonable to expect that the heteroatom would show a net gain of electrons and C-3 would lose electrons. This is the case for **4–8**, indicating that the charges are at least consistent with these compounds being aromatic. On the other hand, the inverse charge distributions in **3** suggest that the molecule is not aromatic, the conclusion previously obtained by Staley *et al.*⁸

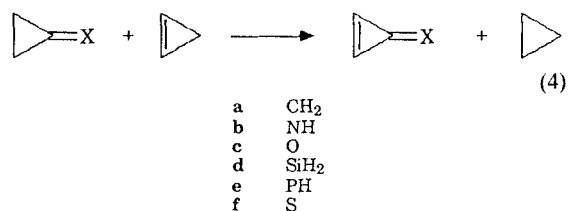
The charge on P in **7** is +1.09. Even though this P atom carries a positive charge, it is the least positively charged P atom we have seen. (Note that integrated charges tend to indicate greater ionicity than other methods.) Relative to all other phosphalkenes and phosphalkynes previously examined, electron density is transferred from the ring to P, indicating definite participation of **2b**.

The large differences in the populations in the two silicon compounds (**6** and **12**) together with the very long C-3–Si bond might suggest large aromaticity in **6**. On the other hand, **6** is non-planar, differentiating it from the other methylenecyclopropenes and typical aromatic systems. Is there a simple way to reconcile these results?

The valence bond model developed by Trinquier and Malrieu³⁶ accurately predicts the nonclassical bent structure of **6**. In this model, no true double bond is formed; rather, a longer C–Si distance is expected. The C=Si bond lengths in silene and **12** are 1.694 and 1.677 Å, respectively. In contrast, the C–Si bond length of 1.886 Å in **6** is much longer. Interestingly, the C–Si distance in **6p** is 1.716 Å, only slightly longer than a typical C=Si bond. There is little C–Si double bond character in **6**.

Comparisons of **6** with **6p** are most instructive. The structure of **6p** appears to be very similar to those of **3–5**, **7** and **8**. However, it is a transition state, lying 7.07 kcal mol⁻¹ above **6**. The integrated populations of C-3 and Si in **6p** are 6.98 e and 11.60 e, respectively. The three-membered ring is thus very electron rich and antiaromatic. Silicon is too electropositive to accept electrons from the ring and the stabilizing charged resonance structures (**1b–e**) do not participate. Bending the structure to give **6** decreases the s-character of bonds from C-3 and allows for a transfer of electrons from the ring to silicon, thereby decreasing the antiaromaticity. In order to determine the nature of **6**, one must balance the conflicting data: the molecule is decidedly nonplanar, yet the C–C distance, charge distribution and delocalization energy (see below) indicate a definite aromatic contribution. We consider the nonplanar geometry and the fact that **6p** is antiaromatic to tip the balance towards the conclusion that **6** is nonaromatic.

The final test of aromaticity is the resonance energy (*RE*). The definition of *RE* is inherently arbitrary, since it can only be evaluated relative to some reference. Previous attempts to obtain *RE*s of the substituted methylenecyclopropenes made use of the reaction energy of



equation (4). Staley *et al.*⁸ called the energy obtained in equation (4) the 'delocalization energy', recognizing that other effects besides resonance are included. The reaction energy using equation (4) obtained at the HF/6-31G* level with correction for zero-point energy (calculated at HF/3-21G//HF/3-21G) for **3–8** are given in Table 5.

We have detailed the effects of some of the approximations inherent in this reaction.²² The reaction not only measures resonance energy, but also has an energy component due to differences in ring strain energy (RSE), σ -delocalization and hybridization between the reactants and the products. No method for quantifying the effects of the non-conservation of RSE and σ -delocalization is available, but they are likely to be small. The energetic effect of non-conservation of hybridization can be estimated using Benson's⁴⁴ group equivalents. Group equivalents are available for correcting the reaction energy for X=CH₂ and O, but not for the other systems. This correction reduces the energy of equation (4a) by 7.8 kcal mol⁻¹ and of equation (4c) by 9.9 kcal mol⁻¹. It is reasonable to expect the correction for the other compounds to be of the same magnitude, *ca* 8.8 kcal mol⁻¹, and the corrected energies are also listed in Table 5. These corrected energies will be referred to as the *DE* of the corresponding substituted methylenecyclopropene with the caveat that this energy only approximates the true *RE*.

Greenberg *et al.*¹⁴ calculated the energy of reactions (4a) and (4c) at HF/6-31G* as 11.3 and 27.7 kcal mol⁻¹, respectively, differing from our results only by the incorporation of zero-point energy.

Table 5. Energies (kcal mol⁻¹) of equation (4) at HF/6-31G*

Equation	X	<i>E</i>	<i>E</i> (corr.) ^a
4a	CH ₂	-11.2	-3.4
4b	NH	-18.2	-9.4
4c	O	-26.4	-16.5
4d ^d	SiH ₂	-12.3	-3.5
4e	PH	-20.2	-11.4
4f	S	-29.7	-20.9

^aCorrected for non-conservation of groups; see text.

^bUsing **6**, the energy is -19.4 kcal mol⁻¹ and *E*(corr.) = -10.6 kcal mol⁻¹.

Budzelaar *et al.*¹⁵ reported the energy of reaction (4b) at HF/3-21G as 13.8 kcal mol⁻¹. The best estimates of the energy of reactions (4a) and (4c) are 8.5 (Ref. 17) and 24.1 kcal mol⁻¹ (Ref. 8), respectively. These calculations were performed at the MP2/6-31G* level. These MP2/6-31G* data differ very little from our HF/6-31G* results, indicating that correlation effects will be small and will not bias our conclusions.

The *DE* of **3** is only 3.4 kcal mol⁻¹, suggesting little aromatic stabilization. In fact, all the structural electron density distribution and energetic criteria consistently corroborate Staley *et al.*'s conclusion⁸ that **3** is not aromatic.

The *DEs* of **4** and **5** are 9.4 and 16.5 kcal mol⁻¹, respectively. Since oxygen is more electronegative than nitrogen, participation of the charged resonance structures is enhanced in **5** relative to **4**. One should also recognize that σ -resonance⁸ (in-plane π -resonance) is likely to be larger in **5** than **4** and partially to account for its larger *DE*. This delocalization is also reflected in the other aromatic criteria: greater charge transfer from C-3 to X and greater C-1-C-3 contraction in **5**. Both molecules display aromatic properties and **5** is more aromatic than **4**.

The energy corresponding to equation (4d) is -3.5 kcal mol⁻¹. Although the reaction is exothermic, it is so close to thermoneutral that no significant stabilization is witnessed. The lack of *DE* further supports the contention that **6p** is antiaromatic. If we substitute **6** for **6p**, the reaction energy is -10.6 kcal mol⁻¹. The bent structure of **6** arises to reduce the antiaromatic nature of the planar form.

The *DE* of **7** is 11.4 kcal mol⁻¹, slightly larger than **4**. Phosphorus is larger and more polarizable than nitrogen, thereby enhancing the former's ability to stabilize the charged resonance structures, leading to a larger *RE*. The aromatic criteria of **7** are all consistent. The P-C bond is long and has a bond order of only 1.2.²⁵ The C-1-C-3 bond is short and projects to a '0% aromaticity' of 47 per cent. The phosphorus population is very large, owing to charge transfer from the ring. These criteria together with the significant *RE* clearly indicate that **7** is aromatic (contrary to our initial expectation) and should be a serious synthetic candidate.

Finally, the *DE* of **8** is 20.9 kcal mol⁻¹, the largest of the systems examined here. The trends in *DE* are readily interpreted in terms of electronegativity and polarizability. Increasing electronegativity allows the heteroatom to stabilize the charged resonance structures better; thus the *DE* of **8** is greater than that of **7**, just as the *DE* of **5** is greater than that of **4**. The second-row atoms are larger and more polarizable than the first-row atoms, again allowing them to stabilize the charged resonance structures better; the *DE* of **8** is greater than that of **5**. As with **7**, all the geometric, energetic and density evidence indicates that **8** is aromatic.

CONCLUSIONS

We have analyzed the geometries, electron density distributions and energetics of six heterosubstituted methylenecyclopropanes to evaluate the aromaticity of these systems.* Methylenecyclopropene **3** has little *DE* and a charge distribution that is the reverse of that expected for an aromatic system. We confirm Staley *et al.*'s⁸ conclusion that **3** is not aromatic. Both **4** and **5** have large *DEs*, large electron populations on the heteroatom, short C-1-C-3 bonds and long C-3-X bonds and are therefore aromatic, although it is difficult to quantify the degree of aromaticity.

The ground-state structure of **6** is non-planar. The planar form is a transition state and is antiaromatic. The electropositive silicon atom cannot accept enough electrons in the planar form to allow participation of the stabilizing charges resonance structures (**1b-e**). The molecule distorts from planarity to reduce the antiaromaticity (evidenced in a large transfer of electrons from the ring to silicon). Compound **6**, like its first-row analogue, is nonaromatic.

All aromatic criteria consistently indicate that both **7** and **8** are aromatic. Even though the net charge on P in **7** is positive, the P charge is the smallest yet found, corresponding to significant transfer of density from the ring via charged resonance structures. The *RE* of **8** is the largest of the molecules examined here. Both of these molecules should be stable and should be serious synthetic candidates.

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* The optimized geometries of all the reported structures are available from the authors.

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