by volume and smaller proportionate quantities were used for crude product IIa). Products were obtained only from the *n*-pentane (first) and methanol (last) eluants. Final yields: aromatic adamantanecarbinyl products (**4a,b**), IIa, 0%, IIb, 96–97%; aminated aromatic products (**5a,b**), IIa, 0–9%, IIb, 0–3%. Aniline and *p*-toluidine were identified by comparison to authentic materials.

Characterization of 4a: mp 42–43 °C (lit. mp 43–44 °C,[30] mp 42–44 °C[31]); IR (melt) 3050, 2920, 2850, 1600, 1500, 1455, 1355, 1350, 1320, 1310, 1235, 780, 705, 615; NMR ($CDCl_3$) δ 7.3–7.0 (m, 5), 2.4 (s, 2), 2.0–1.6 (m, 15); mass spectrum, *m/e* (relative intensity) 226 (8), 211 (3), 167 (4), 155 (6), 141 (6), 135 (100), 115 (6), 107 (8), 93 (16), 91 (20), 79 (19), 67 (10), 55 (8), 44 (14), 41 (17).

Anal. Calcd for $C_{17}H_{22}$: C, 90.20; H, 9.80. Found: C, 89.90; H, 10.10.

The NMR spectrum was essentially identical with that of authentic material.[32]

Characterization of 4b: NMR ($CDCl_3$) δ 7.2–6.8 (4), 2.3–2.1 (5), 2.1–0.8 (15); mass spectrum, *m/e* (relative intensity) 240 (8), 225 (6), 181 (6), 169 (7), 135 (100), 115 (6), 107 (9), 93 (9), 90 (14), 81 (8), 79 (8), 77 (12), 69 (8), 67 (11), 57 (9), 55 (13), 44 (22), 41 (23).

Anal. Calcd for $C_{18}H_{24}$: C, 89.92; H, 10.08. Found: C, 89.93; H, 10.05.

(30) Osawa, E.; Majerski, Z.; Schleyer, P. v. R. *J. Org. Chem.* **1971**, *36*, 205.
(31) Stepanov, F. N.; Dikolenko, E. I.; Danilenko, G. I. *J. Org. Chem. USSR (Engl. Transl.)* **1966**, *2*, 640.
(32) Majerski, Z., personal communication.

Competitive Alkylations of Aromatic Substrates by 3–$AlCl_3$. Anhydrous aluminum chloride (0.49 g, 3.68 × 10^{-3} mol) was quickly added to a solution of **3** (0.30 g, 1.57 × 10^{-3} mol) dissolved in a 1:1 mixture of toluene–benzene, 1.233 mol each) preheated to 45 °C with exclusion of moisture. The temperature was quickly raised to 80 °C and maintained there for 1.5 h. The general isolation procedure was followed. Yield ratios were determined by GLC analysis (Table II).

Alternatively, **3** dissolved in an appropriate mixture of toluene–benzene (for 1:1, 0.513 mol each; for 1:10, 0.10:1.00 mol, respectively) was added during 1.5 h to a homogeneous solution of anhydrous aluminum chloride (0.72 g, 2.25 × 10^{-3} mol) in a mixture of toluene–benzene (for 1:1, 1.37 mol each; for 1:10, 0.25:2.50 mol, respectively) preheated to 67 °C. Moisture was excluded. The temperature was quickly raised to 80 °C and then maintained there for 1.5 h. The general isolation procedure was followed. Yield ratios were determined by GLC analysis (Table III).

Reactions similar to those described for **3** were also run with either **9** or **12**. The appropriate procedure and data are presented in Table I.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank Dr. Zdenko Majerski for a sample of 1-benzyladamantane and Dr. Massimo Bezoari for helpful comments.

Registry No. 3, 63534-35-0; **4a**, 7131-11-5; **4b**, 76429-91-9; **5a**, 62-53-3; **5b**, 106-49-0; **6**, 14504-80-4; **7**, 768-95-6; **9**, 27011-47-8; **12**, 770-70-7; **32**, 828-51-3; $AlCl_3$, 7446-70-0.

Isotopic Perturbation of the Carbon-13 Nuclear Magnetic Resonance Spectrum of a Pyramidal Dication

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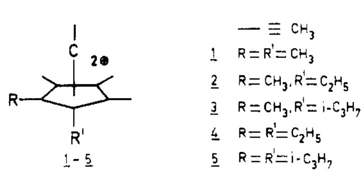
Received July 14, 1980

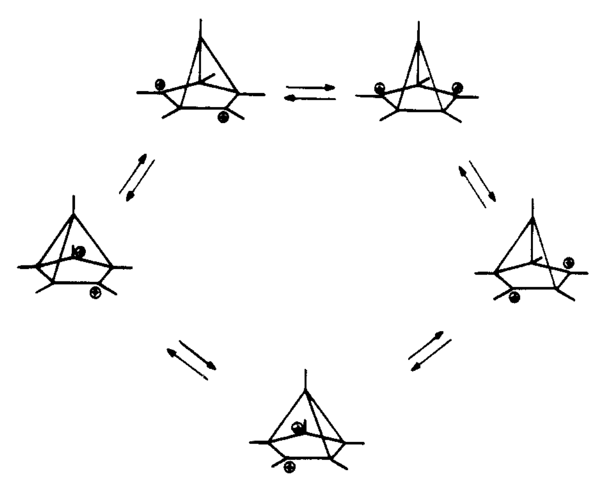
The recently developed method of deuterium-induced perturbation of ^{13}C NMR chemical shifts, which allows distinction between classical and nonclassical cations, has been applied to a pyramidal dication (**1**). The results obtained are in agreement with a symmetrical structure for this species.

We recently reported the synthesis and chemical behavior of $(CCH_3)_6^{2+}$ (**1**)[1] as well as of some derivatives of this class of ions with general formulas $[(CCH_3)_5CR]^{2+}$ (**2**, **3**) and $[(CCH_3)_4C_2R_2]^{2+}$ (**4**, **5**).[2,3]



There are several indications that dication **1** has a nonclassical structure (a single energy minimum), and

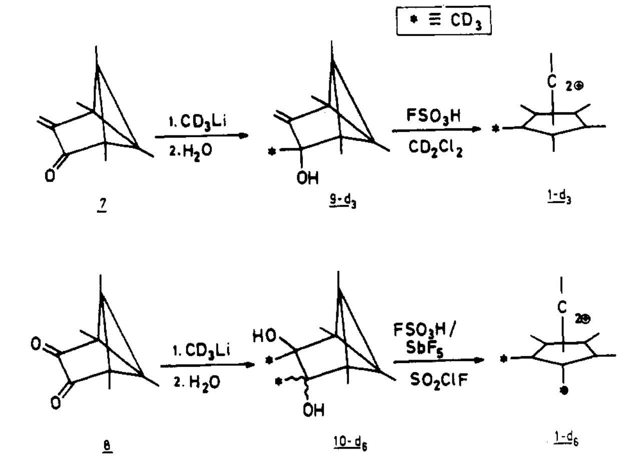
Scheme I



these include the inconsistency of the values of the ^{13}C NMR chemical shifts calculated by using Olah's rule[4,5] with

(1) (a) Hogeveen, H.; Kwant, P. W. *Tetrahedron Lett.* **1973**, 1665; (b) *J. Am. Chem. Soc.* **1974**, *96*, 2208; (c) *Acc. Chem. Res.* **1975**, *8*, 413.
(2) (a) Giordano, C.; Heldeweg, R. F.; Hogeveen, H. *J. Am. Chem. Soc.* **1977**, *99*, 5181. (b) Heldeweg, R. F. Ph.D. Thesis, University of Groningen, 1977.
(3) For reasons of simplicity we have used a representation of the pyramidal dications in the way indicated (the similarity with organometallic chemistry is clear). The positions of the substituents may be indicated as basal (at the five-membered ring) and apical (at the top).

Scheme II



the experimental ones, the ^{13}C NMR chemical shift of the apical methine carbon atom, and low-temperature ^1H NMR measurements. However, the possibility of a fivefold-degenerate rearrangement, in which five carbon atoms become equivalent on the NMR timescale due to rapid Wagner–Meerwein shifts, could not definitely be excluded (Scheme I).

The ^1H NMR spectra[7,8] of solutions of 1 (FSO_3H/SO_2ClF, $FSO_3H/SbF_5/SO_2ClF$, $HF/SbF_5/SO_2ClF$, SbF_5/SO_2ClF) on going from −80 to −140 °C show a broadening[1b,9] of the two absorptions due to the two types of methyl groups in dication 1 that exceeds that of the added reference compound $(CH_3)_4N^+Cl^-$. A circumambulatory motion in dication 1, as shown in Scheme I, can be excluded as the origin of this line broadening, because in that case only the signal due to the basal methyl groups would show a broadening.[10] The fact that the signal due to a monocation like $(CH_3)_4N^+Cl^-$ exhibits less broadening on lowering the temperature than those due to dication 1 may be rationalized in terms of differences in solvation: electrostatic interaction between the superacid solvent molecules and cationic species will be larger for doubly than for singly charged particles.[11]

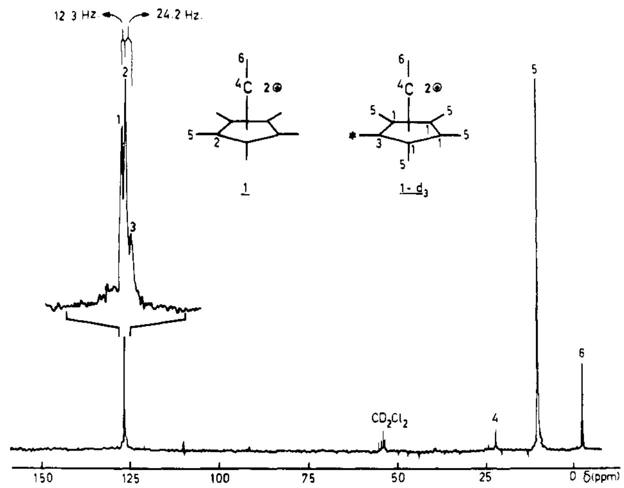


Figure 1. 90.52-MHz ^{13}C NMR spectrum of a mixture of 1 and 1-d_3 at −60 °C.

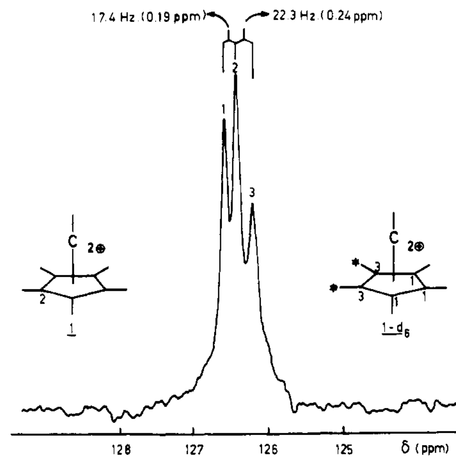


Figure 2. Low-field ^{13}C NMR signals of a mixture of 1 and 1-d_6 at −60 °C.

In order to further substantiate the nature of dication 1, we applied Saunders' major new tool[12] for distinguishing rapidly equilibrating cations from symmetrical ones by a deuterium-induced perturbation of ^{13}C NMR chemical shifts. Single carbon peaks of the unlabeled cations are split into two signals for the deuterium-substituted cations, and the separation is a very strong indication of the nature of the cation. Relatively large splittings (even 100 ppm) are found for classical ions undergoing rapid shifts (double energy minimum), while static and nonclassical (bridged) ions (single energy minimum) give rather small splittings (smaller than 2 ppm). Intermediate cases are also found, e.g., for the 1,2-dimethyl-2-norbornyl cation[12a] and the 1,2-dimethyl-2-bicyclo[2.1.1]hexyl cation,[13] showing the partially delocalized nature of these species. Furthermore, the splittings for the rapidly equilibrating cations are temperature dependent, as expected for an equilibrium process.

The precursors for labeled dications were synthesized by starting with enone 7 or diketone 8.[2,14] Treatment of

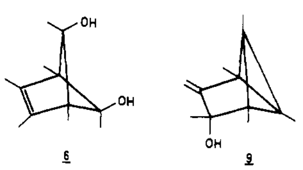
(4) The attribution of a nonclassical structure on the basis of Olah's rule is not entirely secure. For example, using both Olah's rule[5] and the criterion of effects of the dihedral angle and strain on the magnitude of the coupling constants, one ends up with conflicting interpretations in the case of the cyclopropylcarbinyl cation.[5,6]

(5) (a) Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 5801. (b) Olah, G. A.; Kelly, D. P.; Jeuell, C. L.; Porter, R. D. *Ibid.* **1970**, *92*, 2544. (c) Olah, G. A.; Jeuell, C. P.; Kelly, D. P.; Porter, R. D. *Ibid.* **1972**, *94*, 146.

(6) Brown, H. C. *Tetrahedron* **1976**, *32*, 179.

(7) The spectroscopic data for 1 are the following: ^1H NMR (−70 °C) δ 2.21 and 2.90 (ratio 1:5); ^{13}C NMR (−70 °C) δ 126.3 and 22.5 (s, ratio ca. 5:1), 10.6 and −2.0 (q, ratio ca. 5:1). These values differ slightly from the originally reported ones[1] due to the present use of external Me_4Si (10% solution in CD_3COCl) as the reference at δ 0.00.

(8) Suitable precursors for dication 1 are diol 6 (see ref 1) and alcohol 9 (see ref 2). Diol 6 is synthesized according to: Junker, H.-N.; Schäfer, W.; Niedenbrück, W. *Chem. Ber.* **1967**, *100*, 2508.



(9) Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 4752.

(10) Compare: (a) Childs, R. F.; Sakai, M.; Winstein, S. *J. Am. Chem. Soc.* **1968**, *90*, 7144; (b) Childs, R. F.; Winstein, S. *Ibid.* **1968**, *90*, 7146.

(11) Lunazzi and Brownstein have obtained strong evidence, on the basis of NMR line-broadening measurements, for the existence of two differently solvated types of acetyl cations in SO_2 solution: Lunazzi, L.; Brownstein, S. *J. Am. Chem. Soc.* **1969**, *91*, 3034.

(12) (a) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070. (b) Saunders, M.; Kates, M. R. *Ibid.* **1977**, *99*, 8071. (c) Saunders, M.; Kates, M. R.; Wiberg, K. B.; Pratt, W. *Ibid.* **1977**, *99*, 8072. (d) Saunders, M.; Chandrasekhar, J.; Schleyer, P. v. R. In "Rearrangements in Ground and Excited States"; De Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 1.

(13) Schmitz, L. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1980**, *102*, 1645.

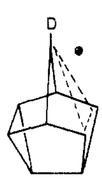
(14) (a) Heldeweg, R. F.; Hogeveen, H. *Tetrahedron Lett.* **1975**, 1517. (b) Heldeweg, R. F.; Hogeveen, H.; Schudde, E. P. *J. Org. Chem.* **1978**, *43*, 1912.

7 and 8 with CD_3Li followed by the addition of water resulted in the formation of allylic alcohol 9-d_3[2a] and glycol 10-d_6[2b] (the latter as a cis–trans mixture; see the Experimental Section and Scheme II, respectively).

A solution of dication 1-d_3 was prepared by treating a solution of 9-d_3 in CD_2Cl_2 with FSO_3H at low temperature. The ^1H NMR spectrum at −50 °C showed two singlets in a ratio of 1.0:4.1, as expected for dication 1-d_3 with the CD_3 group in a basal position.[7] In the 90.52-MHz ^{13}C NMR spectrum of 1-d_3 in FSO_3H at −60 °C a splitting was observed of 41.4 Hz (0.46 ppm) for the low-field signal.[7] The ^{13}C NMR spectrum at −60 °C of a 2:3 mixture of 1 and 1-d_3 (prepared from a mixture of 9[2a,8] and 9-d_3) indicates for the labeled cation a downfield shift of 12.3 Hz (0.14 ppm) for the resonance of the basal carbon atoms bonded to the CH_3 groups relative to the corresponding signal of the unlabeled cation; the peak of the carbon atom bonded to the CD_3 group in 1-d_3 appears upfield (24.2 Hz, 0.27 ppm; see Figure 1). The slight variation of the size of the two splittings in the separate experiments (0.46 and 0.41 ppm) is considered insignificant.

Dication 1-d_6, with both CD_3 groups in basal positions, was obtained upon addition of FSO_3D/SbF_5[15] (molar ratio 1:1) to glycol 10-d_6 in SO_2ClF at low temperature. In the ^1H NMR spectrum at −50 °C, two singlets in the ratio of 1.0:2.9 are observed.[7] The 90.52-MHz ^{13}C NMR spectrum of this cation shows a splitting of 39.5 Hz (0.44 ppm) for the low-field resonance[7] that remained unchanged (0.44 ± 0.01 ppm) in the temperature region −60 to −10 °C. A 2:3 mixture of dications 1 and 1-d_6, obtained by the reaction of 6[8] and 10-d_6 with $FSO_3D/SbF_5/SO_2ClF$ shows a ^{13}C NMR spectrum the relevant part of which is given in Figure 2. The magnitudes of the shifts of cation 1-d_6 are nearly identical with those for cation 1-d_3; viz., a downfield shift of 17.4 Hz (0.19 ppm) and an upfield shift of 22.3 Hz (0.24 ppm) are observed for cation 1-d_6.

In our opinion these experiments are in agreement with a symmetrical, bridged structure for cation 1 (single energy minimum) rather than with a mixture of rapidly equilibrating classical cations. This is based upon comparison with the examples presented by Saunders and co-workers[12] (e.g., cations 11,[16] δ <0.1, and 12,[12c] δ 1.6), by Sorensen (cation 13,[17] δ 0.5), and by Günther et al. (cation 14,[19] δ 0.4).



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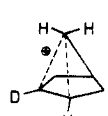

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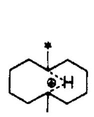

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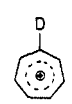
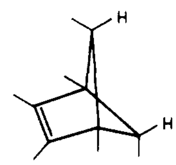


14

It should be pointed out that the validity of Saunders' isotopic perturbation method has not been verified for cases with both a double positive charge as well as a fivefold degeneracy.[25] However, the combined effect of changes in charge per carbon atom as well as in the degree of degeneracy is illustrated by the results of the cyclohexenyl cation[12b] and the tropylium ion 14:[19] both ions show a very small isotopic perturbation (0.5 and 0.4 ppm, respectively), indicating no important influence of these effects.

In addition, we have applied to cation 1 the very recently reported[18] method of comparing the total ^{13}C NMR chemical shift sum of a cation with that of the corresponding neutral hydrocarbon. Schleyer, Olah, Lenoir, and co-workers[18] have found for a great number of classical cations large (>350 ppm) total ^{13}C NMR chemical shift differences, while for nonclassical cations much smaller values (often smaller than 200 ppm) have been calculated. They conclude their method to be "a rough, but useful structural index" for classifying cations.

The total ^{13}C NMR chemical shift sum of cation 1 compared to those of the corresponding hydrocarbons 15[20] and 16[21,22] affords calculated chemical shift differences of 54.6 and 195.7 ppm, respectively (per unit charge).



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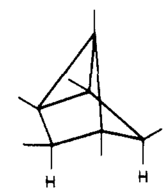

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In conclusion, we feel that the data reported in this paper are convincing evidence that the pyramidal dication 1 occupies a single energy minimum and therefore must have the fivefold symmetry already proposed.

Experimental Section

General Remarks. The low-temperature ^1H NMR spectra were recorded at 60 MHz on a JEOL C-60 HL spectrometer and the ^{13}C NMR spectra at 90.52 MHz on a Bruker HX-360. Chemical shifts (δ) are given in parts per million downfield from internal Me_4Si for the neutral compounds and external Me_4Si for the cations. All superacids used were purchased from Cationics Inc.

Preparation of a CD_3Li Solution. A solution of CD_3Li in ether was prepared from CD_3I (E. Merck, minimum of 99% D) and Li as described for CH_3Li.[23]

Alcohol 9-d_3 was prepared by adding an excess (2–3 equiv) of CD_3Li in diethyl ether to a cold (−50 °C) stirred solution of 500 mg (3.1 mmol) of enone 7[14] in 30 mL of diethyl ether under nitrogen. The solution was warmed to room temperature, and water (5 mL) was added. After extraction with ether (2 × 20 mL), drying of the combined organic layers over anhydrous K_2CO_3, filtration, and evaporation of the solvent under reduced pressure, the crude product 9-d_3 was obtained in a quantitative yield. Recrystallization from *n*-pentane at −30 °C afforded pure alcohol 9-d_3 in 66% yield (368 mg, 2.0 mmol). The spectroscopic data of 9-d_3 agree well with those of the unlabeled compound:[2a] ^1H NMR ($CDCl_3$) δ 4.92 (s, 1 H), 4.66 (s, 1 H), 1.40 (s, 3 H), 1.32 (s, 3 H), 1.10 (s, 3 H), 1.06 (s, 3 H); mass spectrum, m/e 181 (M^+).

Glycol 10-d_6 was prepared by starting from 250 mg (1.52 mmol) of diketone 8[14] with excess CD_3Li (4–6 equiv) and following the procedure described above for alcohol 9-d_3. A 1:1 mixture of the crude cis and trans isomers of glycol 10-d_6 was obtained in a quantitative yield. Recrystallization from *n*-pentane (−30 °C) gave pure glycol 10-d_6 (as a cis–trans mixture) in 84% yield (285 mg, 1.28 mmol). Fractional recrystallizations gave the pure isomers of 10-d_6 in low yields (10–20%). The spectroscopic data are in agreement with those of the unlabeled compounds.[2b,24]

(15) The D line of deuterated superacid was used in this case for locking purpose.

(16) Kates, M. R. Ph.D. Thesis, Yale University, 1978.

(17) Sorensen, T. S., submitted for publication in *J. Am. Chem. Soc.* (as quoted in ref 18).

(18) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Surya Prakash, G. K.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683.

(19) Günther, H.; Seel, H.; Günther, M.-E. *Org. Magn. Reson.* **1978**, *11*, 197.

(20) (a) Hogeveen, H.; Kwant, P. W.; Thio, J. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 152. (b) Kwant, P. W. Ph.D. Thesis, University of Groningen, 1974.

(21) Taucher, P.; Hüttel, R. *Tetrahedron Lett.* **1972**, 4733.

(22) Kok, D. M.; Zwart, L., unpublished results.

(23) Schöllkopf, U. In "Methoden der Organische Chemie (Houben-Weyl)"; George Thieme Verlag: Stuttgart, 1970; Vol. 13/1, p 135.

(24) Bolster, J. M., unpublished results.

Cis isomer: ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 3 H), 1.19 (s, 3 H), 1.00 (s, 6 H); mass spectrum, *m/e* 202 (M^+).

Trans isomer: ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 6 H), 1.00 (s, 6 H); mass spectrum, *m/e* 202 (M^+).

Preparation of Dication Solutions. In a 10-mm NMR tube was dissolved 100 mg of alcohol **9**-d_3 in 0.5 mL of CD_2Cl_2 and the mixture cooled to −196 °C. FSO_3H (2 mL) was added, and the sample was warmed to about −95 °C. A precooled glass rod was employed to mix and homogenize the contents of the tube carefully, resulting in a solution of cation **1**-d_3. A mixture of ions **1** and **1**-d_3 was prepared analogously by using 40 mg of alcohol **9**[2a] and 60 mg of alcohol **9**-d_3.

Ion **1**-d_6 was generated upon dissolution of 50 mg of glycol **10**-d_6 in 1.5 mL of SO_2ClF and cooling of the mixture to −196 °C in a 10-mm NMR tube. FSO_3D/SbF_5 (1:1 molar ratio) was introduced, and the sample was slowly warmed to −125 °C. The resulting mixture was carefully homogenized with the the aid of a glass rod. A mixture of ions **1** and **1**-d_6 was prepared analogously by using 40 mg of diol **6**[8] and 60 mg of **10**-d_6. The best spectra of the dication solutions were obtained by employing the superacids mentioned. Other combinations of superacid, cosolvent, and precursor sometimes gave undesired byproducts.

(25) The authors thank the referee for raising these points.

Acknowledgment. The authors express their thanks to Professor M. Saunders for correspondence on this subject. E.M.G.A.v.K. is grateful to Professor M. Saunders for a stimulating stay in his laboratory at Yale University, Mr. K. Dijkstra (Department of Physical Chemistry, Groningen) has kindly recorded the 90.52-MHz ^{13}C NMR spectra.

Registry No. 1, 51257-59-1; **1**-d_3, 76010-09-8; **1**-d_6, 76010-08-7; **6**, 38525-05-2; **7**, 56745-77-8; **8**, 56745-78-9; **9**, 63963-73-5; **9**-d_3, 75934-45-1; *cis*-**10**-d_6, 75934-46-2; *trans*-**10**-d_6, 75934-47-3; CD_3Li, 15772-82-4.

Hindered Rotation in Substituted Benzyl Halides

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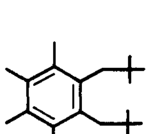
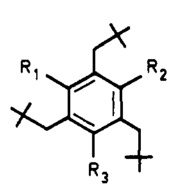
The barriers to internal rotation about sp^2(phenyl)–sp^3 carbon–carbon single bonds in a series of 2-(trichloroethyl)-3,4,5,6-tetramethylbenzyl halides (I) have been determined by using dynamic NMR spectroscopy. The magnitude of the barrier increases proportionally with the size of the halomethyl group. This leads to the tentative conclusion that steric crowding rather than dipolar repulsion determines the magnitude of the rotational barrier.

Introduction

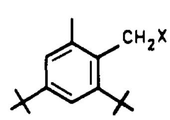
Hindered rotation about sp^2(phenyl)–sp^3 carbon–carbon single bonds has been studied by NMR techniques in a number of benzyl derivatives,[1] such as substituted neopentylbenzenes **1**[2,3] and **2**[3] and halides **3**[4] The barrier to



1



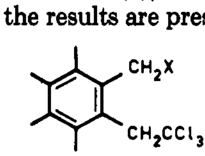
2 (R=H, alkyl, halogen)



3 (X = I, Br, Cl)

internal rotation of the neopentyl groups in compound **1** was calculated to be $\Delta G_{298}^{\ddagger}$ = 16.3 kcal/mol.[3b] The rotamer of lowest energy in the case of **1** was considered to have the neopentyl groups on opposite sides of the benzene ring. The magnitude of the barrier is most likely determined by the steric interactions between the neopentyl groups and the *o*-methyl substituents during the passage of the neopentyl past the methyl groups.[3a,b] This is supported by the finding that in the parent 1,2-dineopentylbenzene in which the ortho substituents are hydrogen atoms, the internal rotation could not be frozen out down to −90 °C.[3b] Also for benzyl halides **3** the conclusion was reached that the magnitude of the barrier to rotation of the CH_2X group is largely determined by the steric interaction between X and the smaller ortho substituent, viz., the methyl group.[4] The barrier in **3** increases with increasing size of the substituent X; it varies from E_a = 11.3 kcal/mol for X = Cl to E_a = 15.9 kcal/mol for X = I. Conversely, the heights of such rotational barriers give an indication of the "effective size" of the substituent.[3b,5]

Recently we reported[6] the preparation of compounds **5** and **6** which show a substantial barrier to rotation about the phenyl–CH_2 bonds. In principle, the origin of the barrier might be attributed to steric crowding as well as to dipolar repulsion between X and CCl_3 groups. In order to evaluate the influence of the substituent X on the barrier height, the dynamic behavior for a series of benzyl halides of type I with X = I (**4**), Br (**5**), Cl (**6**), and F (**7**) was examined and the results are presented in this article.



I

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