APPLICATIONS OF QUANTUM CHEMISTRY—III*

ROTATION BARRIERS AND THERMODYNAMIC STABILITIES FOR CONJUGATED CARBOCATIONS

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Abstract—Barriers to C⋯C bond rotation and heat of formation are calculated by SCF π-electron methods for a variety of conjugated carbocations. The predicted barriers are analyzed in terms of the resonance and aromaticity of the chains and rings involved.

EXPERIMENTALLY, the barriers to C⋯C bond rotation are known accurately for several methyl-substituted allylic cations,[1–3] and from a combination of this data with thermochemical information, the barrier in the unsubstituted allyl cation itself has been estimated.[4] Unfortunately, barriers for other unsubstituted conjugated carbocations are unavailable as yet, although rough estimates have been reported for methyl-substituted pentadienyl and hexatrienyl cations[2] and for the diphenyl-cyclopropenium cation.[5] Although *ab initio* molecular orbital calculations yield realistic barriers for cations,[6,7] extension of such computations beyond three and four carbon atom networks is impractical at present.

For these reasons, barriers to C⋯C bond rotation in a series of conjugated carbocations have been calculated (Table 1) by two semiempirical SCF-LCAO-MO theories, both of which are known to predict accurate bond lengths and bond angles for neutral conjugated hydrocarbons—the Dewar[8] and the NNDO[9] π-electron methods. In contrast to Huckel methods which are acknowledged to be suspect in calculations for ionic species,[10,11] both of the theories used herein include explicitly both electron–electron repulsions and σ bond compression energies in the evaluation of the total bonding energy for each ion.[8,9] In addition, the set of SCF bond lengths which yields the optimum molecular energy is determined by both methods *via* use of a linear bond length bond order correlation for the distance R_{uv} between each pair of bonded carbon atoms,†

$$R_{uv} = A - BP_{uv} \cos \phi$$

where ϕ is the angle of twist across the u—v bond. The values of A, B, and of all other parameters required for the present calculations were taken from the literature.[8,9]

Although neither method used allows for any hyperconjugative interaction between a CH_2^+ group and the —CH≡CH_2 unit twisted perpendicular to it, the rotation barriers (38 and 29 kcal mole⁻¹) calculated for the allyl cation **1** agree well with the "experimental" value[4] of 38–43 kcal mole⁻¹ and with the barrier of 35–42 kcal mole⁻¹ calculated using *ab initio* methods.[6,7] Given this agreement for **1**, some

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* Part II: N. C. Baird and R. M. West, *J. Am. Chem. Soc.* **93**, 3072 (1971)

† Calculated bond distances for individual systems are available upon request from the author.

reliance can be placed upon the calculations for the systems involving a greater degree of conjugation (Table 1). It is interesting that the barriers predicted by the Dewar method are consistently ~ 10 kcal mole^{-1} larger than those deduced from the NNDO method; the lack of variation in this difference is surprising since the method of handling overlap integrals and differential overlap in the two theories is very different.[8, 9] A discrepancy with this sign is not unexpected, however, since barriers in neutral polyenes are overestimated by Dewar's method (if configuration interaction and allowance for steric interactions are not included) and are underestimated using the NNDO procedure.[12]

TABLE 1. CALCULATED HEATS OF FORMATION AND ROTATION BARRIERS (IN kcal mole^{-1})
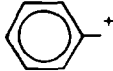
| Carbocation | ΔH_f Dewar method[a] | Energy to twist bond[b] by 90° | | | |
		1,2	2,3	3,4	4,5 or exocyclic bond[c]
1		225	38 (29)	— —	— —	— —
2		222	51 (42)	24 (15)	— —	— —
3		226	57 (19)	18 (9)	32 (23)	— —
4		233	61 (54)	15 (6)	37 (28)	24 (15)
5		262[d]	— —	— —	— —	56 (48)
6		220	— —	— —	— —	45 (37)
7		245[d]	— —	— —	— —	59 (54)
8		221	55 (47)	20 (11)	— —	28 (20)
9		230	29 (19)	— —	— —	18 (10)
10		263[d]	— —	— —	— —	— —
11		268[d, e]	— —	— —	— —	19 (11)
12		279[d, e]	— —	— —	— —	15 (8)
13		255[d]	— —	— —	— —	— —

TABLE 1 (continued)

| Carbocation | ΔH_f Dewar method[a] | Energy to twist bond[b] by 90° | | | |
		1,2	2,3	3,4	4,5 or exocyclic bond[c]
14 (cyclopentadienyl cation, φ)		—	—	—	—
	$247^{d,e}$	—	—	—	32
		—	—	—	(23)
15 (cycloheptatrienyl cation)	219^d	—	—	—	--
		—	—	—	—
16 (cycloheptatrienyl cation, φ)	$231^{d,e}$	—	—	—	15
		—	—	—	(7)

[a] Calculated using $W_c = -9.84$ eV; see text for details.

[b] The values not enclosed in parentheses are from the Dewar method, whereas those enclosed in parentheses are from the NNDO method.

[c] Corresponds to the energy for rotation of the *exo*-methylene group in **5, 6,** and **7** and to rotation of a single phenyl group from conjugation in **8, 9, 11, 12, 14,** and **16**.

[d] A ring strain energy correction has been applied in calculating this value—see text for details.

[e] A correction for steric strain is probably required here, although none has been applied.

The 1,2 bond rotation barriers quoted in Table 1 for the allyl (**1**), pentadienyl (**2**), heptatrienyl (**3**), and nonatetraenyl (**4**) cations indicate that the energy required to twist the *terminal* C≡C bond by 90° increases substantially with increasing conjugation; the limiting values of ~65 and ~60 kcal mole^{-1} for the Dewar and NNDO methods respectively are of the same order of magnitude as the calculated barriers in ethylene of 80 and 58 kcal mole^{-1} respectively[12] (experimental value $= 65$ kcal mole^{-1} for ethylene[13]). Unfortunately there exists only sparse experimental data with which the calculated cation barrier trends can be compared. Deno *et al.* have established that the lower limit for the 1,2 rotation barrier in 1,1,5,5-tetramethylpentadienyl cation is at least 1 kcal mole^{-1} greater than the barrier in the 1,1,3,3-tetramethylallyl cation. The lower limit established for the 1,1,7,7-tetramethylheptatrienyl cation lies below the barrier value for the corresponding allylic system, however, so that the overall trend is neither really confirmed nor denied by existing experimental data.

In contrast to the large energy barriers predicted for twisting of terminal bonds, the 2,3 bond barriers in the pentadienyl and longer cation chains are relatively small and decrease with chain length (Table 1). For example, the 2,3 barrier in **2** is 14 kcal mole^{-1} less than for the allyl system, and is 27 kcal mole^{-1} less than for terminal bond rotation in the same ion. Both the small 2,3 barriers and the intermediate values predicted for the twisting of bonds further toward the center of **3** and of **4** are readily rationalized by the extent of positive charge delocalization in the twisted conformations. For example, twisting of the end bond in **3** localizes the + charge on one carbon; twisting the 2,3 bond results in delocalization of the + charge over five centers, and twisting the 3,4 bond results in delocalization over three carbons.

Although the stabilization of a CH_2^+ group by a polyene chain is predicted to increase monotonically with the number of conjugated carbon atoms, this trend does *not* apply when the CH_2^+ is being stabilized by a monocyclic ring system. In particular, the barrier to CH_2 rotation in the methylenecyclobutadienyl cation **5** is larger than in the benzyl cation **6** (Table 1), but is slightly smaller than in the methylenecyclo-octatetraenyl cation **7**. Analysis of the calculated electronic and geometric structures for these systems indicated that the aromaticity/antiaromaticity of the ring system is responsible for those variations. In the case of **5**, the antiaromaticity of the four-membered ring is *significantly reduced* by conjugation to the CH_2^+ unit; the calculated bond lengths predict a structure which simulates an allyl cation conjugated weakly
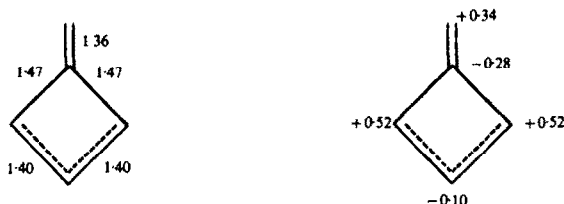

FIG 1. Calculated bond lengths and net π charges (Dewar method) for **5**

to an exocyclic double bond (Fig 1); the positive charge is almost completely localized on 3 of the 5 carbons; indeed the other two carbons are predicted to bear net negative π charges (Fig 1). A simple perturbation MO calculation[12] predicts that the anti-aromaticity of the allyl-ethylene structure of **5** is one-half that (of 16 kcal mole[−1]) for cyclobutadiene itself;[12] the 5 ± 1 kcal mole[−1] increase in the calculated barrier for **5** compared to **2** is in good agreement with this estimate.

In contrast, conjugative stabilization of the CH_2^+ group in the benzyl cation **6** must result in some loss in the aromaticity of the benzene ring itself; thus the barrier for benzyl is *less* by 12 kcal mole[−1] than for its open-chain analog **3**. Nevertheless, the barrier in **6** is predicted by both SCF methods to be greater than that for the allyl cation, in disagreement with the simple HMO result (barriers of 0·72 β and 0·83 β respectively).

To complement the calculations by Hoffmann *et al.*[11] who used the Extended Huckel Method (steric strain and hyperconjugation included, but electron–electron repulsions and sigma-bond compression energy neglected), the degree to which phenyl stabilizes various cations has been investigated by the Dewar and NNDO methods (which neglect the first two effects mentioned but which do include the latter two explicitly). The SCF barriers to 90° phenyl group rotation in benzyl, *trans*-1-phenylallyl, phenylcyclopropenium and phenyltropylium cations (Table 1) are all substantial and positive, in contrast to the EHT values of $\sim$9, $\sim$3, $\sim$0, and $\ll$0 kcal mole[−1] respectively.[10] The SCF barriers for this series correlate well with the net positive charge on the C atom to which the phenyl is bonded. The positive charge versus rotation barrier correlation also applies in comparing the energy to twist a single phenyl group out of conjugation in *trans, trans*-1,3-diphenylallyl cation **9** with that in the diphenylcyclopropenium cation **12**. Although the calculated barrier for **9** is greater

than that for 12, the *difference* is probably less than required by the experimental data for these two systems.[5] Quite obviously, all-valence-electron MO calculations (e.g. by the MINDO[14] or *ab initio* methods) are required to sort out the simultaneous effects of steric interaction, hyperconjugation, and electron–electron repulsion in phenyl-substituted cations.

Dewar *et al.* have shown previously that their SCF π-electron method yields accurate heats of formation (ΔH_f) for conjugated carbocations provided that the one-center core-electron attraction integral, W_{cr} is evaluated empirically using the experimental ionization potential of -9.84 eV for the methyl radical.[15] In Table 1, the ΔH_f for each cation considered has been evaluated by this procedure; strain energy corrections of 66, 26, 6, 6, and 6 kcal mole^{-1} have been made for cations containing 3-, 4-, 5-, 7-, and 8-membered rings[9c,14] respectively. The calculated ΔH_f for the allyl cation of 225 agrees very well with the most recent experimental determination[16] of 226 ± 1 kcal mole^{-1}. The calculated ΔH_f for the cyclopropenium cation 10 of 263 is less positive than the experimental value[17] of 271 ± 1. The discrepancy here may arise from the difficulty in estimating the strain energy for a completely unsaturated three-membered ring; the value of 66 kcal mole^{-1} used herein is the result of extrapolating the experimental strain energies[14a,c] in compounds containing 0, 1, and 2 unsaturated carbon atoms. With respect to the aromaticity of the $C_3H_3^+$ system, it is interesting to note that the total calculated bonding energy (before correction for strain) is 38 kcal mole^{-1} more stable than that for an allyl cation, the ends of which are united by a "single" C—C bond.

In good agreement with experiment, the ΔH_f's for the benzyl and tropylium cations are predicted to be essentially identical; both calculated values are 7 kcal mole^{-1} too positive, however, relative to the most recent experimental determinations of 213 and 212 kcal mole^{-1} respectively.[16] The predicted stabilities of the two $C_5H_5^+$ cations 5 and 13 are also similar; were it not for the large strain associated with a four-membered ring, 5 would be more stable than 13. Given the low antiaromaticity of 5, this ion (along with the $C_4H_4^{++}$ system) should be rather more stable than other cyclobutadiene systems. For example, the energy required to dissociate heterolytically H$^-$ from the methyl group of methylcyclobutadiene should be lower than for systems in which the methyl group is bound to a nonaromatic or aromatic ring. Presumably, a more practical synthetic route to 5 would involve an *exo*-methylenecyclobutene precursor.

The cyclopentadienyl cation 12 is an interesting system in several respects. Like the corresponding 4π electron molecule cyclobutadiene, the most stable singlet state is subject to Jahn–Teller distortion which would stabilize the "pentadienyl-like" geometry* 13a and/or the "allyl-ethylene" geometry 13b relative to the completely symmetrical D_{5h} form.

13a   13b

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* The author is indebted to a referee for bringing this structure to his attention, and for details concerning unpublished CNDO calculations regarding its stability.

Both the Dewar and the NNDO calculations predict that the 13a and 13b conformations are essentially isoenergetic; the total energy for the optimum set of bond lengths in 13a (Fig 2a) is preferred to that for the optimum structure 13b (Fig 2b) by

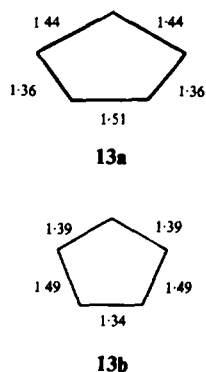FIG 2. Optimum bond lengths calculated (Dewar method) for 13a and 13b

1·0 and 0·6 kcal mole^{-1} respectively according to the two methods. The preference for the pentadienyl form is predicted to be somewhat larger in the phenyl-substituted cyclopentadienyl cation 14, since the net positive charge available for delocalization over the benzene ring is larger at the 1 position of 13a than at any position in 13b (Fig 2).

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