Novel Aromatic Systems. II.[1a] Cyclobutenyl Cations and the Question of Their Homoaromaticity. Preparation and Study of the Homocyclopropenium Ion, the Simplest Homoaromatic System

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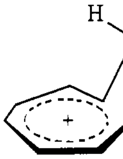
Abstract: A series of cyclobutenyl cations have been prepared and studied by ^{13}C and ^{1}H NMR spectroscopy. The data for the 1,3-diphenyl-2,4-diR-cyclobutenyl cations (**7**, R = Ph, CH_3, H) are characteristic of alkenyl (allyl) cations with undetectably small contributions from 1,3 π overlap. Exclusive methyl substitution, as in the 1,3-dimethylcyclobutenyl cation (**9**) and the 1,2,3,4-tetramethylcyclobutenyl cation (**10**-H) lead to decreased importance of allylic delocalization and accordingly greater 1,3 π overlap and homoaromatic charge delocalization. The series culminates in the parent (unsubstituted) cyclobutenyl cation (**5**-H) which exhibits truly aromatic delocalization. The 270-MHz ^{1}H NMR spectra of **5**-H show temperature dependence and, at −110°, the puckered (nonplanar) homoaromatic ion was "frozen out". Complete line-shape analysis of the 270-MHz ^{1}H NMR spectra (DNMR 3) gave a value for $\Delta G^{\ddagger} = 8.4$ kcal mol^{-1} for the ring-flipping process. The carbon chemical shifts and $^{1}J_{CH}$ values for **9**, **10**-H, and **5**-H are discussed in terms of charge distribution and rehybridization due to increasing importance of the puckered homoaromatic forms. **5**-H, the homoaromatic analog of the cyclopropenium ion, is thus the simplest homoaromatic system.

The concept of homoaromaticity is by now a familiar one in organic chemistry.[2] The general formulation of homoaromatic systems as a cyclic Hückeloid ($4n + 2$) array of π electrons interrupted in one or more places by an intervening sp^3-hybridized carbon has been treated theoretically in a number of studies.[3] Experimental studies of these systems have dealt mainly with the six π-electron homotropylium ion (**1**)[2,4] and the ten π-electron cyclooctatetraene dianion (**2**).[2a,5] Several bishomoaromatic ions, such as **3**[6] and **4**,[2a,7] have also been prepared and studied. Homoaromatic ions are characterized by cyclic charge delocalization, as shown in **1–4**, although the delocalization is not as complete as in the parent aromatic systems, namely the tropylium ion (for **1** and **3**), cyclooctatetraene dianion (for **2**), and the cyclopentadienyl anion (for **4**).



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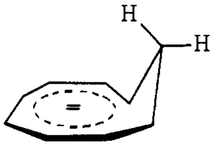

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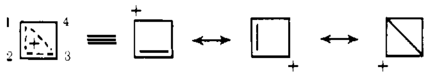
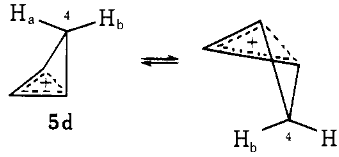
In this paper, we report a systematic experimental investigation of the bonding character in the simplest potentially homoaromatic two π-electron system, the monohomocyclopropenium ion (**5**-H). It is of historical interest that the concept of homoaromaticity was first proposed for this two π-electron system: Roberts and Applequist[8] suggested that the high solvolytic rates of certain 3-substituted cyclobutenes were due to the intermediacy of homocyclopropenium ions (cf. **5**-H). **5**-H can be envisioned as a resonance hybrid of the cyclobutenyl cations **5a** and **5b** and the 1,3 π-overlap contributor **5c**. In recent years, a number of highly substituted cyclobutenyl cations have been prepared under stable-ion conditions and characterized by uv,[11a-c] ^{1}H NMR,[11a-e] and ^{13}C NMR[11f,g] spectroscopy. The most convincing evidence for homoaromatic character was reported by Katz and Gold[11b] for the 4-substituted 1,2,3,4-tetramethylcyclobutenyl cations, which displayed a λ_{max} in the uv absorption spectra intermediate between the values observed for the cyclopropenyl and allyl cationic analogs.



5-H 5a 5b 5c



5d 5e

The question of 1,3 π overlap in alkenyl (allyl) cations has been critically examined, both theoretically[12] and experimentally. The evidence is overwhelmingly against the participation of 1,3 overlap in acylic alkenyl[11f,13] and cyclopentenyl and higher homologous cycloalkenyl cations.[11d,14] It would be expected[12c,e] that, as the proximity of C_1 and C_3 increased, the importance of 1,3 π overlap should accordingly increase and thus 1,3 π overlap is more likely in cyclobutenyl cations than in the acyclic and larger cyclic alkenyl cations. However, the possibility of 1,3 overlap involving bonding between C_1 and C_3 intermediate between σ and π type[15a] must also be considered, as indicated by the recent ab initio calculations of Hehre,[15b] which suggest that the energy minimum for the parent cation **5**-H corresponds to the nonplanar structures **5d** and **5e**.[15b-d]

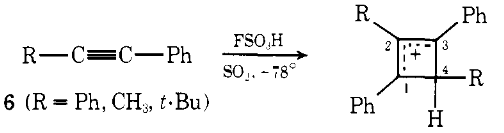
Our experimental search for homoaromaticity in cyclobutenyl cations has probed along two lines. Firstly, 1,3 overlap should lead to increased charge density at C_2 at the expense of C_1 and C_3, i.e., **5c** relative to **5a** and **5b**. For this study, ^{13}C NMR spectroscopy was employed as it is currently the best available technique for the detection of charge distribution patterns.[16] Secondly, the prediction[15c] of degenerate nonplanar structures for **5**-H (i.e., **5d** and **5e**) with a low interconversion barrier suggested that temperature dependence of the NMR spectra should be studied. In the case of **5**-H, separable resonances for H_{4a} and H_{4b} (cf.

5d) should be observed in the ^{1}H NMR spectrum at temperatures where the ring flipping is "frozen out".

We report the successful preparation of the parent homocyclopropenium ion **5**-H and the observation in this ion of both these phenomena, verifying the truly homoaromatic nature of **5**-H. The energy barrier for the interconversion **5d** $\rightleftharpoons$ **5e** was also determined. In addition, we report the study of a series of cyclobutenyl cations where the behavior can be seen to progress from classical allylic delocalization (i.e., **5a** $\leftrightarrow$ **5b**), through species displaying increasing contributions from 1,3-orbital overlap and, finally, the homoaromatic homocyclopropenium ions.

Results and Discussion

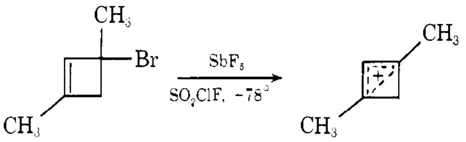
1. Preparation of the Ions. Many cyclobutenes are readily synthesized by the dimerization of alkynes in the presence of electrophilic reagents. Under superacidic conditions, some of these reactions can be terminated at the cyclobutenyl cation stage and thus afford a convenient preparation of cyclobutenyl cations. Diphenylethyne (**6**-Ph),[11c,17] 1-phenylpropyne (**6**-CH_3),[17] and 3,3-dimethyl-1-phenylbutyne (**6**-*t*-Bu)[11c] cyclize in FSO_3H-SO_2 at −78° to give exclusive formation of the cyclobutenyl cations **7**-Ph,[11c,17] **7**-CH_3[17] and **7**-*t*-Bu,[11c] respectively.


6 (R = Ph, CH₃, *t*-Bu)

7 (R = Ph, CH₃, *t*-Bu)

The 1,3-diphenylcyclobutenyl cation (**7**-H) has also been reported previously;[11d] **7**-H cannot be generated directly from phenylethylene,[17] necessitating a more involved synthesis.[11d] **7**-Ph and **7**-CH_3 were prepared for this study, while data for **7**-H[11d] and **7**-*t*-Bu were taken from literature sources.

The preparation of cyclobutenyl cations not substituted at C_2 and C_4 usually involves a complex synthetic problem (cf. **7**-H). The 1,3-dimethylcyclobutenyl cation (**9**) was prepared from 1,3-dibromo-1,3-dimethylcyclobutane which was first converted to 3-bromo-1,3-dimethylcyclobutene (**8**)[18] and then ionized with SbF_5 in SO_2ClF at −78° to **9**.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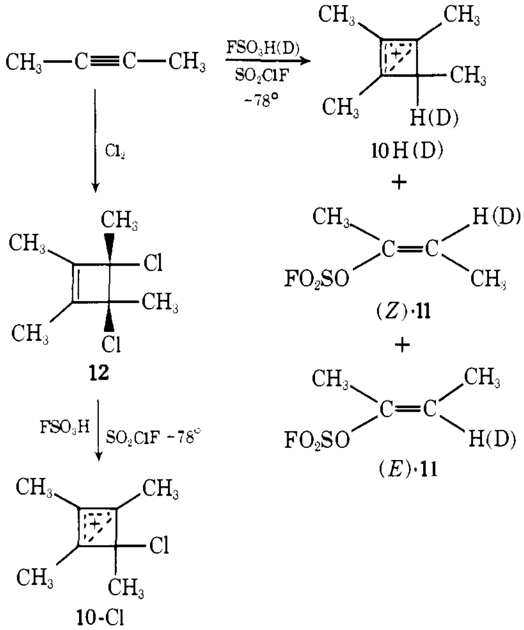
The 1,2,3,4-tetramethylcyclobutenyl cation[11b] (**10**-H) and its 4-deuterio analog **10**-D can be prepared directly from 2-butyne using FSO_3H or FSO_3D, respectively, in SO_2ClF at −78°.[17] Although the major pathway in these reactions leads to formation of the 2-butenyl fluorosulfates (*E*)-**11** and (*Z*)-**11** (the ratio **10**-H:(*Z*)-**11**:(*E*)-**11** = (1: 6.75:1),[17] the carbon and proton resonances for **10**-H are clearly differentiated from those due to (*Z*)-**11** and (*E*)-**11**. The 4-chloro-1,2,3,4-tetramethylcyclobutenyl cation (**10**-Cl) was readily prepared by ionization of *trans*-3,4-dichlorotetramethylcyclobutene (**12**, from 2-butyne and chlorine)[10a] with FSO_3H in SO_2ClF at −78°.

The 4-chlorocyclobutenyl cation (**5**-Cl) was prepared by ionization of *cis*-3,4-dichlorocyclobutene (**13**)[19] with SbF_5 in SO_2ClF at −78°. The parent cation **5**-H was itself obtained from 3-acetoxycyclobutene (**14**)[20a] with FSO_3H-SbF_5 in SO_2ClF at −78°; the reaction was accompanied by the competing process of ring cleavage to form protonated 2-butenyl (**15**).[20b] The resonances due to the by-product, protonated acetic acid, and the acetylium ion (formed by dehydration of acetic acid) were effectively removed by using the trideuteroacetate of **14**[20c] (**14**-d_3) as precursor.

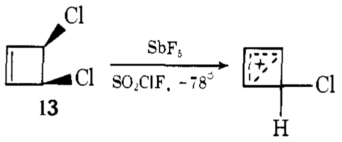

10H(D)

(*Z*)-11

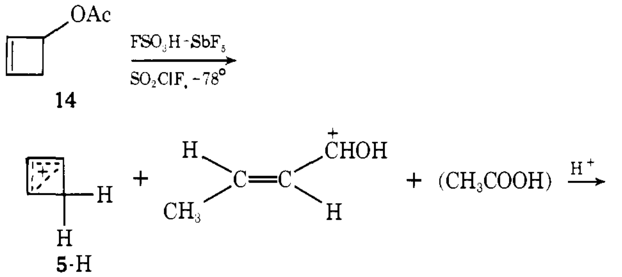
(*E*)-11

12

10-Cl


13

5-Cl


14

5-H

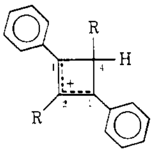
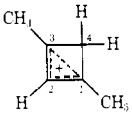
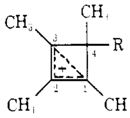
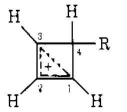
$$CH_3CO_2{}^+H_2 \xrightarrow{H^+} CH_3\overset{+}{C}O + H_3{}^+$$

All the cyclobutenyl cations showed considerable stability, and their solutions could be heated to 20° in some cases. Although a number of other structural variations could have been envisaged, we believe that *all* the significant features likely to be encountered in cyclobutenyl-homocyclopropenium ions are present in the series of ions **7**, **9**, **10**, and **5**. The ^{1}H and ^{13}C NMR data for the ions are summarized in Tables I and II, respectively.

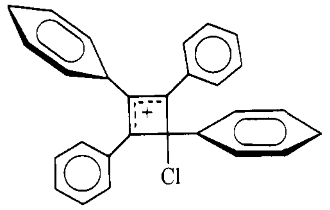
2. The Relationship between Structure and Charge Distribution in Cyclobutenyl Cations. As the starting point of our discussion, we are first considering systems which would be expected to show the highest contribution from classical allylic delocalization, (i.e., **5a** $\leftrightarrow$ **5b**) and correspondingly the least contributions from 1,3 π overlap (**5c**) or homoaromatic charge delocalization.

The presence of phenyl groups at C_1 and C_3 which can conjugatively delocalize charge from these positions should strongly favor allylic delocalization. The X-ray crystal structure of the 4-chloro-1,2,3,4-tetraphenylcyclobutenyl cation (**16**) has been determined,[21] showing the C_1 and C_3 phenyl groups to be nearly coplanar with the *planar* cyclobutenyl ring, while the C_2 phenyl group is twisted approximately 60° out of this plane and thus unable to effectively conjugatively delocalize charge from C_2.

Table I. ^1H NMR Data[a] for the Cyclobutenyl Cations

Ion		Proton chemical shifts, multiplicities, and coupling constants[a]		
		$C_{1,3}$ substituent	C_2 substituent	C_4 substituents
	7-Ph[b]	H_{ortho}, 7.92, d; H_{meta}[h]; H_{para}, 7.72, t	Ph, 7.25–7.7, m	H_4, 5.77; Ph, 7.25–7.7, m
	7-CH_3[b]	H_{ortho}, 8.04, d; H_{meta}, 7.61, t; H_{para}, 7.80, t	CH_3, 2.42, d, $J_{H_4, CH_3} = 2.3$	H_4, 4.40, m; CH_3, 1.47, d, $J_{H_4, CH_3} = 6.9$
	7-H[c]	H_{ortho}, 8.25, d; H_{meta}, 7.82, t; H_{para}, 8.02, t	H_2, 8.12	H_4, 4.18
	9[d]	CH_3, 2.93	H_2, 8.03	H_4, 3.90
	10-H[e]	CH_3, 2.63	CH_3, 2.37, d, $J_{H_4, CH_3} = 3.8$	H_4, 4.53, m; CH_3, 1.39, d, $J_{H_4CH_3} = 6.5$
	10-D[f]	CH_3, 2.60	CH3, 2.35	CH_3, 1.4
	10-C_1[e]	CH_3, 2.91	CH_3, 2.43	CH_3, 2.28
	5-H[g]	$H_{1,3}$, 7.95, g, $J_{1,2} = J_{1,4} = 1.6$	H_2, 9.72, dt, $J_{2,4} = 0.4$	H_4, 4.53, dt
	5-C_1[d]	$H_{1,3}$, 8.38, $J_{1,2} = 1.6$	H_2, 9.80, d, $J_{2,4} = 4.0$	H_4, 6.62, d

[a] Chemical shifts are in parts per million relative to external Me_4Si, coupling constants are in hertz. Signals are singlets unless shown. d = doublet, t = triplet, q = quartet, m = multiplet. [b] In $FSO_3H–SO_2$ at –40°. [c] Data from ref 11d, converted from τ to δ scale. [d] In $SbF_5–SO_2ClF$ at –40°. [e] Data from ref 11b, converted from τ to δ scale. The spectra obtained in this work were identical. [f] In $FSO_3D–SO_2ClF$ at –40°. [g] In $HSO_3F–SbF_5–SO_2ClF$ at –40°. [h] Obscured by C_2– and C_4–Ph proton resonances.



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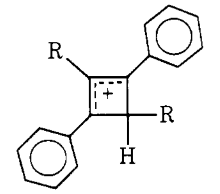
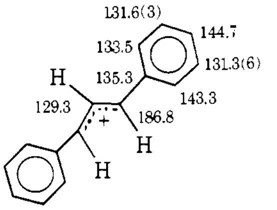


7 (R = Ph, CH_3, H, *t*-Bu)



17[13b]

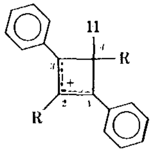
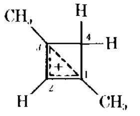
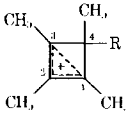
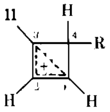
Charge distribution differences in 7-Ph, 7-CH_3, and 7-H[11d] should therefore be directly related to the effectiveness of the $C_{1,3}$-phenyl groups to achieve coplanarity with the cyclobutenyl ring which will accordingly depend on the relative steric interactions between these groups and the C_2 substituent. This latter factor can be estimated, from molecular models, to vary in the order H < Ph < CH_3.[22] The ^1H NMR data for these ions, particularly the H_{ortho} and H_{para} shifts (Table I), are in complete accord with the expected order of steric effects. Although no ^{13}C NMR data are available for 7-H, the ^{13}C NMR data for 7-CH_3 and 7-Ph (Table II) are consistent with the allylic nature of the ions, indicating minimal charge development at C_2 and heavy localization of charge on $C_{1,3}$ and their attached phenyl groups, and can be seen to be analogous with the 1,3-diphenylpropenyl cation (**17**).[13b] The nonequivalence of the C_{ortho} resonances for the $C_{1,3}$-phenyl groups in 7-Ph,[23] combined with the observation by Farnum that 7-H has two H_{ortho} resonances below –40°[11d] shows that free rotation of these groups is not occurring.

The ^{13}C NMR spectrum of 7-*t*-Bu has been reported previously;[11g] steric hindrance to phenyl coplanarity would be expected to be greatest here, and the C_{para} resonance (Table II) is indeed shielded relative to 7-Ph, 7-CH_3, and **17**, consistent with diminished charge localization in the phenyl rings of 7-*t*-Bu. Furthermore, the relative $C_{1,3}$ and C_2 shifts are reversed from 7-Ph and 7-CH_3. However, to interpret this result, consideration must be given for corrections due to the substituent effects introduced by the *tert*-butyl groups. The difficulty of precisely estimating substituent effects operating on the ^{13}C NMR shifts in carbocations is well recognized,[24] but we can obtain approximate values for these effects by comparing the ^{13}C NMR data of 7-CH_3 and **17** with 7-*t*-Bu. The change of 7-CH_3 to 7-*t*-Bu represents the replacement of the six methyl hydrogen atoms with methyl groups and consequently the introduction of three additional β substituents (a well-documented deshielding influence on carbon shifts)[16] to C_2 and six additional γ substituents (a known, well-documented shielding influence)[16,23b] to $C_{1,3}$. Estimation of the deshielding factor for C_2[25a] and the shielding factor for $C_{1,3}$[25b] at about 20 ppm each seems reasonable and, if these corrections are applied to the $C_{1,3}$ and C_2 shifts of 7-*t*-Bu, values similar to 7-CH_3 are obtained.[25c] Although it cannot unequivocally be shown that charge has been delocalized to C_2 at the expense of $C_{1,3}$ in 7-*t*-Bu, the uncertainty in our estimates of substituent correction factors coupled with the remaining differences between 7-*t*-Bu and 7-CH_3 suggests a small contribution from 1,3 π overlap in 7-*t*-Bu.

We conclude that, in the absence of severe steric interactions, cyclobutenyl cations, substituted at C_1 and C_3 by phenyl groups, like their alkenylic and larger ring homologs, exhibit classical allylic delocalization with negligible 1,3 π overlap, in accord with the conclusions of previous studies.[11d,g,13b] Thus one structural condition such that 1,3 overlap may become important has also been recognized, namely steric inhibition of resonance stabilization by substituents at C_1 and C_3.

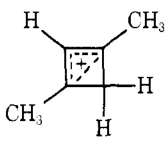
Cyclobutenyl cations substituted at C_1 and C_3 by groups which are less effective at stabilizing charge than phenyl groups should accordingly show a greater contribution from 1,3 overlap. The 1,3-dimethylcyclobutenyl cation (**9**) was prepared, and the ^{13}C NMR spectrum still continues the trend of $C_{1,3}$ resonating at lower field than C_2 (Table II).

Table II. ^{13}C NMR Data for the Cyclobutenyl Cations Carbon-13 Chemical Shifts and Relevant Coupling Constants[a]

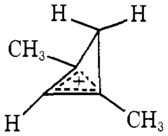
		Cyclobutenyl carbons					$C_{1,3}$ substituent				C_2 substituent		C_4 substituent	
		$C_{1,3}$	C_2	$\Delta\delta_{C_1-C_2}$	C_4	CH_3	C_{ipso}	C_{ortho}	C_{meta}	C_{para}	CH_3*	Other	CH_3	Other
	7-Ph[b]	190.0	152.3	+38.6	52.5 $^1J_{CH}$ = 148.0		*h*	138.7, 137.3	*h*	143.8		C_{ipso}, 135.2; *h*		C_{ipso}, 135.2; *h*
	c	188.2	153.0	+35.2	53.3		129.7	138.1		143.8				
	7-CH_3[b]	196.3	150.6	+45.7	44.7 $^1J_{CH}$ = 145.5		131.5	136.9	131.2	142.7	13.6 $^1J_{CH}$ = 130.1		16.1 $^1J_{CH}$ = 129.4	
			$^2J_{C,CH_3}$ = 6.5		$^2J_{C,CH_3}$ = 4.2									
	7-*t*-Bu[c]	167.0	179.3	−12.3	68.2		125.1	138.1	130.8	139.7	29.9	C_α, 36.8	27.1	C_α, 34.3
	9[d]	197.6	163.1	+34.5	51.4	19.7								
			$^1J_{CH}$ = 198.2		$^1J_{CH}$ = 160.7	$^1J_{CH}$ = 132.6								
	10-H[e]	171.3	171.3	0.0	57.8	13.5					12.9		11.1	
					$^1J_{CH}$ = 172.2									
	10-D[f]	171.1	171.25	−0.15	57.2	13.5					12.9		11.0	
	10-Cl[e]	191.5	174.4	+17.1	76.0	14.0					9.8		27.3	
						$^1J_{CH}$ = 132.9					$^1J_{CH}$ = 132.7		$^1J_{CH}$ = 131.7	
	5-H[g]	133.5[i]	187.6	−54.1	54.0									
		$^1J_{CH}$ = 207.1[i]	$^1J_{CH}$ = 226.6 $^2J_{CH}$ = 14.6[j]		$^1J_{CH}$ = 174.0 $^3J_{CH}$ = 10.4									
	5-Cl[d]	141.6	178.7	−37.1	63.7									
		$^1J_{CH}$ = 212.5[k]	$^1J_{CH}$ = 230.6		$^1J_{CH}$ = 220.0 $^3J_{CH}$ = 16.3[k]									

[a] Chemical shifts are in parts per million relative to external Me_4Si, coupling constants are hertz. [b] In FSO_3H-SO_2 at −70°. [c] Data from ref 11g, converted to parts per million relative to external Me_4Si, using δ_{CS_2} (Me_4Si) = 193.7. The carbons are not specifically assigned are omitted. [d] In SbF_5-SO_2ClF at −60°. [e] In FSO_3H-SO_2ClF at −70°. [f] In FSO_3D-SO_2ClF at −70°. [g] In FSO_3H-SO_2ClF at −60°. [h] The aromatic resonances not assigned belong to the following set; δ 131.9, 131.1, 130.4, 129.6, 190.0, 128.4. [i] This value is slightly different from the value of 130.0 published in our preliminary communication, ref 1a; so are also $^1J_{CH}$'s for 5-H and are considered more accurate since they were obtained at narrower spectral widths. [j] No additional long-range couplings were completely resolved. [k] Corrected value from that published in ref 1a. In addition, reexamination of the proton-coupled ^{13}C NMR spectrum of 5-Cl yielded a resolvable long-range coupling only to C_4. Couplings $C_1 = C_3$ and C_2 were approximately 7 Hz, but poorly resolved.

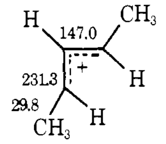
However, a comparison with the 2-pentenyl cation (**18**),[13b] the acyclic analog of **9**, immediately reveals $C_{1,3}$ has become substantially shielded in **9** and correspondingly C_2 has been deshielded. Since substituent effects in **9** and **18** should be similar, ion **9** thus represents the first unequivocal demonstration that charge has been transferred to C_2 at the expense of $C_{1,3}$ and shows the importance of 1,3 overlap in this system. The ${}^1J_{CH}$ value for C_4 in **9** is substantially larger than the corresponding values for **7**-Ph and **7**-CH_3 and indicates increasing strain at this carbon. This could be due solely to the additional contribution from 1,3 π overlap, but some measurable contribution from the puckered (nonplanar) homoaromatic structure **9a** cannot be ruled out. Nonplanarity is not suggested, however, by the temperature independent nature of the ^1H NMR spectrum, even to −120° where viscosity broadening begins to occur.[26]



9

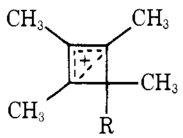


9a

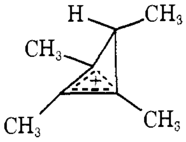


18[13b]

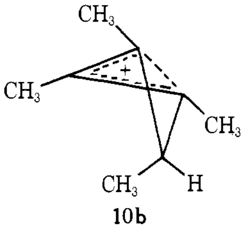
A further increase in 1,3 overlap is expected when C_2 is substituted by a group capable of stabilizing charge. The 1,2,3,4-tetramethylcyclobutenyl cations **10**-H, **10**-D, and **10**-Cl illustrate this further step in the delocalization trend. In **10**-H, the carbon resonances for C_1, C_2, and C_3 are coincidental (Table II), suggesting similar charge at each carbon, a result certainly consistent with the conclusions reached earlier by Katz and Gold[11b] from the u.v. spectra of **10**-H and related ions. The carbon shifts cannot, however, be quantitatively correlated with charge at these carbons because of the potential importance of nonplanar forms **10a** and **10b**. Ring puckering from the planar form must necessarily involve rehybridization of C_1 and C_3 from "pure" sp^2, and this introduction of more p character will result in a substantial upfield shift of these resonances.[27] Thus if nonplanar homoaromatic structures make substantial contributions, the carbon shifts of $C_{1,3}$ will become more shielded than expected on the basis of a charge decrease alone.



10 (R = H, D, Cl)



10a



10b

The degeneracy of $C_{1,3}$ and C_2 resonances in **10**-H is removed in **10**-D by the small specific deuterium isotope shifts. The observed α-, β-, and γ-deuterium isotope shifts of 0.6, 0.2, and 0.05 ppm, respectively, are all to higher field and are similar to reported values.[28] The deshielding of C_4 and $C_{1,3}$ in **10**-Cl relative to **10**-H (Table II) is in accord with the usual deshielding of directly attached and adjacent carbons by chlorine substitution.[29] As observed for **9**, the ^1H NMR spectra of **10**-H and **10**-Cl are temperature independent.[26]

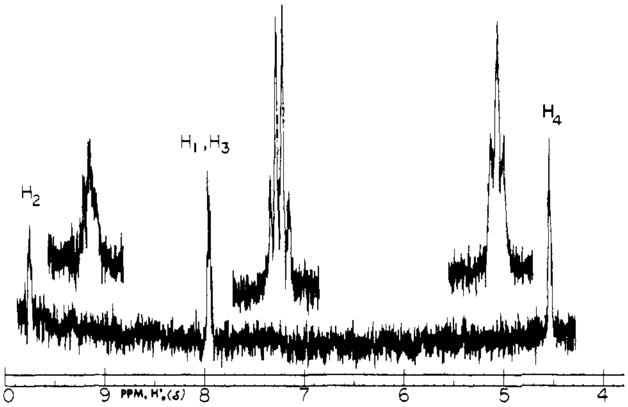
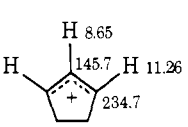
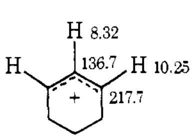


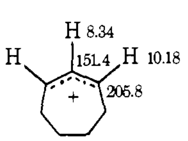
Figure 1. The 100-MHz ^1H NMR spectrum of the homocyclopropenium ion at −60°. The inserts are the spectral portions assigned to H_2, $H_{1,3}$, and H_4 expanded at 250-Hz sweep width.



20[14a]



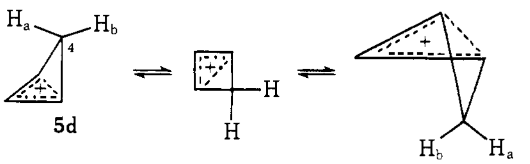
21[14a]



22[14b]

The trends observed above culminate in the case of the parent cyclobutenyl cation **5**-H. The resonances for both H_2 and C_2 are substantially deshielded relative to $H_{1,3}$ and $C_{1,3}$, respectively (Tables I and II), in sharp contrast when compared with the cyclopentenyl (**20**),[14a] cyclohexenyl (**21**),[14a] and cycloheptenyl (**22**)[14b] cations as shown below on the relevant formula. The 100-MHz ^1H NMR spectrum and the FT ^{13}C NMR spectrum for **5**-H are shown in Figures 1 and 2. $C_{1,3}$ now resonate at unusually high field for carbons bearing partial positive charge, consistent with rehybridization to higher p character at these carbons. Moreover, both the 60- and 100-MHz ^1H NMR spectra are temperature dependent; within the temperature range −60 to −110°, the H_2 and $H_{1,3}$ resonances remain unchanged (i.e., do not broaden), while the shielded methylene signal gradually became broader and finally merged into the base line at −110°. At this temperature, difficulties due to limited solubility and viscosity broadening were encountered, but the process is completely reversible and raising the temperature to −60° regenerated the original spectrum. Since the rate of exchange at coalescence for a two-site exchange process is approximately proportional to the difference in resonating frequency of the two exchanging sites, we further studied the temperature dependence of the ^1H NMR spectrum of **5**-H at 270 MHz. The 270-MHz spectra recorded at various temperatures are shown in Figure 3. The coalescence temperature, as anticipated, has now increased to an accessible region and complete line-shape analysis of these spectra gave a value of $\Delta G^\ddagger$ for the process **5d** $\rightleftharpoons$ **5e** of 8.4 kcal mol^{-1}. The complete analysis is described in the Appendix.

We have consequently achieved observation of both our prerequisite conditions for homoaromaticity discussed in the introductory section, showing **5**-H to be the truly homoaromatic homocyclopropenium ion. At temperatures where the "frozen-out" ion **5d** (or **5e**) can be observed (e.g., Figure 3, T −115°), H_{4a} and H_{4b} resonate at δ 4.12 and 4.94 ppm, respectively.[30] These shifts can be compared with the corresponding values of δ −0.67 and 5.10 ppm for the homotropylium ion (**1**).[2a] Although the chemical shifts for the outer (exo) protons are similar for these two ions, the shielding experienced by the endo protons is substantially



5d **5**-H **5e**

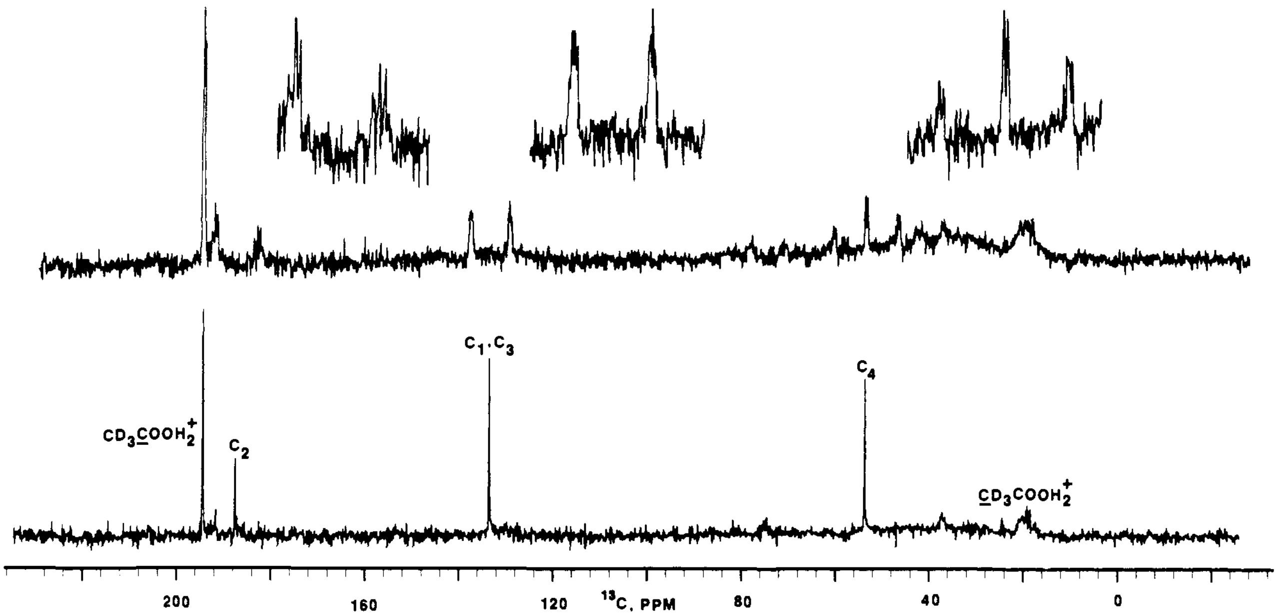


Figure 2. The 25.16-MHz ^{13}C NMR spectrum of the homocyclopropenium ion at −60°. The lower portion is the proton noise-decoupled spectrum, and the upper is the fully coupled gyro-gate spectrum; the inserts are the expanded spectral portions assigned to C_2, $C_{1,3}$, and C_4, respectively recorded in the gyro-gate mode.

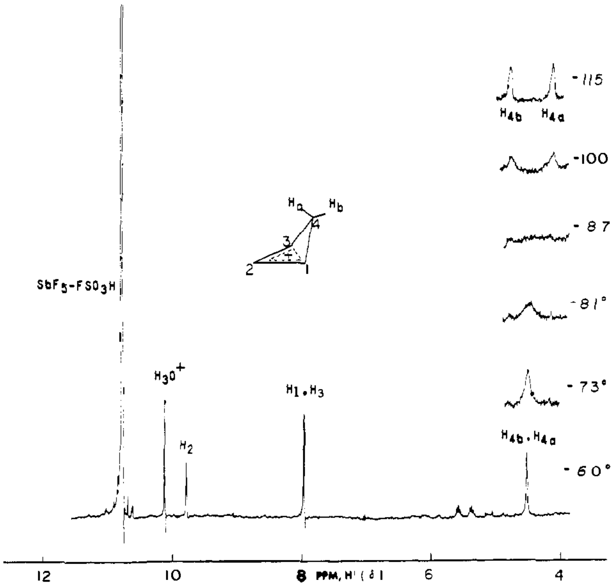
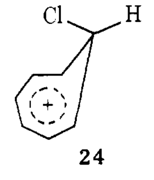


Figure 3. The 270-MHz ^1H NMR spectrum of the homocyclopropenium ion recorded at various temperatures. The complete spectrum at −60° is shown. The temperature dependence of the resonances due to H_{4a} and H_{4b} is shown, at the same sweep width, at temperatures ranging from −73 to −115° above the spectral portion for H_{4a}, H_{4b} at −60°. The resonances assigned to H_1, H_3, and H_2 were not temperature dependent.

different. An obvious explanation for this difference is that C_8 in **1** is bent further out of the C_1–C_7 plane than is C_4 from the C_1–C_3 plane in **5d**, and $H_{8,\text{endo}}$ in **1** is consequently further over the shielding region of the aromatic ring than is H_{4a} in **5d**. However, since it has been shown that the shielding affect of a ring current is proportional to the area of the ring and the number of electrons being delocalized in the ring, differences resulting from these contributions must also be operative.

Close scrutiny of the NMR parameters for **5**-H shows the obvious similarity with the cyclopropenium ion (**23**).[9a] The carbon shift for C_2 is similar to that for **23** (δ 176.8 ppm)[32] while $^1J_{CH}$ for C_2 is exceptionally large (226.6 Hz), approaching the value observed in **23** (265,[9a] 262 Hz[32]). Indeed, both $^1J_{CH}$ for $C_{1,3}$ and C_2 in **5**-H are larger than $^1J_{CH}$ for the bridgehead carbons of bicyclo[1.1.0]butane (205 Hz).[33] The small vicinal vinylic coupling (Table I) can be compared with the negligible value for **23**[9a] and the values for cyclopropenyl (0.5–1.5 Hz)[31b] and cyclobutenyl (2.5–3.7 Hz)[31b] systems.

The ^{13}C and ^1H NMR data for the 4-chlorohomocyclopropenium ion (**5**-Cl, Tables I and II) also show the homoaromaticity of this ion. $C_{1,3}$ and C_4 are deshielded relative to **5**-H by the usual chlorine atom substituent effects,[29a] while the $^1J_{CH}$ value for C_4 demonstrates the well-known dependence upon electronegativity.[29b] However, the ^1H NMR spectrum shows no dependence in the temperature range −20 to −120°, most likely due to overwhelming preference for one conformer.[26] In the homotropylium analogs **24** and **25**, the energy difference between these isomers is such that **24** is converted quantitatively and irreversibly to **25** at 30° with a half-life of 37 min.[4b]



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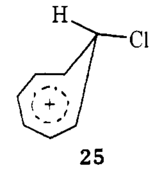
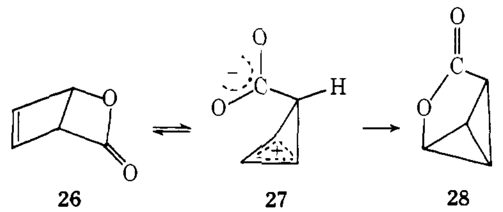


25

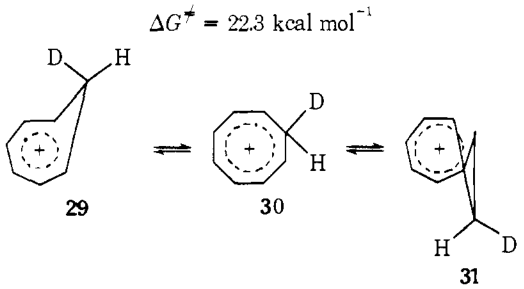
In 1967, Corey and Pirkle[34] observed that bicyclo[2.2.0]pyran-2-one (**26**) rearranged in aprotic solvents to tricyclo[$2^{3,6}$.1.1.0]pyran-2-one (**28**). The mechanism of this rearrangement was shown by deuterium labeling to involve heterolytic cleavage, and the results derived above for **5**-Cl suggest, in the case of **26**, the intermediacy of the nonplanar homocyclopropenium ion pair **27** which can subsequently cyclize onto C_2, yielding **28**. We regard this result as a fur-



26 **27** **28**

ther indication that homocyclopropenium ions are involved as intermediates in many chemical transformations of cyclobutenes.[8]

3. The Relative Energies of the Planar Cyclobutenyl Cation (with 1,3 π Overlap) and the Puckered Homocyclopropenium Ion. The $\Delta G^\ddagger$ value determined for the ring flipping of the puckered homocyclopropenium ion (**5d** $\rightleftharpoons$ **5e**), 8.4 kcal mol^{-1}, must approximate the difference between these nonplanar structures and the planar cyclobutenyl cation with strong 1,3 π overlap (i.e., **5**-H), the presumed intermediate in this process.[35] This can be compared with the analogous ring flipping for the homotropylium ion. A value of $\Delta G^\ddagger = 22.3$ kcal mol^{-1} has been determined from the equilibration of the 8-*endo*-deuterio-**29** with the 8-*exo*-deuterio isomer **31** via the intermediacy of the planar heptatrienyl cation **30**.[2a] This difference of 22.3 kcal mol^{-1} ensures that ions such as **30** are never observed, regardless of substitution pattern. However, the $\Delta G^\ddagger$ difference between **5d** (= **5e**) and **5**-H is sufficiently small that suitable substitution could reverse or accentuate their relative energies.



In the preceding section, we were concerned primarily with establishing the charge delocalization *trends*. Ion structures were only assigned to the more or less limiting examples, namely the 1,3-diphenyl derivatives **7**, where these π-delocalizing substituents lowered the energy of the *planar* cyclobutenyl cation far below the puckered forms and there were negligible 1,3 π-overlap contributions, and the puckered homoaromatic parent ions **5**-H and **5**-Cl, respectively.

We have clearly demonstrated that **9** and **10**-H (and **10**-D, **10**-Cl) exhibit enhanced charge density at C_2 by participation of 1,3 overlap but have not attempted to define the exact nature of the 1,3 overlap in these ions. The inability to observe temperature dependence of the ^{1}H NMR spectra of **9** and **10**-H is strong evidence that they do not exist exclusively as the puckered homoaromatic structures. In the preceding discussion, it was shown that the puckering of ions **5d** = **5e** is manifested by strong shielding of $C_{1,3}$ due to rehybridization of these carbons. We can therefore investigate the contribution from homoaromatic forms in **9** and **10**-H, at least in an approximate manner, by considering the total magnitudes, (i.e., $2\delta_{C_{1,3}} + \delta_{C_2}$) of the $C_{1,3}$ and C_2 shifts. The values obtained from Table II are 558.3 (**9**), 513.9 (**10**-H), and 454.6 ppm (**5**-H), respectively, showing that contributions from $C_{1,3}$ rehybridization are becoming increasingly more important. The $^1J_{CH}$ values for C_4, 160.7 (**9**), 172.2 (**10**-H), and 174.0 Hz (**5**-H), and for C_2, 198.2 (**9**) and 226.6 Hz (**5**-H), certainly support this conclusion.

We conclude from the data described above that methyl substitution at C_1 and C_3 has lowered the energy of the planar forms with 1,3 π overlap relative to the puckered homoaromatic form. Both structures are now of comparable energy and in dynamic equilibrium, the relative proportion of each structure depending upon additional substitution patterns. The exclusive adoption of a puckered, more strained equilibrium geometry for **5**-H (i.e., **5d** = **5e**) must be attributed to the realization of increased delocalization in this conformation. Presumably, the increase in the total overlap between C_1 and C_3 which is now intermediate between σ and π type[15a] more than compensates for the expected decrease in the π overlap between C_1, C_2 and C_2, C_3. An ab initio study of the effect of methyl substitution concentrating on the difference produced by substitution at C_1, C_2, or C_4 should be particularly informative.

In conclusion, we have prepared a series of cyclobutenyl cations which exhibit all the delocalization modes from classical allylic to homoaromatic stabilization. Substitution of phenyl groups at C_1 and C_3 strongly favors allylic delocalization, and no contributions from 1,3 π overlap can be observed. Exclusive methyl substitution leads to decreasing importance from allylic delocalization and, accordingly, greater importance from 1,3 π overlap and homoaromatic charge delocalization. We have successfully prepared the parent (unsubstituted) cyclobutenyl action and have verified the homoaromaticity predicted for this ion.[8] The homocyclopropenium ion, the homoaromatic analog of the cyclopropenium ion, is thus the simplest homoaromatic system.

Experimental Section

Diphenylethyne (**6**-Ph), 1-phenylpropyne (**6**-CH_3), and 2-butyne were commercially available samples. 3-Bromo-1,3-dimethylcyclobutene was synthesized from 1,3-dibromo-1,3-dimethylcyclobutane according to the procedure of Griesbaum.[18] *trans*-3,4-Dichloro-1,2,3,4-tetramethylcyclobutene (**12**),[10a] *cis*-3,4-dichlorocyclobutene (**13**),[19] and 3-acetoxycyclobutene (**14**)[20a] were prepared according to literature methods. The preparation of 3-(acetoxy-d_3)cyclobutene (**14**-d_3) employed the procedure described for **14**[20a] with the modification that acetic anhydride-d_6 was utilized for the acetylation of dimethyl tricyclo[4.2.2.0^{2,5}]deca-7,9-dien-3-ol-7,8-dicarboxylate (instead of acetic anhydride). The ^{1}H NMR spectrum of **14**-d_3 indicated that deuterium incorporation was greater than 93%. Fluorosulfuric acid was doubly distilled, and antimony pentafluoride triply distilled before use. FSO_3H–SbF_5 refers to 1:1 *M* solution of these two reagents.

Preparation of Ions. (a) In FSO_3H–SO_2 (or SO_2ClF) Solution. To an approximately threefold molar excess of 1:1 (by volume) solution of FSO_3H in SO_2 (or SO_2ClF) at −78° was added dropwise, with vigorous Vortex stirring, a 20% solution of diphenylethyne (**6**-Ph), or 1-phenylpropyne (**6**-CH_3) in SO_2, or 2-butyne or *trans*-3,4-dichloro-1,2,3,4-tetramethylcyclobutene (**12**) in SO_2ClF, at −78°. The resulting solutions were transferred immediately to precooled NMR tubes for direct study.

(b) In SbF_5–SO_2ClF. 3-Bromo-1,3-dimethylcyclobutene (**8**) and *cis*-3,4-dichlorocyclobutene (**13**) were ionized in SbF_5–SO_2ClF solution in a manner analogous to that described above for FSO_3H–SO_2 solutions.

(c) In FSO_3H–SbF_5–SO_2ClF. 3-Acetoxycyclobutene (**14**) and 3-(acetoxy-d_3)cyclobutene (**14**-d_3) were ionized in FSO_3H–SbF_5–SO_2ClF solution in a manner analogous to that described above for FSO_3H–SO_2 solutions.

Nuclear Magnetic Resonance Spectroscopy. (a) Proton Nuclear Magnetic Resonance Spectra. ^{1}H NMR spectra were obtained on either a Varian Associates Model A56/60 or HA-100 NMR spectrometer. The 270-MHz ^{1}H NMR spectra were obtained on a Bruker Model HX-270 NMR spectrometer at the University of Chicago. All these instruments were equipped with variable temperature accessories, and proton chemical shifts are referred to external (capillary) Me_4Si.

(b) Carbon Nuclear Magnetic Resonance Spectra. ^{13}C NMR spectra were obtained by the Fourier transform method on a Varian Associates Model XL-100 NMR spectrometer equipped with a broad-band proton decoupler and variable temperature probe. The complete details of the instrumentation and techniques employed have been described previously.[36] ^{13}C NMR chemical shifts were measured from external (capillary) Me_4Si. Proton–carbon coupling constants were measured directly from spectra recorded in the gyro-gate mode of operation.

Acknowledgments. Support of this work by the National Science Foundation is gratefully acknowledged. We thank Professor W. J. Hehre for communication of unpublished

results of ab inito calculations on the homocyclopropenium ion during 1974, Dr. S. Sternhell for helpful discussions relating to the ^1H NMR temperature-dependence study of the homocyclopropenium ion, and Professor P. Eaton for arranging the use of the Bruker HX-270 NMR spectrometer at the University of Chicago operated under a grant from the National Institutes of Health. We also thank Mr. R. Dykstra for technical assistance in recording the 270-MHz ^1H NMR spectra. The generous gift of 1,3-dibromo-1,3-dimethylcyclobutane by Professor K. Griesbaum is also gratefully acknowledged.

Appendix

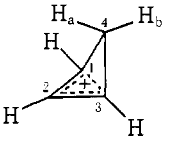
The $\Delta G^\ddagger$ values for the degenerate ring flipping of the homocyclopropenium ion (**5d** ⇌ **5e**) were determined from the 270-MHz ^1H NMR spectra recorded at −84, −87, −90, −93, −95, and −100°. The complete line-shape analysis was achieved by direct comparison of the experimental spectra with spectra calculated by the DNMR3[37] program adapted to CWRU's Univac 1108 computer equipped with a CALCOMP plotter. The rate constants thus obtained were converted to $\Delta G^\ddagger$ values using the Eyring equation,[38] assuming a transmission coefficient of unity. A $\Delta G^\ddagger$ value of 8.4 ± 0.5 kcal mol^{-1} was obtained for all spectra at the temperatures described above. Because it was not possible under these conditions to experimentally resolve the multiplet structure of the H_{4a} and H_{4b} resonances under conditions of their magnetic nonequivalence, the following assumptions were made in the line-shape analysis:

The necessity to reduce the total system to four spins forced the omission of H_2; this resonance is only a weakly coupled first-order perturbation upon H_1, H_3, H_{4a}, and H_{4b} and accordingly should not affect the final results.

T_2 for all protons = 1.0 sec

$$J_{H_1,H_{4a}} = J_{H_3,H_{4a}} = J_{H_1,H_{4b}} = J_{H_3,H_{4b}} = 1.60 \text{ Hz}$$

$$J_{H_{4a},H_{4b}} = -10.00 \text{ Hz}$$



The value for ($\nu_{H_{4a}} - \nu_{H_{4b}}$) used in the line-shape analyses, 216.3 Hz, was obtained from the spectrum at −115°; further cooling to −125°, where the sample froze, did not change this value.

$J_{H_{4a},H_{4b}}$ was varied from 0.00 to −20.00 Hz for the calculated spectra near coalescence, but the $\Delta G^\ddagger$ value did not change within experimental error. Similarly, rate constants at the coalescence temperature for $J_{H_{4a},H_{4b}}$ being varied from 0.00 to −20.00 Hz were obtained from the approximation[39]

$$k_{\text{coal}} = \pi\{[(\nu_{H_{4a}} - \nu_{H_{4b}})^2 + 6J^2_{H_{4a},H_{4b}}]/(2)\}^{1/2}$$

In all cases, conversion of the rate constants obtained in this manner resulted in a value of $\Delta G^\ddagger$ = 8.4 kcal mol^{-1} within experimental error.

References and Notes

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(25) (a) The β-substituent effect was estimated from the difference in the C_4 shifts for **7**-CH_3 and **7**-*t*-Bu (23.5 ppm, Table II). (b) The γ-substituent effect was estimated from the $\delta\Delta_{\text{ortho}}$ value for **17** (9.8 ppm). Since there is such an interaction from *each tert*-butyl group at C_1 and C_3, this shielding factor is accordingly doubled. (c) Although our total correction factor of 40 ppm probably represents a maximum estimation, the value derived by the authors in ref 11g (13 ppm) is clearly much too low; they do not appear to have recognized the γ-substituent effect contribution.

(26) Ring inversion would probably be undetectable by NMR in this temperature range if the barrier to inversion in a symmetrical ion (such as **9a** or **5d**) was less than 4.5 kcal/mol or, in unsymmetrical ions such as **10**-H, **10**-Cl and **5**-Cl, if one of the conformers were as little as 1.5 kcal/mol more stable than the other since this would result in a population range of 93–99% for the major conformer.

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Conformation and Di-π-methane Reactivity. Mechanistic and Exploratory Organic Photochemistry[1]

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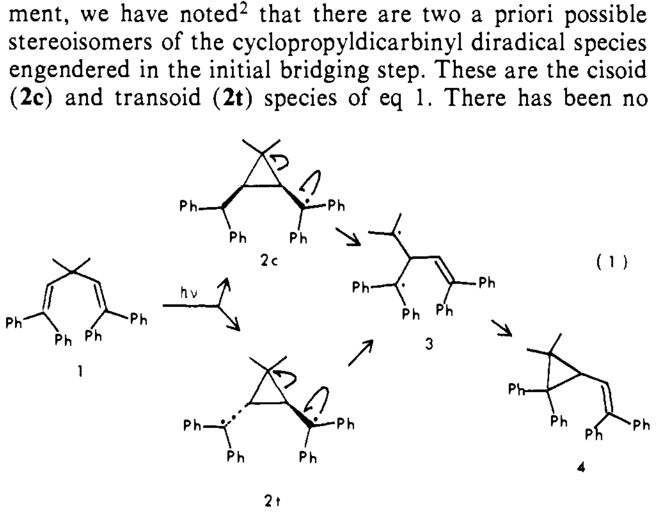
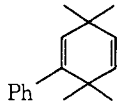
Abstract: In order to test the effect of conformation on the di-π-methane rearrangement, a number of dienes with fixed geometries were synthesized for study. 1-Phenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene, 1,5-diphenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene, and 3,3-dimethyl-1-phenyl-1,4-cyclohexadiene were used as dienes capable of bridging to form the *cis*-cyclopropyldicarbinyl diradical species. 1,1-Dimethyl-3-phenyl-1,4,4a,5,6,7-hexahydronaphthalene was employed as a diene capable of leading on to a trans-bridged cyclopropyldicarbinyl diradical species. For these compounds, excited singlet and triplet reactions were investigated, and the di-π-methane rearrangement products encountered were identified by independent synthesis. Singlet and triplet quantum yields were obtained in order to assess reactivity. Additionally, the rates of excited singlet processes were investigated using single photon counting with deconvolution. The unimolecular rates of excited singlet rearrangement, rates of singlet decay, and rates of fluorescence were determined directly. Evidence was obtained that both cisoid and transoid diradical species can intervene successfully in the di-π-methane rearrangement. Rate differences are interpreted in terms of steric and electronic factors.

In our previous studies on the di-π-methane rearrangement, we have noted[2] that there are two a priori possible stereoisomers of the cyclopropyldicarbinyl diradical species engendered in the initial bridging step. These are the cisoid (**2c**) and transoid (**2t**) species of eq 1. There has been no firm evidence bearing on this point. One suggestive observation[3] is that methyl substitution on the methane carbon (i.e., C-3) facilitates the rearrangement. In our previous reports,[3,4] we ascribed the requirement for methyl substitution to electronic effects which facilitate the opening of the cyclopropyldicarbinyl diradical **2** of eq 1. However, the central methyl effect, a priori, might be rationalized on the basis of such substitution enhancing formation of a conformer of diene reactant required for reaction. Thus, one could conceive of a Thorpe–Ingold effect[5] in which central methyl substitution would affect the probability of obtaining one of the two cyclopropyldicarbinyl diradical species (i.e., **2c** or **2t**).



Consequently, it seemed desirable to compare di-π-methane systems designed to permit generation of only cisoid or transoid cyclopropyldicarbinyl species (i.e., only **2c** or **2t**). With this approach, we could determine if one geometry was inherently unfavorable.

For this study, we selected 1-phenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene (**5**), 1,5-diphenyl-3,3,6,6-tetramethyl-1,4-cyclohexadiene (**6**), 3,3-dimethyl-1-phenyl-1,4-cyclohexadiene (**7**), and 1,1-dimethyl-3-phenyl-1,4,4a,5,6,7-hexahydronaphthalene (**8**). Of these, the first three (i.e., **5–7**)



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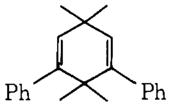

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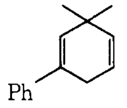

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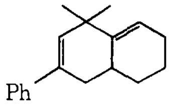

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