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Interactions in Carbocations and Hückel's $4n+2$ Rule*

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The molecular orbital model of hyperconjugation was utilized in rationalizing some long range interactions in carbocations. Conveniently such interactions can be detected by measuring secondary kinetic deuterium isotope effects. Hückel's $4n + 2$ rule can be extended to interactions between the cationic center and pseudo-π orbitals of CH_3, CH_2 and CH groups respectively. Thus, in analogy to hyperconjugation one can envisage homohyperconjugation as the probable cause of normal γ-deuterium isotope effects. Results are presented of studies of these effects in the adamantane and norbornane system. The stability of the 1-adamantyl cation can be ascribed to a favorable $4n + 2$ configuration of σ-electrons comprising the β,γ-carbon carbon and/or γ-carbon hydrogen bonds. It is however not possible to distinguish between these alternatives since both could explain the observed γ-isotope effects. In contrast, the four CH_2 groups flanking C_7 in the 7-norbornyl cation form an antiaromatic $4n$ pseudo-π system which could explain the exceptional instability of this cation. Interactions of the empty *p*-orbital with the subjacent $4B_2$ pseudo-π orbitals give rise to small normal γ-deuterium isotope effects of homohyperconjugative origin. In this system, due to symmetry constraints hyperconjugative interaction with the ribbon orbitals of the σ-framework is not possible.

Carbocations are inherently unstable species and their formation from parent hydrocarbons by hydride abstraction in the gas phase is strongly disfavored energetically when compared with the formation of radicals. The experimental heat of formation, ΔH_f, (298 K for CH_3^+ was found to be 261 kcal/mol** while the conversion of CH_3^+ to the radical

$$CH_3^+ + e^- \longrightarrow CH_3 \cdot$$

is exothermic by 227 kcal/mol[1] which gives an estimate of the electron affinity of the empty p-orbital in the cation. Among carbocations the methyl cation is clearly the least stable and doubt has been expressed whether it can exist at all in the condensed phase[2]. Cacace et al. described an ingenious procedure

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** 1 kcal = 4.184 kJ.

which allows experimental studies of the methyl cation. Radioactive decomposition of tritiated methane, a relatively slow process, generates tritiated

$$CT_4 \xrightarrow{-\beta^-} CT_3{}^3He^+ \longrightarrow CT_3{}^+ + {}^3He$$

methyl cations which can be captured by suitable nucleophiles[3]. The synthetic and mechanistic applications of this technique are likely to yield important information on the behavior of carbocations in the gas phase.

The instability of $CH_3{}^+$ can be rationalized in valence bond terms. Resonance stabilization by the »no-bond« canonic structure as the only available means for charge dispersal must be negligible.

Theoretical arguments corroborate the prediction based on the simple VSEPR model that the methyl cation is planar. As will be seen later, this conclusion is not necessarily valid for strained carbocations.

The lack of a suitable mechanism for resonance stabilization in the methyl cation can be amended by appropriate substitution. Thus, the heat of formation of $CH_3CH_2{}^+$ is 917 kJ mol⁻¹ (219 kcal/mol) or 172 kJ mol⁻¹ (41 kcal/mol) less than that of $CH_3{}^+$ while a methoxy group stabilizes the methyl cation by as much as 407 kJ mol⁻¹ (97 kcal/mol)[4]! The valence bond description gives an adequate »explanation«.

$$H_3C—CH_2{}^+ \leftrightarrow H^+H_2C=CH_2$$

$$H_3CO—CH_2{}^+ \leftrightarrow H_3CO^+=CH_2$$

The differences in stabilities of these cations are reflected in the corresponding solvolytic reactivities. CH_3OCH_2Cl solvolyses in ethanol about 10^{13} times faster than n-propyl chloride[5].

Alkyl groups, as exemplified above, stabilize the cationic center to a lesser extent than some heteroatoms which have the ability to delocalize the positive charge more effectively. In molecular orbital terms this stabilization results from the interaction of the empty orbital at the cationic center with the filled orbitals of the adjacent σ C-H (or C-C) bonds[6]. At first approximation this can be regarded as a HOMO-LUMO interaction between the $2p_y$ or $2p_z$ pseudo-π orbitals of the methyl group with the p_y or p_z function of the cation (Figure 1).

This interaction provides the molecular basis for the stabilizing effect of α-alkyl substituents on carbocations, commonly described as hyperconjugation[7]. In addition to this type of interaction, i. e. electron donation from the adjacent σ C-H (or C-C) bond, alkyl groups adjacent to an electron deficient center also exert an inductive stabilization through the framework of σ-carbon-carbon bonds.

Measurements of gas phase acidities lead to an estimate that the average stabilization resulting from α-methyl substitution amounts to about 15 kcal/mol, which is equivalent to a rate enhancement of 10^{11} relative to hydrogen. In solvolysis the attenuating effect of the solvent becomes apparent lowering this value on average by 10^5 to 10^6 [8]. Because the molecular basis of the methyl group effect is probably best understood of all substituent effects, methyl substitution is used as the standard probe for charge delocalization in heterolytic transition states.

From the molecular orbital description of hyperconjugation (Figure 1) certain conclusions can be made.

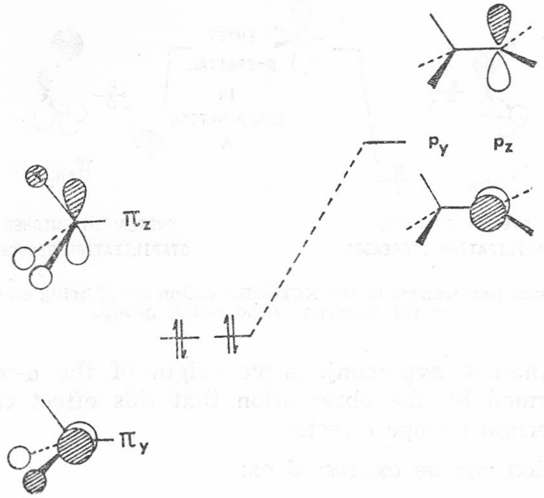


Figure 1. Orbital interactions between the filled pseudo-π orbitals of the methyl group and the empty p-orbital of the carbocation.

(i) The magnitude of hyperconjugative (stabilizing) interaction depends on the dihedral angle between the empty (LUMO) p-orbital and the pseudo-π (HOMO) orbital of the methyl group. The best overlap between these two orbitals is achieved when this angle is 0^0 or 180^0 [7].

(ii) Electron withdrawal from the adjacent C-H bond into the vacant p-orbital causes a weakening of this bond and consequently a lowering of the appropriate vibrational force constant[9]. This change in the force constant can be detected by measuring kinetic isotope effects in carbonium ion forming reactions using deuterium labeled substrates.

(iii) Hyperconjugative interactions are small when compared with steric and inductive effects of alkyl groups. Neither C-H nor C-C hyperconjugation are important stabilizing factors. Thus in the ethyl cation the sixfold rotational barrier is practically zero and in the *n*-propyl cation it is less than 3 kcal/mol[10]. However, strong electron donating or electron withdrawing groups show definite conformational preferences[7]. In the cation conformation A will be preferred if X is an electron donating group while conformation B will be more stable for X being an electron withdrawing group (Figure 2).

It appears that the stabilizing influence of hyperconjugation is quite significant in strained transition states. In some cases geometrical distortions due to hyperconjugation lead to 1,2-shifts possibly via bridged transition states or intermediates. It is however difficult to distinguish between stabilization without bridging (hyperconjugation) and with bridging (participation)[7,11].

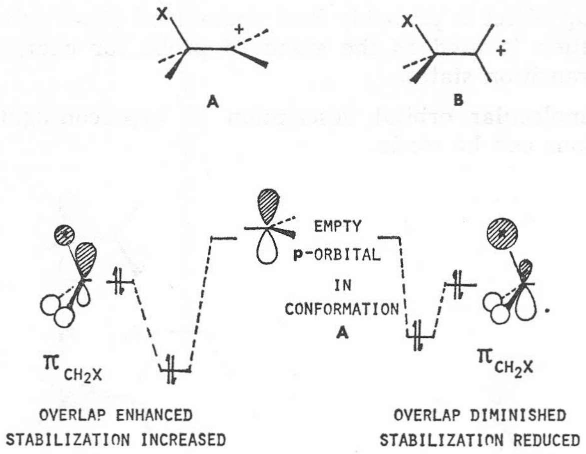


Figure 2. Conformational preferences in the $XCH_2CH_2^+$ cation for X being an (A) electron donating or (B) electron withdrawing group.

The predominantly hyperconjugative origin of the α-metyl group rate effect was confirmed by the observation that this effect can be correlated with CD_3 β-deuterium isotope effects[12].

This correlation can be expressed as:

$$\log k_{CH_3}/k_{CD_3} = 0.02024 \log k_{CH_3}/k_{H}$$

and is based on rate measurements on a group of structurally different substrates (Table I and Figure 3).

From this linear relationship it was possible to develop mathematical expressions which correlate the magnitude of the β-deuterium isotope effect with the dihedral angle between the adjacent p-orbital of the carbocation and the adjacent C—H (D) bond[13,14]. Implied in this approach was the separation of the conformationally independent inductive deuterium isotope effect (k_I) from the conformationally dependent hyperconjugative effect (k_o).

$$\log k_{\vartheta} = \log k_{I} + \log k_{o} \cos^2 \vartheta$$

The $\cos^2 \vartheta$ relationship follows from the simple perturbation molecular orbital theory according to which the energy of stabilizing a two-electron interaction between a vacant p-type orbital ψ_p and a filled orbital of π symmetry ψ_π is given by

$$\delta = \frac{|\psi_p H \psi_\pi d\tau|^2}{(E_p - E_\pi)}$$

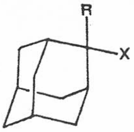
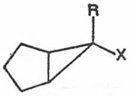
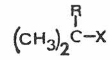
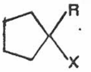
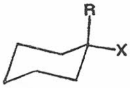
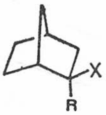
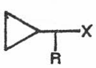
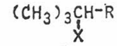
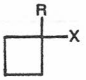
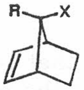
Introduction of the Wolfsberg-Helmholtz approximation[15] yields an expression for the energy of hyperconjugation which depends on the square of the overlap of the interacting orbitals

$$\delta = \frac{|\psi_p \psi_\pi d\tau|^2}{(E_p - E_\pi)}$$

As the angular dependence of the overlap goes as the cosine of the angle between the interacting orbitals, the hyperconjugative energy should follow a cos $^2\vartheta$ relationship.

TABLE I

α-Methyl Group Rate Effects and CD_3/CH_3 *Isotope Effects*

	COMPOUND (R = H, CH_3, CD_3)	k(CH_3/H)	k(CH_3/CD_3)
1		$10^{8.12}$	1.48
2		$10^{7.0}$	1.42
3	 $(CH_3)_2\overset{R}{C}\text{-}X$	10^6	1.33
4		$10^{4.44}$	1.25
5		$10^{4.36}$	1.21
6		$10^{4.27}$	1.22
7		$10^{3.62}$	1.18
8	 $(CH_3)_3\underset{X}{C}H\text{-}R$	10^2	1.09
9		$10^{2.11}$	1.09
10		10^2	1.09

The graphical representation of the angular dependence of β-deuterium isotope effects is given in Figure 4 for a range of different CH_3/H rate ratios.

Theoretical evidence from molecular orbital calculations supports the »cos $^2\vartheta$ rule« and also shows that this rule can be applied to radicals and carbocations as well[14].

That methyl group orbitals of π symmetry could be made responsible for ground state conformations of some molecules was suggested by Pople et al.[16].

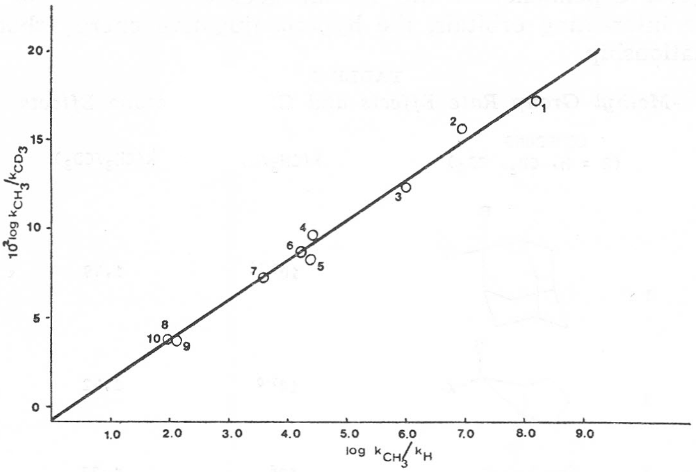


Figure 3. The linear relationship between log (k_{CH_3}/k_H) and log (k_{CH_3}/k_{CD_3}).

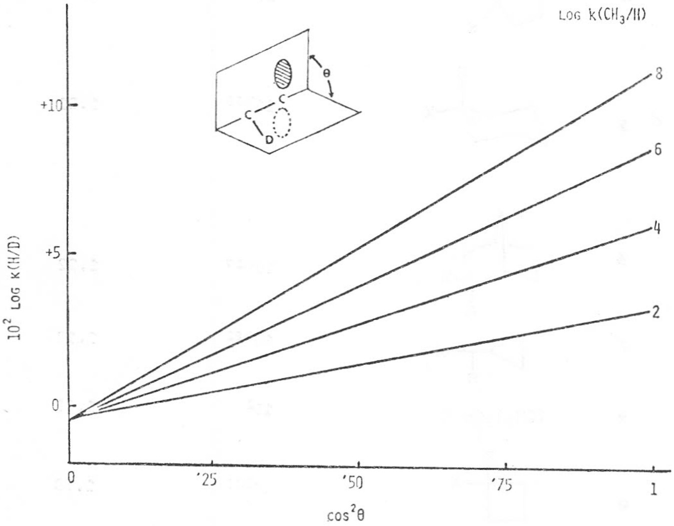


Figure 4. Angular dependence of log $k_{(H/D)}$ for different values of log $k_{(CH_3/H)}$.

Ab initio calculations at the STO-3G level show that conformations of double rotor molecules CH_3—X—CH_3 are determined by the electron contribution of the central grouping X. For X = O, NH, CH_2 this contribution will approach 2 electrons and the cycle formed by the 2pπ orbitals on the methyl group will contain 6π electrons and be »aromatic« in conformation A. For X = CH^+ as in the 2-propyl cation, the cycle will contain 4π electrons, be »antiaromatic« and prefer conformation B (Figure 5).

Implied in this reasoning is the extension of Hückel's rule to atomic orbitals of the 2pπ type involved in the CH-σ bond. It should be pointed out

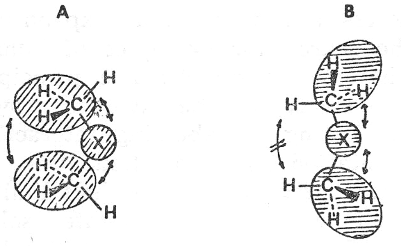


Figure 5. Orbital orientation for two different conformations of a CH_3-X-CH_3 molecule.

that we also used these same orbitals in rationalizing hyperconjugation and its angular dependence.

That Hückel's $4n + 2$ rule can also be applied to ions is known since the aromaticity of the tropylium ion was recognized[17]. Later Goldstein and Hoffmann[18] presented theoretical evidence that a pericyclic topology is not a necessary prerequisite for aromatic stabilization. With the recognition of other topological possibilities in spirocyclic, longicyclic and laticyclic interactions aromaticity ceased to be a phenomenon restricted to one plane (Figure 6).

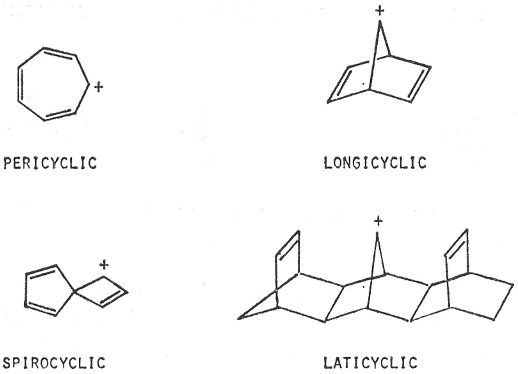


Figure 6. Different topologies for aromatic stabilization.

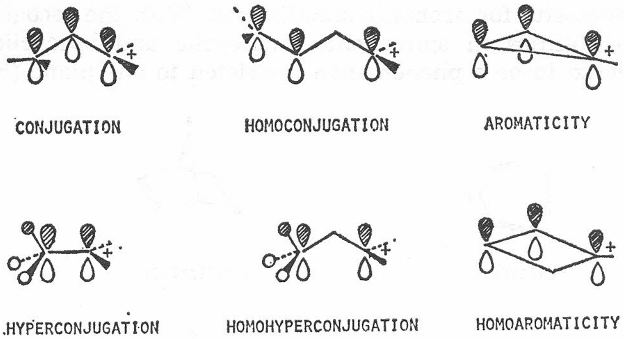
This has not been the only extension of the concept of aromaticity. Some 20 years ago the unusual solvolytic behavior of the bicyclo[3.1.0]-hexyl cation led Winstein to advance the concept of homoaromaticity[19]. It was recognized that this cation is in fact the »non-classical« tris-homo counterpart of the cyclopropenyl cation (Figure 7).

Figure 7. Homoaromatic orbital stabilization in the bicyclo [3.10] hexyl cation.

It is apparent that the interaction leading to stabilization of the bicyclic cation differs from the overlap in the parent cyclopropenyl ion on two accounts. Firstly, the orbitals involved are the Walsh orbitals of the cyclopropane ring system and therefore not of the ordinary π type, and secondly the system is not planar thus exhibiting a one side overlap of increased σ contribution.

With variable success and with great expenditure of theoretical and experimental effort the search for examples of homoaromatic stabilization continued well into the present time[19c]. The principal issue has been the question of (i) how extensively can the involved π system be disrupted and distorted while still exhibiting a stabilizing interaction, and (ii) how such an interaction can be detected and quantified.

In the context of this presentation we shall limit our discussion to the problem of interactions in carbocations generated solvolytically focusing on systems where electron delocalization can be detected by measuring secondary kinetic deuterium isotope effects. The conceptual connection between hyperconjugation, conjugation and aromaticity is provided by the similarity of π-orbitals in conjugated and aromatic systems and the 2pπ orbitals of C—H bonds in their saturated counterparts. Analogously, homoconjugation and homoaromaticity could be linked with homohyperconjugation. The following examples illustrate these points (Figure 8).


CONJUGATION HOMOCONJUGATION AROMATICITY

HYPERCONJUGATION HOMOHYPERCONJUGATION HOMOAROMATICITY

Figure 8. Different stabilizing interactions in carbocations.

If the same mode of interaction exists between a β-CH bond and the cationic center as with a γ-CH bond in the homologue, deuterium substitution should give rise to a normal ($k_H/k_D > 1$) isotope effect (Figure 9).

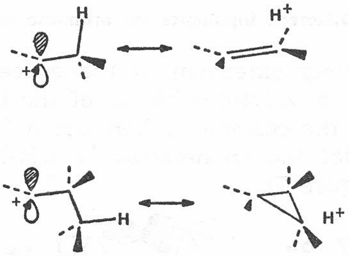
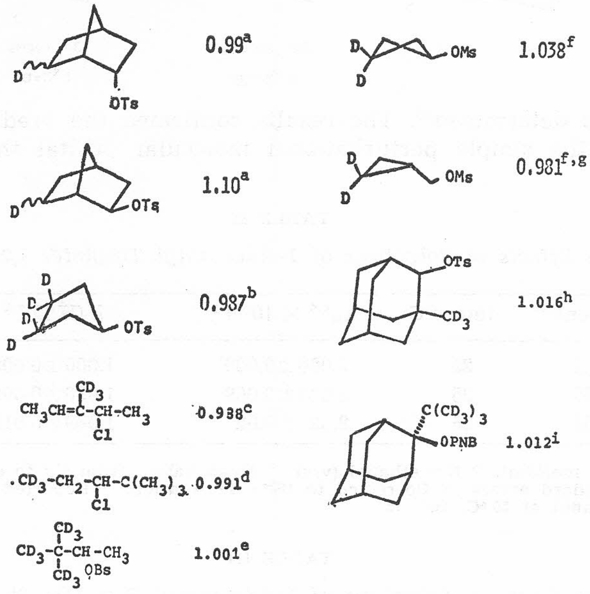


Figure 9. C—H Hyperconjugation vs. C—H homohyperconjugation.

Quantum mechanical considerations predict a rapid fall-off of through space interactions at distances greater than 250 pm or more than three carbon atoms apart. It is evident that such long range interactions should be critically dependent on the proper orientation of interacting orbitals. Although hyperconjugation is usually considered as a 1,2 or β-effect, in rigid systems where adverse entropy effects could be minimized, interactions from the γ-position may also be expected. Cases where deuterium rate effects from γ or even more remote positions were observed can be found in the literature[20-27] (see Figure 10), but homohyperconjugation was never explicitly invoked as the cause of these effects. Furthermore, inverse effects ($k_H/k_D < 1$) were considered as the normal kinetic response to γ-deuteration[28]. Normal effects ($k_H/k_D > 1$) were usually interpreted as being due to some specific interpretations as in the case of γ-deuterated norbornyl derivatives[20]. Here σ-bond participation leading to a nonclassical cation was the obvious rationalization for the observed effect (Figure 11).

γ-ISOTOPE EFFECTS
(per atom D)



[a]ref. 20; [b]ref. 21; [c]ref. 22; [d]ref. 9; [e]ref. 23; [f]ref. 24;
[g]ref. 25; [h]ref. 26; [i]ref. 27.

Figure 10. Some selected γ-isotope effects per atom D.

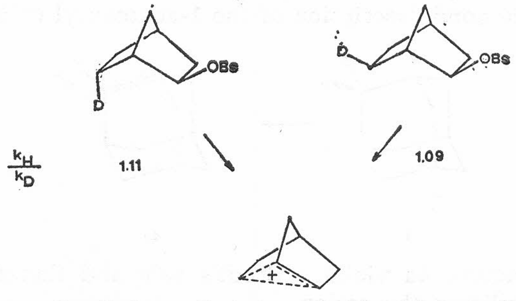
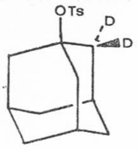


Figure 11. γ-Isotope effects in *exo*-norbornyl derivatives.

In order to test the hyperconjugative and homohyperconjugative interactions 1-adamantyl derivatives 1—3 were solvolyzed and the corresponding



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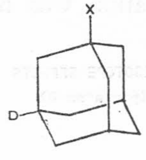
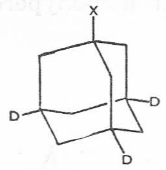


2a X= OTs
b X= Br



3a X=OTs
b X=Br

isotope effects determined[29]. The results confirmed the predictions made on the basis of the simple perturbational molecular orbital theory (Tables II and III).

TABLE II

Isotope Effects in Solvolysis of 1-Adamantyl Tosylates 1,2a, *and* 3a

compd[a]	solvent[b,c]	temp/°C	k_{H}[c,d] × $10^4/\mathrm{s}^{-1}$	k (H/D)[c,d]	$k\,(\mathrm{H/D})_{\mathrm{cor}}$[e]
1	96 E	25	2.020 ± 0.009[f]	1.000 ± 0.0086	1.000
2a	96 E	25	2.020 ± 0.009	1.036 ± 0.009	1.041
3a	96 E	25	2.03 ± 0.02	1.069 ± 0.012	1.073

[a] 0.002—0.003 mol/dm^3. [b] E = ethanol (v/v). [c] Mean values from six to eight measurements. [d] Errors are standard errors. [e] Corrected to 100% deuteration. [f] Reported value 2.07×10^{-4} s^{-1} in 95% (v/v) ethanol at 20 °C, ref. 15.

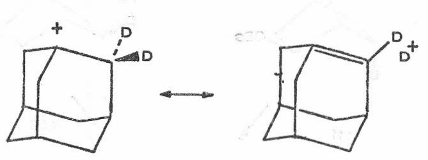
TABLE III

Isotope Effect in Solvolysis of 1-Adamantyl Bromides 2b *and* 3b[a]

compd[a]	solvent[b,c]	temp/°C	k_{H}[d,e] × $10^4/\mathrm{s}^{-1}$	k (H/D)[d,e]	$k\,(\mathrm{H/D})_{\mathrm{cor}}$[f]
2b	80 T	25	0.880 ± 0.004	1.026 ± 0.022	1.03
3b	80 T	25	0.880 ± 0.004	1.050 ± 0.028	1.053

[a] For a list of solvolytic rates of 1-adamantyl bromide in different solvents see: D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Amer. Chem. Soc.* 92 (1970) 5977. [b] 0.002—0.003 mol/dm^3. [c] T = 2,2,2-trifluoroethanol (w/w). [d] Mean values from four measurements. [e] Errors are standard errors. [f] Corrected to 100% deuteration.

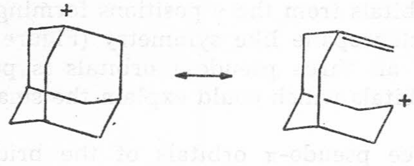
The absence of any significant β-effect can be easily understood on the basis of the valence bond description of the 1-adamantyl cation:



4 4a

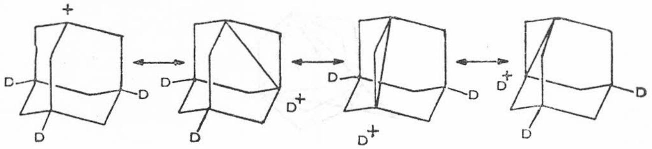
The canonical structure 4a violates Bredt's rule and therefore cannot be of importance in stabilizing the cation.

For the observed γ-effects the valence bond method offers two explanations. If electron donation from the β-γ C-C bond is stabilizing the cationic center, resonance stabilization by carbon-carbon hyperconjugation should be important.



4 4b

An equally good explanation can be based on homohyperconjugative stabilization from the γ-C-H (D) bond(s).



4c-d

Using the homohyperconjugative model as the basis for the γ-effects the following molecular orbital description of this interaction can be advanced.

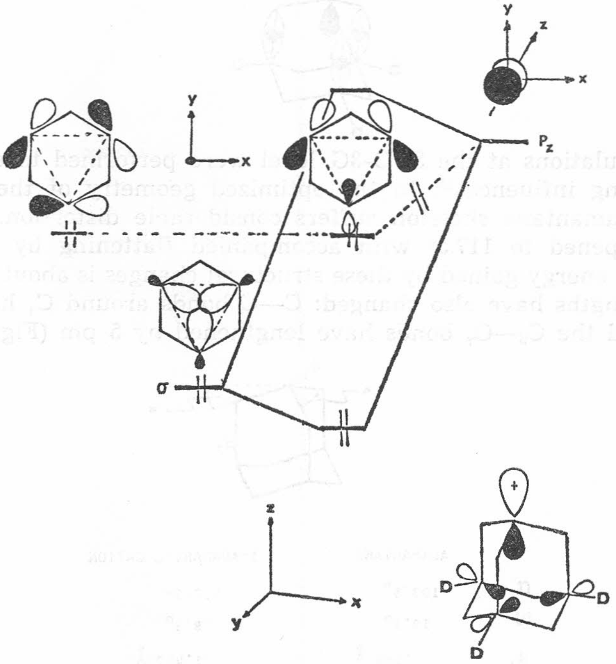
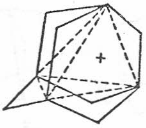


Figure 12. Orbital interactions between the cationic center and the γ-C—H(C—D) pseudo-π orbitals in the 1-adamantyl cation.

The pseudo π-orbital of the γ-CH(D) bond has the right orientation with the backlobe of the p-orbital at C_1^+. This interaction should be unhindered by solvent molecules which cannot easily occupy the space inside the adamantyl skeleton. Also, the symmetry of adamantane provides for a possible interaction of all three of these orbitals from the γ-positions forming a pseudo Walsh-type configuration with cyclopropane like symmetry (Figure 12). However, simultaneous interaction of all three pseudo-π orbitals is possible only with the subjacent level of π orbitals which could explain the smallness of the observed effect.

By using the three pseudo-π orbitals of the bridgehead CH(D) bonds we are in fact constructing a Hückel $4n + 2$ system of laticyclic topology[18]. This kind of stabilization implies a delocalization of the positive charge over the four bridgehead carbon atoms in a formally hexahomotetrahedranyl cation **5**.



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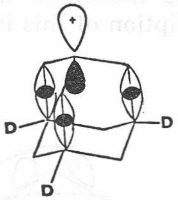
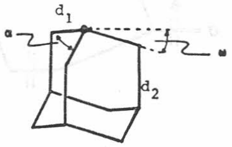
Not surprisingly, similar reasoning could be applied to the hyperconjugative model. The three, β,γ-σ-CC bonds form a pericyclic 6 electron Hückel system properly aligned for interaction with the vacant p-orbital at C_1.

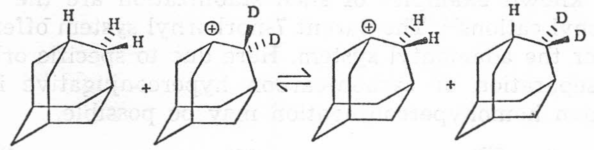


Ab initio calculations at the STO-3G level were performed to examine these same stabilizing influences[29]. In the optimized geometry of the 1-adamantyl cation the adamantane skeleton suffers considerable distortion. Bond angles at C_1 have opened to 117.5° with accompanied flattening by 11.2° towards planarity. The energy gained by these structural changes is about 28.6 kcal/mol. Some bond lengths have also changed: C—C bonds around C_1 have shortened by 4.3 pm and the C_β—C_γ bonds have lengthened by 5 pm (Figure 13).



Theoretical isotope effects were calculated for the two isodesmic equilibrium reactions (1) and (2)[30].

(1)



(2)

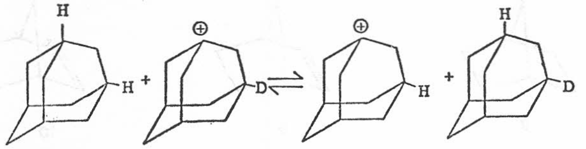


TABLE IV

Theoretical Isotope Effects and Force Constants

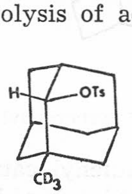
	k_{CD}/N m^{-1}		
	adamantane	1-adamantyl cation	$K_{eq}(k_H/k_D)^a$
reaction 1	725.8	726.6	1.001(1.000)
reaction 2	728.7	741.1	1.014(1.041)

[a] Effect per D atom substitution; experimental value in parentheses.

For both reactions the results are in agreement with the experimentally observed β and γ effects (Table IV). These and accompanying studies on γ-substituted adamantyl derivatives[29] indicate that the main stabilizing interaction in the adamantyl cation arises from carbon-carbon hyperconjugation but some homohyperconjugative electron donation from the γ-CH bonds cannot be excluded.

It deserves mentioning that while this work was in progress experimental results became available which strongly suggest that the 1-adamantyl cation is intrinsically more stable than the tert. butyl cation[31].

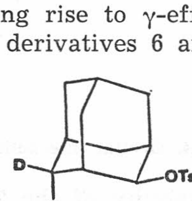
Similar long range interactions giving rise to γ-effects have also been observed in the solvolysis of adamantyl derivatives 6 and 7.



6

k_H/k_{D_3} 1.05[26]

(60% dioxane, 50 °C)



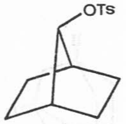
7

k_H/k_{D_2} 1.04[34]

(70% TFE, 60 °C)

From the similarity of π and pseudo-π orbitals, homohyperconjugative interactions and consequently normal γ-deuterium isotope effects may also be expected in systems where charge delocalization by neighboring double bond participation is known to occur.

The best known examples of such stabilization are the 7-norbornyl and 7-norbornadienyl cations[35]. The parent 7-norbornyl system offers one additional advantage over the adamantyl system. Here due to specific orbital »non-interactions«[36] a separation of carbon-carbon hyperconjugative interaction from carbon-hydrogen homohyperconjugation may be possible.



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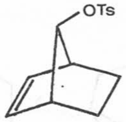

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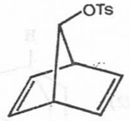


10

	8	9	10
k_{rel}	1	10^{11}	10^{14}

In solvolysis tosylates 9 and 10 react 10^{11} and 10^{14} times faster than the parent saturated 7-norbornyl tosylate (8) (Figure 13). The high reactivity of 7-norbornenyl derivatives relative to 7-norbornyl derivatives can be attributed to the homoaromatic stabilization of the cation. The bridge orbital interaction is of proper symmetry[37] to allow for a *bis*-homoconjugative interaction of $4n + 2$ pericyclic topology which is similar to the one in the bicyclo [3.1.0] hexyl cation (vide supra) (Figure 14).

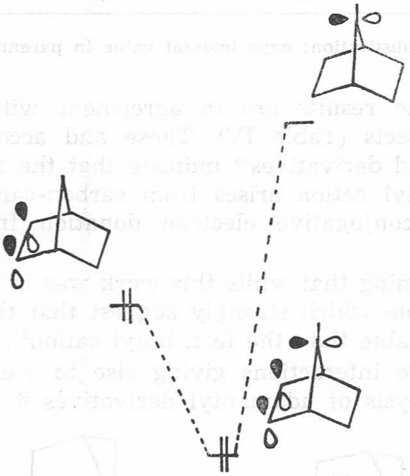
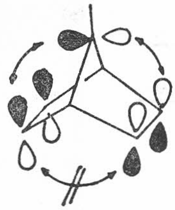


Figure 14. Orbital interactions in the 7-norbornenyl cation.

The additional stability of the 7-norbornadienyl cation, a $4n$ π electron system, cannot be explained in these terms. This ion is of longicyclic topology[18] and required the modification of the Hückel's rule as formulated by Goldstein and Hoffmann[18,38]. »A fully unsaturated bridged bicyclic ion is expected to be stabilized if any two of its three bridges differ in mode. Thus, if two each possess $4n$ π electrons (mode 0), the third must posses $4n + 2$ (mode 2) and vice versa«. Accordingly, the 7-norbornadienyl cation is a bicycloaromatic species, and should also be stabilized[18]. The stabilization introduced by the second double bond is however smaller than the one for the first (10^3 vs. 10^{11} in relative rates). The orbital interaction diagram offers an explanation. In the symmetrical ion the interaction between the two mode 0 ribbons is destabilizing while that between the empty *p*-orbital at C_7 and either of the 2^0 ribbons is stabilizing.



In order to escape this situation the ion choses the alternative unsymmetric geometry where the interaction with one double bond is increased but with the other decreased. In the first interaction (A in Figure 15) a bishomocyclopropenyl cation is formed whose LUMO orbitals, again of pseudo-Walsh type, have the proper symmetry for interaction with the HOMO orbital of the second double bond (B). The stabilization thus occurs in two stages and this simple PMO-model adequately explains the differences in reactivities between 7-norbornene and 7-norbornadiene derivatives. The reasoning applied here parallels the one suggested by Loew and Wilcox for the resolution of the »quadricyclyl cation puzzle«[39].

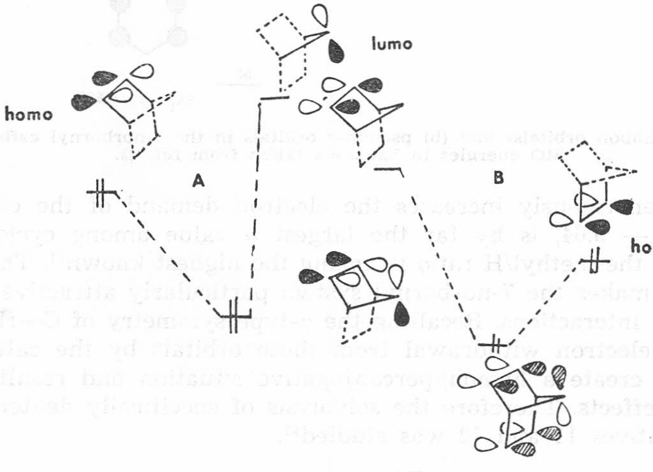


Figure 15. Orbital interactions in the 7-norbornadienyl cation.

The extreme solvolytic unreactivity of 7-norbornyl derivatives — the tosylate has a half life in acetic acid at 25 °C of 3 455 200 years — has intrigued chemists for a long time. An attractive explanation for the destabilization in the 7-norbornyl cation was suggested by Hoffmann, Mollère and Heilbronner[36]. It is blamed on the inability of the high lying set of degenerate ribbon orbitals of the σ-bonds in the underlying cyclohexane ring (in boat conformation) to interact with the p-function at C_7 (Figure 16a). Both, the AA and SS ribbons are of wrong symmetry for such interactions. This lack of any means for

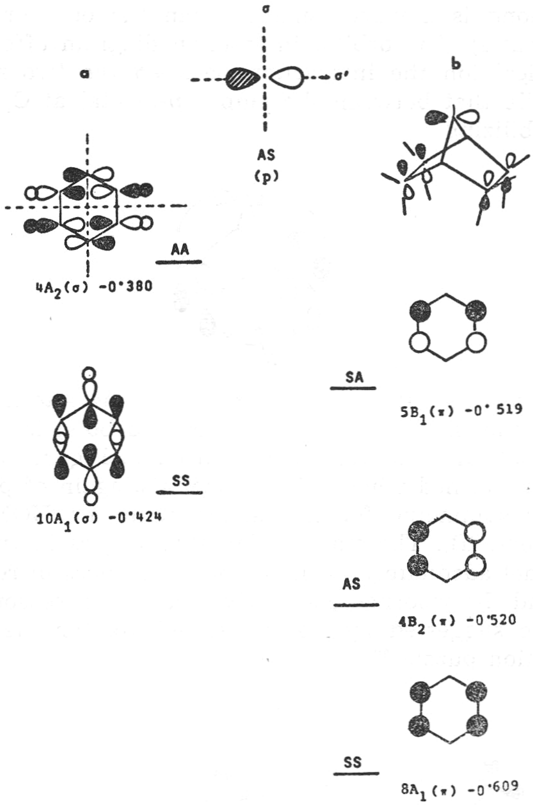
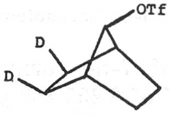
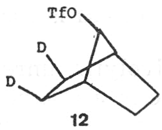


Figure 16. (a) »Ribbon orbitals« and (b) pseudo-π orbitals in the 7-norbornyl cation. Calculated MO energies in hartrée-s taken from ref. 43.

stabilization enormously increases the electron demand of the cation. Hammett's value — 5.64, is by far the largest ϱ value among cycloalkyl derivatives[40], and the methyl/H ratio is among the highest known[41]. This exceptional behavior makes the 7-norbornyl system particularly attractive for studies of long-range interactions. Recalling the π-type symmetry of C—H orbitals in CH_2 groups, electron withdrawal from these orbitals by the cationic center at C_7 should create a homohyperconjugative situation and result in normal γ-deuterium effects. Therefore the solvolysis of specifically deuterated 7-norbornyl derivatives 11 and 12 was studied[42].



11



12

$k(H/D_2)$ 1.026 ± 0.007 1.039 ± 0.009 (65 °C, 80 T)

The result of this investigation confirmed our prediction. The magnitude of the effects is small. Because of symmetry constraints, similar to those in the 1-adamantyl cation, interaction can occur only with the subjacent $4B_2$

pseudo π orbitals of the C-H(D) bonds (Figure 16b) but not with ribbon orbitals of carbon-carbon bonds. The slightly larger effect in the *syn* derivative can be accounted for by invoking steric factors[27] which would render the *syn* side more crowded in the ground state than in the transition state, because of interactions between the *exo* hydrogen atom and the relatively bulky leaving group. That the pseudo-π orbitals cannot stabilize the system in spite of the favorable symmetry (which is not the case with ribbon orbitals) can be ascribed to the fact that since each CH_2 group provides 2 electrons the laticyclic system can be regarded as being antiaromatic. Here we are assuming that the ion is symmetric (C_{2v} group) as supported by recent ab initio calculations[44]. This is by no means a proven statement because other theoretical methods (MINDO/2 and MINDO/3) as well as some earlier solvolytic studies[45] ascribe a bent structure to the cation. To what extent are the solvolytic results an artefact due to solvent interactions remains to be seen. Work in this direction is in progress. It is however the observation of normal γ-deuterium isotope effects which makes this result particularly interesting. From orbital symmetry consideration the only reasonable mechanism for electron withdrawal from the γ-position seems to be the homohyperconjugative interaction with the respective C-D(H) bonds. A small contribution of a steric effect arising from the *exo*-orientation of deuterium atoms cannot be excluded and it remains to be seen how endo deuterium labeled 7-norbornyl derivatives will behave.

Acknowledgment. — I thank my colleagues and co-workers, who are named in the references, for their intellectual and experimental contribution to our work. Financial support was furnished by the Research Council of Croatia. Special thanks go to the donors of the Van't Hoff Fund for a personal grant which was used for enhancing the long range through space interaction between our group in Zagreb and Professor Hehre's at University of California Irvine!

REFERENCES

1. F. P. Lossing and G. P. Semeliuk, *Can. J. Chem.* **48** (1970) 955.
2. T. S. Sorensen and A. Rauk, in: A. P. Marchand and R. E. Lehr, Eds., *Pericyclic Reactions,* Vol. 2, Academic Press Inc., New York 1977, Chapter 1.
3. F. Cacace, G. Ciranni, and M. Schüller, *J. Amer. Chem. Soc.* **97** (1975) 4747; F. Cacace, *Advan. Phys. Org. Chem.* **8** (1970) 79.
4. For a recent review see:P. Vogel, in: C. Wentrup, Ed., *Reactive Zwischenstufen II,* Georg Thieme Verlag, Stuttgart 1979, p. 239.
5. A. Streitwieser, Jr., *Solvolytic Displacement Reactions,* McGraw-Hill Book Co., Inc., New York 1962, p. 103.
6. R. S. Mulliken, *J. Chem. Phys.* **1** (1933) 492; **3** (1935) 520; **7** (1939) 339.
7. R. Hoffmann, L. Radom, J. A. Pople, P. von R. Schleyer, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.* **94** (1972) 6221.
8. J. L. Fry, J. M. Harris, R. C. Bingham, and P. von R. Schleyer, *J. Amer. Chem. Soc.* **92** (1970) 2540 and references therein.
9. V. J. Shiner, *Jr. ACS Monogr. No. 167,* Chapter 2, (1970).
10. L. Radom, D. Poppinger, and R. C. Haddon, in G. A. Olah and P. von R. Schleyer, Eds., *Carbonium Ions,* Vol. 5, Wiley-Interscience, New York 1976, Chapter 38.
11. J. Chandrasekhar and P. von R. Schleyer, *Tetrahedron Lett.* (1979) 4057.
12. a) K. L. Servis, S. Borčić, and D. E. Sunko, *Tetrahedron* **24** (1968) 1247; b) R. D. Fischer, R. C. Seib, V. J. Shiner, Jr., I. Szele, M. Tomić, and D. E. Sunko, *J. Amer. Chem. Soc.* **97** (1975) 2408.
13. D. E. Sunko, I. Szele, and W. J. Hehre, *J. Amer. Chem. Soc.* **99** (1977) 5000.
14. D. J. DeFrees, W. J. Hehre, and D. E. Sunko, *J. Amer. Chem. Soc.* **101** (1979) 2323.

15. M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.* **20** (1952) 837.
16. D. Cremer, J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Amer. Chem. Soc.* **96** (1974) 6900.
17. W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.* **76** (1954) 3203.
18. M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.* **93** (1971) 6193.
19. a) S. Winstein, *J. Amer. Chem. Soc.* **81** (1959) 6524; b) S. Winstein, *Quart. Rev. Chem. Soc.* **23** (1969) 141; c) For a recent review see also: L. A. Paquette, *Angew. Chem., Int. Ed.* **17** (1978) 106.
20. a) B. L. Murr, A. Nickon, T. Swarz, and H. N. Werstiuk, *J. Amer. Chem. Soc.* **89** (1967) 1730; b) J. M. Jerkunica, S. Borčić, and D. E. Sunko, *ibid.* **89** (1967) 1732.
21. S. Borčić, *Croat. Chem. Acta* **35** (1963) 67.
22. R. H. Griffin and J. G. Jewett, *J. Amer. Chem. Soc.* **92** (1970) 404.
23. V. J. Shiner, Jr, R. D. Fisher, and W. Dowd, *J. Amer. Chem. Soc.* **91** (1969) 7748; V. J. Shiner, Jr. and R. C. Seib, *Tetrahedron Lett.* (1979) 123.
24. B. Goričnik, Z. Majerski, S. Borčić, and D. E. Sunko, *J. Org. Chem.* **38** (1973) 1881.
25. S. Borčić, M. Nikoletić, and D. E. Sunko, *J. Amer. Chem. Soc.* **84** (1962) 1615.
26. D. Kovačević, B. Goričnik, and Z. Majerski, *J. Org. Chem.* **43** (1978) 4008.
27. R. C. Badger and J. L. Fry, *J. Amer. Chem. Soc.* **101** (1979) 1680.
28. D. E. Sunko and S. Borčić, ref. 9, Chapter 3.
29. D. E. Sunko, S. Hiršl-Starčević, S. K. Pollack, and W. J. Hehre, *J. Amer. Chem. Soc.* **101** (1979) 6163.
30. For the description of the method see: D. J. DeFrees, D. Z. Hassner, W. J. Hehre, E. A. Peter, and M. Wolfsberg, *J. Amer. Chem. Soc.* **100** (1978) 641.
31. a) D. Mirda, D. Rapp, and G. M. Kramer, *J. Org. Chem.* **44** (1979) 2619; b) T. W. Bentley, C. T. Bowen, W. Parker, and C. I. F. Watt, *J. Amer. Chem. Soc.* **101** (1979) 2486; c) The first report indicating that 1-adamantyl cation could be more stable than the tert. butyl cation can be found in the paper by Beauchamp et al.[32]. It was gratifying to observe the change in reactivities of 1-adamantyl derivatives when ethanol was replaced by trifluoroethanol as the solvolytic solvent[31b] thus confirming reservations regarding the validity of direct comparison of solvolytic rates with thermodynamic stabilities. In ethanol 1-adamantyl chloride is about 3000 times *less* reactive than tert. butyl chloride[33]!
32. R. H. Staley, R. D. Wieting, and J. L. Beauchamp, *J. Amer. Chem. Soc.* **99** (1977) 5964.
33. R. C. Bingham and P. von R. Schleyer, *J. Amer. Chem. Soc.* **93** (1971) 3189.
34. Unpublished work with M. Bicaj.
35. a) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.* **77** (1955) 4183; b) S. Winstein and C. Ordronneau, *J. Amer. Chem. Soc.* **82** (1960) 2084; see also ref 19b; d) P. R. Story and B. C. Clark, Jr., in: G. A. Olah and P. von R. Schleyer, Eds., *Carbonium Ions,* Vol. 3, Wiley-Interscience, New York 1972, Chapter 23.
36. R. Hoffmann, P. D. Mollère, and E. Heilbronner, *J. Amer. Chem. Soc.* **95** (1973) 4860.
37. R. Hoffmann, *Accounts. Chem. Res.* **4** (1971) 1.
38. M. J. Goldstein, S. Tomoda, and G. Whittaker, *J. Amer. Chem. Soc.* **96** (1974) 3677.
39. L. M. Loew and C. F. Wilcox, Jr., *J. Amer. Chem. Soc.* **97** (1975) 2296.
40. W. F. Slivinski, T. M. Su, and P. von R. Schleyer, *J. Amer. Chem. Soc.* **94** (1972) 133.
41. a) H. Tanida and T. Tsushima, *J. Amer. Chem. Soc.* **94** (1972) 133; b) P. G. Gassman and A. F. Fentiman, *J. Amer. Chem. Soc.* **92** (1970) 2529; c) D. E. Sunko, I. Szele, and M. Tomić, *Tetrahedron Lett.* (1972) 1827; d) J. Lhome, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.* **91** (1969) 1548.
42. Unpublished work with H. Vančik and V. Deljac.
43. For the MO calculations of orbital energies in norbornane see J. M. Lehn and G. Wipff, *Theor. Chim. Acta* **33** (1974) 43.

44. a) G. Wenke and D. Lenoir, *Tetrahedron* 35 (1979) 489 and references therein; b) J. E. Williams, Jr., R. Sustmann, L. C. Allen, and P. von R. Schleyer, *J. Amer. Chem. Soc.* **91** (1969) 1037.
45. a) P. G. Gassman, J. M. Hornback, and J. L. Marshall, *J. Amer. Chem. Soc.* **90** (1968) 6238; b) F. B. Miles, *J. Amer. Chem. Soc.* **90** (1968) 1265.

SAŽETAK

Interakcije u karbokationima i Hückelovo $4n+2$ pravilo

D. E. Sunko

Molekularno-orbitalni model hiperkonjugacije omogućuje tumačenje nekih interakcija dalekog dosega u karbokationima koje se mogu otkriti mjerenjem sekundarnih deuterijskih izotopnih efekata. Hückelovo $4n+2$ pravilo moguće je proširiti i na interakcije tzv. pseudo-π-orbitala CH_3, CH_2 CH-skupina, pa analogno homokonjugaciji može postojati i homohiperkonjugacija koja je vjerojatno jedan od uzroka γ-deuterijskim izotopnim efektima. Opisani su rezultati istraživanja tih efekata na adamantanskom i norbornanskom sistemu. Dok se stabilnost 1-adamantil-kationa može pripisati povoljnoj $4n+2$ konfiguraciji σ-elektrona β,γ-CC ili γ-CH veza, u 7-norbornil-kationu četiri CH_2-skupine predstavljaju $4n$ pseudo-π-sistem što bi moglo objasniti njegovu izvanrednu nestabilnost.

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