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Methyl-Substituted Allyl Cations. A Comparison of Experimental Stability, Rotational Barrier, and Solvolysis Data with ab Initio Calculations

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Abstract: Three sources of quantitative data for methyl-substituted allyl cations are available experimentally: Gas phase heats of formation, rotational barriers in solution, and rates of solvolysis. NMR chemical shifts also provide an index of charge distribution. This paper draws all these lines together in comparison with results of STO-3G ab initio molecular orbital calculations performed on planar and perpendicular methyl-substituted allyl cations. Sequential substitution of the terminal positions by one, two, three, and four methyl groups stabilizes allyl cations electronically by 17, 15, 13, and 11 kcal/mol, respectively; a methyl group on the central carbon has a much smaller stabilizing effect (∼5 kcal/mol). The steric strain for the first *endo*-methyl group was determined to be 3 kcal/mol, whereas a second *endo*-methyl experiences a somewhat greater strain of 5 kcal/mol. Allyl solvolysis rates correlate well with gas phase allyl cation stability data, but there is a reduction in magnitude due to solvation. The calculated rotational barriers also are 4–12 kcal/mol higher than the activation free enthalpies determined in superacid solution; the difference provides further evidence for differential solvation effects—the more highly delocalized planar forms are solvated to a lesser extent than their rotational transition states. The rotational barrier of the parent allyl cation is predicted to be 34 kcal/mol in the gas phase but to decrease to 23.7 ± 2 kcal/mol in superacid solution.

Allyl cations, the prototype π delocalized carbenium ions, have been studied experimentally for many decades.[1] The solvolysis studies, which first proved the existence of allyl cations as short-lived reactive intermediates, preceded generation and direct observation of stable allyl cations in superacid media.[1] In recent years, many thermodynamic data on allyl cations in the gas phase have become available, particularly by means of ion cyclotron resonance measurements.[2]

Previous theoretical studies have concentrated on the parent allyl cation.[3-8] With few exceptions,[9a] methyl-substituted allyl cations have only been investigated by semiempirical methods[10,11] or by ab initio calculations without geometry optimization.[12] Since these calculations give considerable deviations with experimentally determined energy differences, we undertook a comprehensive ab initio MO study of methyl-substituted allyl cations with geometry optimization in order to assess and to augment the experimental data.

Methods

All ab initio MO calculations on planar and perpendicular allyl cations were performed by utilizing the STO-3G minimal basis set[13] and the Gaussian 70 series of programs.[14] For the planar allyl cations, the heavy atom framework was fully optimized, until the total energy was constant to better than 10^{-5} au, bond lengths to 0.001 Å, and angles to 0.1 degrees; standard bond lengths and angles were used for the CH bonds (Table I). The energy values thus obtained were only slightly higher than those of completely optimized structures, e.g., **1** (ΔE = 0.5 kcal/mol), **4** (ΔE = 0.7 kcal/mol), and **6** (ΔE = 1.0 kcal/mol).[15] The fully optimized structures are included in Table I.

The geometries of the perpendicular allyl cations were based on the completely optimized structure of the parent system.[7] This geometry proved to be satisfactory also for substituted cations, since complete optimization of perpendicular **5** and **8** (rotation of CH_2 group) resulted in energies only 0.5 and 1.8 kcal/mol, respectively, below those given in Table IV.

Since the errors introduced by our less than complete optimization appear to be small and more or less constant, they tend to cancel in many of the energy comparisons. In section A2, it will be shown that the relative energies of allyl cations, thus calculated, coincide with experimental gas phase data, which justifies the approximations employed.

Results and Discussion

A. Planar Allyl Cations. 1. Geometry. Heavy-Atom Framework. The results of STO-3G calculations on the planar allyl cations are summarized in Table I. All allyl cations were assumed to have planar heavy-atom ground states. This was justified on the basis of the planar preference of a member of the set more prone to twisting: An energy increase was calculated when the 3,3-dimethylallyl cation (**8**), which has a relatively low rotational barrier (see below), was twisted by only 15° around the C-2–C-3 bond. In contrast, INDO predicted

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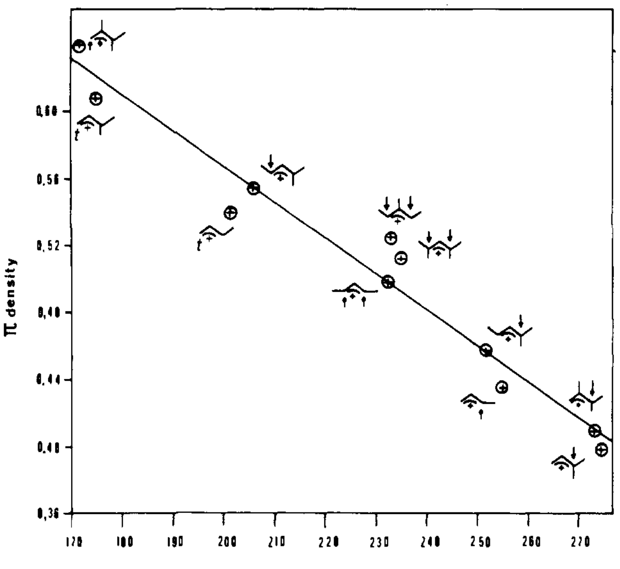


Figure 1. Correlation between ^{13}C NMR shifts and π densities.

to possess a 30° twisted ground state;[11] we believe this to be an artifact due to the excessively low barriers erroneously given by this method.[16]

Methyl substitution at C-1 (or C-3) results in an elongation of the adjacent allylic C-C bond and shortening of the remote bond (Table I). In valence bond terminology, the canonical structure **2′** is favored over **2″** because of the stabilizing effect

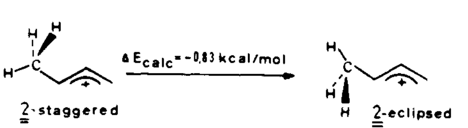
2′ 2″

of the alkyl group. As a consequence, a methyl group increases the positive charge at the substituted allyl terminus and decreases the charge at the opposite end, as demonstrated by the calculated π densities (Table I). The ^{13}C NMR spectra of allyl cations, which show a deshielding of the substituted allylic carbon and a shielding of the opposite terminus, have been interpreted analogously.[17] Figure 1 shows a linear correlation between the observed ^{13}C NMR chemical shifts[18] and the calculated π densities (charge density at the p_π orbital calculated by the Mulliken procedure[19]). Regression analysis yields the equation, $\delta = 456 - 450\ \pi$ density, and a correlation coefficient $r^2 = 0.961$.

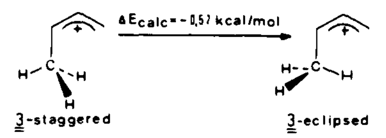
In contrast, bond lengths and ^{13}C NMR chemical shifts remain almost unchanged on substitution at the 2 position.

The sequential widening of the $C^1C^2C^3$ angle in the series **5** → **6** → **7** can be attributed to increasing steric strain. The increase of angle β from **5** to **6** and of angle β′ from **6** to **7** (Table I) also have steric origins.

Methyl Conformations. The preference of the eclipsed over the staggered conformations of the methyl groups of both crotyl cations **2** and **3** has been calculated previously.[9] Although the differences are not large, methyl groups, not sterically interacting with other substituents, generally should prefer eclipsed conformations. This conclusion is in accord with the results of the sickle-shaped 1,3-dimethylallyl cation **6**.[20]



2-staggered 2-eclipsed



3-staggered 3-eclipsed

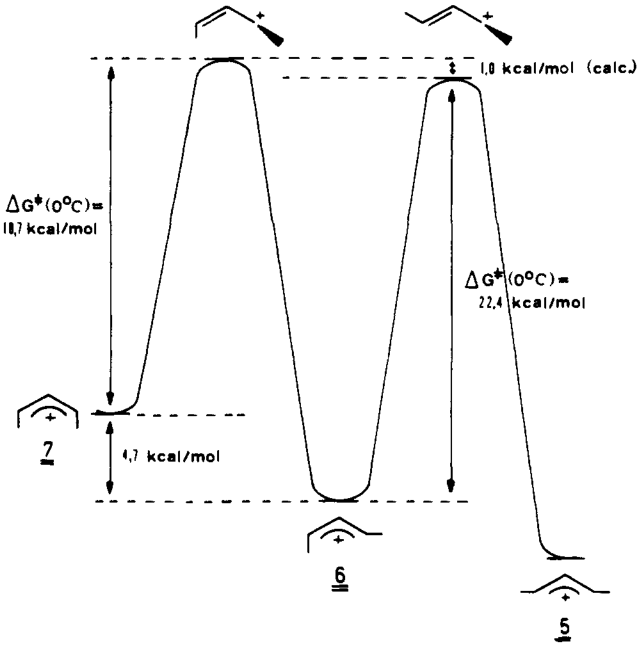
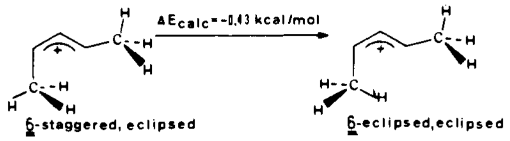
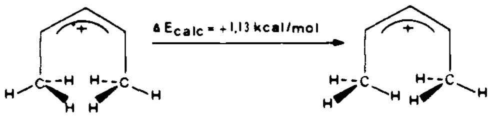


Figure 2. Analysis of relative energies of 1,3-dimethylallyl cations.



6-staggered, eclipsed 6-eclipsed,eclipsed

However, for the U-shaped cation **7**, the doubly staggered form is indicated to be more stable.[20] Because of this large energy



7-staggered, staggered 7-eclipsed, staggered

difference, the *s*, *s* conformation has been assumed for calculations of all cations with two *endo*-methyl groups (**12**, **15**, **17**). The *Z,s-E,e* conformer depicted for **8** (Table I) is 0.5 kcal/mol more stable than the *Z,e-E,s* or the *Z,s-E,s* conformer. Consequently, this conformation was also selected for the calculation of the cations **11**, **12**, and **16**. Rotation of the 3-methyl in **9** involves a barrier of 0.1 kcal/mol and the 2-methyl and 3-methyl conformations in cations **13**, **14**, and **16** were aligned as in **9**.

2. Energy. Steric Strain. As previously discussed for the crotyl cations, methyl groups prefer *exo-* over *endo*-allyl cation positions.[9a] According to Table II, this preference amounts to 3 kcal/mol and is almost independent of the system. The slightly smaller difference between **13** and **14** can be explained by steric crowding in **13** due to the three *cis*-methyl groups. Introduction of a second *endo*-methyl group increases the strain by 5 kcal/mol as shown by the examples in the lower part of Table II.

A closely similar value has already been derived from experimental data. Schleyer and Saunders measured the rates of isomerization of **7** to **6** and of **6** to **5** and interpreted the difference of the Arrhenius activation energies (6.5 kcal/mol) as $\Delta\Delta H_f°$ of **6** and **7**.[21] In Figure 2 we present a slightly different interpretation of these experimental data. Because of the potentially large experimental error in E_a, $\Delta G^{\ddagger}$ is em-

Table I. Ab Initio Geometries and Energies (STO-3G) of Methyl-Substituted Allyl Cations[a]

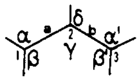
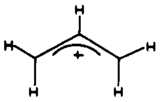
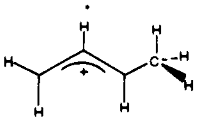
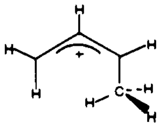
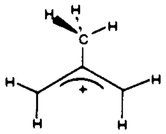
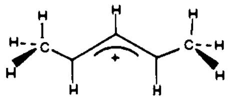
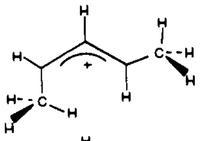
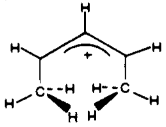
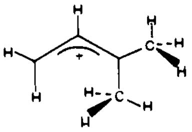
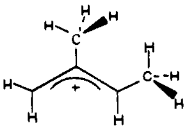
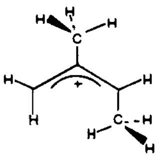
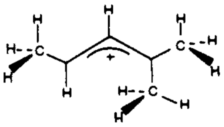
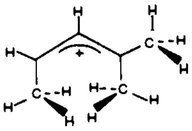
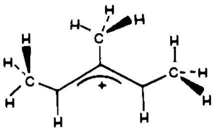
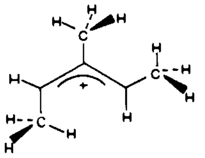
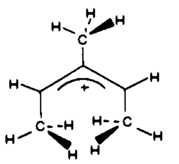
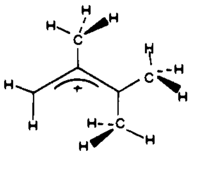
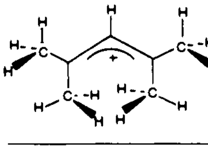
		a b	α β	α' β'	γ δ	π density C-1 C-3	total energy (au)
	**1**	1.385* 1.385	120.0 120.0	120.0 120.0	119.0* 120.5*	0.466 0.466	−114.80881[b]
	**2**	1.370* 1.404*	120.0 120.0	124.5* 118.4*	119.2* 119.7*	0.539 0.435	−153.41630[c]
	**3**	1.368* 1.410*	120.0 120.0	115.8* 129.0*	122.8* 117.5*	0.541 0.423	−153.41157[d]
	**4**	1.391* 1.390*	120.0 120.0	120.0 120.0	115.2* 122.8*	0.490 0.498	−153.39745[e,f]
	**5**	1.386* 1.386	124.5* 117.8*	124.5* 117.8*	119.5* 120.3*	0.498 0.498	−192.02040[g]
	**6**	1.389* 1.386*	115.6* 128.8*	123.5* 118.2*	123.7* 118.4*	0.492 0.495	−192.01546[h,i]
	**7**	1.389* 1.389	115.4* 129.3*	115.4 129.3	127.1* 116.5	0.492 0.492	−192.00765[j]
	**8**	1.355* 1.429*	120.0 120.0	119.2* 123.3*	122.6* 117.3*	0.608 0.398	−192.01470[k]
	**9**	1.374* 1.412*	120.0 120.0	126.2* 117.8*	115.0* 122.5*	0.575 0.452	−192.00276
	**10**	1.374* 1.412*	120.0 120.0	115.7* 130.0*	119.2* 120.0*	0.563 0.449	−191.99765
	**11**	1.371* 1.404*	124.6* 119.6*	119.1* 123.8*	122.9* 117.9*	0.554 0.457	−230.61585[l]
	**12**	1.375* 1.410*	114.6* 130.5*	118.5* 125.1*	127.8* 115.8*	0.554 0.457	−230.60797
	**13**	1.392* 1.392	126.1* 117.7*	126.5* 118.0*	114.4* 122.5*	0.525 0.522	−230.60288

Table I (*Continued*)

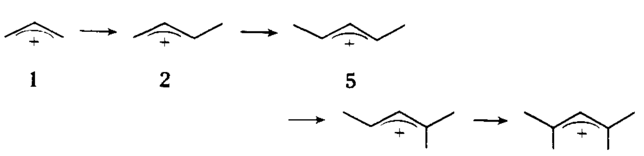
		a *b*	α β	α′ β′	γ δ	π density C-1 C-3	total energy (au)
	**14**	1.395* 1.394*	115.4* 130.6*	125.8* 118.7*	119.0* 121.4*	0.517 0.515	−230.59912
	**15**	1.390* 1.390*	114.7* 130.1*	114.7 130.1	123.4* 118.3	0.511 0.518	−230.59150
	**16**	1.360* 1.437*	120.0 120.0	120.4* 125.5*	120.3* 120.6*	0.639 0.409	−230.59661
	**17**	1.394* 1.394	118.1* 126.3*	118.1 126.3	128.9* 115.6	0.512 0.512	−269.20541[m]

[a] Asterisks signify optimized parameters; values without asterisks were standard or taken from the parent: C–CH_3 = 1.52 Å, C-1–H = 1.10 Å, C-2–H = 1.084 Å, H_2C–H = 1.09 Å, tetrahedral angles in CH_3 groups. [b] Complete opt $E = -114.80953$: ref 7. [c] $E = -153.41436$: ref 9a. $E = -153.41377$: ref 12. $E = -153.41560$: ref 23. [d] $E = -153.40964$: ref 9a. $E = -153.40480$: ref 23. [e] $E = -153.39761$: ref 23. [f] Complete opt: $\alpha = \alpha' = 121.6$, $\beta = \beta' = 122.0$, C–CH_3 = 1.530, H–CH_2 = 1.088, 1.088, 1.085, H–CH_2C^2 = 110.2, 110.2, 110.0; other parameters unchanged; $E = -153.39854$. [g] $E = -192.01528$: ref 12. [h] $E = -192.00880$: ref 12. $E = -192.01358$: ref 20. [i] Complete opt: $a = b = 1.386$, $\alpha = 116.1$ $\beta = 129.3$, $\alpha' = 124.3$, $\beta' = 119.4$, $\gamma = 123.0$, $\delta = 118.7$, CH_3–C^1 = 1.512, H–$CH_2(C^1)$ = 1.091, 1.091, 1.083, H–CH_2–C^1 = 108.0, 108.0, 113.5, CH_3–C^3 = 1.508, H–$CH_2(C^3)$ = 1.092, 1.092, 1.085, H–CH_2–C^3 = 108.5, 108.5, 111.6; other parameters unchanged; $E = -192.01702$. [j] $E = -191.95703$: ref 12. $E = -192.00441$: ref 20. [k] $E = -192.01036$: ref 12. [l] $E = -230.60996$: ref 12. [m] $E = -269.15662$: ref 12.

ployed. $\Delta S^{\ddagger}$ is thus assumed to be similar for the two isomerization reactions. Our calculations indicate the transition states not to be equal in energy, as was assumed earlier,[21] but to differ by 1 kcal/mol (see Table IV). On this basis, a corrected experimental energy difference of 4.7 kcal/mol, almost identical with the calculated difference (4.9 kcal/mol), is obtained. Standard geometry calculations significantly overestimated the difference in stability between **6** and **7** (31.4 kcal/mol).[12]

The activation free enthalpies of the stereomutations **15** → **14** and **14** → **13** differ by 5.5 kcal/mol,[22] a value similar to the calculated $\Delta H_f°$ of **14** and **15** (4.8 kcal/mol). No correction for the transition states is needed since there are two cis substituents at the double bond of the perpendicular ion in both cases.

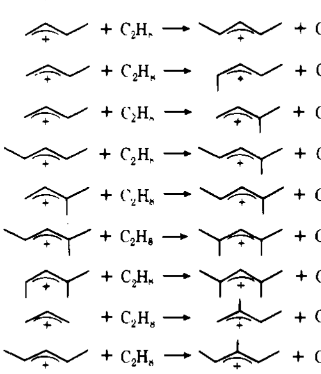
Methyl Stabilization. The stabilization of allyl cations by methyl groups can be evaluated from STO-3G energies (Table I) on the basis of isodesmic reactions 1–10. Stabilization by successive terminal methyl substitution for these steps are 17, 15, 9.5, and 6 kcal/mol, respectively (eq 1, 2, 5, 7).



1 **2** **5** **11** **17**

In the last two steps, electronic stabilization is counterbalanced by steric destabilization due to the introduction of endo substituents. Such steric effects are absent if only substitution by *exo*-methyl groups is considered: eq 1, 2, 6, and 8 indicate an electronic stabilization of 17, 15, 13, and 11 kcal/mol for the first, second, third, and fourth terminal methyl group, respectively. If the 1-methyl allyl cation is further methylated at the 1 *or* 3 position, there is no significant change in energy as long as the steric strains are identical (eq 3 and 4).

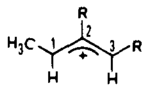
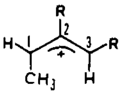
As expected, 2-methylation has a smaller effect, 5.3 kcal/mol in the case of **1** (eq 9) and 1.4 kcal/mol for 2-methylation of **5** (eq 10).

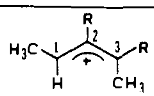
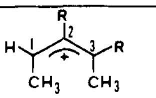


	ΔE_{calcd} (kcal/mol)	ΔE_{exp} (kcal/mol)	
	−17.1	−17.4 to −18.4	(1)
	−15.0	−11.9 to −14.4	(2)
	−11.9		(3)
	−11.4	−10.2 to −15.4	(4)
	−9.5	−7.4 to −8.9	(5)
	−13.1	−6.4 to −10.6	(6)
	−5.8	−7.4	(7)
	−10.8		(8)
	−5.3	−10.4	(9)
	−1.4	−4.4 to −5.9	(10)

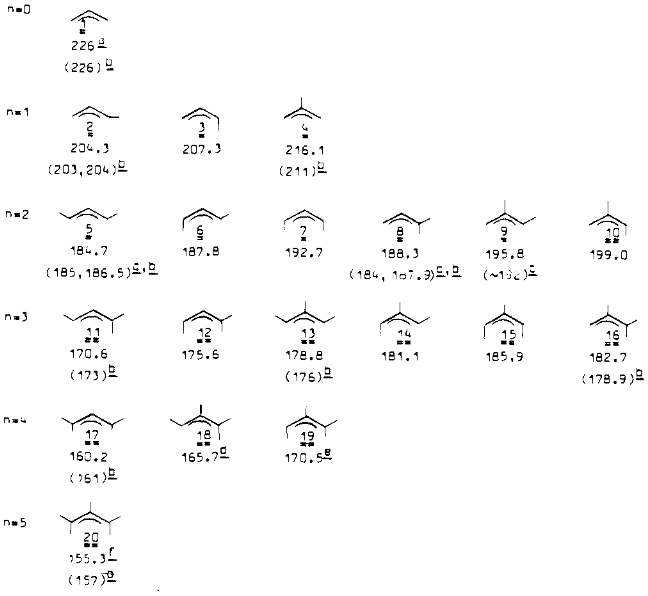
Comparison with Gas-Phase Data. The stabilization energies defined by eq 1–10 can alternatively be derived from gas-phase data. Their interpretation is problematic, however, since in

Table II. Relative Energy of Stereoisomeric Allyl Cations

2-R	3-R			ΔE_{calcd} (kcal/mol)
H	H	**2**	**3**	3.0
CH_3	H	**9**	**10**	3.2
H	CH_3	**5**	**6**	3.1
CH_3	CH_3	**13**	**14**	2.3

2-R	3-R			ΔE_{calcd} (kcal/mol)
H	H	**6**	**7**	4.9
CH_3	H	**14**	**15**	4.8
H	CH_3	**11**	**12**	5.0

Scheme I. Calculations of ΔH_f° of Methyl-Substituted Allyl Cations (Experimental Numbers in Parentheses)

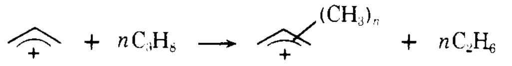


[a] Reference compound. [b] Reference 2. [c] Reference 26. [d] Estimated from **17** and the difference **12–14.** [e] Estimated from **17** and the difference **12–15.** [f] Estimated from **18** and the difference **11–17.**

most cases inconsistent experimental results (see Scheme I) lead to differing stabilization energies.

For eq 1-8 (terminal methyl substitution), the agreement between calculated and experimental numbers appears to be very good. The maximum deviations are only −2.5 kcal/mol (eq 6) and +1.6 kcal/mol (eq 7) and these may be due to a slight inaccuracy of the experimental ΔH_f° value in **11** since the deviations are in opposite directions. An error in the calculated energy of **11** is improbable, because **11** fits very well in the series of the other calculated systems, as shown above.

2-Methyl substitution is generally calculated to be less stabilizing than experimentally observed; in these cases, a systematic error of 3–5 kcal/mol may be present in the calculations. Equations 1-10 can be generalized by eq 11. Since ΔH of eq 11 can be calculated from STO-3G energies,[24] one



(11)

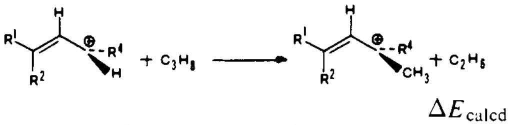
can obtain ΔH_f° of the methyl-substituted allyl cations from the calculated ΔH and the experimental heat of formation of the parent allyl cation,[2] ethane, and propane.[25] Equation 12,

$$\Delta H_f^\circ(\text{kcal/mol}) = 627.49E_{\text{total}}\,(\text{au}) + 24\,204.125n + 72\,267.38 \quad (12)$$

which is derived on this basis, was used to calculate the heats of formation of the methyl-substituted allyl cations (Scheme I). Since the agreement between the calculated ΔH_f° values and the available experimental numbers is quite good, it can be assumed that the predictions in Scheme I are also reliable.

Comparison with Solvolysis Data. Solvolysis reactions of allylic chlorides and allylic *p*-nitrobenzoates have been shown to proceed via allyl cations in aqueous formic acid and aqueous acetone, respectively.[27] Table III shows relative rate constants and relative activation free enthalpies of these reactions. In Figure 3, $\Delta\Delta G^{\ddagger}$ is plotted against the ΔH_f° difference of the allyl cations and the corresponding precursors. A slope of 0.52 for solvolysis of the allyl chlorides in aqueous formic acid and of 0.41 for the allylic *p*-nitrobenzoates in aqueous acetone indicates that the carbocation character is only partially developed in the solvolysis transition states. Recently, Arnett, Petro, and Schleyer reported a linear correlation of the heats of ionization of various alkyl halides under superacidic conditions with the corresponding activation free energies of the solvolysis reactions.[29] The slope of the line (0.89) was larger than in our cases; the difference may be due to solvation effects in superacid solutions.

B. Perpendicular Allyl Cations. The calculated total energies of perpendicular allyl cations are summarized in Table IV. The stabilizing effect of methyl on the cationic center is demonstrated by eq 13. Comparison with eq 14 shows that the calculated ΔE of eq 13 is identical with the stability difference of the ethyl and 2-propyl cation (R^4 = H, eq 13) or the 2-propyl and *tert*-butyl cation (R^4 = CH_3, eq 13). Since this energy difference is that obtained experimentally, we can conclude that ΔE of eq 13 is also in agreement with experiment. Sub-



(13)

R^1	R^2	R^4	ΔE_{calcd} (kcal/mol)[24]
H	H	H	−24.2
CH_3	H	H	−23.6
H	CH_3	H	−23.3
CH_3	CH_3	H	−23.1
H	H	CH_3	−20.1
CH_3	H	CH_3	−18.8

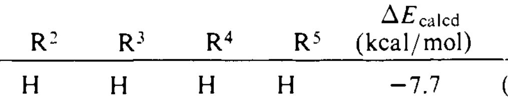
(14)

R = H ΔE_{calcd} = −24.7 kcal/mol;[30]

ΔE_{exp} = −22.4 kcal/mol[25,31]

R = CH_3 ΔE_{calcd} = −19.6 kcal/mol;

ΔE_{exp} = −18.4 kcal/mol



(15)

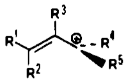
R^1	R^2	R^3	R^4	R^5	ΔE_{calcd} (kcal/mol)	
CH_3	H	H	H	H	−7.7	(15a)
H	CH_3	H	H	H	−6.9	(15b)
CH_3	H	H	CH_3	H	−7.1	(15c)
H	CH_3	H	CH_3	H	−6.1	(15d)
CH_3	H	H	CH_3	CH_3	−5.8	(15e)
H	H	CH_3	CH_3	CH_3	−3.8	(15f)

Table III. Relative Rate Constants and Activation Free Energies of Various Allylic Chlorides[a] and *p*-Nitrobenzoates[b]

	k_{rel}	$\Delta\Delta G^{\ddagger}$	$\Delta H_f°$ (precursor)[c]	$\Delta H_f°$ (cation)[d] $-\Delta H_f°$ (prec)
$CH_2{=}CHCH_2Cl$	1.0	0.0	−1.6	227.6
$CH_2{=}C(CH_3)$-CH_2Cl	0.5	0.44	−10.1	226.2
$CH_2{=}CHCH$-$(CH_3)Cl$	5.67×10^3	−5.44	−10.2	214.5
$CH_2{=}CHC$-$(CH_3)_2Cl$	8×10^7	−11.45	−18.3	206.6
$CH_3CH{=}CH$-CH_2Cl	3.55×10^3	−5.14	−9.5	213.8
$(CH_3)_2C{=}CH$-CH_2Cl	1.5×10^7	−10.40	−17.0	205.3
$CH_2{=}CHC$-$(CH_3)_2OPNB$	1.0	0.0	−50.2	238.5
$CH_2{=}C(CH_3)C$-$(CH_3)_2OPNB$	0.72	0.19	−58.7	241.4
$CH_3CH{=}CHC$-$(CH_3)_2OPNB$	2.2×10^3	−4.54	−58.1	228.7
$(CH_3)_2C{=}CHC$-$(CH_3)_2OPNB$	2.3×10^4	−5.93	−65.6	225.8

[a] Rate constants in 0.5% aqueous formic acid at 44.6°C: ref 27a. [b] Rate constants in 80% aqueous acetone at 25 °C: ref 27b. [c] Estimated from group increments for the allyl chlorides and the corresponding alcohols for the nitrobenzoates: ref 28. [d] $\Delta H°_f$(calcd) from Scheme I.

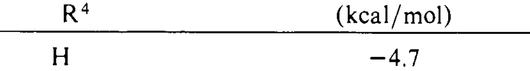
Table IV. Ab Initio Calculations (STO-3G) on Perpendicular Allyl Cations[a]



R^1	R^2	R^3	R^4	R^5	total energy (au)
H	H	H	H	H	−114.75468
H	H	H	CH_3	H	−153.37342
CH_3	H	H	H	H	−153.34716
H	CH_3	H	H	H	−153.34596
H	H	H	CH_3	CH_3	−191.98571
CH_3	CH_3	H	H	H	−191.93376[b]
CH_3	H	H	CH_3	H	−191.96502[c]
H	CH_3	H	CH_3	H	−191.96339
CH_3	CH_3	H	CH_3	H	−230.55075
CH_3	H	H	CH_3	CH_3	−230.57527
H	H	CH_3	CH_3	CH_3	−230.57196

[a] All calculations carried out with partial geometry optimization. Bond angle $R^4C^3R^5$ was optimized if either R^4 or R^5 were methyl. All other parameters were taken from the completely optimized geometry of the perpendicular parent system (ref 7). [b] Complete opt $E = -191.93661$ au. [c] Complete opt $E = -191.96582$ au.

stitution of the formally uncharged double bond has a smaller effect (eq 15, 16). A *trans*-methyl group (position R^1) stabilizes primary, secondary, and tertiary cations by 7.7, 7.1, and 5.8 kcal/mol, respectively (eq 15a,c,e). The effect of a *cis*-methyl group ($R^2 = CH_3$) is approximately 1 kcal/mol smaller (eq 15b,d); a 2-methyl group ($R^3 = CH_3$) stabilizes perpendicular allyl cations by 3.8 kcal/mol (eq 15f). Equation 16



(16)

R^4	ΔE_{calcd} (kcal/mol)
H	−4.7
CH_3	−4.5

Table V. Theoretical Evaluations of the Rotational Barrier of the Allyl Cation

$\Delta E^{\ddagger}$ (kcal/mol)	method	geometry	ref
42	ab initio	standard	3
11	CNDO	optimized	4
29	NNDO	part. opt	5
38	Dewar	part. opt	5
14	MINDO/2	not defined	6
19.7	INDO	part. opt	11
17.3	MINDO/3	part. opt	32
34.4	ab initio (STO-3G)	optimized	7
35.0	ab initio (4-31G)	STO-3G opt	7
34.8	ab initio (6-31G*)	STO-3G opt	7
34.0	ab initio (4-31G)	4-31G opt	36
36.6	ab initio (4-31G/MP2)	4-31G opt	36
34.1	ab initio (4-31G/MP3)	4-31G opt	36
33.2	ab initio (4-31G/MP4/DQ)	4-31G opt	36
33.8	ab initio (4-31G/MP4/SDQ)	4-31G opt	36
34.0	ab initio (6-31G*)	4-31G opt	36

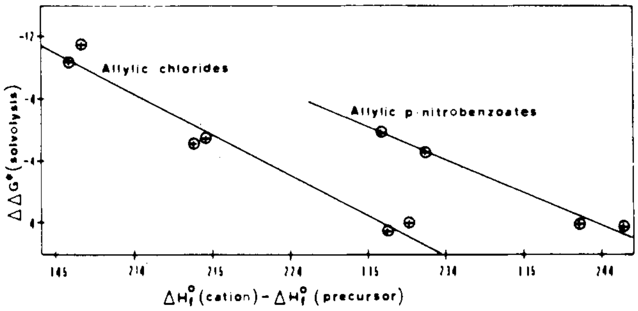
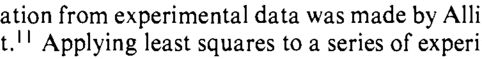


Figure 3. Correlation between activation free enthalpies of the solvolysis reactions of allylic chlorides and *p*-nitrobenzoates and gas-phase stabilities of the cations.

shows that a stabilization of 4.6 kcal/mol by a *trans*-methyl is expected if position R^2 is already methyl substituted.

C. Rotational Barriers. The rotational barrier of the parent allyl cation has previously been calculated by a variety of methods; values from 11 to 42 kcal/mol have been obtained (Table V). Because of the low chemical stability of the parent allyl cation, no experimental data are available. Barriers of 11.5 and 7.8 kcal/mol have been calculated by MINDO/3 for the (*Z,Z*)-1,3-dimethylallyl cation (**7**) and the 1,1,3,3-tetramethylallyl cation (**17**),[10] respectively. Experimentally, much larger activation free energies of 18.7 and 17.5 kcal/mol have been observed.[21,33] INDO gives a rotational barrier of 4.1 kcal/mol for the 1,1-dimethylallyl cation **8**, which seems to be much too low when one considers the experimental value of 11.7 kcal/mol for **16**.[22]

Based on thermodynamic data of allyl cations and the experimentally known rotational barrier of **16**, a rotation barrier of 38-43 kcal/mol has been estimated for the parent allyl cation,[34] but this number is too high due to the use of an older heat of formation for the allyl cation. The presently accepted value[35] yields an estimate, calculated by using the same procedure (eq 17) of 24.7-25.7 kcal/mol (11.7 + 12 + 1-2



(17)

kcal/mol). Another estimate of the rotational barrier of the allyl cation from experimental data was made by Allinger and Siefert.[11] Applying least squares to a series of experimentally known rotational barriers, they concluded that a methyl group at the rotating carbon lowers the barrier by 6.6 kcal/mol, whereas a methyl group at the nonrotating terminal carbon

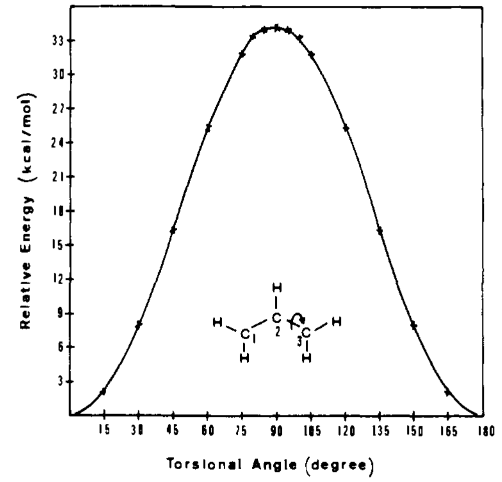


Figure 4. Energy of the allyl cation as a function of the torsional angle of the planes HC^1C^2 and HC^3H.

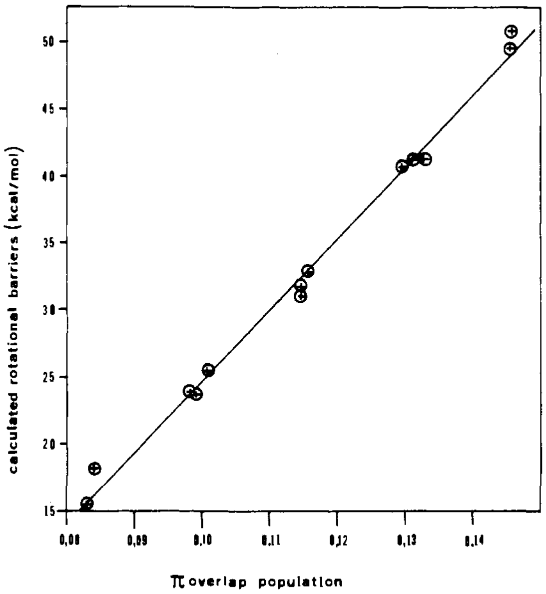


Figure 5. Correlation between calculated rotational barriers and π-overlap population.

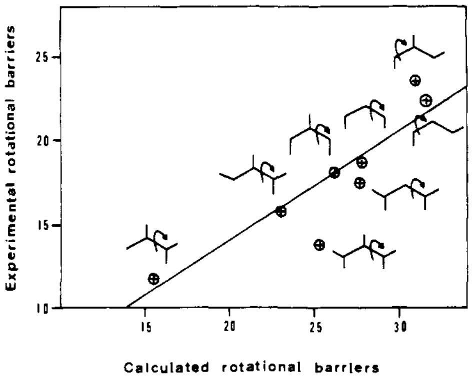


Figure 6. Correlation between calculated and experimental rotational barriers (kcal/mol).

raises the barrier by 3.2 kcal/mol. Steric effects were also considered. A barrier of 27.9 kcal/mol was deduced for the parent allyl cation in solution. While Allinger's assumption of a constant increment for sequential methyl substitution is not accurate, cancellation of errors led to a value which is in reasonable accord with our conclusions.

Figure 4 shows the energy of the allyl cation as a function of the torsional angle. At each point, a complete optimization has been carried out. It can be seen from Figure 4 that the 90° twisted form corresponds to the energy maximum. Therefore, the rotational barriers given in Table VI have been calculated as the energy differences between the planar and perpendicular conformations of the allyl cations (from Tables I and IV). Stabilization energies from the isodesmic reactions 13-16 were used to estimate the energies of the perpendicular cations whose values are not given in Table IV.

Table VI shows that terminal methyls facilitate the rotation of the adjacent allylic bond and raise the barrier for the remote one. The reason is indicated by the comparison of the isodesmic reactions 1-8 and 13-16: methyl at the rotating end stabilizes the transition state (20-24 kcal/mol) more than the ground state (6-17 kcal/mol), while methyl at the nonrotating end stabilizes the ground state (6-17 kcal/mol) better than the transition state (4-7 kcal/mol). Figure 5 shows a linear correlation ($r^2 = 0.990$) of the Mulliken π overlap population of the originally p_π orbitals in the planar form with the calculated barriers. Only allyl cations with one *endo*-methyl were employed in Figure 5 so that steric effects cancel. Regression analysis gives eq 18.

$$\text{rotational barrier (kcal/mol)} = 266.2\ \pi \text{ overlap population} - 28.6 \quad (18)$$

Interestingly the intercept of eq 18 does not equal zero. This implies that, in the absence of π overlap, the allyl cation would prefer the perpendicular conformation, where the cationic center would be stabilized by hyperconjugation with the C-H and the C-C σ-bonds.

In Figure 6 the experimental rotational barriers are plotted against the calculated values. Except for the pentamethylallyl cation **20**, where the calculated value is based on several assumptions and therefore not as reliable, a linear correlation between calculated and experimental rotational barriers is found. Deviations are within experimental error. However, calculated and experimental values are not identical. Is this due to an artifact of our calculations? Higher level calculations with and without correlation do not change the barrier of the parent allyl cation by more than 1 kcal/mol (Table V).[36] Therefore we interpret the differences between the calculated and observed barriers as being due to a solvation effect. The transition state, with the charge less delocalized, experiences a stronger solvation effect than the planar cation. This interpretation is in accord with Arnett and Petro's demonstration of a solvent effect in the ionization of alkyl halides in superacid media.[37] Neglecting **20**, the graph of Figure 6 is represented by eq 19.

$$\text{rotational barrier in soln (kcal/mol)} = 0.2 + 0.69 \text{ calcd barrier} \quad (19)$$

On this basis we predict an activation free energy of 23.7 kcal/mol for the rotation of a methylene group of the parent allyl cation in superacid solution.

It should be mentioned that rotation of one allylic bond is not the only stereomutation mechanism possible. Ring closure to a cyclopropyl cation followed by ring opening has been predicted for the 2-methylallyl cation **4**.[38]

D. Resonance Energy. In view of a recent discussion,[39] we wish to emphasize the relationship between the actual energy and the resonance energy of a system. Resonance energy has been defined as the quantity obtained by subtracting the actual energy of a molecule from that of the most stable contributing structure.[40] If we accept this definition, then the perpendicular allyl cation can be used as a model for the "nonresonating allyl cation".[41] After correcting for steric effects, the values in the

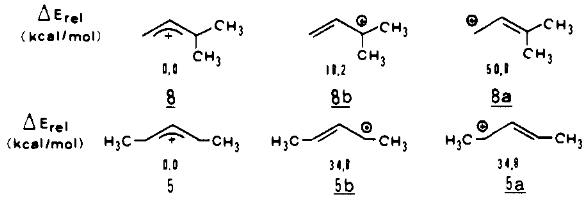
Table VI. Rotational Barriers (kcal/mol) and Mulliken π Overlap Populations of Allyl Cations[a]

system	πC^1C^2	calcd barriers C^1–C^2	πC^2C^3	calcd barrier C^2–C^3	$\Delta G^{\ddagger}$(exptl)
1	0.2332	34.0	0.2332	34.0	
2	0.2626	43.4	0.2006	26.9	
3	0.2656	41.2	0.1964	23.9	
4	0.2308	35.5[b]	0.2324	35.5[b]	
5	0.2310	34.8	0.2310	34.8	
6	0.2296	31.7	0.2312	32.7	22.4[c]
7	0.2308	27.8	0.2308	27.8	18.7[c]
8	0.2916	50.8	0.1678	18.2	
9	0.2628	44.5[b]	0.1980	27.0[b]	
10	0.2622	41.3[b]	0.1992	23.8[b]	
11	0.2590	40.8	0.2008	25.5	
12	0.2588	35.7[b]	0.1988	21.5[b]	
13	0.2308	33.3[b]	0.2298	33.3[b]	
14	0.2298	31.0[b]	0.2292	31.0[b]	23.6[d]
15	0.2310	26.2[b]	0.2326	26.2[b]	18.1[d]
16	0.2908	49.4[b]	0.1662	15.5	11.7[d]
17	0.2276	27.7[b]	0.2276	27.7[b]	17.5[e]
18		38.2[b]		23.0[b]	15.8[d]
19		33.4[b]		18.2[b]	
20		25.3[b]		25.3[b]	13.8[d]

[a] For carbon numbering, see Table I. [b] Calculated by the formula: barrier = 260 −4.6*n* − stab. energy (perp cation) − $\Delta H_f°$ (planar cation), with *n* = number of methyls and the following stab energies, R^4: 24.2; $R^4 + R^5$: 44.3; R^3: 3.8; R^1 or R^2: 7.7, 7.1, and 5.8 for primary, secondary, and tertiary cations, respectively. $R^1 + R^2$: values above +4.6 kcal/mol. For each two cis substituents on the double bond: −1 kcal/mol. [c] $\Delta G^{\ddagger}$ (0 °C) calculated from the Arrhenius activation parameters in ref 21. [d] Reference 22. [e] $\Delta G^{\ddagger}$ (0 °C) calculated from the Arrhenius activation parameters in ref 33.

fourth column of Table VI can be taken to be the resonance energies.

In unsymmetrical systems, like **8**, where the canonical structures have a large energy difference, the resonance energy (as defined above) is relatively small (18.2 kcal/mol),[42] whereas, in symmetrically substituted allyl cations, the resonance energy is much larger (34.8 kcal/mol for **5**). *The total energy of allyl cations, however, does not depend on the magnitude of the resonance energy.* Both **6** and **8**, the symmetrical and nonsymmetrical dimethylallyl cations, both with one *endo*-methyl, have almost identical energy (Table I). The same holds for **14** and **16**. The higher resonance energy of **5**, therefore, compensates for the energy difference between the secondary ion **5a** and the tertiary ion **8b**. The actual energy, rather than the "resonance energy", is of primary concern to chemists.



Conclusion

Ab initio calculations even at the STO-3G minimal basis set level reproduce relative gas-phase stabilities of methyl-substituted allyl cations very well. In cases of contradictory experimental results, they may even serve to identify the correct value. The experimentally observed trends of solvolysis rates and rotational barriers are also reproduced by the calculations. The differences in solution are smaller than those indicated in the gas phase. This suggests the solvation of the more delocalized planar allyl forms to be less than that of the more highly localized transition states.

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Isopropylation of Halobenzenes by *sec*-$C_3H_7^+$ Cations. Evidence for a Participation of the Substituent in a Gas-Phase Alkylation

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Abstract: Isopropylation of the halobenzenes (PhF, PhCl, and PhBr) by isopropyl cations, generated in the diluted gaseous phase from the radiolysis of propane, leads to formation of the corresponding halocumenes. The regioselectivity of the substitution changes from apparent kinetic control, i.e., ortho >80% at 760 Torr, to thermodynamic control i.e., meta, as the overall pressure is lowered to 20 Torr. The results of competitive alkylation experiments with toluene show the reactivity trend PhF > PhCl $\simeq$ PhBr. Appreciable yields of anisole, increasing in the order PhF > PhCl $\simeq$ PhBr, are measured when the system is radiolyzed in the presence of CH_3OH. The formation of $PhOCH_3$ is traced to the attack of methanol on the aromatic ring, activated toward nucleophilic displacement by a specific interaction of *sec*-$C_3H_7^+$ ions with the halogenated substrates. The same interaction helps also to explain the exceptionally high reactivity of the ring positions ortho to a n-donor substituent.

Introduction

Coordination effects[1,2] have long been postulated to account for high ortho/para ratios in the liquid-phase alkylation of aromatic compounds bearing n-donor substituents, such as anisole and chlorobenzene.[3] Recent studies by our group on gas-phase electrophilic aromatic substitution led to isolation of *tert*-butyl phenyl ether as the main product from the alkylation of phenol by unsolvated *tert*-butyl cations, providing direct evidence for predominant attack to the OH group, under conditions favoring kinetic control.[4] Accordingly, in the case of anisole,[5] where no neutral end product can directly arise from *tert*-butylmethylphenyloxonium ions, substantial amounts of *o-tert*-butylanisole have been recovered, confirming preferential reactivity of the charged electrophile toward the n-donor substituent. Analogous conclusions have been reached in the isopropylation of the same substrates by gaseous *sec*-$C_3H_7^+$ cations,[6] which can undergo either proton transfer and condensation with both "n" and "π" nucleophilic sites of phenol and anisole.

The present work has been undertaken to collect further evidence on the specific interactions of carbenium ions and n-donor substituents in the gas-phase electrophilic aromatic substitution, particularly in cases where proton transfer to the substituent is expected to be endothermic.

For this purpose, the alkylation of the halobenzenes (PhX, X = F, Cl, Br) by isopropyl cations from the radiolysis of propane has been studied in the diluted gaseous phase, where the absence of the counterion and of appreciable solvation effects brings into sharper focus the correlation between ion-molecule interactions and the formation of final neutral products.

According to a well-established technique, introduced by Ausloos and co-workers,[7] high yields of *sec*-propyl ions can be obtained from the gas-phase radiolysis of propane. This method has already been exploited,[6,8] in combination with suitable analytical techniques, to study gas-phase electrophilic aromatic substitution by *sec*-$C_3H_7^+$ ions, and consists in carrying out the radiolysis of a system, prepared by mixing trace concentrations of the substrate(s) and of appropriate additives with a large excess of C_3H_8 and a few torr of oxygen, to cut off the radical component of the process.

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