Hyperconjugation and Homohyperconjugation in the 1-Adamantyl Cation. Qualitative Models for γ-Deuterium Isotope Effects

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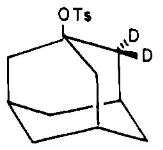
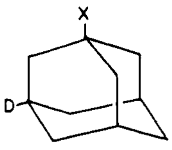
Abstract: An experimental and theoretical study of the modes of stabilization of the carbocation-like transition state in the solvolysis of 1-substituted adamantyl systems is presented. Experimental determination of β- and γ-deuterium isotope effects are used as a probe for hyperconjugative and homohyperconjugative stabilization. Ab initio molecular orbital theory is utilized to examine these same stabilizing influences. Our findings indicate carbon–carbon hyperconjugative stabilization to be the major mode of cation stabilization in the adamantyl system.

It is well established that solvolytic transition states possess a large degree of carbocation ion character.[2a] The hyperconjugative electron demand of such transition states can be examined by kinetic secondary β-deuterium isotope effect measurements.[2b] The recently evaluated angular dependence of these effects in conjunction with their linear relationship to α-methyl group rate effects significantly broadens the applicability of this mechanistic probe.[3] We have demonstrated how reliable estimates of transition-state geometries can be obtained by correlating β effects in secondary substrates with CH_3/H or CH_3/CD_3 rate ratios. However, the alternative possibility of estimating the electron deficiency at the cationic carbon by means of β effects has been much less explored, and is used only qualitatively in mechanistic studies of reactions which proceed by neighboring group participation.[4,5] Molecular orbital theory has also been used as a probe for hyperconjugative stabilization of adjacent charge centers.[3,6] Theoretically derived force constants have allowed calculations of β-deuterium isotope effects on several equilibrium systems.[6a-c]

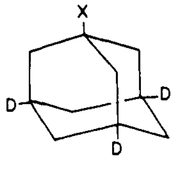
Contrary to β effects, a mechanistic rationalization of more remote secondary deuterium isotope effects has seldom been attempted.[7] It is reasonable to expect that such long-range effects should in some way also be a measure of charge at the carbocation center, as well as an indication of the extent of charge delocalization by the molecular framework. The mechanism of such long-range effects is not initially obvious.

The solvolysis of specifically β- and γ-deuterated 1-adamantyl derivatives, **1–3**, affords two sets of data which will be rationalized in terms of hyperconjugative and homohyperconjugative through-space interactions.



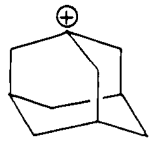


2a X= OTs
b X= Br



3a X= OTs
b X= Br

The choice of 1-adamantyl derivatives has several clear-cut advantages. The rigid cage-like structure of the carbon framework should prohibit rear-side solvation of the ion pair as a mode of stabilization. Further, this rigid structure simplifies theoretical calculations owing to the absence of various conformers. Also steric and electronic factors should suppress possible Wagner–Meerwein rearrangements. For all the above reasons, isotope effects in **1, 2,** and **3** should be devoid of complicating factors and the magnitude of the β effect in **1** should give a good measure of electron deficiency at the cationic center in **4**.



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The importance of this estimate is augmented by the recent observation by Beauchamp et al.[8] that **4** is 10.8 kcal/mol more stable than *tert*-butyl cation. Again, the rigidity of the adamantyl framework makes it amenable to studies of long-range through-space effects such as homohyperconjugation, as well as investigation of carbon–carbon hyperconjugation as a stabilizing influence in the carbocation-like transition states.

It should, of course, be noted that considerable information on this system is already available from the work of Schleyer[9a] and of Grob[9b] and their collaborators, who studied the solvolytic reactivity, remote substituent effects, and fragmentation patterns of various adamantane derivatives. The reader is referred elsewhere to detailed discussions.[9]

Experimental Section

The synthesis of the specifically deuterated 1-adamantyl derivatives **1–3** was accomplished by suitable modification of the procedures described for the preparation of the corresponding protio derivatives. The synthetic steps are outlined in Scheme I and described in detail in the Experimental Section.

General. The purity of all compounds was checked by GLC or TLC. Structure determination was performed by NMR, infrared spectra, and mass spectrometry. For this purpose the following instrumentation was used: Varian A-60A and Varian EM-360 NMR spectrometers, Perkin-Elmer M-257 spectrophotometer, and Varian CH-7 mass spectrometer. The kinetic studies were performed on a Radiometer SBR 2c titrigraph with a PHM-25 pH meter coupled to a TTT-1 titrator and a SBU-la buret.

Kinetic Measurements. The previously described procedure was used.[10] Six to eight measurements were performed for each compound alternating the solvolysis of labeled and unlabeled substrate. The rate data were evaluated by a nonlinear least-squares sum-fitting program. Tosylates **1, 2a,** and **3a** were solvolyzed in 96% ethanol at 25 °C while bromides **2b** and **3b** were solvolyzed in 80% trifluoroethanol at 25 °C. The rate constants and the corresponding isotope effects are presented in Tables I and II.

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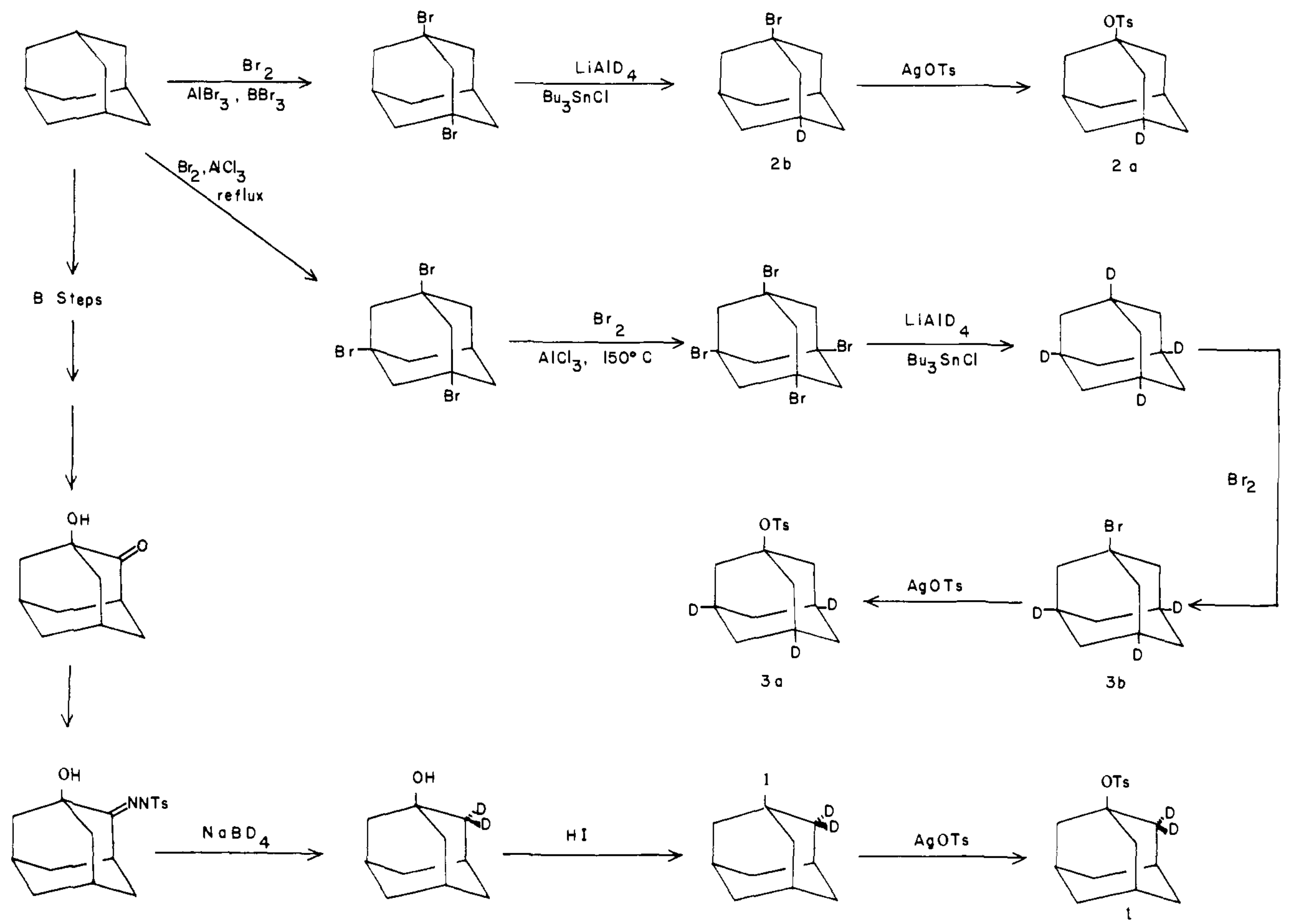
Scheme I



1-Hydroxy-2-adamantanone.[11] Jones' reagent (8 mL) was added dropwise with vigorous stirring to a solution of 1,2-adamantanediol (2.2 g, 13.1 mmol) in acetone (60 mL) until a persistent reddish-brown color appeared. Stirring was continued for 15 min and the excess oxidant destroyed by dropwise addition of 2-propanol (5 mL). Water (100 mL) was added and the products were extracted into chloroform (3 × 80 mL). The chloroform solution was washed with a solution of $NaHCO_3$ and dried over $MgSO_4$. Removal of solvent afforded 1.40 g (65%) of a crude product (85% pure by GLC). Final purification was performed by chromatography of an ethyl acetate solution through Al_2O_3 (activity II/III) and elution with ethyl acetate-pentane, yield 1.02 g (47%) of the pure product. The ^1H NMR and IR spectra were identical with those of an authentic specimen.[11]

1-Hydroxy-2-adamantanone Tosylhydrazone.[12] To a solution of 1-hydroxy-2-adamantanone (0.325 g, 1.96 mmol) in methanol (5 mL), 0.396 g (1.98 mmol) of *p*-toluenesulfonyl hydrazide was added. The mixture was stirred for 12 h at 60–65 °C, then cooled, and the product precipitated by adding water (5 mL). The precipitate was dissolved in ether (100 mL), washed with water (2 × 25 mL), dried over $MgSO_4$, and evaporated. The residue (0.61 g) was recrystallized from 1:1 ether-hexane mixture. The yield of the pure product was 0.52 g (73%)

1-Hydroxyadamantane-*2,2-d$_2$*.[13] The tosylhydrazone (0.40 g, 1.2 mmol) was dissolved in CH_3OD (7.5 mL) and to the resulting solution sodium borodeuteride (0.40 g, 10.4 mmol) was slowly added with stirring and gentle heating (30 °C). Stirring was continued overnight at 60–65 °C. After D_2O (2 mL) was added, the product was extracted with ether (3 × 30 mL), and the extracts were washed with water (2 × 30 mL) and dried ($MgSO_4$). The crude product (0.15 g, 86%), obtained after removal of the solvent, was purified by chromatography over Al_2O_3 (activity III) using 4:1 pentane-ether as eluent. The recovered product (0.11 g, 68%) was 98% pure by GLC. It contained 92.5% d_2 by mass spectrometry.

1-Iodoadamantane-*2,2-d$_2$*.[14] A mixture of 1-hydroxyadamantane-*2,2-d$_2$* (0.250 g, 16.2 mmol) and HI (5 mL, 47%) was heated with stirring to 50 °C for 3 h. The product was extracted with pentane, and the pentane solution was washed with water and dried over $MgSO_4$. Removal of solvent yielded 0.36 g (84%) of 95% pure 1-iodo derivative.

1-Adamantyl-*2,2-d$_2$* Tosylate.[15] This derivative is very sensitive to humidity and its synthesis was performed in a drybox using carefully dried reagents.

1-Iodoadamantane-*2,2-d$_2$* (0.25 g, 0.95 mmol) and silver tosylate (0.29 g, 1.26 mmol) in 20 mL of hexane were stirred for 36 h at room temperature under exclusion of light. The precipitate was filtered off and washed with hexane and the combined filtrates were evaporated. After recrystallization from hexane 0.25 g (82%) of the pure tosylate was obtained.

1,3-Dibromoadamantane.[16] Adamantane (13.6 g, 0.1 mol) was added in small portions to a stirred mixture of dry bromine (50 mL), aluminum tribromide (0.11 g), and boron tribromide (2.4 mL, 0.026 mol). The reaction was performed under exclusion of moisture in an atmosphere of dry nitrogen. Subsequently the mixture was refluxed for 2 h and the stirring continued for an additional 1 h and then the mixture poured on ~300 mL of crushed ice. Carbon tetrachloride (400 mL) was added, and the organic layer was separated and washed repeatedly with a saturated solution of $NaHSO_3$ (3 × 80 mL) in order to remove excess of bromine. The original aqueous layer was extracted with CCl_4, and the combined extracts were washed successively with a 5% solution of $NaHCO_3$ and water and then dried over $MgSO_4$. The crude yellow dibromide obtained after removal of solvent was recrystallized from methanol, yield 23.7 g (80.6%) of a 96% (GLC) pure product.

1-Bromoadamantane-*3-d$_1$*.[17] A solution of tri-*n*-butyltin chloride (0.2 g, 0.61 mmol) in 20 mL of dry ether was added with stirring to a suspension of $LiAlD_4$ (0.36 g, 8.3 mmol) in dry ether (20 mL). After 10 min a solution of 1,3-dibromoadamantane (0.9 g, 3.06 mmol) in ether (30 mL) was added and the mixture stirred under reflux. The progress of the reaction was monitored by GLC (DEGS column, 150 °C). The reaction was complete in 2 h. After decomposition with water and the usual workup, the ethereal extract was washed with a saturated solution of NaCl (3 × 30 mL) and dried ($MgSO_4$). The crude product was purified by column chromatography over silica gel-charcoal (5:1) with pentane-ether (98:2) as eluent. The higher frac-

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

compd[a]	solvent[b]	temp, °C	$k_H{}^{c,d} \times 10^4$, s^{-1}	$k(\mathrm{H/D})^{c,d}$	$k(\mathrm{H/D})_{\mathrm{cor}}{}^{e}$
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/L. [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 25 °C, ref 15.

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

compd[b]	solvent[c]	temp, °C	$k_H{}^{d,e} \times 10^4$, s^{-1}	$k(\mathrm{H/D})^{d,e}$	$k(\mathrm{H/D})_{\mathrm{cor}}{}^{f}$
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. Am. Chem. Soc.*, **92,** 5977 (1970). [b] 0.002-0.003 mol/L. [c] T = 2,2,2-trifluoroethanol (w/w). [d] Mean values from four measurements. [e] Errors are standard errors. [f] Corrected to 100% deuteration.

tions which do not contain adamantane were combined and evaporated. In this manner 0.3 g (47%) of a 96% pure product was obtained which contained 0.88 atoms D per molecule.

1-Adamantyl-*3-d*$_1$ Tosylate.[15] The tosylate was prepared from the bromide by a procedure analogous to that described for the conversion of 1-iodoadamantane. From 0.22 g (1.02 mmol) of the bromide and 0.324 g of silver tosylate, 0.228 g (89%) of the pure tosylate was obtained.

1,3,5-Tribromoadamantane.[18] Adamantane (10 g, 7.35 mmol) was slowly added to a stirred solution of aluminum bromide (3.0 g) in dry bromine (40 mL). The mixture was refluxed for 4 h, then cooled and worked up in the same manner as described for 1,3-dibromoadamantane. The crude, brown product was recrystallized from methanol, yield 12.8 g of a mixture of bromides which contained 1,3,5-tribromo- (80%), 1,3,5-tetrabromo- (15%), and 1,3-dibromoadamantane (2%). This mixture was used without purification for the next step.

1,3,5,7-Tetrabromoadamantane.[13] The crude tribromoadamantane from the previous preparation (2.0 g) was heated in a sealed ampule with $AlBr_3$ (1.2 g) and 5 mL of bromine for 3 h at 150 °C. After cooling, the content of the ampule was poured on crushed ice (50 g) and extracted with CCl_4 (150 mL) and excess of bromine in the organic layer was destroyed by washing with a cold saturated solution of $NaHSO_3$. The aqueous layer was extracted once more, and the combined extracts were washed with a solution of $NaHCO_3$ and water. After drying with $MgSO_4$, the solvent was evaporated. The residue (2.5 g) containing 25% of the unreacted tribromide was brominated again as described above and the product purified by chromatography of its solution in pentane over a mixture of silica gel and charcoal (10:1). In this manner 1.9 g (75%) of 98% pure 1,3,5,7-tetrabromoadamantane was obtained.

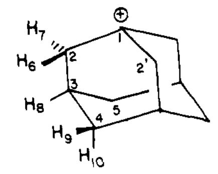
Adamantane-*1,3,5,7-d*$_4$.[17] To a stirred suspension of $LiAlD_4$ (0.22 g, 4.9 mmol) in dry ether (20 mL), in an atmosphere of nitrogen, tri-*n*-butyltin chloride (0.72 g) in ether (4 mL) was added. After 15 min 1.2 g (2.44 mmol) of 1,3,5,7-tetrabromoadamantane was added in one portion. The mixture was kept under reflux and the progress of the reaction was monitored by GLC (QF-1 column, 110 °C). After 34 h the reduction was complete and excess deuteride was destroyed with water. The usual workup of the organic layer afforded 0.2 g (70%) of 98% pure product containing 94% d_4 and 4% d_3 adamantane.

1-Bromoadamantane-*3,5,7-d*$_3$. Tetradeuterioadamantane (0.204 g, 1.5 mmol) in 3 mL of dry bromine was stirred at room temperature for 1 h and then worked up as described for the dibromo derivative.[16] The crude product was purified by column chromatography over silica gel with pentane as eluent, yield 0.24 g (73%) of a 98% pure product containing 94.5% d_3 and 4.2% d_2 molecules.

1-Adamantyl-*3,5,7-d*$_3$ Tosylate.[17] From 0.24 g (1.1 mmol) of 1-bromoadamantane-*3,5,7-d*$_3$ and 0.34 g (1.3 mmol) of silver tosylate using the procedure described above 0.27 g (84%) of the pure tosylate was obtained.

Theoretical Procedures

All calculations were performed using the STO-3G basis set[19] and the GAUSSIAN 77 package of programs.[20] Adamantane was given standard model geometry[21] and C-H bond lengths were optimized to yield methine CH bond lengths of 1.090 Å and methylene CH bond lengths of 1.087 Å. The optimization of 1-adamantyl cation was more extensive. One cyclohexane ring was given standard model geometry except for the methine hydrogens. The remainder of the molecule was allowed to reorganize its structure, while maintaining overall C_{3v} symmetry. The final structure is shown in Table III and **4A**. Energies for both adamantane and 1-adamantyl cation as well as energies for 1-substituted adamantanes and 3-substituted 1-adamantyl cations are listed in Table IV.



4A

Table III. STO-3G Optimized Geometry[a] of 1-Adamantyl Cation

bond lengths[b]		bond angles[c]	
rC_1C_2	1.497	$\angle C_2C_1C_2'$	117.5
rC_2C_3	1.590	$\angle C_1C_2C_3$	98.3
rC_3C_4, rC_3C_5	1.540[d]	$\angle C_2C_3C_4$, $\angle C_2C_3C_5$	109.9
rC_2H_6, rC_2H_7	1.088	$\angle C_1C_2H_9$, $\angle C_1C_2H_6$	112.8
rC_3H_8	1.091	$\angle C_2C_3H_8$	106.4
rC_4H_9, rC_4H_{10}	1.090[d]	$\angle H_8C_3C_4$, $\angle H_8C_3C_5$	110.6
		$\angle H_6C_2H_7$	111.0
		$\angle H_6C_2C_3$, $\angle H_7C_2C_3$	110.6
		$\angle H_9C_4H_{10}$	109.47[d]
		$\angle C_4C_3C_5$	109.47[d]

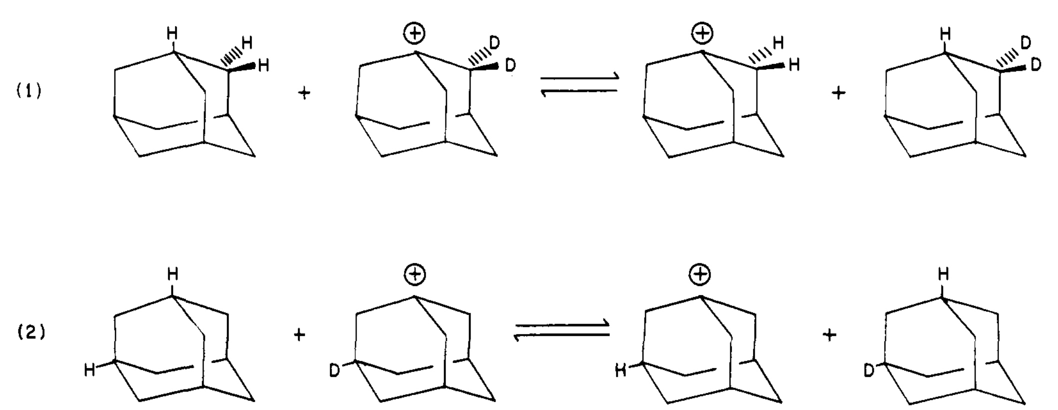
[a] Overall C_{3v} symmetry maintained; numbering based on **4A**. [b] In ångstroms. [c] In degrees. [d] Held fixed at standard model.

Table IV. STO-3G Energies (hartrees) of 3-Substituted 1-Adamantyl Cations and 1-Substituted Adamantanes[a]

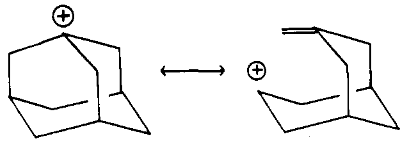
substituent	1-adamantyl cation	adamantane
H	−382.694 40	−383.513 93
CN	−473.221 84	−474.060 03
NH_2	−437.004 40	−437.824 58
CH_3	−421.276 43	−422.083 96

[a] Standard molecular geometries employed for substituents; skeleton optimized as in text.

Scheme II



Some discussion of the structure of the 1-adamantyl cation is warranted at this point. It is apparent that there has been considerable distortion of the adamantane skeleton as the cationic center attempts to achieve planarity. Bond angles at the carbocation center have opened to 117.5°. A previous extended Hückel theory calculation[22] gave this angle is 117.0°. The energy gained upon this flattening, relative to a nonoptimized, pyramidal 1-adamantyl cation, is some 28.6 kcal/mol. There have also been some major changes in bond lengths. Bonds to the carbocation center have shortened by 0.043 Å and the β-γ carbon-carbon bonds have lengthened by 0.050 Å. One explanation can be afforded by resonance forms such as[44a] **4A** and **4B**. We will focus our attention on such a phenomenon when we discuss γ-deuterium isotope effects in the context of stabilization of the cationic center.

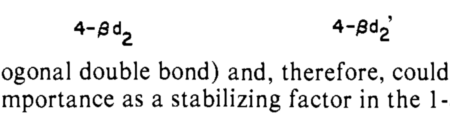


4A 4B

Theoretical isotope effects for the equilibrium reactions (1) and (2) are calculated as detailed previously.[7] (See Scheme II.) These are tabulated in Table V.

Discussion of Results

β Effects. The absence of any measurable β effects in the solvolysis of **1** is indicative of a compensating interaction of two opposite effects, a hyperconjugative effect [$k(\mathrm{H/D}) > 1$] of two deuterium atoms occupying at C_2 a position with dihedral angles of 60° with respect to the p orbital and a conformationally independent inductive effect [$k(\mathrm{H/D}) < 1$] caused by the slightly greater electron-releasing power of deuterium relative to hydrogen.[3] By taking 0.985 as the value for the inductive effect of one deuterium atom in the β position,[23] the hyperconjugative effect which will bring the total effect to unity is 1/0.985 = 1.015. For comparison the corresponding hyperconjugative effect for the 60° C–D bond in the *tert*-butyl cation is 1.04/0.985 = 1.056. The simplest way to accommodate the absence of a β effect in the 1-adamantyl cation would be to resort to the valence bond description of hyperconjugation. The canonical structure **4-$\beta d_2'$** violates Bredt's rule (yields an orthogonal double bond) and, therefore, could be of only minor importance as a stabilizing factor in the 1-adamantyl cation. Additionally one might rationalize the experimental β isotope effect by assuming much more extensive charge delocalization in the *tert*-adamantyl cation relative to *tert*-butyl.



4-βd_2 4-$\beta d_2'$

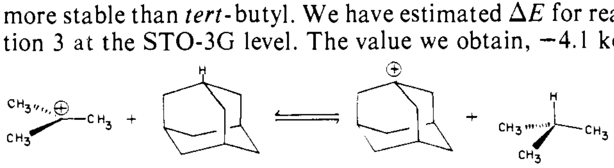
The calculated (STO-3G basis set) β-deuterium equilibrium isotope effect of 1.001 is in agreement with the experimentally observed kinetic effect of 1.000. Indeed, structures such as **4-$\beta d_2'$** would indicate substantial lengthening of the βC–D(H) bond relative to neutral adamantane. The calculations show no such lengthening. In order to express this delocalization, manifested in the small β effects, in a more convenient way we should make use of the fact that these effects are linearly correlated to methyl group rate effects.[3,24] Since, on the other hand, methyl group rate effects are a reliable measure of the electron deficiency of secondary carbonium ions,[25] any β effect $k(\mathrm{H/D})_\theta$ in systems of known conformation has formally its "methyl group equivalent." This can be shown by comparing eq 1 and 2.

$$\log k(\mathrm{CH_3/H}) = 49.407 \log k(\mathrm{CH_3/CD_3}) \tag{1}$$

$$\log k(\mathrm{CH_3/CD_3}) = [\log k(\mathrm{H/D})_\theta + 0.006\,56/0.666 \cos^2\theta] - 0.0195 \tag{2}$$

Equation 1 is the Servis-Borčić-Sunko (SBS) correlation[24] while eq 2 is derived from the expression used for calculating the angular relationship of β effects.[3] It is evident that in secondary systems the methyl group equivalent effect will be identical with the methyl group rate effect determined in this case indirectly from β-deuterium isotope effects measured on secondary derivatives. However, this approach should in principle be also applicable to tertiary systems such as 1-adamantyl where direct measurement of the electron deficiency of the tertiary carbocation by methyl group rate effects is not possible.

By substituting the observed value for $k(\mathrm{H/D})_{60\,°\mathrm{C}} = 1$ into eq 1, a methyl group equivalent effect of $10^{0.983}$ or $\Delta\Delta G^{\ddagger}(25\ °\mathrm{C}) = 1.34$ kcal/mol is obtained. The corresponding value for *tert*-butyl taken from the $\mathrm{CH_3/CD_3}$ isotope effect of 1.323 or the $\mathrm{CH_3/H}$ rate effect of 10^6 is 8.2 kcal/mol.[3] By this criterion the *tert*-adamantyl cation is by 8.2 − 1.34 = 6.86 kcal/mol more stable than *tert*-butyl. We have estimated ΔE for reaction 3 at the STO-3G level. The value we obtain, −4.1 kcal mol^{-1}, is smaller than the 10.8 kcal mol^{-1} difference in bromide affinities obtained by Beauchamp using ion cyclotron resonance spectroscopy.[8a] The discrepancy between theory and experiment may be due to the simplicity of the theoretical model, or possibly to errors inherent in the nonequilibrium experimental techniques. Note that the theoretical calculations refer to the energetics of hydride transfer, whereas the ex-



(3)

Table V. Theoretical Isotope Effects and Force Constants

	k_{CD}, mdyn/Å		
	adamantane	1-adamantyl cation	$K_{eq}(k_H/k_D)^a$
reaction 1	7.258	7.266	1.001 (1.000)
reaction 2	7.287	7.411	1.014 (1.041)

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

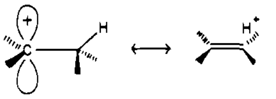
perimental measurements pertain to bromide exchange. However, available gas phase thermochemical data[8] on the relative hydride and bromide affinities of related systems indicate that the two sets of data correlate linearly.

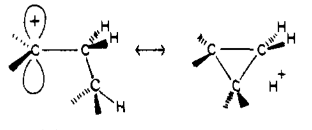
Kinetic data from solvolyses of 1-adamantyl and *tert*-butyl derivatives do not support the conclusion that the *tert*-adamantyl cation is the more stable (e.g., *tert*-butyl chloride is 10^3 times more reactive than 1-adamantyl chloride). This, however, does not necessarily invalidate the arguments based on the present results because the cage structure of the 1-adamantyl cation does not permit solvent participation from the rear, and, therefore, is not as effectively stablized by the medium as is the *tert*-butyl cation. Inhibition of solvation has already been ascribed as the cause behind the well-known Baker-Nathan ordering of carbocation stabilities observed in solution. It should further be noted that β secondary deuterium isotope effects appear to be much less sensitive to the solvent than do relative rates.

γ Effects.[48] Hyperconjugation as a through-space interaction is critically dependent on the distance and orientation of interacting orbitals.[23,27] It is generally accepted that such interactions are more pronounced in excited species (carbocations, carbanions, and radicals) than in the ground state of molecules.[28]

The perturbation theory offers a satisfactory description of hyperconjugation,[27] and recent work from our laboratories demonstrated how this approach can be used to define the angular dependence of hyperconjugative deuterium isotope effects in carbonium ion reactions.[3]

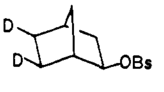
Within the framework of a hyperconjugative picture, there are two obvious modes in which γ-deuterium substitution could produce an isotope effect. In the same sense that a β-substituted cation induces a force constant change in the C-H(D) bond participating in hyperconjugative stabilization, a γ-substituted cation will also cause a change in C-H force constants due to homohyperconjugative stabilization.





From quantum mechanical considerations we expect to observe a rapid fall-off of through-space interactions at distances greater than 2.5 Å or more than three carbon atoms apart. Therefore, hyperconjugation is usually looked upon as a β or 1,2 effect. However, in systems where rotations around carbon-carbon single bonds are restricted and thus the adverse entropy factor eliminated, interactions from the γ position may also be expected. Indeed, these homohyperconjugative interactions have been observed in ESR spectra of radical anions where they induce large hyperfine splittings.[29] Also, changes in ionization potentials in some methyl-substituted dienes were attributed to this through-space 1,3 interaction between a π orbital and the pseudo-π orbital of a methyl group.[30] In carbocation chemistry very few examples of this homohyperconjugative interaction can be found and these are mostly confined to isotope-effect.[31-34] Only in some specific cases were normal isotope effects observed, but homohyperconjugation was never specifically invoked as the cause of any γ effects;[3,5] on the contrary, inverse effects [k(H/D) < 1] were considered as the normal kinetic response to deuteration at the γ position.[35]

The most dramatic example of a normal γ-deuterium isotope effect was the 10% rate retardation observed in the solvolysis of deuterated *exo*-2-norbornyl derivatives **5**-**7**.[32,33]



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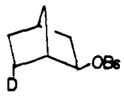

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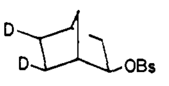
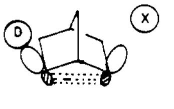


7

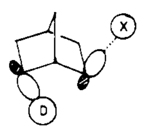
(k_H / k_D) 1.09 1.11 1.09

These effects, which were absent in the corresponding endo isomers, were rationalized in terms of force field changes at C_6 due to a β,γ-carbon-carbon σ bond participation leading to the nonclassical cation **8**.[5,36] Here the main argument against a through-space "backlobe effect" of the C_6-H(D) bond[37] was the identical magnitude of the effect observed in the endo derivative where such "backlobe" interaction is not present.

8

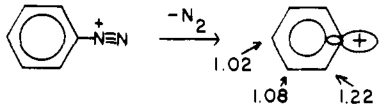


exo-6d



endo-6d

A more recent example of a γ effect which is even more relevant to the present studies can be found in the work of Swain et al.[34] on the mechanism of dediazonization of phenyldiazonium ions. The large normal [k(H/D) > 1] isotope effects from the β, γ, and δ position were taken as the supporting evidence for the intermediacy of a phenyl cation **9**.[39] The magnitude of these effects is linked to the unusual sp^2 geometry of the vacant orbital in **9** which is orthogonal to the π system and thus acts as a very efficient electron sink withdrawing electrons not only from the β C-H(D) bond(s) but also from γ and δ positions. The direction of these effects [k(H/D) > 1] affirms their hyperconjugative origin.



9

Using the homohyperconjugative model as the basis for the γ effects observed in the solvolysis of **2** and **3** the following molecular orbital description of this interaction can be advanced. The pseudo-π orbital of the C_3-H(D) bond has the right orientation for interaction with the backlobe of the empty p orbital at C_1. Owing to the favorable structure of the adamantyl molecule this interaction occurs unhindered by solvent molecules through the empty space inside the adamantyl skeleton cage. Furthermore, the symmetry of adamantane provides for a possible interaction of all three of these orbitals from the three γ positions forming a pseudo-Walsh-type configuration with cyclopropane-like symmetry (Figure 1).

If we allow for a simultaneous interaction of all three pseudo-π orbitals, then, because of symmetry constraints, the p function can interact only with the subjacent level of π orbitals (π_1), which may explain the smallness of the observed effects. If, on the other hand, stabilization occurs with one pseudo-π orbital at the time, then the largest effect will be observed with the monodeuterated substrate, with each suc-

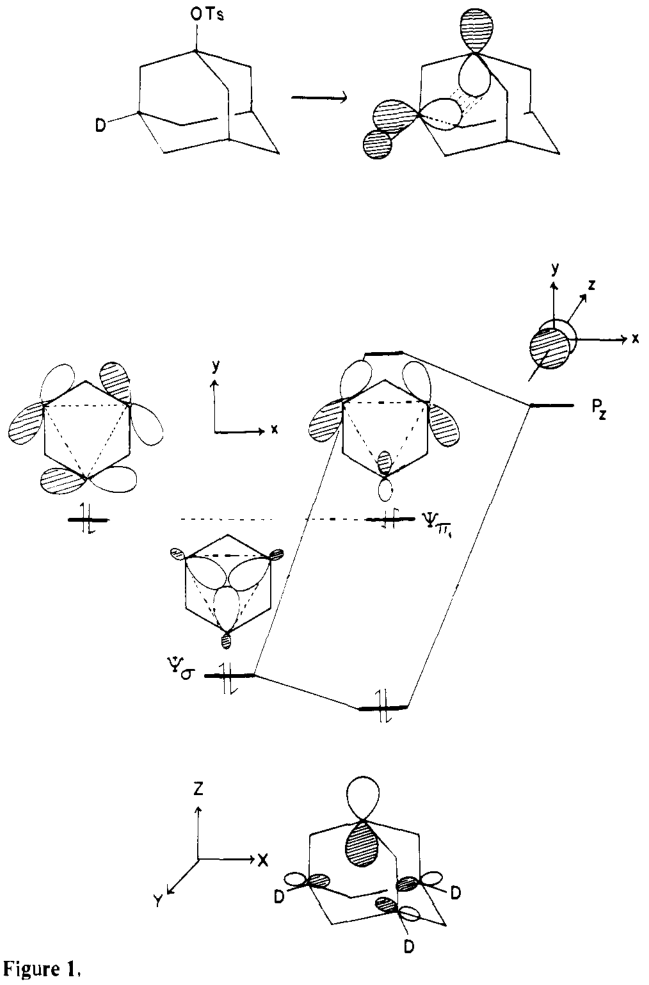
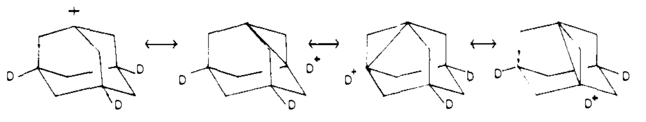
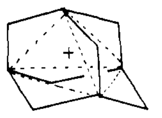


Figure 1.

cessive deuteration lowering the effect. The presently available data do not allow a distinction between these two alternatives.[39] A satisfactory description of the effects is also given by the valence bond picture of the contributing canonical structures.



Since by using the three pseudo-π orbitals of the bridgehead C-H(D) bonds we are, in fact, constructing a Hückel $4q + 2$ system of laticyclic topology,[40] this kind of stabilization implies delocalization of the positive charge over the four bridged carobns of a hexahomotetrahedranyl cation.[41] From extended Hückel calculations this delocalization amounts to a stabilization energy of 1.2 kcal/mol.[22]



In our opinion, it is, however, the positive sign of these effects [$k(\mathrm{H/D}) > 1$] which makes this result particularly valuable since it gives us an idea about the hitherto obscure origin of γ isotope effects. Hereby γ effects are related to β effects in the same way as homoconjugation is related to conjugation and therefore can adequately be rationalized as being due to homohyperconjugation. One additional degree of freedom, the rotation around the carbon-carbon σ bond, and the greater distance from the positive center are, we believe, the main reasons in restricting these effects to rigid (poly)cyclic systems which for a maximum effect should be devoid of other means of stabilization. Because of the similarity of the pseudo-π orbitals of carbon-hydrogen bonds with the π orbitals of a double bond, we predict that γ effects greater than unity will show up in solvolyses of deuterated saturated analogues of compounds which manifest a pronounced anchimeric assistance by neighboring double bonds.[42] In strict analogy to hyperconjugation and neighboring hydrogen participation, the homohyperconjugative isotope effects should be larger in systems which allow for a relaxation of the molecule by participation (such as the *exo*-2-norbornyl[31,32]) than in systems where relaxation by rearrangement is not possible (such as 1-adamantyl).

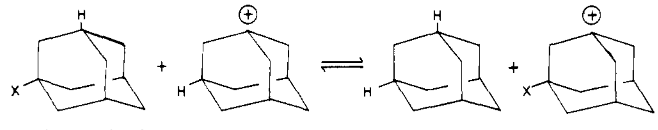
Table VI. Stabilization Energies for 3-Substituted 1-Adamantyl Cations

substituent	energy, kcal/mol
CH_3	1.23
NH_2	0.41
CN	−11.71

Table VII. Potential Constants (kcal/mol) for C-N Rotation

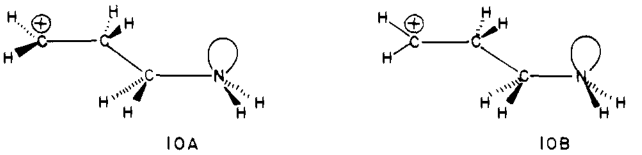
molecule	V_1	V_2	V_3
perpendicular cation (**10A**)	2.69	4.19	−2.60
bisected cation (**10B**)	5.76	2.15	−2.67
neutral	0.66	0.03	−2.95

The other possible means for rationalizing the presence of a γ isotope effect lies again in hyperconjugation. Carbon-carbon hyperconjugation or vertical stabilization is usually considered as being more important than carbon-hydrogen hyperconjugation.[43] In the adamantyl cation it would, however, imply contribution of structure **4B,** which has been suggested to be unimportant, based on the fact that the rate of solvolysis of 1-bromoadamantane decreases upon introduction of a methyl group at the γ position.[44] This is at odds with the calculated structure of 1-adamantyl cation. We have, therefore, calculated the stabilization energy for methyl, cyano, and amino substitution at the γ carbon using the previously determined equilibrium geometries. The results are listed in Table VI.



As expected, the cyano group is strongly destabilizing while the methyl and amino groups are stabilizing. These results suggest positive charge development at the γ carbon. A previous study on substituted *n*-propyl cations with similar geometries showed an analogous trend.[45]

One could argue that the observed effects are long-range inductive effects. To ascertain whether these effects were inductive or resonance in nature, we undertook a further study. Using the 3-amino-1-propyl cation as a model, we calculated the C-N rotational potentials for the forms **10A** and **10B** as well as for the corresponding neutral molecule.[46] Results are listed in Table VII. We first note that V_3 is negative in all three molecules, indicating a preference for the staggered form (θ = 60, 180°) over eclipsed conformers (θ = 0, 120°). This value is essentially the same in all three systems. As stated in a previous study,[46] the positive sign of the V_2 term in the rotational barrier of amines indicates a stabilizing mechanism involving



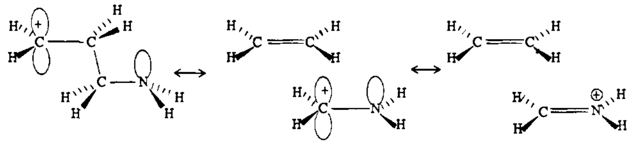
10A 10B

Table VIII. STO-3G Energies (hartrees) and Rotational Barriers (kcal/mol) between Perpendicular and Cis Cation at Several CC-N: Dihedral Angles

	STO-3G energies		barrier
θ, deg	**10A**	**10B**	**10A-10B**
0	−170.300 25	−170.295 45	3.01
60	−170.298 30	−170.294 88	2.15
120	−170.292 03	−170.286 03	3.77
180	−170.300 10	−170.290 56	5.99

donation of n electrons into an adjacent 2p orbital, this being favored in the cis ($\theta = 0^\circ$) or trans ($\theta = 180^\circ$) periplanar forms over the perpendicular form ($\theta = 90^\circ$). It is clear from the difference in magnitude of the V_2 terms in the perpendicular and bisected cations (**10A** and **10B**, respectively) that the preference for such charge donation by the amino group is more pronounced in the former cation.

We can rationalize this difference based on the ability of the two isomeric cations to undergo carbon-carbon hyperconjugative stabilization. In the case of the perpendicular cation, we can draw hyperconjugative resonance forms such as **10A**, **$10A_1$**, and **$10A_2$**, where forms such as **$10A_1$** do possess an empty 2p orbital suitably disposed for overlap with the lone pair on nitrogen, as in **$10A_2$**. In the case of the bisected cation, **10B**, the empty 2p orbital on carbon is orthogonal to the carbon-carbon single bond and cannot participate in such hyperconjugative resonance forms as above. The small V_2 term we do see in the bisected cation can be accounted for by inductive charge removal from the carbon 2p orbital adjacent to nitrogen, by the carbenium ion centers. The V_1 term has been attributed[46] to minimization of the overall dipole of the molecule. It is also possible that, since we are dealing with a pyramidal nitrogen, overlap would be better with the backlobe of the lone pair which is directed toward the carbon-carbon single bond. This accounts for the sign of the V_1 term which favors the front lobe of the lone pair being 180° from the carbon-carbon single bond. If there is charge donation from the nitrogen to the carbon 2p orbital in the perpendicular cation, upon change in the CCN:dihedral angle we should see changes in the 2p population[46] on N (1.7069, 1.7213, and 1.6923 for θ = 0, 90, and 180°, respectively) and in the π (C-N) overlap populations (0.0124, 0.0019, and 0.0163 for θ = 0, 90, and 180°, respectively). One can also see from the difference in energies between the perpendicular and bisected cation, **10A** and **10B**, in Table VIII that, for all C-N rotamers, the perpendicular cation is the favored system, this being the form which can most benefit from carbon-carbon hyperconjugative stabilization.



10A $10A_1$ $10A_2$

All of the above leads one to conclude that there is substantial carbon-carbon hyperconjugative stabilization in this model system, structurally analogous to the 3-amino-1-adamantyl cation. The bond-length changes calculated for the 1-adamantyl cation, together with the stabilization energies for the cation, lead one to believe that this system as well shows carbon-carbon hyperconjugative stabilization of the cationic center. There still lies the discrepancy between the predicted stabilizing influence of γ-methyl group on the 1-adamantyl cation and the observed solvolytic rate decrease. As has been previously mentioned, simple inductive arguments are not satisfactory in explaining the solvolysis results. It should be noted that the theoretical calculations portray free carbocations whereas in solution the incipient ion center may be incompletely formed and as such its geometry and charge distribution may be significantly different. Gas-phase experiments would certainly serve to clarify the situation.

The experimentally observed γ isotope effect may be explained by suggesting that resonance forms which invoke carbon-carbon hyperconjugation cause major changes in hybridization at the γ position. These hybridization changes will in turn change bending and stretching force constants for hydrogen (or deuterium) attached to the γ carbon. These changes would be like those experienced by hydrogen attached to a center undergoing solvolysis, where similar isotope effects (in this case α secondary) have been noted.[47]

Conclusion

In this study we have examined the stabilization of the 1-adamantyl cation via several long-range interactions. We find that, both theoretically and experimentally, the adamantyl cation shows little stabilization from carbon-hydrogen hyperconjugation. This is noted in the absence of β-deuterium isotope effects and in the lack of bond lengthening in the β C-H bond in the cation. We have also investigated the possibility of other long-range stabilization mechanisms such as homohyperconjugation and carbon-carbon hyperconjugation. Both arguments seem valid and further experiment is warranted to determine which of these two mechanisms is the more important. We are presently addressing ourselves to this problem both theoretically and experimentally.

Acknowledgments. This work was supported in part by the Research Council of Croatia, the National Institutes of Health (NIH PL-480 Grant 02-011-1), the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. S.H-S. wishes to thank Dr. Z. Majerski for his interest and kind help in some portion of the experimental work.

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(48) In the course of an exchange of information regarding this work the present authors learned from Professor P. v. R. Schleyer that approximately 10 years ago D. L. K. M. Lam working in his group found large effects in the solvolysis of both 3-deuterio-1-adamantyl and 4-deuterio-1-bicyclo[2.2.2]octyl tosylates. However, "the accuracy of the measurements . . . were not sufficiently high to justify publication."

Conformational Effects upon the Charge-Transfer Transitions of the Hexamethylbenzene–Tetracyanoethylene Crystalline Complex

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Abstract: Piezomodulated and direct reflection spectra from the (010) face of the hexamethylbenzene (HMB)–tetracyanoethylene (TCNE) electron donor–acceptor single crystal were measured from 10 000 to 45 000 cm^{-1} at 300 K. High-resolution spectra were obtained for the charge-transfer transition polarization direction over the visible region at 5 K. Results are compared to AIM-Xα-SCF calculations on the complex. Evidence for three separate charge-transfer transitions which may be associated with three specific triads of molecules is presented.

I. Introduction

A previous study[1] from this laboratory has shown that the interpretation and assignments of charge-transfer (CT) transitions in electron donor–acceptor (EDA) complexes can be greatly enhanced by the study of those complexes which display symmetry in the crystal. The case first considered, that of the EDA complex of anthracene with tetracyano-*p*-quinodimethane ($TCNQ^0$),[1] showed that, consistent with symmetry considerations, the lowest energy CT transition originated from the penultimately filled molecular orbital of anthracene and terminated with the lowest unoccupied molecular orbital (LUMO) of the $TCNQ^0$. The transition from the highest occupied molecular orbital (HOMO) of anthracene to the LUMO was found to be forbidden.

Of particular interest in the study of aπ–bπ EDA complexes have been the complexes of methyl-substituted benzenes with tetracyanoethylene (TCNE).[2,3] An interesting finding in earlier papers is the evidence for the presence of two charge-transfer bands in many of these complexes. This was rationalized by Voigt and Reid[3] and Orgel[4] as due to splitting of the doubly degenerate (e_g) highest occupied molecular orbitals of appropriately substituted benzenes (C_{3v} symmetry or higher) which is caused by the different interactions of the substituents and the degenerate orbitals. However, Voigt and Reid pointed out that another, albeit more subtle, effect could be induced by "geometric" perturbation where the C=C bond of the TCNE would have the plane containing the bond parallel to the plane of the ring but with the bond axis oriented with its projection on the ring plane either intersecting atoms or bisecting bonds. The energetics of the CT interaction would be

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