Modern Molecular Mechanics and ab Initio Calculations on Benzylic and Cyclic Delocalized Cations

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Calculations of optimized force field (MMP2 extended to carbocations) and ab initio (MP2/6-31G*) geometries as well as π-electron densities of various benzyl and cyclic delocalized cations agree well. The MMP2 heats of formation reproduce the available experimental values. MMP2 π-resonance energies are consistent with those obtained by isodesmic equations from experimental and ab initio data. When carbon π-charges are lower than 0.2, the influence of phenyl substituents is attenuated. Thus, the triphenylmethyl cation resonance stabilization value (−41.6 kcal/mol average for each phenyl ring) is much less than that of the benzyl cation (−76.4 kcal/mol) and the benzhydryl cation (average stabilization value of −51.4 kcal/mol). MMP2 aromatic stabilization energy estimates of the benzyl and tropylium cations as well as benzene agree well with the assessments of aromaticity by the nucleus independent chemical shift (NICS) criterion, which is based on the magnetic shieldings computed at ring centers. The MMP2 method allows quantitative evaluations of homoconjugative interactions. The stabilization in the homotropylium cation due to 1,7 homoconjugative overlap is estimated to be quite appreciable, −13.4 kcal/mol.

Introduction

This paper employs a newly parametrized empirical force field, which has been shown to compute carbocation[1] geometries and π-electron densities well,[2] to examine the benzyl, tropylium, and homotropylium cations. Allinger's MMP2 program,[3] which combines a classical molecular mechanics treatment with an SCF procedure for π-systems of unsaturated molecules, was used as the basis for the parametrization. Hyperconjugation was introduced via a quantum chemical term.[2] This new method allows a force field treatment of delocalized carbocations, such as allyl,[4] benzyl, and 1,3-pentadien-5-yl[5] as well as the calculation of resonance energies,[4−6] which are quite large in such species.[7,8] In contrast, early force field parametrizations[9] were not devised to reproduce carbocation geometries and hyperconjugation effects, but rather to compute strain energies.[10]

The first carbocations observed in solution were highly resonance stabilized. While Norris[11] and Kehrmann[12] nearly a century ago discovered that triphenylmethanol and triphenylmethyl chloride give yellow solutions in sulfuric acid, von Baeyer first recognized that cations were responsible.[13] Conductivity measurements[14] demonstrated the salt-like behavior.[15] Much later, X-ray investigations[16−18] showed the three-dimensional structure of the triphenylmethyl cation with a propeller-like out-of-plane distortion of the three phenyl rings.[19,20] Gas phase ion heats of formation are known for only a few cyclic delocalized carbocations,[21] and the energy of the triphenylmethyl cation is not among them. More than 6 decades after the first observation of the triphenylmethyl cation, benzhydryl and alkylated benzyl cations[22] could be formed and studied by ^{1}H NMR spectroscopy under superacidic conditions by Olah and co-workers.[23,24] Attempts to prepare such species with aluminum chloride were not sucessful.[25,26] Only recently a X-ray structure of the parent cumyl cation has been reported.[18] However, benzyl cations[27] have been observed in numerous gas-phase ion studies[28] and by Steenken and McClelland's fast UV methods.[29]

High level ab initio calculations[30] now provide an alternative source of carbocation structure and energetic information.[31] For example, the close agreement between the experimental chemical shifts of allyl cations with those obtained by GIAO-MP2 calculations[32,33] showed that these MP2(full)/6-31G* geometries of delocalized cations are reliable.[34] For a large number of carbocations, ^{13}C chemical shifts obtained by GIAO-MP2 calculations on MP2(full)/6-31G* optimized geometries were close to experimental values.[35] Therefore, such geometries can be used to test the accuracy of the force field results.

MMP2 also allows the study of nonbonded resonance,[5] (i.e., π-overlap between atoms that are not connected by a σ-bond) and homoconjugation[36−38] effects in allyl and other delocalized open chain cations. Homoconjugation, proposed for carbocations by Applequist and Roberts[39] as well as by Simonetta and Winstein[40] about four decades ago (e.g., for homoallyl cations), was extended to homoaromaticity[41] some years later. Cyclic delocalized cations do exhibit homoaromatic behavior; the predictions have been confirmed by ab initio calculations (e.g., the homotropylium cation).[37a,b] Our force field method complements ab initio calculations by providing estimates of nonbonded resonance and homoconjugation energies.

Methods

All ab initio calculations with GAUSSIAN 92[42] and GAUSSIAN 94[43] used Convex C220, Hewlett-Packard 735, and Cray YMP-864 computers. The 6-31G* basis set[44] was employed for all optimizations both at the RHF and RMP2(full) levels (i.e., with the second-order Møller−Plesset perturbation correction based on the restricted Hartree−Fock wave function).[45] Correlated ab initio methods are necessary for the optimization of delocalized cations.[7,46] The energies discussed in the text

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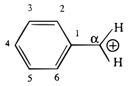
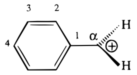
TABLE 1: C−C Bond Lengths and π-Electron Densities at MP2(full)/6-31G* (MP2) and MMP2 of the Benzyl Cation and Its Rotamer



	MP2	MMP2
	π-Electron Densities	
Cα	0.533	0.603
C1	1.115	1.090
C2	0.783	0.792
C3	1.034	1.019
C4	0.700	0.686
	Bond Lengths/Å	
Cα−C1	1.372	1.373
C1−C2	1.436	1.439
C2−C3	1.378	1.379
C3−C4	1.408	1.410



	MP2	MMP2
	π-Electron Densities	
Cα	0.057	0.0004
C1	1.153	1.243
C2	0.999	0.986
C3	0.949	0.945
C4	0.925	0.896
	Bond Lengths/Å	
Cα−C1	1.421	1.445
C1−C2	1.412	1.399
C2−C3	1.393	1.394
C3−C4	1.394	1.398

refer to calculations on the RMP2(full)/6-31G* optimized geometries using fourth-order Møller−Plesset correction including single, double, and quadruple excitations (MP4sdq).[47] All optimized structures were characterized by frequency calculations at HF/6-31G*//HF/6-31G*. π-Electron densities were obtained from natural bond orbital (NBO)[48] analysis of RHF/6-31G* wave functions using MP2(full)/6-31G* optimized structures. Calculations of nucleus independent chemical shifts (NICS)[49] were performed with the GAUSSIAN 94[43] program. The force field calculations were performed with a modified Convex version of the MMP2-82 program.[50]

Benzyl Cations

The Parent Benzyl Cation. MMP2 and MP2(full)/6-31G* optimizations gave the expected C_{2v} symmetry for the benzyl cation **1**, as computed earlier.[2,49b,51−53] Although the thermochemistry of $C_7H_7^+$ ions is still not well established,[54] the MMP2 heat of formation of **1** (215.4 kcal/mol) excellently corresponds with experimental data (215 kcal/mol[21b]) and a recently reported ab initio estimate (217.0 kcal/mol[54]). Table 1 shows C−C bond lengths and π-electron densities obtained by the MMP2 and MP2 methods, which agree remarkably well.

The resonance energy, E_{res}, of **1** was calculated by comparing the MMP2 π-energy of **1** with those of benzene and ethene, eq 1 (Table 2 lists data for a number of delocalized cations and neutral molecules).

$$E_{\mathrm{res}} = E_\pi(\text{benzyl cation}) - 3E_\pi(\text{ethene}) = -107.2\ \text{kcal/mol} \tag{1}$$

Since the MMP2 π-resonance energy of benzene (E_π(benzene) − $3E_\pi$(ethene)) is −30.8 kcal/mol, the stabilization energy of the positive charge by a phenyl ring, E_{stab}, is −76.4 kcal/mol (eq 2).

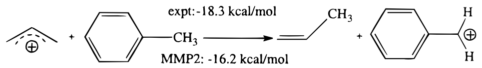
$$E_{\mathrm{stab}} = E_\pi(\text{benzyl cation}) - E_\pi(\text{benzene}) = -76.4\ \text{kcal/mol} \tag{2}$$

The isodesmic eq 3 gives −75.9 kcal/mol from experimental data (MP4sdq/6-31G*//MP2(full)/6-31G*: −75.4 kcal/mol). This matches the MMP2 result, although polarization effects also should contribute to the stabilization of the larger benzyl cation.

$$\mathrm{Ph\text{-}CH_3} + \mathrm{CH_3^+} \xrightarrow[\text{MMP2: -75.4 kcal/mol}]{\text{expt: -75.9 kcal/mol}} \mathrm{Ph\text{-}CH_2^+} + \mathrm{CH_4} \tag{3}$$

ΔH_f^o(expt), kcal/mol:	+12.1 ±0.1[55]	+261 ± 0.4[56]	+215 ± 2.0[57]	-17.8 ± 0.1[55]
ΔH_f (MMP2), kcal/mol:	12.1	260.9	215.4	-17.8[58]

The MMP2 stabilization energy of the benzyl cation is much larger than that of the allyl cation (−53.2 kcal/mol, cf. ref 4) (i.e., the larger phenyl substituent stabilizes a methyl cation more effectively than the smaller vinyl group (difference −23.2 kcal/mol)). The relative stabilization energy can also be obtained from eq 4, which gives −18.3 kcal/mol from experimental data (MP4sdq/6-31G*//MP2(full)/6-31G*: −18.0 kcal/mol) and supports the MMP2 result.

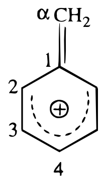


(4)

ΔH_f (expt), kcal/mol:	+226 ± 2	+12.1 ± 0.1	+4.8 ± 0.1	+215 ± 2
ΔH_f (MMP2), kcal/mol:	+225.0	12.1	5.5	+215.4

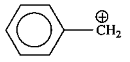
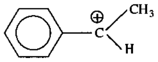
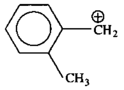
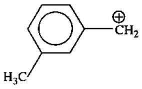
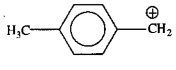
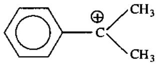
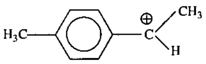
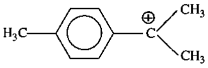
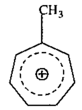
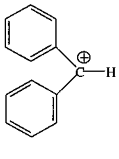
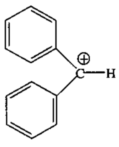
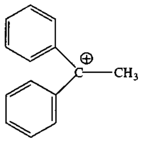
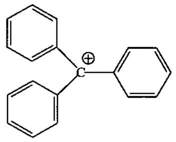
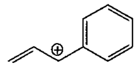
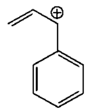
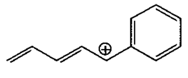
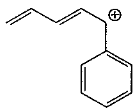
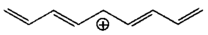
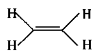
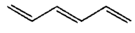
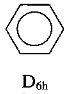
The large stabilization of the positive charge in the benzyl cation reduces the “aromaticity” of the benzene substituent significantly. Aromatic stabilization can be analyzed quantitatively by means of the nucleus independent chemical shifts (NICS) criterion (i.e., the computations of absolute magnetic shieldings at ring centers), which are proving to be a simple and effective aromaticity probe.[49] Negative NICS values suggest aromaticity (diatropic ring current), while positive NICS values are typical for antiaromatic molecules. Table 3 compares NICS (GIAO−SCF/6-31+G*//Becke3LYP/6-311+G**) of the benzyl cation with those of toluene.

The largest absolute magnetic shielding of toluene was calculated to be −11.2 ppm at a position 1.0 Å perpendicular to the ring center and for the benzyl cation −7.5 ppm at a similar 1.0 Å point above the ring. The values at the ring centers, −9.7 and −3.3 ppm, respectively, differ even more (cf. Table 3), but are influenced by contributions of the C−C and C−H σ-bonds.[49d] These results suggest that the aromaticity of the benzyl ring moiety is substantially reduced relative to toluene. MMP2 can be used to evaluate the aromatic stabilization energy in **1** by comparing the computed π-energy (−274.0 kcal/mol, Table 2) with that of the isoelectronic π-system of the acyclic *all-trans*-1,3,5-heptatrien-7-yl cation (−262.8 kcal/mol, Table 2). The π-energy difference, −11.2 kcal/mol, is only 68% of the MMP2 benzene aromaticity (E_π(benzene) − E_π(1,3,5-hexatriene) = −16.4 kcal/mol). This reduced *aromatic* stabilization energy in **1** is a consequence of the large resonance stabilization demand of the positive charge. Therefore, the best single description of **1** is the quinoid structure **1a**. The C_α−C_1 bond (MMP2:



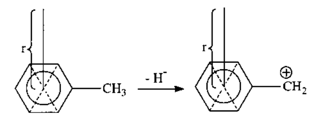
1a

TABLE 2: MMP2 π-Energies, E_π,[a] σ-Energies, E_σ,[a] Total Electronic Energies, $E_\sigma + E_\pi$,[a] and Steric Energies, E_{st},[a] Ab Initio Energies, EMP2[b,c,d] and EMP4,[d,e] Number of Imaginary Frequencies, NIMAG, Zero Point Energies, ZPE,[a] of Delocalized Carbocations and Neutral Molecules

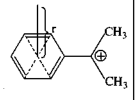
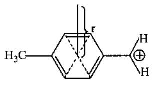
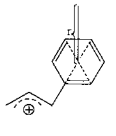
Molecule	E_π *E_σ* **$E_\pi + E_\sigma$**	E_{st}	EMP4 *EMP2*	NIMAG *ZPE*
 **1** C_{2v}	-274.0 *-584.5* **-858.5**	-8.7	-269.78713 *-269.77676*	0 *78.9*
 **5** C_s	-281.2 *-573.4* **-854.6**	-12.1	-308.98145 *-308.96618*	0 *97.6*
 **2** C_s	-276.8 *-573.9* **-850.7**	-12.7	-308.97372 *-308.95774*	0 *97.5*
 **3** C_s	-274.1 *-581.8* **-855.9**	-8.5	-308.97229 *-308.95763*	0 *97.3*
 **4** C_s	-278.6 *-573.7* **-852.3**	-13.7	-308.97869 *-308.96230*	0 *97.2*
 **6** C_2	-287.8 *-560.1* **-847.8**	-14.4	-348.17000 *-348.14973*	0 *116.2*
 **7** C_1	-285.3 *-562.9* **-848.3**	-14.1	-348.17129 *-348.15023*	0 *115.9*
 **8** C_1	-291.4 *-549.7* **-841.1**	-19.4	-387.35868 *-387.33283*	0 *134.6*
 **18** D_{7h}	-278.5 *-590.0* **-868.5**	-11.6	-269.80245 *-269.79675*	0 *79.9*
 **19** C_s	-285.0 *-574.3* **-859.3**	-14.6	-308.98860 *-308.97808*	0 *97.7*
 **9** C_2	-497.9 *-1173.0* **-1670.9**	-11.5	-500.14660 *-500.14885*	0 *134.1*
 **10** C_{2v}	-495.4 *-1175.6* **-1671.0**	-9.9	-500.14352 *-500.14449*	1 *134.0*
 **12** C_1	-503.9 *-1158.5* **-1662.4**	-15.2	- *-539.32980*	0 *152.6*
 **11** D_3	-717.6 *-1753.6* **-2471.2**	-12.2	- *-730.41929*	0 *188.7*
 **13** C_s	-345.8 *-752.0* **-1097.8**	-6.4	-346.96104 *-346.94957*	0 *101.8*
 **14** C_1	-348.6 *-747.0* **-1095.6**	-3.6	-346.95307 *-346.94221*	0 *101.8*
 **16** C_s	-413.0 *-919.8* **-1332.8**	-7.4	-424.12970 *-424.11644*	0 *124.4*
 **17** C_1	-414.7 *-916.5* **-1331.2**	-5.9	-424.12072 *-424.10862*	0 *124.4*
 C_{2v}	-108.8 *-164.0* **-272.8**	-1.6	- -	- -
 C_{2v}	-190.6 *-329.8* **-520.4**	0.8	- -	- -
 C_{2v}	-262.8 *-496.7* **-759.5**	-0.5	- -	- -
 C_{2v}	-330.2 *-664.1* **-994.3**	-1.4	- -	- -
 D_{2h}	-55.6 *-73.8* **-129.4**	0.4	- -	- -
 C_{2h}	-181.2 *-403.3* **-584.5**	-5.4	- -	- -
 D_{6h}	-197.6 *-497.5* **-695.1**	-2.6	- -	- -

[a] Values in kcal/mol. [b] MP2(full)/6-31G*//MP2(full)/6-31G*. [c] Ab initio energy for the triphenylmethyl cation at MP2(fc)/6-31G*//MP2(fc)/6-31G*. [d] Ab initio energies are given in atomic units. [e] MP4sdq/6-31G*//MP2(full)/6-31G*.

TABLE 3: Dependence of Negative NICS Absolute Magnetic Shieldings δ (GIAO-SCF/6-31+G*//Becke3LYP/6-311+G) on the Distance, *r*, from the Ring Centers in Toluene, the Benzyl, the Cumyl, the *p*-Methylbenzyl, and the 1-Phenylallyl Cations**



r / Å	δ / ppm	δ / ppm
0.0	-9.7	-3.3
0.5	-11.3	-5.8
1.0	-11.2	-7.5
1.5	-8.1	-6.1
2.0	-5.2	-4.1
2.5	-3.2	-2.8
3.0	-2.1	-1.9
3.5	-1.4	-1.3

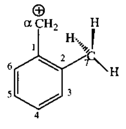
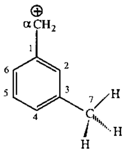
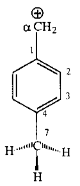
			
r / Å	δ / ppm	δ / ppm	δ / ppm
0.0	-6.7	-3.6	-7.0
0.5	-9.1	-6.3	-9.4
1.0	-10.0	-7.9	-10.2
1.5	-7.4	-6.1	-7.9
2.0	-4.7	-3.9	-5.0

1.373 Å. MP2(full)/6-31G*: 1.372 Å.) is only moderately longer than that of the ethene C=C bond (MMP2: 1.339 Å. MP2(full)/6-31G*: 1.335 Å.) The rather long C1−C2 bond (MMP2: 1.439 Å. MP2(full)/6-31G*: 1.436 Å.) supports this conclusion impressively. More evidence is discussed below. Very recently, Olah has called attention to the "important contribution" made by a similar quinoid resonance structure to the 2,4,6-trimethylbenzyl cation.[24]

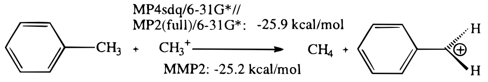
The MMP2 total benzyl cation stabilization energy, −76.4 kcal/mol (eq 2), is much larger than the rotational barrier of the benzyl cation, 48.7 kcal/mol at MP4sdq/6-31G*//MP2(full)/6-31G* (MMP2: 50.2 kcal/mol). The computed barrier is almost independent of the basis set[59,60] (the MINDO/3[61] value, 22.3 kcal/mol, is too low[61b]). The rotated benzyl cation transition structure is stabilized by hyperconjugative interactions of two C−C σ-bonds and by large polarization effects of the benzene π-electrons. Hence, the resonance stabilization due to the benzene ring should be considerably larger than the 48.7 kcal/mol rotational barrier, and the MMP2 estimate of −76.4 kcal/mol seems reasonable. Moreover, a recently developed orbital deletion procedure (ODP[62a]) showed bond equalization in the benzene ring when the p orbital of the exocyclic carbon was deleted and, therefore, stressed the importance of resonance stabilization in the benzyl cation **1**.[62b] The π-electron densities of the benzene ring carbons in the perpendicular rotamer decrease with increasing distance from the exocyclic carbon because of the polarization by the positive charge (cf. Table 1). All the benzene ring C−C bond lengths in the rotamer are close to those of neutral benzene (MP2(full)/6-31G*: 1.395 Å. MMP2: 1.396 Å.) The NICS value in the benzene ring center of the rotated form (−9.5 ppm) is nearly the same as the toluene value (−9.7 ppm), which indicates that the aromaticity of the benzene ring in the rotamer is almost that of neutral toluene.

According to the isodesmic eq 5, the benzyl cation rotamer is stabilized relative to the methyl cation. Strong polarization effects of the benzene π-electrons are responsible for this stabilization. The MMP2 as well as the MP2(full)/6-31G* π-electron densities demonstrate this polarization effect clearly (cf. π-electron densities, Table 1).

TABLE 4: Bond Lengths and π-Electron Densities of the *o*-, *m*-, and *p*-Methylbenzyl Cations at MP2(full)/6-31G* (MP2) and at MMP2, Relative Energies, E_{rel}[a,d] and ΔH_f(rel),[b,d] Experimental Heats of Formation, ΔH_f(exp),[c,d] and MMP2 Heats of Formation, ΔH_f(MMP2)[d]

	 **2**		 **3**		 **4**	
	Bond lengths / Å					
Bond	MP2	MMP2	MP2	MMP2	MP2	MMP2
Cα-C1	1.370	1.372	1.372	1.374	1.370	1.370
C1-C2	1.450	1.443	1.435	1.439	1.436	1.441
C2-C3	1.387	1.387	1.384	1.379	1.374	1.377
C3-C4	1.402	1.405	1.414	1.411	1.416	1.419
C4-C5	1.408	1.416	1.406	1.409	-	-
C5-C6	1.374	1.374	1.378	1.380	-	-
C1-C6	1.440	1.445	1.436	1.438	-	-
C2-C7	1.497	1.482	-	-	-	-
C3-C7	-	-	1.501	1.489	-	-
C4-C7	-	-	-	-	1.490	1.482
	π-Electron densities					
Carbon	MP2	MMP2	MP2	MMP2	MP2	MMP2
Cα	0.561	0.613	0.542	0.602	0.571	0.623
C1	1.117	1.111	1.107	1.082	1.114	1.101
C2	0.743	0.688	0.817	0.833	0.785	0.775
C3	1.063	1.080	1.004	0.958	1.053	1.069
C4	0.692	0.673	0.710	0.716	0.665	0.587
C5	1.047	1.027	1.032	1.010		
C6	0.787	0.808	0.788	0.798		
E_{rel}	3.12		4.02		0.	
ΔH_f(rel)	2.99		3.35		0.	
ΔH_f(exp)	203		204		200	
ΔH_f(MMP2)	203.6		203.9		200.6	

[a] MP4sdq/6-31G*//MP2(full)/6-31G*. [b] MMP2 relative heats of formation. [c] See ref 21b. [d] Values in kcal/mol.

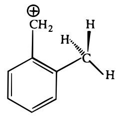


(5)

ΔH_f (MMP2), kcal/mol: 12.1 260.9 -17.8[58] 265.6

Methyl Group Substitution

Methyl Group Substitution on the Benzene Ring. The C_s *o*-methylbenzyl cation **2** prefers the conformation were one methyl C−H bond is eclipsed with the *meta* carbon slightly. The methyl group helps stabilize the π-charge at the α-carbon (cf. Tables 1 and 4). Small variations in the C−C bond lengths result.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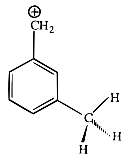
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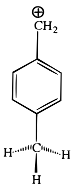
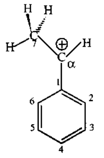
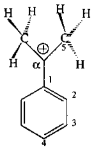

4

The favored C_s *m*-methylbenzyl cation conformation **3** has one methyl C−H bond eclipsed with the *ortho* carbon both according to MP2(full)/6-31G* and to MMP2 optimizations. The conformer with C_s symmetry and one methyl C−H bond eclipsed with the *para* carbon is a transition state for methyl rotation; the barrier is 0.47 kcal/mol at MP4sdq/6-31G*//MP2-(full)/6-31G* (the MMP2 heats of formation for both structures are identical). The methyl group reduces the π-electron density

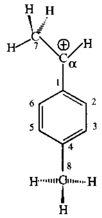
TABLE 5: C−C Bond Lengths and π-Electron Densities of α-Methylbenzyl Cations at MP2(full)/6-31G* (MP2) and MMP2



5



6



7

Bond lengths / Å

Bond	MP2	MMP2	Bond	MP2	MMP2	Bond	MP2	MMP2
Cα-C1	1.389	1.384	Cα-C1	1.409	1.396	Cα-C1	1.385	1.381
C1-C2	1.430	1.436	C1-C2	1.427	1.434	C1-C2	1.431	1.438
C2-C3	1.381	1.381	C2-C3	1.382	1.382	C2-C3	1.377	1.378
C3-C4	1.403	1.407	C3-C4	1.402	1.406	C3-C3	1.410	1.416
C4-C5	1.406	1.408	Cα-C5	1.485	1.491	C4-C5	1.415	1.417
C5-C6	1.380	1.381				C5-C6	1.376	1.379
C1-C6	1.429	1.436				C1-C6	1.430	1.438
Cα-C7	1.468	1.465				Cα-C7	1.471	1.465
						C4-C8	1.492	1.482

π-Electron densities

Carbon	MP2	MMP2	MP2	MMP2	MP2	MMP2
Cα	0.501	0.494	0.479	0.416	0.534	0.513
C1	1.134	1.155	1.147	1.199	1.138	1.169
C2	0.816	0.803	0.834	0.815	0.796	0.787
C3	1.023	1.016	1.021	1.014	1.052	1.069
C4	0.740	0.710	0.772	0.727	0.703	0.610
C5	1.030	1.017			1.043	1.068
C6	0.802	0.806			0.814	0.785

of the *meta* carbon slightly. Table 4 lists bond lengths and π-electron densities of the *o*-, *m*-, and *p*-methylbenzyl cations at MP2(full)/6-31G* and at MMP2.

The C_s *p*-methylbenzyl cation **4** has one methyl C−H bond perpendicular to the benzyl system. The π-charge at the *para* carbon is stabilized by C−H hyperconjugation; this leads to elongations of the *para*−*meta* C−C bonds and to moderate shortenings of the *meta*−*ortho* C−C bonds. The larger *para* carbon π-charge in **4** compared with **1** influences the aromaticity of the benzene ring only insignificantly. The NICS values computed for **1** and **4** are almost identical (cf. Table 3).

The two methods agree with experimental data in giving the same energy sequence for the three isomers (cf. Table 4). MMP2 suggests that the *p*-methylbenzyl cation is stabilized better by hyperconjugation than **2** and **3**.

Methyl Group Substitution at the Exocyclic Carbon. The C_s α-methylbenzyl cation **5** and C_2 α,α-dimethylbenzyl cation **6** increase the π-charge stabilization of the exocyclic carbon. At both MP2(full)/6-31G* and MMP2, **5** has one methyl C−H bond eclipsed with the benzyl system. Table 5 lists C−C bond lengths and π-electron densities of both cations obtained by the two different theoretical methods.

Both methods agree that the π-charge at the exocyclic carbon increases with increasing methyl group substitution.[63] This stabilization due to C−H hyperconjugation elongates the Cα−C1 bonds. The MMP2 π-energies become more negative along the benzyl **1**, α-methylbenzyl **5**, and α,α-dimethylbenzyl **6** cation series (cf. Table 2): **5** is 1.7 kcal/mol more stable than **4** at MP4sdq/6-31G*//MP2(full)/6-31G* (MMP2: 2.9 kcal/mol); the experimental heats of formation (**5**: 199 ± 2 kcal/mol.[21b] **4**: 200 ± 2 kcal/mol.[21b]) are consistent, but are not highly accurate.

Methyl group substitution at the exocyclic carbon reduces the π-charge localized in the benzene ring. Therefore, the benzene ring aromaticity in **6** should be larger than that in **1**. In agreement with this expectation, the NICS absolute magnetic shieldings computed at the aromatic ring center and at positions perpendicular to this ring center of **6** are almost the same as those of toluene and significantly larger than those of the parent benzyl cation (cf. Table 3).

A recently reported X-ray structure of cumyl hexafluoroantimonate(V), similar to the theoretical structure, showed a small twisting of the exocyclic carbon plane relative to the benzene ring plane (exptl: 8°. MMP2: 6.4°. MP2(full)/6-31G*: 7.4°.)[18] The X-ray C_1 point group for **6** evidently is due to the involvement of many strong H···F contacts to SbF_6^- anions in the crystal structure.

The C_1 α-methyl-*p*-methylbenzyl cation **7** (cf. Table 5) and C_1 α,α-dimethyl-*p*-methyl benzyl cation **8** have one *para* methyl C−H bond almost perpendicular to the benzyl system according to MP2(full)/6-31G* and to MMP2. The MMP2 heat of formation of **7** (186.0 kcal/mol) agrees well with experimental data (186.2 kcal/mol[21b]) and is 1.2 kcal/mol lower than that of **6** (MMP2 heat of formation: 187.2 kcal/mol; the energy difference is 0.81 kcal/mol at MP4sdq/6-31G*//MP2(full)/6-31G*). Figure 1 lists key geometry parameters and π-electron densities of **8**. The MMP2 heat of formation of **8** (176.4 kcal/mol) agrees with the experimental value (174 ± 2 kcal/mol[21b]).

Substitution by Phenyl Groups

The moderate twisting of both phenyl rings (MP2(full)/6-31G*: 19.4°. MMP2: 18.9°) out of the plane of the central carbon of the C_2 benzhydryl cation **9**, which has been studied by experimental laser flash photolysis of *trans*-2,3-diphenylaziridinimines[64] as well as by kinetic[65] and fast UV investigations,[66] weakens the resonance stabilization. Analogous geometries have been obtained with smaller basis sets.[67] Structure **9** is 1.89 kcal/mol (MP4sdq/6-31G*//MP2(full)/6-31G* + ZPE (RHF/6-31G*)) lower in energy than the planar C_{2v} conformer **10** (MMP2: 1.38 kcal/mol) which serves as the transition state for phenyl rotation. The π-electron density of the central carbon of the C_2 conformer (MP2(full)/6-31G*: 0.579; MMP2: 0.620.) is only insignificantly higher than that of the benzyl cation α-carbon (MP2(full)/6-31G*: 0.533. MMP2: 0.603.). The MMP2 π-charge of a phenyl ring, 0.318 (MP2(full)/6-31G*: 0.294), is delocalized mainly at the *para* position (MMP2: 0.194. MP2(full)/6-31G*: 0.184.). The MMP2 phenyl ring π-charge of 0.603 (MP2(full)/6-31G*: 0.551) in **1** is only slightly lower than the sum of the π-charges of the two phenyl rings in **9**. Figure 1 lists geometry parameters and π-electron densities of **9** and many other cations discussed in this article.

Resonance energy evaluations also give estimates of the charge stabilization by the two phenyl rings. The total charge stabilization energy, E_{stab}, can be calculated by eq 6 (cf. π-energies, Table 2).

$$E_{\mathrm{stab}} = E_{\pi}(\text{benzhydryl cation}) - 2E_{\pi}(\text{benzene}) = -102.7\ \text{kcal/mol} \quad (6)$$

The MMP2 value is only 26.3 kcal/mol larger than the stabilization by the benzene ring in **1** (eq 2). The value, −91.6 kcal/mol, obtained by isodesmic equation eq 7, is somewhat lower than that given by eq 6 due to steric interactions.

$$CH_3^+ + Ph_2CH_2 \xrightarrow{-91.6\ \text{kcal/mol}} Ph_2CH^+ + CH_4 \quad (7)$$

ΔH$_f$ (MMP2), kcal/mol: +260.9 +38.6 +225.7 -17.8 (expt)

The second phenyl ring in Ph_2CH^+ stabilizes the positive charge only moderately. This is shown by the −16.2 kcal/mol exothermicity of eq 8.

$$Ph\text{-}CH_2^+ + Ph_2CH_2 \xrightarrow{-16.2\ \text{kcal/mol}} Ph_2CH^+ + PhCH_3 \quad (8)$$

ΔH$_f$ (MMP2), kcal/mol: +215.4 +38.6 +225.7 +12.1

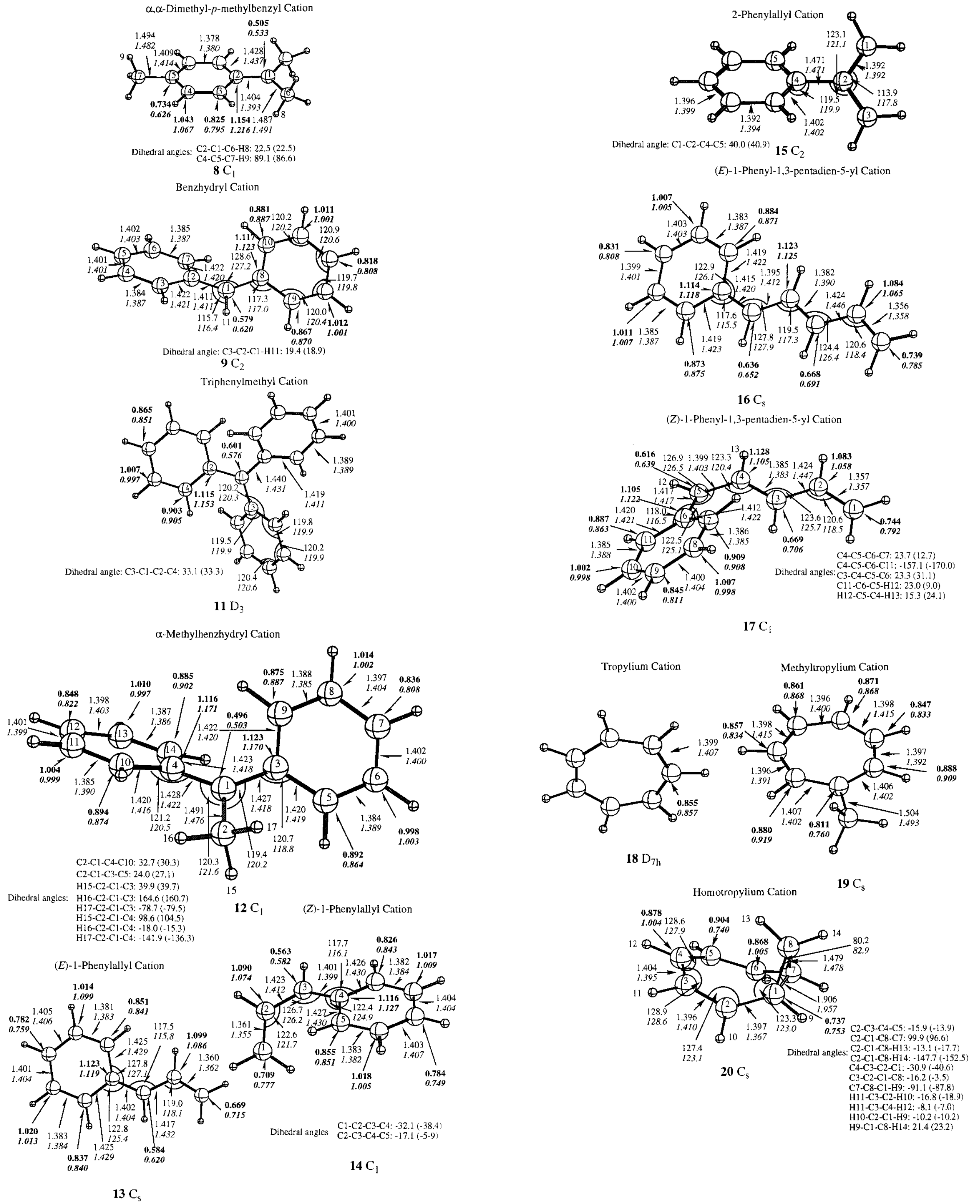


Figure 1. Geometries: bond lengths in angstroms; angles and dihedral angles in degrees; the MMP2 dihedral angles are given in parentheses (Italic: values at MMP2. Bold: π-electron densities.) of some cyclic delocalized cations at MP2 (full)/6-31G* (Values for the triphenylmethyl cation at MP2(fc)/6-31G*.) and MMP2.

In agreement with the X-ray structure,[19] the three benzene rings of the D_3 triphenylmethyl cation **11** are strongly distorted of out of the plane of the four central carbons (cf. **9**, Figure 1). The C−C bond lengths of the central carbon and the benzene ring *ipso*-carbons (X-ray: 1.45 Å. MMP2: 1.431 Å. MP2-(fc)/6-31G*: 1.440 Å.) as well as the twist angles of the phenyl rings out of the central carbon plane (X-ray: 33°. MMP2: 33.3°. MP2(fc)/6-31G*: 33.1°.) agree well. The high reactivity of triphenylmethyl derivatives in solvolysis reactions has long been known experimentally.[68] Kinetic investigations of solvolysis rates have clearly shown the considerable ability of triarylmethyl systems to stabilize a positive charge.[69] Although triphenylmethyl chloride solvolyzes 130 000 times faster than benzhydryl chloride and solution pK_a differences demonstrate increased stabilization,[69] the average resonance energy per phenyl ring is lower in **11** than that in **9**, showing attenuation. The π-charges (MMP2: 0.192. MP2(fc)/6-31G*: 0.200.) of the individual phenyl rings in **11** are significantly lower than those of the phenyl rings in **1** (MMP2: 0.603. MP2(full)/6-31G*: 0.551.) and **9** (MMP2: 0.318. MP2(full)/6-31G*: 0.294.). The C−C bond lengths of the central carbon toward the phenyl rings are elongated (MMP2, **1**: 1.373 Å. **9**: 1.411 Å. **11**: 1.431 Å.).

Resonance energies document the decreasing efficiencies of charge stabilization per phenyl with the increasing number of rings. The total charge stabilization energy, E_{stab}, can be calculated by eq 9.

$$E_{\text{stab}} = E_\pi(\text{triphenylmethyl cation}) - 3E_\pi(\text{benzene}) = -124.8 \text{ kcal/mol} \quad (9)$$

An isodesmic equation (eq 10) gives a lower value (−102.2 kcal/mol) due to steric contributions.

$$\begin{array}{lcccccc} & CH_3^+ + & Ph_3CH & \xrightarrow{-102.2\text{ kcal/mol}} & Ph_3C^+ + & CH_4 & (10) \\ \Delta H_f\text{(MMP2), kcal/mol:} & +260.9 & +67.2 & & +243.7 & -17.8\text{ (expt)} & \end{array}$$

The additional resonance effect, E_{res}, due to the third benzene ring, is given by eq 11.

$$E_{\text{res}} = E_\pi(\text{triphenylmethyl cation}) - E_\pi(\text{benzhydryl cation}) - E_\pi(\text{benzene}) = -22.1 \text{ kcal/mol} \quad (11)$$

This value is 4.2 kcal/mol lower than that for the second phenyl ring in the benzhydryl cation (−26.3 kcal/mol) and illustrates the attenuation of the phenyl stabilization. The value given by eq 12 is somewhat lower (−10.6 kcal/mol) as a result of energy-raising steric contributions.

$$\begin{array}{lcccccc} & Ph_3C^+ + & Ph_2CH_2 & \xrightarrow{-10.6\text{ kcal/mol}} & Ph_3CH + & Ph_2CH^+ & (12) \\ \Delta H_f\text{(MMP2), kcal/mol:} & +243.7 & +38.6 & & +67.2 & +225.7 & \end{array}$$

When hyperconjugation of six C−C σ-bonds was excluded (a feature allowed by the program), the π-energy was raised by 2.3 kcal/mol. The hyperconjugation contribution obtained by NBO analysis[48] via Fukui's method[70] (this method assumes a $f^2/\Delta\epsilon$ dependence of orbital interactions, where f is the fock matrix element and $\Delta\epsilon$ is the energy difference of the participating orbitals) on the MP2(fc)/6-31G* structure was 4.7 kcal/mol. The MMP2 heat of formation of **11** is 243.7 kcal/mol, but the experimental value is not known.

The methyl group in the C_1 α-methylbenzhydryl **12** cation distorts the two phenyl rings differently out of the plane of the three central carbons (cf. Figure 1). The methyl group stabilizes the π-charge of the exocyclic carbon slightly and elongates the bonds between the exocyclic carbon and the phenyl rings moderately. Consequently, larger distortions of the phenyl rings out of the central carbon plane, which decreases the resonance energy by 2.0 kcal/mol compared with **9**, result. The MMP2 heat of formation of **12** (214.1 kcal/mol) agrees well with the experimental value (213.6 ± 2 kcal/mol[21b]).

Phenyl Substitution at Delocalized Open Chain Polyenyl Cations

The 1-Phenylallyl Cations. The (*E*)-1-phenylallyl cation **13** has C_s symmetry at both MP2(full)/6-31G* and MMP2 (cf. Figure 1) and is best described as an α-vinylbenzyl cation. The two allyl C−C bond lengths differ by 0.06 ± 0.01 Å (C1−C2, MP2(full)/6-31G*: 1.417 Å. MMP2: 1.432 Å. C2−C3, MP2(full)/6-31G*: 1.360 Å. MMP2: 1.362 Å.) and the allyl C2−C3 bond length is rather close to that of an isolated C═C double bond (ethene, MMP2: 1.339 Å. MP2(full)/6-31G*: 1.335 Å.). The π-electron density of the allyl carbon substituted by the phenyl ring is close to that of the exocyclic benzyl carbon (MP2(full)/6-31G*: 0.533. MMP2: 0.603.). The total phenyl ring charge is +0.320 at MMP2 (MP2(full)/6-31G*: +0.373).

The additional resonance stabilization energy, E_{stab}, due to phenyl substitution, calculated by eq 13 (cf. Table 2), is quite large.

$$E_{\text{stab}} = E_\pi(1 - \text{phenylallyl cation, } \mathbf{13}) - E_\pi(\text{allyl cation}) - E_\pi(\text{benzene}) = -39.4 \text{ kcal/mol} \quad (13)$$

This stabilization is significantly greater than the resonance effects of the second phenyl ring in **9** and the third phenyl ring in **13** but less than that in the benzyl cation **1**.

The aromatic stabilization energy of the benzene ring in **13** can be evaluated by comparing its MMP2 π-energy with that of the acyclic *all-trans*-1,3,5,7-nonatetraen-9-yl cation π-system (cf. Table 2). The differences in π-energies give an aromatic stabilization of −15.6 kcal/mol, insignificantly lower than that of benzene (−16.4 kcal/mol). This large benzene ring aromaticity relative to that in **1** is a consequence of the lower stabilization by the benzene ring (−39.4 kcal/mol) in **13** compared to that in **1** (−76.4 kcal/mol). The NICS values of **13** are only slightly lower than those of toluene (cf. Table 3), which confirms the MMP2 aromaticity impressively.

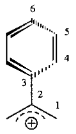
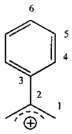
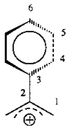
The phenyl ring in the C_1 (*Z*)-1-phenylallyl cation **14** is distorted out of the allyl plane at MP2(full)/6-31G* and at MMP2 (cf. Figure 1). The (*E*)-isomer is 5.0 kcal/mol more stable than the (*Z*)-isomer at MP4sdq/6-31G*//MP2(full)/6-31G* (MMP2: 4.8 kcal/mol). MMP2 attributes this difference both to steric (2.8 kcal/mol is mainly due to torsional strain) and to electronic π-effects (2.0 kcal/mol decrease due to the distortion of the π-system from planarity).

2-Phenylallyl Cation. MMP2 as well as MP2(full)/6-31G* favors C_2 symmetry for the 2-phenylallyl cation **15** (cf. Figure 1) with a significantly reduced allyl C−C−C angle (MP2(full)/6-31G*: 113.9°) and moderate deviations of the phenyl C−C bond lengths from the benzene value. The structures and energies of the planar C_{2v} 2-phenylallyl cation **16** and the perpendicular C_{2v} rotamer **17** also are given in Table 6 along with the π-electron densities of these three 2-phenylallyl cation conformers.

The MMP2 rotational barrier (1.3 kcal/mol) is somewhat lower than the ab initio value (2.1 kcal/mol). MMP2 suggests that the unfavorable π-energy is the main disadvantage of **16**. The steric energy of the C2 structure is 1.1 kcal/mol lower than that of the planar conformer. The C_{2v} structure **17** has the best π-energy, but unfavorable σ-and steric energies destabilize **17**.

The stabilization energy, E_{stab}, of the phenyl substituent on the allyl system given by eq 14 is −11.2 kcal/mol for the C_2

TABLE 6: π-Electron Densities at MP2(full)/6-31G* (MP2) and at MMP2, ab Initio Energies, EMP2^{a,f} and EMP4,^{b,f} Relative Energies, E_{rel}^{b,e} and ΔH_f(rel),^{c,e} MMP2 π-Energies, E_π,^{e} σ-Energies, E_σ,^{e} and Steric Energies, E_{st},^{e} of 2-Phenylallyl Cation Conformers^d

	 C_2 **15**		 C_{2v} planar **16**		 C_{2v} perpendicular position of the benzene ring towards the allyl system **17**	
	π-Electron densities					
Carbon	MP2	MMP2	MP2	MMP2	MP2	MMP2
C1	0.474	0.524	0.486	0.557	0.457	0.497
C2	1.086	0.996	1.069	0.967	1.086	1.006
C3	1.091	1.143	1.094	1.136	1.107	1.167
C4	0.996	0.986	0.988	0.976	0.990	0.988
C5	0.967	0.963	0.967	0.966	0.963	0.966
C6	0.942	0.914	0.931	0.900	0.946	0.925
EMP2	-346.90601		-346.90232		-346.90314	
EMP4	-346.91729		-346.91388		-346.91463	
E_{rel}	0.0		2.14		0.67	
ΔH_f(rel)	0.0		1.30		0.31	
E_π	-317.6		-315.4		-320.6	
E_σ	-752.8		-754.7		-751.1	
E_{st}	-6.5		-5.4		-4.6	

[a] MP2(full)/6-31G*//MP2(full)/6-31G*. [b] MP4sdq/6-31G*//MP2(full)/6-31G*. [c] MMP2 relative heats of formation. [d] We could only perform MMP2 single point calculations on the C_{2v} rotamer of the 2-phenylallyl cation optimized at MP2(full)/6-31G*, because MMP2 is not able to freeze more than two dihedral angles simultaneously. [e] Values in kcal/mol. [f] Values in atomic units.

minimum structure **15**. The π-electron densities show only small π-charges on the benzene ring (MMP2: 0.08. MP2(full)/6-31G*: 0.06.).

$$E_{stab} = E_\pi(2 - \text{phenylallyl cation}) - E_\pi(\text{allyl cation}) - E_\pi(\text{benzene}) \quad (14)$$

The MMP2 heat of formation of **15** (250.9 kcal/mol) is larger than that of **13** (219.7 kcal/mol); the difference, 31.2 kcal/mol, agrees well with the MP4sdq/6-31G*//MP2(full)/6-31G* value, 27.5 kcal/mol.

1-Phenyl-1,3-Pentadien-5-yl Cations. The (*E*)-1-phenyl-1,3-pentadien-5-yl cation **18** favors C_s symmetry and a planar π-system at MMP2 and at MP2(full)/6-31G* (cf. Figure 1). The total π-charge delocalization into the benzene ring is lower (MP2(full)/6-31G*: 0.280. MMP2: 0.316.) than that of **13** (MP2(full)/6-31G*: 0.373. MMP2: 0.320.), but the MMP2 difference is quite small.

The MMP2 resonance stabilization, E_{stab}, of the benzene ring, given by eq 15 (cf. π-energies, Table 2), is significantly less favorable than the resonance stabilization by the benzene ring in **13** (−39.4 kcal/mol).

$$E_{stab} = E_\pi(\text{1-phenyl-1,3-pentadien-5-yl cation}) - E_\pi(\text{1,3-pentadien-5-yl cation}) - E_\pi(\text{benzene}) = -24.8\ \text{kcal/mol} \quad (15)$$

The C_1 (*Z*)-1-phenyl-1,3-pentadien-5-yl cation **19** (cf. Figure 1) is 5.6 kcal/mol less stable than **18** at MP4sdq/6-31G*//MP2-(full)/6-31G* (MMP2: 3.0 kcal/mol). According to MMP2, this difference can be attributed to steric and electronic effects resulting from the distortion of the pentadienyl system out of the plane of the benzene ring in **19**. The π-charge delocalization into the benzene ring in **19** is moderately less than in **18** (**18**: MMP2: 0.316. MP2(full)/6-31G*: 0.280. **19**: MMP2: 0.300. MP2(full)/6-31G*: 0.245.).

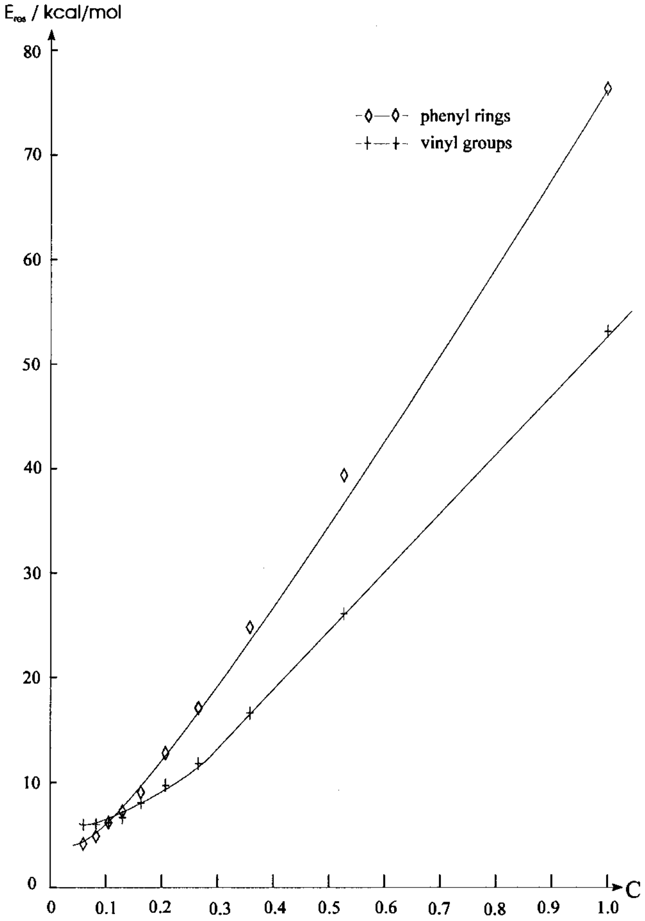


Figure 2. Dependence of resonance energies, E_{res}, of phenyl rings and vinyl groups on the π-charge, *C*, stabilized by these groups.

Resonance Effects of Benzene Substituents. MMP2 computations on delocalized open-chain cations[5] showed that the magnitude of resonance stabilization by vinyl substituents depend strongly on the π-charges of cation carbons to which these groups are attached. A linear relationship over a long range was found between the resonance energy and the MMP2 π-charges. However, when the π-charges of carbon centers are smaller than 0.2, the resonance stabilization energies of vinyl substituents are larger than expected from a linear relationship, since resonance also is important in conjugated neutral molecules (e.g., 1,3-butadiene (MMP2 resonance energy in *s-trans*-1,3-butadiene: −6.7 kcal/mol).

The MMP2 resonance stabilization of a benzene substituent, E_{res}(benzene), in a linear *all-trans*-1-phenylpolyenyl cation 1-Ph-poly(*n*) with *n* linearly conjugated vinyl groups ($Ph{-}^{+}CH{-}(CH{=}CH)_n{-}H$) is given by eq 16,

$$E_{res}(\text{benzene}) = E_\pi(\text{1-Ph-poly}(n)) - E_\pi(\text{poly}(n)) - E_\pi(\text{benzene}) \quad (16)$$

where $E_\pi(\text{poly}(n))$ is the π-energy of a linear *all-trans* cation $CH_2^{+}{-}(CH{=}CH)_n{-}H$.

The correlation of the resulting resonance energies with the π-charges of the terminal carbons of the *all-trans*-polyenyl cation poly(*n*) with *n* vinyl groups attached linearly to a CH_2^+ group are compared in Figure 2. Analogous to eq 16, the resonance effect of a terminal vinyl group, E_{res}(vinyl), in a linear *all-trans*-polyenyl cation poly(n+1) with n+1 vinyl groups attached linearly to a $CH2^+$ group can be calculated by eq 17,

TABLE 7: Charge Stabilizing Resonance Energies of Benzene Rings, E_{res}(benzene), in Linear *all-trans*-(*E*)-1-Phenylpolyenyl Cations Ph$-^{+}$CH$-$(CH$=$CH)$_n-$H and Resonance Energies of Vinyl Groups, E_{res}(vinyl),[a] in Linear *all-trans*-Polyenyl Cations $H_2C^+-(CH{=}CH)_{n+1}-H$ Depending on the π-Charge, *C*, of a Terminal Carbon of a Linear *all-trans*-Polyenyl Cation $H_2C^+-(CH{=}CH)_n$-H

n	*C*	E_{res}(benzene)/kcal/mol	E_{res}(vinyl)/kcal/mol
0	1.0	76.4	53.2
1	0.527	39.4	26.1
2	0.358	24.8	16.6
3	0.266	17.1	11.8
4	0.207	12.8	9.7
5	0.163	9.1	8.1
6	0.130	7.3	6.7
7	0.105	6.2	6.2
8	0.083	4.9	6.0
9	0.060	4.2	6.0

[a] The results for vinyl groups are already published; cf. ref 5.

where E_π(poly(n+1)) is the π-energy of a linear *all-trans* cation $CH_2{}^+-(CH{=}CH)_{n+1}-H$.

$$E_{res}(\text{vinyl}) = E_\pi(\text{poly}(n+1)) - E_\pi(\text{poly}(n)) - E_\pi(\text{ethene}) \quad (17)$$

Table 7 lists the MMP2 resonance energies of benzene rings and vinyl groups and the π-charges stabilized by these groups and Figure 2 illustrates the results.

Benzene rings stabilize π-charges larger than 0.2 more effectively than vinyl groups. Figure 2 demonstrates a linear relationship between resonance stabilization energies and the π-charges stabilized by resonance for vinyl as well as for benzene substituents. The slopes of the straight parts of the lines give a resonance stabilization of −78.2 kcal/π-charge for benzene substituents and of −57.3 kcal/π-charge for vinyl substituents; this demonstrates the inherently larger resonance stabilization of benzene rings compared with vinyl groups.

Tropylium Cations. *Tropylium Cation.* Doering and Knox first synthesized the D_{7h} tropylium cation **20** (cf. Figure 1) via bromation of tropylidene.[71] Vibrational spectroscopy verified the high symmetry.[72] The C−C bond lengths are 1.407 Å at MMP2 (MP2(full)/6-31G*: 1.399 Å). MMP2 reproduces the experimental heat of formation well (H_f(exptl): 203 ± 2 kcal/mol;[21b] MMP2: 202.4 kcal/mol.). The difference in the experimental heat of formation of the isomeric benzyl cation (experimental value: 215 ± 2 kcal/mol kcal/mol.[21b] MMP2: 215.4 kcal/mol.) is reproduced by MMP2 and by ab initio calculations (MP4sdq/6-31G*//MP2(full)/6-31G* + ΔZPE(HF/6-31G*): 8.67 kcal/mol) satisfactorily. The MMP2 π-energy of the tropylium cation is 4.5 kcal/mol lower than that of the benzyl cation (cf. π-energies, Table 2).

The aromatic stabilization energy of the tropylium cation can be calculated by comparing the MMP2 π-energies of the tropylium and the acyclic *all-trans*-2,4,6-heptatrienyl cations (cf. Table 2). The difference between these π-energies suggests an aromatic stabilization energy of −15.7 kcal/mol, slightly lower than that of benzene (−16.4 kcal/mol, based on the difference in the π-energies of benzene and *all-trans*-1,3,5-hexatriene, cf. Table 2). The nucleus independent chemical shifts also indicate a slightly larger aromatic stabilization in benzene (NICS = −9.7 ppm[49b]) than in **20** (NICS = −7.6 ppm,[49b] both at 6-31+G*). Nevertheless, the aromatic stabilization energies of both molecules are significantly larger than the −11.2 kcal/mol deduced above for the phenyl ring in the benzyl cation.

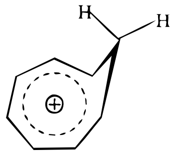
Methyltropylium Cation. MP2(full)/6-31G* and MMP2 optimizations give C_s symmetry for the methyltropylium cation **21** with one methyl C−H bond in the ring plane (cf. Figure 1). The C−C bond lengths and π-electron densities obtained by the two different methods suggest that MMP2 may overestimate hyperconjugation somewhat.

The heat of formation of **21** was calculated from the energy difference with the isomeric cation **5** at MP4sdq/6-31G*//MP2(full)/6-31G* + ΔZPE(RHF/6-31G*) (cf. Table 2) and the experimental heat of formation of the latter (199 ± 2 kcal/mol[21b]). The resulting estimate for **21**, ΔH_f = 194.6 kcal/mol, is in good agreement with the MMP2 value (193.0 kcal/mol). The energy difference between **21** and **5** (MP4sdq/6-31G*//MP2(full)/6-31G*: 4.5 kcal/mol. MMP2: 4.7 kcal/mol favoring the methyltropylium cation.) is lower than that between **1** and **20** (MMP2: 13.0 kcal/mol), which indicates that the methyl stabilization is larger in the benzyl system.

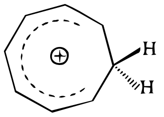
Homotropylium Cation. The homotropylium cation **22**, which has been examined by Cremer and co-workers theoretically (e.g., at MP2(full)/6-31G*),[37a,b] is of interest because of the extensive earlier experimental studies.[73] As confirmed by NBO analysis,[74] the small C−C−C angle of the central tetragonal carbon (MP2(full)/6-31G*: 80.2°) results from the strong stabilization due to homoconjugative interactions. The MP2(full)/6-31G* C−C bond lengths and π-electron densities (**22**, Figure 1) emphasize the aromatic tropylium character of the π-system more than MMP2, which gives greater alternation. Nevertheless, the short 1−7 distance (MP2(full)/6-31G*: 1.906 Å. MP4sdq/6-31G* single-point estimates gave a 1−7 distance of 2.031 Å,[37b] while a 1−7 distance of 2.149 Å could be found by optimizations employing the Becke3LYP[75] density functional method[76] and a 6-311+G** basis set.) is mirrored satisfactorily by MMP2 (1.957 Å, cf. Figure 1).

The MMP2 homoconjugative stabilization energy of **22** −22.8 kcal/mol is higher than the nonbonded resonance effects computed for all other delocalized cations due to the nonbonded overlap of the two trigonal carbons attached to the tetracoordinate carbon. The MMP2 homoconjugation evaluation of −13.4 kcal/mol for this nonbonded 1,7 π-overlap is only slightly lower than the estimates of aromatic stabilization energies of **20** (−15.7 kcal/mol) and of benzene (−16.4 kcal/mol). All other nonbonded π-overlap stabilizations total −9.8 kcal/mol. Hence, **22** can indeed be regarded as a homoaromatic six π-electron system. The MP2(full)/6-31G* geometry of Cremer and co-workers,[37b] which shows almost perfect C−C bond equalization in the seven-membered ring, agrees with this MMP2 conclusion impressively.

Magnetic shielding calculations at the center of the six-membered tricoordinate carbon ring give a −11.1 ppm NICS value. This confirms the appreciable aromaticity of **22** in excellent agreement with the NBO data[74] and the MMP2 results on homoconjugation interactions. In contrast, a planar C_{2v} conformer **23** was found to have a positive absolute chemical shift of +11.0 ppm at the ring center, which may indicate an antiaromatic behavior of **23** due to a participation of the two aliphatic C−H bonds in the π-system and consequently, a



22 C_s



23 C_{2v}

resulting antiaromatic eight π-electron system. This antiaromatic behavior of **23** may contribute to the large ring inversion barrier of **22** (MP4sdq/6-31G*//MP2(full)/6-31G*: 24.85 kcal/mol. Becke3LYP(6-311+G**)+ΔZPE (RHF/6-31G*): 21.34 kcal/mol. Experimental value: 22.3 kcal/mol[77]).

However, the MMP2 inversion barrier, 20.5 kcal/mol, is only somewhat lower than the experimental and ab initio values, even though MMP2 is not parametrized for C−H participation in the π-system. This indicates that the NICS value, +11.0 ppm, may be the result of in plane C−C and C−H σ-bond deshielding effects rather than a consequence of an antiaromatic eight π-electron system. According to MMP2, the steric energy of **23** is only 10.1 kcal/mol higher than that of **22** (angle strain favors **22** by 22.1 kcal/mol, while the torsional energy of **23** is 16.7 kcal/mol more favorable than that of **22**). The MMP2 π-energy of **22** is 20.5 kcal/mol lower than that of **23**. The 1,7 π-overlap in **23** is only −2.1 kcal/mol, which indicates that **23** cannot be regarded as an aromatic six π-electron system.

The MMP2 heat of formation of **22** is 222.7 kcal/mol. The ab initio energy of **22** is 23.4 kcal/mol higher than that of the isomeric α-methylbenzyl cation at MP4sdq/6-31G*//MP2(full)/6-31G* + ΔZPE(RHF/6-31G*) (cf. Table 2). The estimated heat of formation of **22** thus is 222 ± 2 kcal/mol (based on the experimental heat of formation of **5**: 199 ± 2 kcal/mol[21b]).

Conclusions

The force field calculations on delocalized cyclic cations reproduce ab initio (MP2(full)/6-31G*) geometries and π-electron densities remarkably well. The MMP2 π-energies along the benzyl, benzhydryl, and triphenylmethyl cation series show attenuation in the stabilization of the positive charge by phenyl rings. The homotropylium cation is strongly stabilized by the nonbonded π-overlap (−22.8 kcal/mol stabilization) and is truly a homoaromatic six π-electron system. The pure stabilization by 1,7 π-overlap in the homotropylium cation is −13.8 kcal/mol.

As a consequence of the larger aromatic stabilization of the seven-membered ring and the more favorable π-energy, the tropylium cation is 8.7 kcal/mol lower in energy than the benzyl cation. The aromatic stabilization energies of the tropylium cation and benzene are similar. The π-stabilization of carbocation centers with a π-charge larger than 0.2 by benzene conjugation is much larger than vinyl conjugation. Delocalization stabilizes the benzyl cation but reduces the aromatic character of the benzene ring (the aromatic stabilization energy is 5.2 kcal/mol lower than that of benzene). The parent benzyl cation can be best described by a quinoid structure. The more modest phenyl charge stabilization in the 1-phenylallyl cation reduces the aromaticity of the benzene ring only moderately (0.8 kcal/mol). The methyl substituents in the cumyl cation stabilize the benzyl system due to hyperconjugation, but reduce the degree of resonance stabilization of the positive charge by the benzene ring. Consequently, the aromaticity of benzene ring in the cumyl cation approaches that of toluene.

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Supporting Information Available: The Gaussian 94 archive entries for the MP2(full)/6-31G* optimizations and MP4sdq/6-31G*//MP2(full)/6-31G* single point estimates given in this paper (11 pages). Ordering information is given on any current masthead page.

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