INDO Theoretical Studies. VI.[1] Cyclopropenyl, Azirinyl, and Diazirinyl Cations

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Geometry-optimized theoretical calculations, in the INDO approximation, have been carried out on a series of cyclopropenyl cations including $C_3H_3^+$ (1), $C_3F_3^+$ (2), $C_3(NH_2)_3^+$ (3), and $C_3H_2Ph^+$ (9). The most stable geometries of 1-3 had D_{3h} symmetry, but a distorted C_3 ring with a small quinoid contribution was found for **9**. From a study of the π-bond orders, bond lengths, rotational barriers, charge densities, and orbital electron densities, it was shown that F and NH_2 groups conjugate strongly with the ring. However, the resonance interaction of the phenyl substituent was weak and this result is compared to experimental results in the literature. Geometry-optimized INDO calculations on C_2BH_3 (4) and the azirinyl ($C_2NH_2^+$) and the diazirinyl (CN_2H^+) cations (5 and 6, respectively) indicated extensive delocalization within the three-membered rings and suggest that these species are aromatic. Calculations on cyclopropenone (7) indicate very little aromatic nature and very little positive charge buildup on the olefinic ring carbons. However, the carbonyl group is very highly polarized toward oxygen. On the other hand, protonated cyclopropenone (8) resembles a 2 π aromatic system.

Previous studies have indicated that alkyl groups stabilize cyclopropenyl cations[3] more than do phenyl groups.[4-6] This suggested that cyclopropenyl cations, with their closed 2 π aromatic shell, were less susceptible to resonance stabilization than traditional open-shell carbonium ions. Without resonance stabilization by the phenyls' π clouds, alkyl groups would be more effective stabilizing groups *via* their inductive effect. Interest in a wide variety of substituted cyclopropenyl cations has persisted unabated[7-11] and this anomalous stabilizing behavior of the phenyl group has caused extensive discussion.[4-6,12-15]

Simple Hückel MO theory predicts a delocalization energy of 2β for $C_3H_3^+$. Semiempirical SCF-LCAO-MO calculations[16] of Baird[17] predict ΔH_f values of 263, 268, and 279 kcal/mol for the cyclopropenyl, phenylcyclopropenyl, and diphenylcyclopropenyl cations, respectively. Interestingly, Baird calculated out-of-plane rotational barriers of 19 and 15 kcal/mol for the phenyl and diphenylcyclopropenyl cations, respectively. This is consistent with marked phenyl conjugation. Extended Hückel calculations,[15] on the other hand, predicted a shallow minimum when all rings were perpendicular to the C_3 plane in $Ph_3C_3^+$ (*i.e.*, 5.3 kcal/mol). An X-ray diffraction study of $Ph_3C_3^+ClO_4^-$ indicates only a slight noncoplanarity of the phenyl rings, presumably due to nonbonded ortho hydrogen repulsions (rings were rotated 7.6, 12.1, and 21.2° with respect to the C_3 plane).[18] Brief mention has been made of a CNDO study[19] of the trisaminocyclopropenyl cation with predicted 1.36-Å C-C bond lengths. This is in good agreement with the 1.363-Å C-C length found in the X-ray crystal structure of 1,2,3-trisdimethylaminocyclopropenium perchlorate.[20]

No systematic theoretical study of a variety of substituted cyclopropenyl cations has appeared. In view of their high C-C stretching force constant[21] (for $C_3Cl_3^+$ 6.32 mdyn/Å *vs.* 5.59 mdyn/Å for benzene), the high degree of s character in the ring carbon to substituent bonds [$J(^{13}C-H)$ = 265 Hz, 53% s for $C_3H_3^+$],[22] and their great stability, we undertook theoretical studies of such a series in the INDO approximation.[23-25] In addition to $C_3H_3^+$, $C_3F_3^+$, $C_3(NH_2)_3^+$, and $C_3H_2Ph^+$ we performed calculations on C_2BH_3 (isoelectronic with $C_3H_3^+$), cyclopropenone,[26] protonated cyclopropenone,[27] the azirinyl cation ($C_2NH_2^+$), and the diazirinyl cation (CN_2H^+). The azirinyl cations, for which simple Hückel MO calculations predict a 1.58β delocalization energy, have not been observed, but they have been implicated in isomerizations of 3-chloro-1-azirines.[28] Similarly, the diazirinyl cation should be stable according to simple Hückel theory,[29] but extended Hückel calculations predict it to be unstable with respect to distortion to a linear diazomethane cation.[30] Diazirinyl cations are postulated intermediates in reactions of halodiazirines.[31,32]

Results

The program (CNINDO), QCPE No. 141,[33] was modified for use on a Univac 1108.[1] Structures were generated using model builder program QCPE No. 135. The geometries of all ions (except the phenylcyclopropenyl cation) were completely and systematically optimized with respect to all bond lengths and angles.[34,35] The optimum geometries of the cyclopropenyl (1), trifluorocyclopropenyl (2), and trisaminocyclopropenyl (3) cations had symmetrical equilateral triangular rings with the substituent bond axis on a line bisecting the CCC 60° angle and in the C_3 plane (*i.e.*, D_{3h} symmetry). Boracyclopropene (4), the azirinyl cation (5), and the diazirinyl cation each exhibit C_{2v} symmetry. The bond lengths, angles, and charge densities are summarized in Figure 1. Figure 1 also summarizes the geometries and charge densities of cyclopropenone (7) (C_{2v} symmetry), protonated cyclopropenone (8) (C_s overall symmetry with local C_{2v} symmetry) and the phenylcyclopropenyl cation (**9b**). The charge densities are defined as $q - N$ where N = the atomic number.

The π-bond orders of **1-9** are given in Table I and the calculated HOMO to LUMO energy gaps are below 85 nm for **1-9**. We emphasize that these are $E_i - E_j$ (eigenvalue differences) rather than $E_i - E_j - J_{ij} + 2K_{ij}$ as given by Pople[36a] for transition energies. The individual orbital q values have been obtained by calculations using several different axis systems.[36b] This provides a picture of the polarization both of the π and σ bonds in **1-9**. A few results are noted in Table II.

Discussion

Cyclopropenyl Cations 1-3. The only experimental and calculated geometry which may be compared is that of **3** with the X-ray crystal geometry of the trisdimethylaminocyclopropenyl cation.[20] The calculated C-C (1.40) and C-N (1.36) lengths in **3** are comparable to the observed C-C (1.36) and C-N (1.33) lengths. The fact that the observed bond lengths are actually slightly shorter than those calculated suggests that the INDO method will not seriously overestimate resonance effects in this series due to any serious underestimation of bond lengths. The ring bond lengths in the triphenylcyclopropenyl cation are

Table I
Calculated π_y Bond Orders for Structures 1–9

Bond	1	2	3	4	5	6	7	8	9b
C–C	0.667	0.620	0.570	0.737	0.668		0.424[a] 0.856[b]	0.578[a] 0.747[b]	0.581[a] 0.734[b] 0.408[c]
C–F, C–B, or C–O		0.339[d]		0.623[e]			0.761[f]	0.479[f]	
N–C or N–N			0.453[g]		0.666[g]	0.652[g] 0.693[h]			

[a] Indicates C_1–C_2 bond. [b] C_2–C_3 bond. [c] C_1–C_4 bond. [d] C–F bond. [e] C–B bond. [f] C–O bond. [g] N–C bond. [h] N–N bond.

Table II
Selected Orbital Electron Densities (q Values)

Structure	Orbital[a] C(p_y)	C(p_z)	N(p_y) and N(p_z)	B, F, and O p_y	B, F, and O p_z
1	0.667	0.976			
2	0.759	0.747 (C*–F) 0.838 (C*–C)		1.907 (F)	1.334 (F*–C)
3	0.861	0.834 (C*–N)	1.820 [1.055 (N*–C)]		
4	0.737	0.981 (C*–C) 0.993 (C*–B)		0.527 (B)	0.789 (B*–C)
5	0.667	0.959 (C*–C) 0.916 (C*–N)	0.665 [1.253 (N*–C)]		
6	0.614	0.909 (C*–N)	0.693 [1.229 (N*–C)] [1.138 (N*–N)]		
7	0.753 (C_1) 0.856 (C_2)	0.835 (C_1*–O) 0.884 (C_1*–C_2) 0.965 (C_2–C_1) 0.963 (C_2*–C_3)			
8	0.680 (C_1) 0.747 (C_2)	0.791 (C_1*–O) 0.881 (C_1*–C_2) 0.985 (C_2*–C_3) 0.969 (C_2*–C_1)		1.536 (O)	1.175 (O*–C_1)
9b	0.688 (C_1) 0.734 (C_2) 0.897 (C_7)	0.925 (C_1*–C_4) 0.914 (C_4*–C_1) 0.970 (C_2*–C_3)		1.826 (O)	1.244 (O*–C_1)

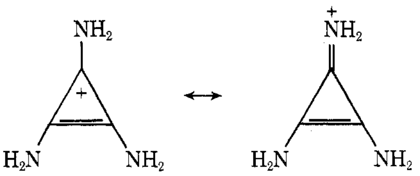
[a] The p_z orbital designation given in brackets means that the orbital is on the starred (*) atom along the bond axis to the other atom designations.

known to be 1.40,[18] showing that only minor changes in ring structure occur as the substituent is varied from NH_2 to phenyl. The calculated C–C ring bond lengths of **1**, **2**, and **3** are 1.38, 1.38, and 1.40 Å, respectively.

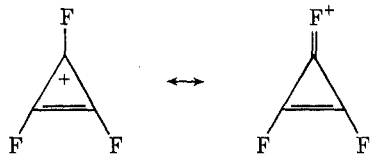
The C–C π-bond orders of **1**, **2**, and **3** are 0.667, 0.620, and 0.576, respectively. When combined with calculated σ-bond orders, which are in the vicinity of 1, the total calculated C–C ring bond orders exceed 1.5. Thus, the high force contents associated with these systems are understandable.

Bonding to Substituents in 1–3. The C–H bonds in **1** are polarized toward carbon as is expected. Each carbon bears a charge of +0.201 while each hydrogen has a +0.132 charge. In **3** the C–N σ bond is polarized toward nitrogen [C(p_z) = 0.834, N(p_z) = 1.055]. However, despite this inductive electron withdrawal by nitrogen, the net charge on each ring carbon is lower in **3** (+0.185) than in **1** (+0.201). This is readily explained by examining the π bond between carbon and nitrogen. Each carbon has 0.834 electrons in its p_y orbital (an increase of 0.17 electrons per carbon over **1**) while the nitrogen has 1.82 π_y electrons (*i.e.*, it has donated about 0.18 π electron to carbon per C–N π bond). This strong resonance donation of electron density to carbon is further indicated by the calculated C–N π-bond order in **3** of 0.453 and 13.9 kcal/mol rotational barrier. Thus, the C–N bond is a combination of σ bond polarized toward N with a π bond formed by back donation of electron density from N to C. When rotated 90°, the charge at the rotated nitrogen is −0.241 *vs.* −0.159 at the other two nitrogens. This is caused by the inability of the rotated nitrogen to back donate electron density to carbon *via* π bonding.

In **2** the same picture exists for the C–F bonds. However, here the π bond is more strongly polarized toward fluorine [$q(C(p_z))$ = 0.747, $q(F(p_z))$ = 1.334] and the back π donation from F to C is less than from an amino group [C–F π-bond order = 0.339, $q(F(p_y))$ = 1.90, $q(C(p_y))$ = 0.759]. Thus, INDO calculations clearly show that resonance hybrid structures **2b** and **3b** contribute strongly to



3a **3b**



2a **2b**

the bonding in **2** and **3**. In **3** a total of 2.58 electrons populate the ring π system and in **2** the total is 2.28 (*vs.* 2 electrons for **1**).

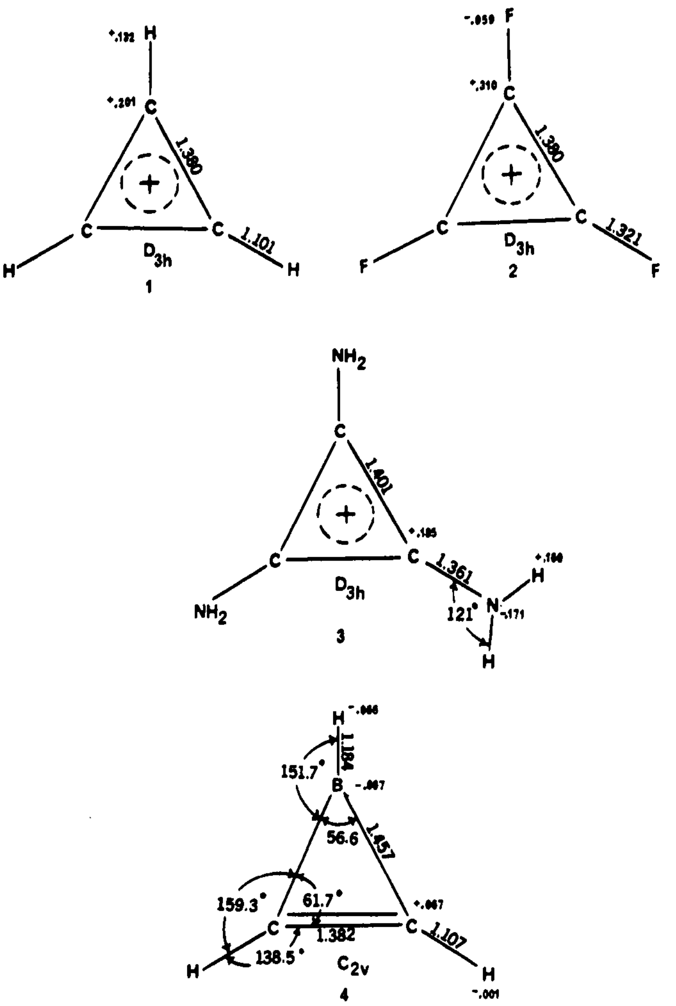
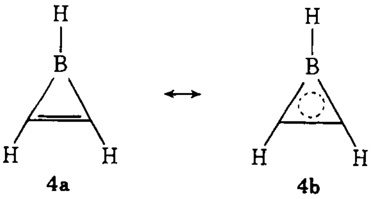


Figure 1a. The calculated geometries and charge distributions of structures 1-4.

Boracyclopropene. INDO calculations clearly portray boracyclopropene's aromaticity. For example, although the B-C σ bond is polarized toward carbon as expected [$C(p_z)$ = 0.993, $B(p_z)$ = 0.737] there is very little charge separation in the molecule. This is due to back π donation of electron density from C to B. Thus boron's "vacant" p_y orbital has 0.527 electrons occupying it *vs.* 0.732 for $q(C(p_y))$. Furthermore the C-C π-bond order (0.737) is not much larger than the C-B π-bond order (0.623).

The calculated C-C length in 4 (1.38) is longer than simple C=C bonds (1.33-1.34) but about that predicted for benzene (1.39). Similarly the calculated C-B length (1.46) is substantially shorter than measured C-B lengths [1.56 for $B(CH_3)_3$].[37] The predicted HOMO to LUMO energy gap (see Results) of 4 is below 85 nm and similar to that of **1**. According to INDO calculations, **4b** is a superior representation of 4 than is **4a**.



4a **4b**

Azirinyl and Diazirinyl Cations. The azirinyl cation has extensive π delocalization, as evidenced by the large and similar C-C and C-N π-bond orders (0.668 and 0.666, respectively). Furthermore, substantial back π donation from N to C exists. The $N(p_y)$ orbital is occupied by only 0.665 electrons and the carbon p_y orbitals contain 0.668 electrons each, for a total of 1.336 π electrons on the carbons. In other words, a 0.336 excess exists over the value of 1.0 predicted by resonance hybrids **5a** and **5b**. This back π donation from N counteracts the polarization of the σ bond [$N(p_z)$ = 1.253, $C(p_z)$ = 0.916] toward N. A substantial amount of positive charge resides on the nitrogen (+0.135), though less than on carbon (+0.275), despite the polarization of the σ bond toward N. Thus, within the INDO framework **5c** makes a substantial contribution to the structure of **5**. Furthermore, the calculated bond lengths support this view. The C-C length (1.36) is only slightly shorter than the C-C length in **1**, and the calculated C-N length (1.36) is close to that found in pyridine (1.35).

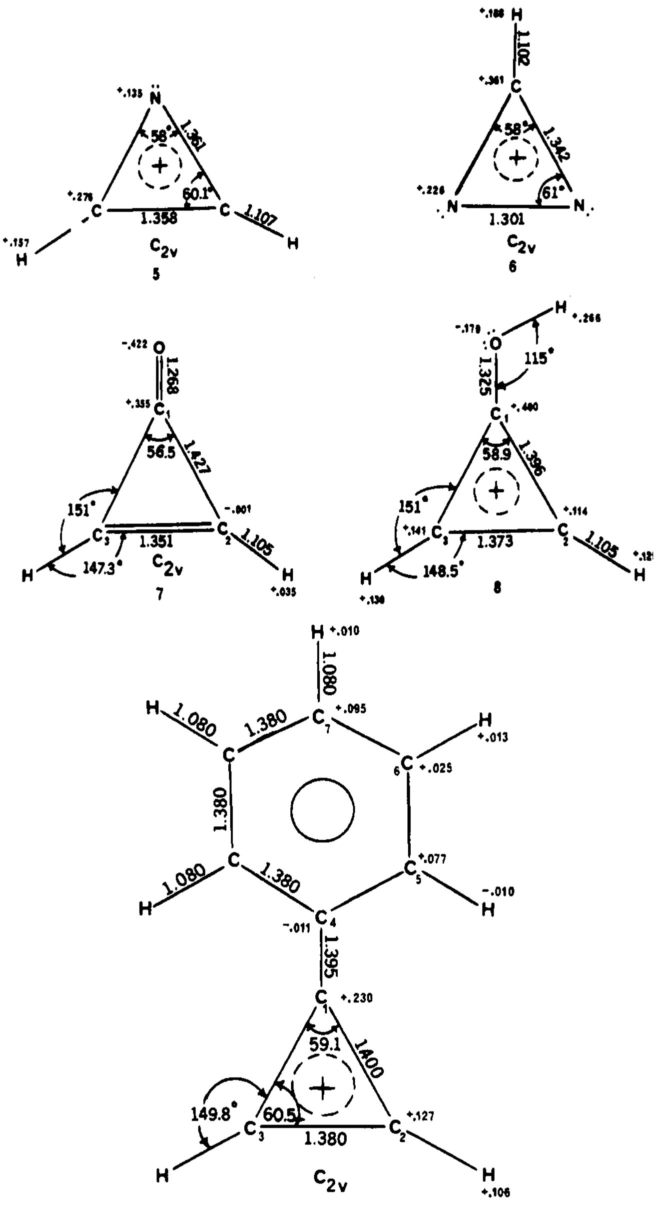
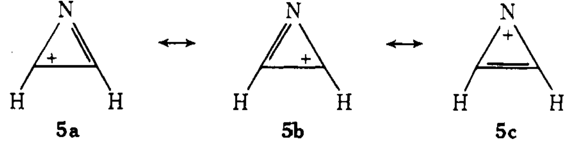
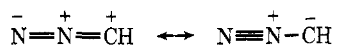


Figure 1b. The calculated geometries and charge distributions of structures 5-8 and **9b**.



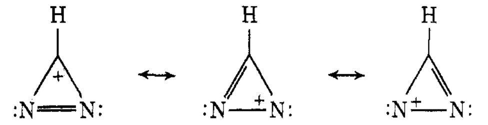
5a **5b** **5c**

The diazirinyl cation exhibits the stable minimized geometry listed in Figure 1. Unlike EHT,[30] no structural instability relative to the diazomethyl cation, **10**, was predicted by INDO. As with species **1-5**, aromaticity is suggested by the similarity and the size of the N-N and C-N π-bond orders (0.693 and 0.652, respectively) and the distribution of π-electron density [$C(p_y)$ = 0.614 and $N(p_y)$ = 0.693] where substantial back π donation of electron density from N to C occurs. Moreover, each nitrogen bears a significant positive charge (+0.226) along with carbon (+0.361). The large charge on N occurs despite a strong polarization of the C-N bonds toward nitrogen [$C(p_z)$ = 0.909, $N(p_z)$ = 1.229]. It is largely a result of back π bonding from N to C. The short calculated C-N distance (1.34) and the N-N length of 1.30 further suggest an aromatic structure. Finally, the HOMO to LUMO eigenvalue difference is very close to that of **5** and similar to that of **1-4**. Taken altogether, a substantial contribution by each hybrid structure **6a-c** is indicated by INDO. These calculations suggest that the azirinyl and diazirinyl cations might be prepared as stable aromatic cations, perhaps in nonnucleophilic media.



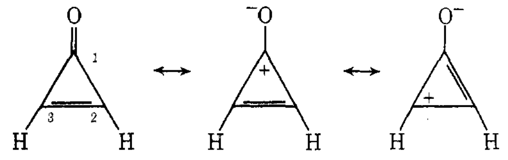
$$\overset{-}{N}=\overset{+}{N}=\overset{+}{C}H \longleftrightarrow N\equiv\overset{+}{N}-\overset{-}{C}H$$

10



6a **6b** **6c**

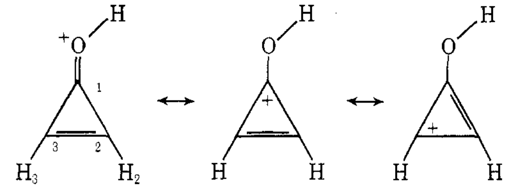
Cyclopropenone and Protonated Cyclopropenone. Cyclopropenone's high boiling point [30° (0.45 Torr)][26] suggests that the molecule is highly polar and supports the notion that structures **7b** and **7c** are strong contributors. However, examination of the calculated charge densities of **7** reveal that the "olefinic" carbons have a tiny negative charge (0.001) and their bound hydrogens only a very small positive charge (+0.035). This suggests that any contribution of **7c** might be small. The large charge separation between oxygen (−0.422) and the carbonyl carbon (+0.355) implicates a large contribution from **7b** and is in agreement with a high boiling point. For comparison, the calculated charge separation in the carbonyl group of formaldehyde is much smaller (*i.e.*, C, +0.21; O, −0.19).[24] That a contribution of the type indicated by **7c** is small in cyclopropenone is further suggested by comparing the π-bond orders between C_1-C_2 (0.424) and C_2-C_3 (0.856). This view is further supported by the calculated lengths (C_1-C_2 = 1.43; C_2-C_3 = 1.35). The long length and small π-bond order in the C_1-C_2 bond argue for a much smaller contribution of **7c** than is found in cyclopropenyl cations **1-3** and their analogs **4-6**.



7a **7b** **7c**

The C_1-O π order and the calculated occupancy of the π orbitals argue that the C_1-O bond is a double bond [$O(p_y)$ = 1.54 and $C_1(p_y)$ = 0.753]. Back π donation from O to C_1 occurs while the C_1-O σ bond is strongly polarized toward O [$C(p_z)$ = 0.835, $O(p_z)$ = 1.175].

Calculations on **8** are particularly interesting when compared to **7**. On protonation there is a substantial increase in the "aromatic" nature of the ring. The calculated charge density at C_1 increases modestly relative to cyclopropenone (**7**) (*i.e.*, 0.400 *vs.* 0.355) while C_2, C_3, H_2, and H_3 now bear sizable positive charges (0.114, 0.141, 0.129, and 0.130, respectively). Furthermore, the C_1-C_2 π-bond order increases (0.578) substantially and the C_2-C_3 π-bond order decreases (0.747) relative to those in **7**. There is a very large change in the C_1-O π-bond order (0.761 in **7** *vs.* 0.479 in **8**). The C_1-O σ-bond polarization increases going from **7** to **8** [$C(p_z)$ = 0.791, $O(p_z)$ = 1.244] but the C_1-C_2 σ-bond polarization is virtually unchanged. These observations indicate that hybrid **8c** has become a far more significant contributor in **8** than **7c** is in **7**.



8a **8b** **8c**

Strong polarization of the π electrons of **8** toward O is also indicated. Despite the fact that the oxygen in **8** is protonated and bears less total electron density than the oxygen in **7**, the electron density in its p_y orbital has *increased* going from **7** to **8** (1.54 *vs.* 1.83 electrons). On the other hand the p_y electron density on the ring in **8** has decreased [$C_1(p_y)$ = 0.68, $C_{2,3}(p_y)$ = 0.75]. A final indication that there has been a substantial shift toward ring aromaticity going from **7** to **8** is the increase in energy of the HOMO-LUMO eigenvalue difference.

Phenylcyclopropenyl Cation. Several geometries of the phenylcyclopropenyl cation, including **9a** and **9b** (for **9b** see Figure 1), were studied but it was not fully optimized.[35] In **9a** the three-membered ring's bond lengths were all held equal at 1.38 Å, whereas in **9b** the three-membered ring's C_1-C_2 and C_1-C_3 lengths were increased to 1.40° while the C_2-C_3 length was maintained at 1.38 Å. The distorted geometry **9b** was more stable than **9a**. Further calculations were carried out where a slight quinoid geometry was introduced to the phenyl ring, and this resulted in a further stabilization (note that **9a** and **9b** have symmetrical phenyl rings assumed). This indicates some conjugation between the two rings. However, the degree of phenyl conjugation with the three-membered ring is modest, as indicated by (a) a π-bond order of 0.408 for the C-C bond joining the two rings; (b) the rather small charge delocalization to the ortho (+0.077) and para (+0.093) positions of the phenyl rings; and (c) the small calculated out-of-plane rotational barrier for the phenyl ring (2 kcal/mol).[38]

The total π-electron population on the three-membered ring is 2.16 [$q(C_1(p_y))$ = 0.688, $q(C_{2,3}(p_y))$ = 0.734], an increase of 0.16 electrons over **1**. This, plus the greater positive charge density at the ortho and para (relative to meta) positions on the phenyl ring, further suggests that some conjugation exists in **9**. However, the extent of conjugation appears far less in **9** than in the phenylcyclobutadienyl dication.[39]

A review of all the calculations reveals that strong conjugation between the substituent (such as F or NH_2) and the ring may occur to provide π-electron density to the cyclopropenyl ring. Furthermore, this is a stabilizing interaction. Thus, INDO theory shows that cyclopropenyl cations are susceptible to resonance stabilization without loss of aromaticity, in agreement with the interpretation of recent experimental results.[9-11,14] However, it is also clear that theory, at the INDO level, predicts only a small resonance interaction of the cyclopropenyl ring with a phenyl substituent. Again, this agrees with experimental results. Evaluation of all the data in the literature, including those on the protonation of cyclopropenones,[8,40-42] reveals the ordering $R_2N \gg c\text{-}C_3H_5 > SR > CH_3 > i\text{-Pr} > t\text{-Bu} > Ph > H$ in ability to stabilize cyclopropenyl cations. Thus, the anomalous position of the phenyl in the above experimental seems to be reflected in the INDO calculations. Certainly it would be desirable to have calculations on other members of this series, but geometry optimization of such systems would be expensive.

While the phenyl group is usually thought to be more effective than the alkyl groups in stabilizing carbonium ion-like transition states[43] (especially those where there is a great electron demand by the charge center), the literature teaches that, in many equilibrium studies, phenyl substituents are inferior to alkyl groups in stabilizing carbonium ions relative to their uncharged precursors. Example equilibrium studies include enthalpies of transferring enols[44] and ketones[45] from carbon tetrachloride to fluorosulfonic acid, the ionic dissociation of p-$RC_4H_4CPh_2Cl$ in SO_2,[46] cyclopentenyl cation $pK_R{}^+$ measurements,[47] and $pK_R{}^+$ measurements on para-substituted tropylium ions.[48] Solvolysis studies of substituted cumyl chlorides[49] also reflect the inferior stabilizing ability of remote phenyls. Insofar as INDO calculations are meaningful, they argue that phenyl groups inherently do not strongly conjugate with the three-membered ring. However, as the electron demand at the ring increases (in going from cyclopropenyl cations to cyclobutadienyl dications) the resonance interaction with phenyl substituents increases sharply.[39]

INDO calculations argue strongly against any major contribution of a cyclopropenium oxide structure (*i.e.*, **7c**) in cyclopropenone. Tobey has previously argued that no abnormal degree of charge separation is needed to explain cyclopropenone's high dipole moment in substituted systems.[50] Indeed, from ^1H and ^{19}F nmr studies, it was pointed out that an exceptional amount of positive charge should not be invoked to explain the observed deshielding of side-chain protons in cyclopropenones.[50] However, chlorine anisotropies, now known to be significant,[51] were neglected in Tobey's analysis. Our calculations do support Tobey's conclusions and resemble arguments advanced by Bertelli in the tropone series.[52] The chemistry of cyclopropenone suggests ambivalent character in this respect. While Diels–Alder addition has been observed on one hand, reaction with bromine affords a cyclopropenium hypobromite.[53]

The well-known correlations between ^{13}C chemical shifts and π-charge densities in aromatic systems[54–56] have used HMO calculations to define the π-charge density at carbon. However, it has now been noted[57] that the correlation, between empirically and theoretically (HMO) derived charge densities is poor for the triphenylcyclopropenyl cation compared to a similar correlation made for the triphenylmethyl cation.[58] The INDO results show that the total charge densities are only partly the result of the π electrons and future chemical shift correlations should be made with this distinction in mind.

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(35) While geometry optimization could lead to structures which might not duplicate known bond lengths,[18,20] we used optimization so that the intrinsic results of the INDO method would be realized. Thus, all ions in a series are able to be compared directly once they have been optimized, as opposed to examining calculated quantities for a series where known geometries were used for some structures and assumed geometries for others. Complete opimization of the phenylcyclopropenyl cation, **9**, would have been prohibitive with respect to computer time. Thus, we employed two geometries (**9a** and **9b**) which were close to an optimized structure.

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not be made until complete geometry optimization studies are made, and the same is true of INDO. In our view, each conformation being compared must be completely geometry optimized with respect to energy and then only those minimized conformations should be compared in stability. Without going through this procedure it is impossible to really see which conformation CNDO/2 (or INDO, etc.) inherently predicts as most stable.
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INDO Theoretical Studies. VII.[1] Cyclobutadienyl Dications

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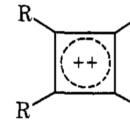
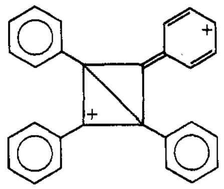
Geometry-optimized INDO calculations have been performed on six cyclobutadienyl dications including $C_4H_4^{2+}$ (3), $C_4F_4^{2+}$ (4), $C_4(CH_3)_4^{2+}$ (5), $C_4(NH_2)_4^{2+}$ (6), $C_4H_3(NH_2)^{2+}$ (7), and $C_4H_3Ph^{2+}$ (8). The magnitude of conjugation by F, NH_2, and Ph groups with the four-membered ring was assessed by examining the calculated π-bond orders, rotational barriers, charge densities, orbital electron densities, and the bond lengths. Within the framework of INDO theory these substituents conjugated strongly to the ring (π effect) while the C–F bonds in 4 and the C–N bonds in 6 and 7 remained polarized toward the substituent. Conjugation to such substituents is stronger in cyclobutadienyl dications than in cyclopropenyl cations. Thus the "aromatic" 2 π system accepts a significant amount of π-electron density from the substituents to increase stability, and "anti-aromatic" destabilization does not appear to be a problem.

Simple molecular orbital theory predicts that planar cyclobutadienyl dications, 1, should be stable delocalized 2 π aromatic systems having 2β units of resonance energy.[3] In contrast to the 6 π cyclobutadienyl dianion, the dication should be more stable because its double positive charge will lower the energy of the bonding orbitals. Furthermore, the highest π orbitals of the dication are not degenerate as they are in the cyclobutadiene; thus they would not be subject to Jahn-Teller distortion.



1

Since 1960 a number of unsuccessful attempts to prepare this class of dications appeared.[4-7] However, in 1969 Olah, *et al.*,[8] reported the successful generation of the tetramethylcyclobutadienyl dication upon addition of tetramethyl-2,3-dichlorocyclobutene to SbF_5–SO_2 at −78°. The pmr of the dication exhibited a sharp singlet at δ 3.68, and it was stable at −78° in solution for at least 2 weeks. The ^{13}C spectrum exhibited ring carbon absorption at −14.4 ppm (from CS_2),[8] which agreed with that predicted based on the linear relationship of measured ^{13}C shifts for $C_5H_5^-$, C_6H_6, $C_7H_7^+$, and $C_8H_8^{2-}$ with a slope of 166 ppm per π electron.[9] Shortly thereafter, Olah and Mateescu[10] reported the generation of the tetraphenylcyclobutadienyl dication from 3,4-dibromotetraphenylcyclobutene in SbF_5–SO_2 at −60° (^{13}C δ +17.6 for ring carbons). HMO calculations[10] predicted π-bond orders of 0.45 between ring carbons and 0.47 between ring and phenyl carbons, and a π-electron density of 0.71 at each ring carbon. Thus the calculations suggested a significant contribution of canonical forms such as 2, with charge delocalization into the phenyl rings.



2

No systematic theoretical study of cyclobutadienyl dications has appeared. In order to study the effects of substituents on the bonding in this class of dications, we performed INDO[11,12] calculations on the parent cyclobutadienyl dication (3) and the tetrafluoro- (4), the tetramethyl- (5), the tetraamino- (6), the monoamino- (7), and the monophenylcyclobutadienyl (8) dications. In these calculations the bond lengths and angles of the ring carbons and the substituent atoms (relative to the four-membered ring) were optimized in a systematic fashion.[13,14] In particular, we examined the extent of delocalization into substituents, in view of the observation that alkyl groups stabilize the 2 π cyclopropenyl cations more than phenyl groups do.[15-17] This anomalous stabilizing behavior has led to extensive discussion in the literature of whether or not cyclopropenyl cations were less susceptible to resonance stabilization than traditional open-shell carbonium ions.[10,15-19] Extension of this question to the 2 π cyclobutadienyl dications is of obvious interest.

Throughout this paper we shall qualitatively represent the results of the INDO calculations in terms of ground-state valence bond resonance hybrids. This is done as a convenient method of representing resonance contributions of various functional groups and to compare the ef-