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Theoretical Studies of the Rotational Barriers of Benzyl Cation, Radical, and Anion and of Singlet and Triplet Phenylcarbene

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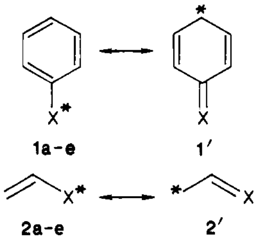
Abstract: Rotational barriers of benzylic cation, radical, and anion and of the singlet and triplet phenylcarbene were calculated by ab initio molecular orbital calculations with the 3-21G basis set. The rotational barriers of benzylic systems are predicted to correlate linearly with the barriers of the corresponding allylic species with a slope of 1.3. Resonance stabilization and inductive effects of the π-system are factors which influence the rotational barriers, stabilities, and geometric features of these species. The rotational barriers of various species are also found to influence their reactivities toward intramolecular cyclization reactions.

According to the simple Hückel theory,[1] the Hückel delocalization energies of the benzyl cation, radical, and anion (**1a–c**)



a, X = CH_2^+; b, X = $CH_2^{\cdot}$; c, X = CH_2^-; d, X = CH (singlet); e, X = CH (triplet)

are all the same, 0.72β, and so the barriers to rotation about the exocyclic double bonds should also be the same. The same is true for the allyl cation, radical, and anion (**2a–c**), which have Hückel delocalization energies of 0.83β.[1] However, the facts are very different from these simple expectations. In this paper, ab initio molecular orbital calculations on these barriers to rotation are reported and analyzed. We have also shown elsewhere how these rotational barriers can have a profound influence on intramolecular reactivities.[2]

Background. Reactive carbonium ions, radicals, and carbanion intermediates are significantly stabilized by conjugate π-systems, as in the cases of **1** and **2**. Resonance theory has been commonly utilized to rationalize and to predict qualitatively the structural features and thermal stabilities of these species.[3] According to resonance theory, the geometry of a delocalized system is intermediate between geometries expected for the resonance structures. The resonance energy (RE) of a system measures the stabilizing effect of electronic delocalization with respect to the corresponding localized or saturated system. For systems **1a–c** and **2a–c**, the resonance energies can be estimated from eq 1 or alternatively from the rotational barriers of the terminal methylene group around the CC bond, which interrupts conjugation.

$$CH_3\text{–}R + R'CH_2{}^* \rightarrow {}^*CH_2\text{–}R + R'CH_3 \qquad (1)$$

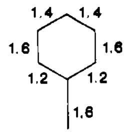
(R = vinyl, phenyl; R′ = ethyl, cyclohexyl, respectively)

Because only the occupancies of the nonbonding orbital are different for **2a–c**, the Hückel theory predicts that the allylic cation, radical, and anion all should have identical CC bond lengths and resonance stabilization energies. The bond length predictions have been recently confirmed for the allyl system,[4] but the stabilization energies are quite different. Wiberg proposed that charge delocalization effects as well as resonance effects stabilize the allyl cation, but that resonance stabilization of the anion is small.[5]

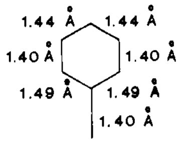
In a series of paper, Shaik and Hiberty et al. have proposed that the nonalternating bond lengths of allyl and other conjugate π-systems are due to the constraints imposed by the σ-frameworks rather than a tendency of the π-system to delocalize.[6]

The importance of resonance stabilization has been studied in many cases.[7-10] Wiberg et al. have discussed the role of resonance interaction in amides and esters. Ab initio calculations on the rotamers of these species indicate that variations of bond lengths and charge distributions are inconsistent with expectation based upon resonance theory.[9] Thomas et al. proposed that resonance stabilization of carboxylate anion plays only minor role in strong acidities of carboxylic acids as compared to alcohols.[10] Thus, a number of doubts have been cast upon the role of resonance in both geometry and stabilization.

Unlike the allylic system **2**, contributions of three resonance structures like **1′**, with exocyclic double bonds, and two like **1**, lead to prediction of partial alternation of single and double bonds in the benzene ring of the benzylic system. Assuming that all five resonance structures contribute equally, we obtained the bond orders shown in **3**, which lead to the rough prediction of bond lengths in **4** based upon Pauling's bond-order–bond-length relationship,[1b,11]



3 (bond orders)



4 (bond lengths)

$$r\,(\text{Å}) = 1.54 - 0.3 \ln n_p \qquad (2)$$

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where n_p is the total bond order and r is the observed length.[11] Note these resonance theory bond orders are quite different from Hückel bond orders. In addition, the phenyl group is larger than the vinyl group and may have greater capacity to stabilize a reactive center by charge dispersion.

In order to gain insights into the geometrical features and the resonance interactions of benzylic species, we have undertaken ab initio molecular orbital calculations on the rotational barriers of benzylic cation, radical, and anion, and of the singlet and triplet phenylcarbene.

For stable molecules in their ground states, experimental techniques generally can be used to measure their conformational preferences. Quantum chemical calculations are often the only tool available to estimate analogous barriers for short-lived excited states of molecules or for reactive intermediates. One potential problem associated with systems of this size is the prohibitive expense of ab initio molecular orbital calculations at the post-Hartree–Fock level and/or with the use of large basis sets. In discussing the magnitude of the rotational barrier, it is therefore first necessary to investigate its dependence on the level of theory employed. The allylic systems **2a–e** are suitable models for their aromatic counterparts, and their much smaller size has made them readily amenable to relatively inexpensive high-level theoretical studies. Here we briefly review how the magnitude of the barrier to rotation in the allylic molecules is affected by the basis set size and the extent of electron correlation.

Allyl Cation. Ab initio molecular orbital studies of the allyl cation, **2a**, have been performed by a number of authors.[12] The highest level calculations to date are those by Pople and coworkers.[12a] The rotational barrier, calculated using the 6-31G**[13] basis set and with inclusion of Møller–Plesset correlation energy correction[14] up to the fourth order, is 34.9 kcal/mol; the Hartree–Fock value is found to be similar, and is not significantly basis-set dependent (3-21G:[13] 34.3 kcal/mol;[12b] 6-31G*:[13] 34.8 kcal/mol;[12c] 6-31G**: 33.7 kcal/mol[12a]). These calculations overestimate the barrier in solution. The energy of solvation is expected to be higher for the perpendicular conformer, in which the positive charge is essentially localized at C_3. Mayr[15] has found a linear relationship between experimental solution values (typically around 20 kcal/mol[16]) and calculated (HF/STO-3G[13]) values:

$$\Delta E_{\text{sol}} = 0.2 + 0.69\Delta E_{\text{calc}} \quad (3)$$

This formula predicts a rotational barrier for the allyl cation in solution of 23.7 kcal/mol.

Jorgensen and Cournoyer reported Monte Carlo simulation studies on the rotational barrier of allyl cation in liquid hydrogen fluoride. As expected, they observed a substantial decrease of the rotational barrier upon the solvation of allyl cation.[17]

Table I. Rotational Barriers (kcal/mol) in the Allyl Cation, Anion, and Radical and in S_1 and T_0 Vinylcarbene[a]

	$C_3H_5^+$	$C_3H_5^-$	$C_3H_5^\bullet$	S_1-C_3H_4	T_0-C_3H_4
barrier:	34.9[b]	19.0[c]	14.1[d]	8.4[e]	4.6[e]

[a] The planar conformer is the energy minimum in each case. [b] MP4/6-31G**//HF/6-31G*: ref 12a. [c] CIPSI/DZ//HF/6-31G: ref 18a. [d] MCSFC/DZP: ref 8a. [e] SDQCI//SCF(DZP): ref 24a.

Allyl Anion. There are less theoretical data concerning the rotational barrier of the allyl anion.[18] The highest level published calculation to date is by Gonzalez-Luque et al.[18a] who used the 6-31G[13] basis set for geometry optimizations and the 6-31G** and the 6-31+G basis sets for energy calculations on the optimized geometries. The plus sign represents diffuse functions, which are included on carbon atoms, and generally provide a better description of negatively charged species. The 6-31G and 6-31+G barriers are quite similar (25.8 and 25.5 kcal/mol, respectively) and are also close to the 6-31G** value of 21 kcal/mol.[18a] We have performed geometry optimizations for allyl anion (planar C_{2v} and pyramidal C_s conformers) with the 6-31+G basis set, which indicates a barrier of 24.8 kcal/mol. This basis set is known to give a considerably improved description of negatively charged species. The effect of electron correlation is expected to be modest, just as in the case of the cation. CI calculations with the DZ basis set predicted a barrier of 19 kcal/mol.[18a] Even for the anion, solvation lowers the energy difference between planar and perpendicular structures. The rotational barrier in allylcesium (18.0 kcal/mol)[19] represents a lower limit to the value for the naked anion in solution.

Allyl Radical. Restricted open-shell Hartree–Fock calculations (ROHF)[20] are inadequate for this conjugated radical. A planar structure with a localized double bond is spuriously preferred to a delocalized structure having C_{2v} symmetry.[21] According to unrestricted Hartree–Fock calculations, which correctly favor the C_{2v} conformer, the rotational barrier is equal to 19.5 kcal/mol with the 4-31G basis set,[22] while the use of a multiconfiguration SCF procedure gives a calculated barrier of 14.1 kcal/mol.[8a] The latter value is in very good agreement with the experimental EPR measurement of 15.0 kcal/mol.[23]

Triplet and Singlet Vinylmethylene. The ground state of vinylmethylene has been calculated by Pacansky and co-workers to be the trans isomer of the triplet, which has C_s symmetry,[24a] with the singlet lying 9.7 kcal/mol above it. The barrier to rotation is equal to 4.6 kcal/mol in T_0, and 8.4 kcal/mol in S_1. In both sets of calculations, single- and double-excitation configuration-interaction wave functions with a DZP[25] basis set were employed. The effect of electron correlation is modest; a similar value for the rotational barrier in the singlet (9.2 kcal/mol) is obtained from Hartree–Fock calculations[24b] using the 4-31G basis set. More recent calculations by Yoshimine and Pacansky,[24d] this time using the 4-31G basis set and a MCSCF procedure followed by extensive inclusion of electron correlation, favor a planar triplet ground state but a nonplanar geometry for the singlet, where the $H_{(\text{methine})}$–C–C–C torsional angle is predicted to be 147°.

In summary, for all allylic species considered, the calculated energy difference between the planar and perpendicular conformer is only slightly affected by the size of the basis set used. Moreover, Hartree–Fock and post-Hartree–Fock calculations are in good agreement in all cases. This justifies the neglect of electron

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Table II. HF/3-21G Rotational Barriers (kcal/mol) in $C_7H_7^+$, $C_7H_7^-$, $C_7H_7^\bullet$, S_1-C_7H_6, and T_0-C_7H_6[a] and Rotational Barriers in the Allyl Cation, Anion, and Radical and in S_1 and T_0 Vinylcarbene

	$C_7H_7^+$	$C_7H_7^-$	$C_7H_7^\bullet$	S_1-C_7H_6	T_0-C_7H_6
barrier:	45.4	28.1	20.0	11.2	5.7
	$C_3H_5^+$	$C_3H_5^-$	$C_3H_5^\bullet$	S_1-C_3H_4	T_0-C_3H_4
barrier:	34.9	19.0	14.1	8.4	4.6

[a] The energy minimum is planar in each case.

correlation and the use of small basis sets in the calculations of the benzylic species that we describe later.

The barrier to rotation increases in the order T_0 vinylcarbene < S_1 vinylcarbene < allyl radical < allyl anion < allyl cation. Table I lists the values for each species according to the highest level calculation available for each case. For each system we give the relative energy of the "perpendicular" conformer (defined as having one of the C_3–H bonds orthogonal to the plane of the carbon atoms) with respect to that of the planar one (the more stable of the two in all cases). A detailed discussion of this ordering will be given in the next section, in conjunction with the results of the calculations on the benzylic systems, which show the same qualitative trend.

Results and Discussion

Benzyl Cation, Radical, and Anion and Phenylcarbenes. The results reported for the allylic systems form the background of the discussion of the calculations on the benzylic species. Here the sizes of the molecules render post-Hartree–Fock calculations prohibitively expensive. However, as shown above, electron correlation is indispensable only in order to correct symmetry breaking in the allyl radical at the UHF level, and the choice of the basis set is not critical. All calculations[26] for these species have thus been performed within the framework of Hartree–Fock theory, using the 3-21G split-valence basis set,[13] with full geometry optimization for each conformer under the appropriate symmetry constraints (C_{2v} symmetry for the planar cation, anion, and radical conformers and for the perpendicular cation; C_s symmetry for all others). Unrestricted Hartree–Fock theory was used for the calculations of triplet phenylcarbene and the benzyl radical. In the latter, the planar conformer suffers spin-contamination from higher energy quartet states.[27] This is a common problem with UHF wave functions[28] when low-lying states of higher multiplicity exist, as is the case with conjugated radicals; however, the spin contamination is not severe (S^2 = 1.28, which means that the wave function is about 18% quartet in character). The rotational barriers are summarized in Table II. For comparison, the calculated barriers in the corresponding C_3 species are also shown. Table III illustrates the relevant geometric features in all benzylic species.

For all of these systems, except the anion, lower level molecular orbital calculations had been performed by other authors. Radom et al.[29] calculated the barrier to rotation in T_0 and S_1 phenylcarbene with the 4-31G basis set on STO-3G geometries. The values found were 3.9 and 2.7 kcal/mol for the singlet and triplet, respectively, somewhat lower than the values we give in Table II. The barrier we computed for the cation (45.4 kcal/mol) is much larger than the one found from semiempirical calculations (22.8 kcal/mol).[30] The same holds for the radical, which we find to have a rotational barrier of 20.0 kcal/mol, while MINDO/3[30] gives an energy difference of only 2.0 kcal/mol between the two conformers.[31]

Our calculations indicate that the perpendicular conformer of the benzyl radical is indeed a maximum. This was tested by rotating the C(ring)–CH_2 bond by 5° and calculating the energy of the new rotamer, which was found to be 0.03 kcal/mol more stable than the perpendicular conformer. This result is in contrast with what has been reported for this species by Khalil and Shanshal,[31] who found from MINDO/3 calculations that the maximum occurs for an angle of rotation equal to 50°, and that the perpendicular conformer is a local minimum which is only 2.0 kcal/mol higher in energy than the planar form. According to the MINDO/3 calculation, the transition state has a rotational angle of 50° and is only 7.0 kcal/mol above the planar conformer. Calculations with AM1[32] (the newest in the Dewar series of semiempirical techniques) *favor* the perpendicular conformer by 1 kcal/mol.[33] These semiempirical methods, however, are known to severely underestimate the rotational barrier in conjugated systems.[34]

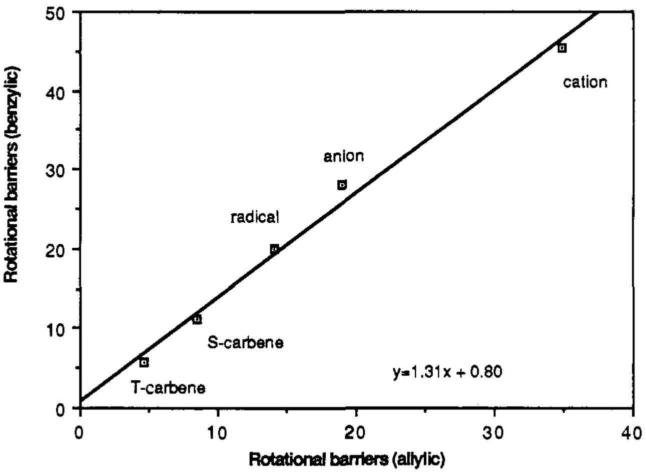

Figure 1. Correlations of rotational barriers of the benzylic and allylic systems.

The rotational barriers of various benzylic species calculated with the 3-21G basis set exhibit a linear correlation with the barriers of the allylic species. The slope of such linear relationship is calculated to be 1.3 as shown in Figure 1. These results indicate that benzene ring is more powerful than the vinyl group in stabilizing a reactive center, but there is a linear response.

The different rotational barriers (Table II) in the five species deserve comment. We will focus on the aromatic systems, but the conclusions are qualitatively applicable to the allylic molecules. The decrease in the rotational barrier in the series cation > anion > radical > singlet carbene is accompanied by a steady increase in the C(ring)–C(exocyclic) bond length in the planar conformers. The values found in the cation (1.356 Å) and the singlet carbene (1.462 Å) are similar to those found in polyenes[35] for localized double (1.35 Å) and single (1.48 Å) bonds, respectively. This signifies a decrease in π-bonding of the ring π-system with the p orbital on the exocyclic carbon atom in this series (hereafter referred to as the p_z atomic orbital). In the planar *triplet* carbene, on the other hand, the bond length is virtually the same as in the radical (1.400 Å; cf. the singlet, where the bond length is 1.462 Å).

The striking similarity in the geometry of the triplet carbene and the radical, in fact, indicates substantial conjugation between the singly occupied p_z orbital and the ring π-system. However, the rotational barrier of the radical is much higher (20 kcal/mol) than that of the carbene (5.7 kcal/mol). This is because there is an analogous interaction even in the perpendicular conformer of the triplet carbene, due to overlap between the ring electrons and the half-filled hybrid orbital. This type of π-bonding is completely eliminated in the perpendicular conformers of the other

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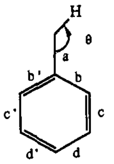
Table III. HF/3-21G Optimized C–C Bond Lengths (Å) in the Benzyl Cation, Anion, and Radical and in Singlet and Triplet Phenylcarbene[a]



species	*a*	*b* (*b'*)	*c* (*c'*)	*d* (*d'*)	θ, deg
cation					
planar	1.356	1.434	1.361	1.400	122
perpendicular	1.450	1.393	1.382	1.384	121
anion					
planar	1.370	1.449	1.368	1.398	122
perpendicular	1.538	1.406 (1.401)	1.385 (1.385)	1.386 (1.386)	106
radical					
planar	1.404	1.427	1.389	1.403	121
perpendicular	1.488	1.389	1.384	1.384	121
S_1 carbene					
planar	1.462	1.400 (1.398)	1.378 (1.381)	1.389 (1.385)	108
perpendicular	1.478	1.392	1.382	1.384	109
T_0 carbene					
planar	1.400	1.426 (1.429)	1.390 (1.390)	1.403 (1.402)	133
perpendicular	1.422	1.421	1.392	1.400	140

[a] In species that do not have a plane of symmetry perpendicular to the ring, the hydrogen atom(s) on the exocyclic carbon are on the same side as bonds a, b, c, and d.

systems. In fact, while the C(ring)–C(exocyclic) bond length in triplet phenylcarbene is 1.422 Å, for the others it ranges from 1.45 to 1.53 Å. The low rotational barrier in the triplet is the consequence of the delocalization present even in this conformer. The increase of the HCC angle, θ, in the perpendicular conformation also signals this conjugation.

The singlet carbene also has a fairly low rotational barrier, but here the reason is that neither conformer enjoys substantial conjugation between the ring π system and the carbene. This is also evidenced by the fairly long exocyclic CC bonds (1.461 and 1.478 Å in the planar and perpendicular conformer, respectively). Even though the planar species is stabilized by the interaction between the vacant p_z orbital and the benzene ring filled orbital of appropriate symmetry, this interaction involves charge separation, as opposed to charge delocalization as in the case of the cation. Thus, although both the cation and the carbene are stabilized by this type of interaction in their planar conformers, the barrier to rotation is much larger in the former (45.4 kcal/mol).

The substantial conjugation which is present in the perpendicular conformer of triplet phenylcarbene suggests that it might be a local energy minimum, rather than a transition state for the interconversion of two planar conformers. However, we calculated the perpendicular conformer to be 0.15 kcal/mol less stable than the rotamer obtained by a 10° rotation about the exocyclic carbon–carbon bond. This indicates that perpendicular triplet phenylcarbene is truly a maximum with respect to the internal rotation. A similar result was found for singlet phenylcarbene. Here we have found a difference of 0.33 kcal/mol between the perpendicular conformer and the rotamer in which the dihedral angle H–C(exocyclic)–C(ring)–C is equal to 80°. These results agree with the conclusions of recent CISD/DZP calculations performed by Pacansky and Yoshimine[24a] on the vinylcarbenes. Interestingly, the authors also performed MRCI/4-31G//MCSCF/4-31G calculations which likewise gave a preference for the planar trans triplet, but predicted a nonplanar minimum-energy geometry for the singlet.[24d] The main reasons for the discrepancy are (i) the use in one case[24d] of the 4-31G basis set, which is a split-valence basis set but has no polarization functions, and is thus inferior to the DZP basis set used in the other[24a] calculation; and (ii) the use of a multiconfiguration SCF wave function with the 4-31G basis set, and only a single determinantal wave function with the DZP basis set. In both papers, configuration interaction including all single and double substitutions was employed to estimate correlation energy corrections; however, only in one case were quadruple excitation corrections also estimated.[24a] On the basis of the MRCI//MCSCF/4-31G basis set, the authors conclude that singlet vinylcarbene is probably nonplanar, suggesting that only in this low-symmetry structure can resonance between the carbene and diradical structures (Figure 2) be a stabilizing factor.

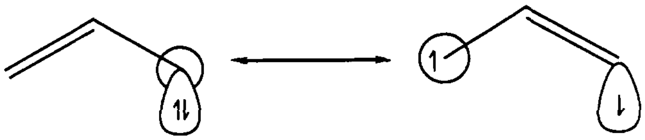


Figure 2. Resonance between singlet carbene and diradical structures.

The decrease in the amount by which the planar conformation is preferred along the series from the cation to the anion to the radical can be rationalized in various ways. In the frontier molecule orbital formalism, the planar cation is strongly favored over the perpendicular because of the strong interaction between the filled orbital of the ring and the energetically low-lying p_z orbital (shown schematically in Figure 3a). In the radical, this becomes a three-electron interaction, which is roughly half as strong (Figure 3b). At the same time, the half-occupied p_z orbital interacts with vacant benzene π^* orbital. The barrier to internal rotation in the radical is actually somewhat less than half that in the cation, since the barrier to rotation in the cation is also influenced by inductive effects, as discussed below. In the anion, a two-electron stabilizing interaction is also present, involving the *filled* exocyclic p orbital and a vacant π orbital of the ring system (Figure 3c). This is the same type of effect that is present in the planar cation, but the rotational barrier in the anion is only about 28 kcal/mol, compared to 45 kcal/mol in the cation. One possible reason for this large difference between the benzyl, and the allyl, anions and cations is the presence in the anion of four-electron repulsion arising from the overlap of the filled exocyclic p_z and ring π orbitals, which destabilizes the planar conformer of the anion.[36] As shown later on, high rotational barriers of cations are further due to the destabilizing interactions present in the perpendicular conformer.

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(36) An example of how repulsion between filled orbitals can be significant even in the presence of attractive interactions is given by the high barrier to acetylene trimerization. For a detailed discussion, see: Houk, K. N. *Top. Curr. Chem.* **1979**, *79*, 1. Recent calculations[6] suggest that the "aromatic" benzene π-sextet is unstable with respect to distortion away from a D_{6h} geometry, for similar reasons.

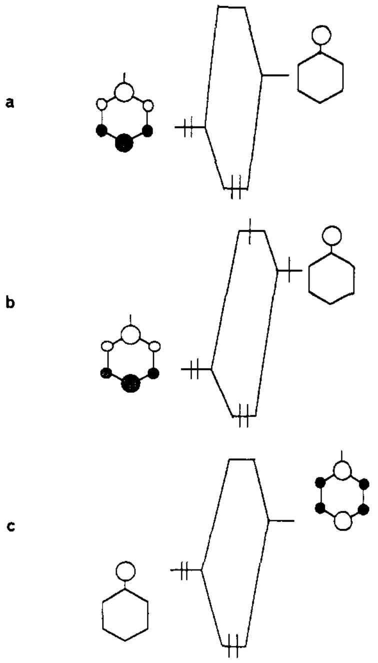

Figure 3. Orbital interactions in benzylic systems: (a) two-electron interaction between the benzene HOMO and the vacant exocyclic p orbital; (b) three-electron interaction between the benzene HOMO and the half-filled exocyclic p orbital; (c) two-electron interaction between the filled exocyclic p orbital and the benzene LUMO.

Table IV. HF/3-21G Resonance Stabilization Energies (RSE) of $C_7H_7^+$, $C_7H_7^-$, $C_7H_7^•$, S_1-C_7H_6, and T_0-C_7H_6[a]

	$C_7H_7^+$	$C_7H_7^-$	$C_7H_7^•$	S_1-C_7H_6	T_0-C_7H_6
RSE:[b]	38.6	44.8	19.6	8.6	17.3

[a] The energy minimum is planar in each case. [b] In kcal/mol.

Stabilization Energies. Stabilization energies, often attributed to resonance stabilization, can be calculated according to eq 1. This procedure, however, is more dependent upon the computational level of theory than calculations of rotational barriers. Nevertheless, we estimated stabilization energies of benzylic systems by the isodesmic reaction (eq 4), which approximates eq

$$CH_3\text{-}Ph + CH_3X^* \rightarrow {}^*X\text{-}Ph + CH_3CH_3 \qquad (4)$$

$$X = CH_2^+,\ CH_2^•,\ CH_2^-,\ CH\ (\text{singlet, triplet})$$

1 by using a methyl group as the reference standard. Table IV summarizes what we will call the resonance stabilization energies of various benzylic species calculated with the 3-21G basis set.

These results clearly support our previous conclusions that benzyl radical and triplet phenylcarbene are stabilized to nearly the same extent, despite the low barrier to rotation of the triplet phenylcarbene. The calculated resonance energies of benzyl cation and anion are significantly larger than those of the neutral species, while the singlet phenylcarbene is stabilized only moderately by delocalization. The resonance energy estimated from isodesmic reaction is in good agreement with the rotational barrier of benzyl radical.

These calculations reveal that the stabilization energies are similar for the benzyl cation and anion. The stabilization energies are smaller than the rotational barrier of cation but larger than the rotational barrier of the anion. These results suggest that the cation is *de*stabilized by 7 kcal/mol and the anion is stabilized by 17 kcal/mol, in their perpendicular conformations. This can be rationalized by the fact that the carbon atoms adjacent to the cation and anion centers are sp^2 hybridized in the benzylic systems. The inductive electron-withdrawing effect of the sp^2-hybridized benzene ring atoms destabilizes an electron-deficient carbonium ion, but stabilizes an electron-rich carbanion center.

The same destabilizing inductive effect is present in the perpendicular conformation of the allyl cation. A rough idea of the importance of this effect can be obtained from measurements of cation stabilities and gas-phase acidities of the allylic species. The difference in the heat of reaction of the allyl and ethyl cations with hydride anion (calculated from thermodynamic data) is about 17 kcal/mol.[37] This value gives a measure of the stabilization due to conjugation present in the allyl cation and absent in the simple primary ethyl cation, and is much smaller than the rotational barrier in the allyl cation (34.9 kcal/mol). The difference of 18 kcal/mol between these two values is a measure of the destabilization of the perpendicular allyl cation conformer, which is caused by the inductive effect of the sp^2-hybridized carbon atoms. On the other hand, the difference in the enthalpy of deprotonation of propene (392 kcal/mol) and methane (417 kcal/mol) is 25 kcal/mol.[38] The acidity of ethane is expected to be similar to that of methane, as is found to be the case for methylamine and ammonia.[38,39] Thus, the value of 25 kcal/mol is a measure of the stabilization due to conjugation in the allyl anion but not in the primary ethyl anion, and is somewhat larger than the rotational barrier in the allyl anion.

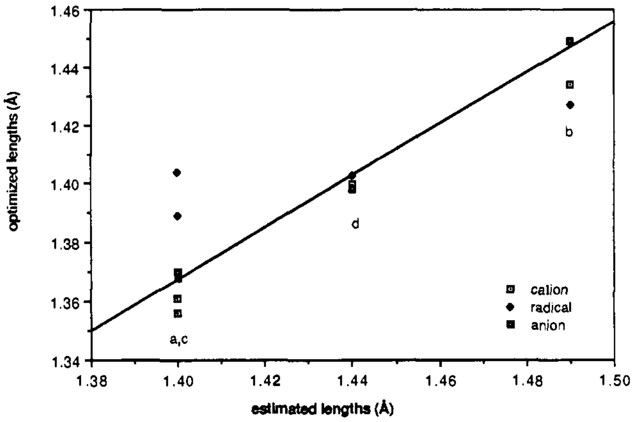

Figure 4. Correlations between the ab initio optimized bond lengths and the bond lengths estimated by resonance theory for benzyl cation, radical, and anion.

The configuration of the exocyclic carbons can be correlated with the optimized bond angles around that carbon. As shown in Table III, these bond angles are essentially unchanged from the planar conformation to the perpendicular one except in the benzyl anion. These results indicate that the exocyclic methylenes in the cation and radical have the same configuration in both rotational conformers. On the other hand, the exocyclic carbon of benzyl anion changes from a sp^2 hybridization in the planar conformation to sp^3 in the nonconjugate conformation.

Our calculations suggest that the rotational barrier of 34.9 kcal/mol in the allyl cation is not just due to the stabilization of the planar form, but also to the *de*stabilization of the perpendicular form. On the other hand, the rotational barrier in the anion is mainly a consequence of the conjugation present in the planar form. The implicit assumption in the above argument is that inductive effects are not important in the planar species, which are stabilized by conjugation. In fact, inductive effects are operative to some extent in the planar conformers as well, but are less significant than in the perpendicular, nonconjugated conformers, where the charge is more localized on the exocyclic carbon.

Bond Alternation in Delocalized π-Systems. Figure 4 plots the optimized bond lengths of benzylic cation, radical, and anion with respect to the bond lengths estimated by the resonance theory. The geometries of the benzyl species follow qualitatively the prediction of resonance theory described earlier in structure **4**. The exocyclic bond, a, and side bonds, c and c′, are always the

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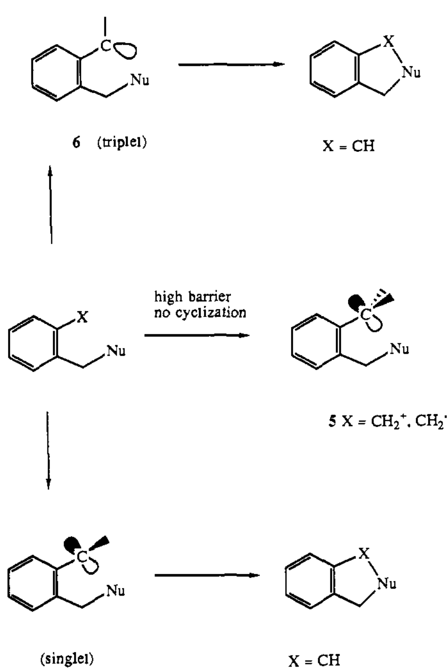

Figure 5. Intramolecular cyclization reactions of various reactive benzylic species.

shortest; the lower ring bonds, d and d′, are intermediate; and the top ring bond, b and b′, are longest. The ring bond lengths of the charged species alternate much more than in the benzyl radical.

Our calculations show that p–π interactions of benzylic species are correlated with the C(ring)–C(exocyclic) bond lengths. That is, the stabilization energies, the rotational barriers, and the exocyclic CC bond lengths are all related to the extent of delocalization. This delocalization causes substantial bond alternation in the benzene rings of the benzyl cation and anion, in which the differences between bond a and bond c are about 0.08 Å. However, the high stabilities of these species suggest that the bond localization apparently does not destroy the aromaticity of the benzene ring.

The extent of bond alternation is less for the radical and phenylcarbenes, in which the differences between bond a and bond c is less than 0.04 Å. The benzyl radical and the triplet carbene have nearly uniform CC bond lengths of ~1.4 Å, which is near to the bond length of benzene, for both the ring and the exocyclic CC bonds. The singlet carbene has similar benzene ring bond lengths, but the exocyclic CC bond is very long (1.46 Å). This geometric feature, together with the low resonance energy of the singlet phenylcarbene, indicates that the p–π interaction is much smaller than in the other cases.

Our calculations support the traditional interpretation that the stability and geometrical features of a delocalized system are mainly determined by the interactions of π orbitals. We have previously shown that the importance of π-interactions is dependent upon the distance between the various π orbitals.[40] The aromaticity of the benzene ring, for example, is realized only when the π orbitals are in their proper distance range.[40,41] We agree in this sense with Shaik et al. that the σ-framework plays an essential role in order to bring stabilizing π-orbital interactions.[6]

Intramolecular Reactivity. It has been found that rotational barriers of the benzylic species have a profound effect upon their reactivities of intramolecular cyclizations.[2] In spite of similar intermolecular reactivities of carbenes and cations,[42,43] arylcarbenes react readily with nucleophilic groups on ortho substituents, whereas simple benzyl cations do not (Figure 5).[2] Since the reaction modes of both species are dictated by an electrophilic vacant 2p orbital, rotation about the exocyclic CC bond of the carbene or cation must occur in order to achieve the reactive conformation **5**. High barriers to rotation imposed in benzyl cations hinder the intramolecular reaction. On the other hand, arylcarbenes have considerably lower rotational barriers than the analogous benzyl cations, so that the reactive conformation is easily attained by the carbene. Similarly, a 90° rotation about an aryl–carbon bond is required in the cyclization of both benzyl and diphenylmethyl 1,5-diradicals.[44] The latter are found to do so easily because of the lower rotational barrier. Cyclization of 2-allylbenzyl radical occurs with an activation energy of 16.3 kcal/mol, about 10 kcal/mol higher than the activation energy for cyclization of the 5-hexenyl radical.[45]

Finally, it should be mentioned that the intramolecular reactivity of triplet carbenes should be expected to be even higher than that of any other species described here, on the basis of this argument. Experimental results indicate that this is indeed the case.[46] In fact, the reaction might take place with no rotation about the bond to the carbenic carbon, since even the minimum-energy conformation has an odd electron in the plane of the ring, suitably oriented for reaction on the double bond. There are therefore two modes of attack possible, in principle. In the first case, the methylene p orbital is attacking the double bond, whereas the second type of approach involves attack by the hybrid orbital which lies in the plane of the methylene atoms. Moreno et al. have recently reported the ab initio transition structure for the addition of triplet methylene to ethylene, which involves the attack of the in-plane orbital of methylene with a 2.3 Å forming CC bond length.[47a] In order to estimate the preference of this attacking mode, we performed model HF/3-21G calculations of the attack of triplet methylene on ethene. The C–C forming bond is fixed at a distance of 2.0 Å, typical for CC partially formed bonds in transition structures. All other parameters are optimized under the constraint of C_s symmetry in both cases. These calculations suggest that attack by the in-plane orbital is preferred by 21.6 kcal/mol, which implies that the minimum-energy conformation of **6** has the exocyclic CH group already suitably oriented for intramolecular insertion in the double bond. The model used is obviously somewhat crude, but the qualitative conclusions should persist even if a higher level of theory were employed. This geometry of approach resembles the transition structure which Fueno and co-workers found from ab initio calculations (MRDCI//HF/4-31G**) for the analogous addition of triplet nitrene to ethylene.[48]

Conclusion

Molecular orbital calculations indicate that the barrier to internal rotation decreases in the order benzyl cation > anion > radical ≫ singlet phenylcarbene > triplet phenylcarbene. For the first four, this is the result of a gradual decrease in the conjugation between the ring π-system and the p_z orbital on the exocyclic carbon atom. In the triplet carbene, the two conformers are close in energy due to the substantial conjugation present in both cases.

The trend is the same as that observed in the allylic species. However, the rotational barriers are systematically higher in the benzylic molecules. This can be rationalized in terms of the

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stronger interaction between the orbitals of the benzene ring and the exocyclic p orbital in the planar conformers, relative to the analogous interaction between the π (or π^*) orbitals of the double bond and the p orbital at C_3 in the allylic systems. In the case of the cation, for example, the benzene HOMO of appropriate symmetry is higher in energy than the allyl π orbital, and the magnitude of the stabilizing interaction between the filled orbital and the vacant p orbital on the cationic center is therefore larger for the aromatic species. Analogous arguments can be applied to the other systems as well. An alternative explanation is that more resonance structures are possible for the benzylic systems than for the allylic ones. The benzyl cation and radical are additionally stabilized since delocalization in the ring places the charge (or odd electron) on *secondary* carbon atoms, which bear the charge (spin) better than the exocyclic primary carbon.

The intramolecular reactivity toward nucleophiles or double bonds on ortho substituents is found to *increase* in the same order as the rotational barrier decreases. This strongly suggests a relationship between ease of internal rotation and intramolecular reactivity.[2,46]

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Solvent Effects on Optical Absorption Spectra: The $^1A_1 \rightarrow {}^1A_2$ Transition of Formaldehyde in Water

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Abstract: We have examined solvation of the singlet ground ($^1A_1$) and excited ($^1A_2$) states of formaldehyde by water using a combination of classical molecular dynamics and ab initio quantum mechanics techniques. Molecular dynamics simulations were carried out for a formaldehyde solute molecule in a bath of 209 water molecules. The solute was represented by Lennard–Jones plus electrostatic terms with net atomic natural charges generated from ab initio Hartree–Fock calculations using a 6-31G+d-type basis set. The SPC model was used to describe the water–water interaction potential. Radial distribution functions show structured binding by several water molecules at the oxygen end of formaldehyde in its ground state. This structure is largely, but not completely, destroyed for formaldehyde in its lowest excited singlet state. The $^1A_1 \rightarrow {}^1A_2$ vertical transition energy of formaldehyde was calculated at the ab initio Hartree–Fock level including the electrostatic interactions with the solvent molecules for 70 configurations along the trajectory. No single water molecule or first solvation shell (cluster model) adequately describes the formaldehyde–solvent interactions in both electronic states. When an ensemble of water configurations is considered, the calculated spectral blue shift and bandwidth of about 1900 and 4400 cm^{-1}, respectively, are in reasonable accord with the available experimental data.

I. Introduction

The modeling of quantum mechanical properties for molecules in liquids is an important and challenging topic. A major difficulty is the very large number of intermolecular interactions that must be considered in order for the results to correctly reflect the physics of the liquid state. A full quantum mechanical treatment of an entire solute–solvent system is far too complicated to carry out, and various approximations must be made. A variety of pure quantum or mixed-mode quantum/classical computational procedures have been proposed.[1-8] Some investigations[9-13] have been performed using fully quantum mechanical calculations on very small systems containing, for example, a single solute clustered with one or several water molecules. Such calculations on small clusters may account for two and perhaps three body interactions, but cannot reproduce the large-scale static or dynamical effects of a full solvent bath. Other investigators[14,15] have incorporated various continuum solvent models in the solute Hamiltonian. This approach does permit certain bulk properties to be simulated by quantum mechanical calculations on the solute alone, but it cannot give any information about the microscopic details of solvation. Problems associated with developing a theoretical framework for modeling electronic transitions in the condensed phase are particularly formidable due to the high computational levels that are often required to describe the excited-state electronic structure of even the isolated solute species correctly. For studying solvent

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