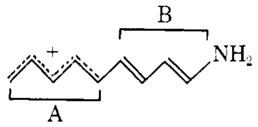


spread over its conjugated fragment without losing any electrostatic energy.

*The electrostatic attraction of the "hole-particle pair" disappears if and only if one of the two subsystems already bears an electric charge,* which may be canceled through the excited state charge transfer. Of course an environmental negative charge certainly exists in the N$^+$ region, which might prevent a neutralization of N$^+$ site, but the rotation around the central bond certainly moves the B part of the molecule, and the N$^+$ site no longer faces its negative environmental counterpart.

From these simple arguments one might understand the very specific role of the retinal *protonated* Schiff base. Neither the retinal nor its nonprotonated Schiff base would present such a charge displacement; in such molecules the + − couple would remain in the rotating bond region. The stability of Salem's structure also possibly explains the very low excitation energy of the molecule and the bathochromic effect of the Schiff base.

Of course the charge migration is overestimated if one imagines it as a jump of a 1.0 e charge from the nitrogen atom to the central carbon atom of the A part. Our calculations on the smallest protonated Schiff base suggest a shorter transfer of a smaller charge ($<0.5$ e). Further calculations on these large systems, allowing correct repolarization phenomena, are necessary, in order to assess the exact extent of the charge migration.

**Acknowledgments.** Thanks are due to the Consiglio Nazionale delle Ricerche (Roma) and the Centre National de la Recherche Scientifique for their financial support, and to L. Salem for his fruitful comments.

## References and Notes

(1) (a) Universita di Modena; (b) Institut de Biologie Physico-chimique; (c) Université Paul Sabatier.
(2) (a) R. Hoffmann, *Tetrahedron*, **22**, 521 (1966); (b) N. C. Baird and R. M. West, *J. Am. Chem. Soc.*, **93**, 4427 (1971); (c) J. Langlet and J. P. Malrieu, *Theor. Chim. Acta*, **33**, 307 (1974).
(3) (a) S. Shih, R. J. Buenker, and S. D. Peyerimhoff, *Chem. Phys. Lett.*, **16**, 244 (1972); (b) J. P. Malrieu, to be published.
(4) R. J. Buenker and J. D. Peyerimhoff, *Chem. Phys.*, **9**, 75 (1976), and experimental references herein.
(5) P. Bruckmann and L. Salem, *J. Am. Chem. Soc.*, **98**, 5037 (1976).
(6) D. F. Evans, *J. Chem. Soc.*, **2**, 1735 (1960).
(7) M. C. Bruni, F. Momicchioli, I. Baraldi, and J. Langlet, *Chem. Phys. Lett.*, **36**, 484 (1975), and references herein.
(8) D. A. Luippold, *Chem. Phys. Lett.*, **35**, 131 (1975).
(9) L. Salem and P. Bruckmann, *Nature (London)*, **258**, 526 (1975).
(10) V. Bonacic-Koutecky, P. Bruckmann, P. Hiberty, J. Koutecky, C. Leforestier, and L. Salem, *Angew. Chem., Int. Ed. Engl.*, **14**, 575 (1975).
(11) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).
(12) R. K. Nesbet, *Rev. Mod. Phys.*, **35**, 552 (1963).
(13) J. E. Lennard-Jones, *Proc. R. Soc. London, Ser. A:*, **198**, 1 (1949); G. G. Hall and J. E. Lennard-Jones, *ibid.*, **202**, 155 (1950); J. E. Lennard-Jones and J. A. Pople, *ibid.*, **202**, 166 (1950); for a review see P. Millie, B. Levy, and G. Berthier, "Localization and Delocalization in Quantum Chemistry", Vol. I, O. Chalvet, R. Daudel, S. Diner, and J. P. Malrieu, Ed., D. Reidel, Dordrecht, 1975, p 59.
(14) See, for instance, W. T. Simpson, *J. Am. Chem. Soc.*, **73**, 5363 (1951); **77**, 6164 (1955); J. N. Murrell, *J. Chem. Phys.*, **37**, 1162 (1962); H. C. Longuet-Higgins and J. N. Murrell, *Proc. R. Soc. London, Ser. A:*, **68**, 601 (1955). For a review, see J. Langlet and J. P. Malrieu, "Localization and Delocalization in Quantum Chemistry", Vol. II, O. Chalvet, R. Daudel, S. Diner, and J. P. Malrieu, Ed., D. Reidel, Dordrecht, 1976.
(15) S. Diner, J. P. Malrieu, and P. Claverie, *Theor. Chim. Acta*, **13**, 1 (1969); J. P. Malrieu, P. Claverie, and S. Diner, *ibid.*, **13**, 18 (1969); S. Diner, J. P. Malrieu, F. Jordan, and M. Gilbert, *ibid.*, **15**, 100 (1969).
(16) J. P. Daudey, *Chem. Phys. Lett.*, **24**, 574 (1974).
(17) B. Huron, J. P. Malrieu, and P. Rancurel, *J. Chem. Phys.*, **58**, 5745 (1973).
(18) J. Langlet and P. Gacouin, *Theor. Chim. Acta*, **42**, 293 (1976).
(19) J. Langlet and P. Gacouin, *Theor. Chim. Acta*, in press.
(20) M. C. Bruni, F. Momicchioli, and J. Langlet, to be published.
(21) G. Del Re, *J. Chem. Soc.*, 4031 (1958).
(22) Ph. Millie and G. Berthier, *Int. J. Quantum Chem.*, **25**, 67 (1968).
(23) J. Langlet, J. P. Daudey, and J. P. Malrieu, *Chem. Phys. Lett.*, **45**, 481 (1977).

---

# Nuclear Magnetic Resonance Conformational Analysis of 1,4-Dihydronaphthalenes

**Peter W. Rabideau,*[1a] Earl G. Burkholder,[1a] Michael J. Yates,[1a,b] and Jonathan W. Paschal[1c]**

*Contribution from the Department of Chemistry, Indiana-Purdue University at Indianapolis, Indianapolis, Indiana 46205, and Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana 46206.* *Received January 11, 1977*

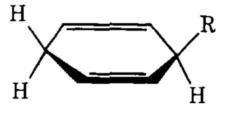
**Abstract:** The question concerning the extent of cyclohexadiene ring puckering in 1-substituted 1,4-dihydronaphthalenes is attended to by NMR analysis of several structures including some rigid, boat-shaped model compounds. A large 1-substituent results in a highly puckered geometry (similar to 9,10-dihydroanthracene), whereas small substituents are accommodated by a less puckered (but not planar) cyclohexadiene ring. Attention is also given to the nature of the homoallylic coupling constants.

Considerable attention has been brought to bear on the conformational analysis of the cyclohexadiene ring systems 1,4-dihydrobenzene (**1**), 1,4-dihydronaphthalene (**2**), and 9,10-dihydroanthracene (**3**). However, despite numerous studies over several years, each of these systems became a center of controversy over some aspect of its stereochemistry.[2] For example, it had generally been accepted that **3** exists as rapidly equilibrating boat conformations, but conflicting reports appeared concerning the preferred conformation of substituted derivatives (**3a**) with regard to pseudoequatorial or pseudoaxial (shown) preference of substituents.[3a] It was later shown by use of nuclear Overhauser enhancements and homoallylic coupling constants ($J_{9,10}$) that pseudoaxial conformations are indeed the preferred geometry.[3b]

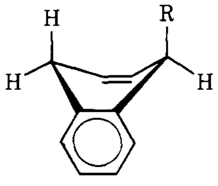
**Table I.** NMR Data (100 MHz) for Various 1,4-Dihydronaphthalenes

| Compd | Coupling constants, Hz | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $J_{1,4}$ | $J_{1,4'}$ | $J_{1,2}$ | $J_{1,3}$ | $J_{2,3}$ | $J_{2,4}$ | $J_{2,4'}$ | $J_{3,4}$ | $J_{3,4'}$ | $J_{4,4'}$ |
| **2a**[a] | 3.8 | 4.4 | 4.6 | 1.2 | 9.6 | 1.2 | 3.0 | 4.6 | 2.4 | 21.9 |
| **4**[b] | 3.5 | 3.7 | 3.8 | $\leq 1$ | 9.9 | | | 3.7 | 2.1 | 21.0 |
| **5**[b] | 1.8 | 3.0 | 5.2 | $\leq 1$ | 9.6 | $\leq 1$ | 2.0 | 5.0 | 2.0 | 20.5 |
| **6**[b] | 8.5 | | 1.6 | 2.8 | 9.6 | 3.1 | | 1.4 | | |
| **7**[b] | | 3.2 | 5.0 | $\leq 1$ | 9.5 | | 2.8 | | 1.2 | |

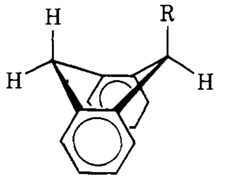
[a] Data from ref 5m. [b] NMR measurements made in the presence of Eu(fod)$_3$. See ref 14 for further description.



1a, R = CO$_2$H
b, R = CH$_2$OH



2a, R = CO$_2$H



3a, R = alkyl

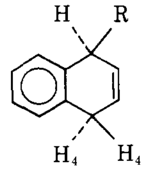
A much more heavily disputed issue has been the geometry of **1** and its simple derivatives. Although generally considered[4] to be boat-shaped for a number of years, a series of reports appeared which were almost equally divided between the boat-shaped and planar geometries.[5] A major difficulty is that NMR analysis provides unusually large coupling constants across the ring (homoallylic coupling constants typically 7–9 Hz), but due to a remarkable number of chemical shift equivalences, initial studies could not provide vicinal or allylic coupling constant information. Furthermore, conclusions concerning geometry based on the homoallylic coupling constant data were questioned due to disagreements[5e,h,i,6] with regard to the "predicted value" for the $^5J_{\text{cis}}/^5J_{\text{trans}}$ value. However, the use of shift reagents with **1b** and related model compounds have indicated a planar geometry for **1a** and **1b.**[7]

It was originally suggested that the geometry of 1,4-dihydronaphthoic acid is boat-shaped[5l] based on considerations of the vicinal and allylic coupling constants. Later, however, in view of an accurately obtained value for the homoallylic $J_{\text{cis}}/J_{\text{trans}}$ ratio, a nearly planar conformation was preferred.[5m] Although this was disputed by some,[2] it did appear consistent with the suggestion that, theoretically, $^5J_{\text{trans}}$ should be slightly larger than $^5J_{\text{cis}}$.[8-10] More recently, however, carbon–carbon spin coupling[11] and carbon–proton spin coupling[12] studies have led to the suggestion that **2a** is, in fact, puckered, although not to the same extent as **3.** Furthermore, very recent INDO calculations[13] indicate that $^5J_{\text{trans}}$ should be somewhat smaller than $^5J_{\text{cis}}$ ($^5J_{\text{cis}}/^5J_{\text{trans}} \approx 1.2$) for a planar **1,** which is in remarkable agreement with experimental findings.[2]

We would now like to present our results with some model compounds and additional 1-substituted 1,4-dihydronaphthalenes, which further elucidate the stereochemistry of this ring system as well as provide some experimental data concerning homoallylic coupling constants.

## Results and Discussion

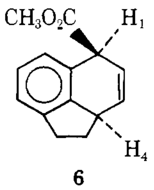
Since all of the controversy concerning the geometry of 1,4-dihydronaphthalenes has centered on a single compound (i.e., **2a**), it seemed reasonable to begin our investigation by examining a second rather simple example to exclude the possibility of peculiarities with **2a.** Thus, compound **4** was prepared and subjected to NMR analysis using shift reagents and triple irradiation,[14] and the coupling constant data is provided in Table I. Most of the coupling constants having stereochemical consequence are slightly smaller for **4** than for **2a,** but are reasonably close. Furthermore, the $^5J_{\text{cis}}/^5J_{\text{trans}}$ ratio (as well as the $J_{3,4}/J_{3,4'}$ ratio) is quite similar for both compounds, and this leads us to conclude that they probably have similar geometries.



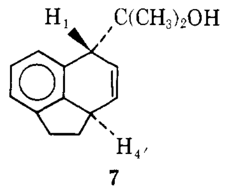
4, R = CD$_2$OH
5, R = C(CH$_3$)$_2$OH

The use of a large substituent provides substantially different results, however, and compound **5** represents the first example of a highly puckered[15] monosubstituted 1,4-dihydronaphthalene. This type of geometry is supported by the fact that the cis homoallylic coupling constant ($J_{1,4}$) has dropped to 1.8 Hz. This is quite reasonable, since as the substituent becomes pseudoaxial (as expected[3]), protons H$_1$ and H$_4$ adopt a pseudoequatorial/pseudoequatorial relationship which minimizes the coupling constant. Furthermore, the observed decrease in $J_{1,4}$ is also consistent with increased puckering according to calculations.[6,12] No doubt, this change in geometry with **5** is due to increased steric interactions with the aromatic ring and H$_8$, an effect which has been shown to be quite important in 9-substituted 9,10-dihydroanthracenes.[3b]

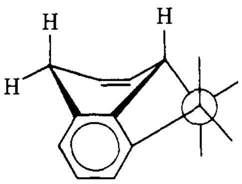
In order to properly evaluate these data, we wanted to obtain NMR parameters for a rigid, boat-shaped model compound. To this end, we prepared the ester **6**[17,19] and the alcohol **7**



**6**



**7**



which both (according to Drieding models) incorporate a boat-shaped cyclohexadiene ring (see figure), and the NMR data is presented in Table I.[20] Of immediate interest are the values of the homoallylic coupling constants, which are 8.5 Hz for the axial/axial relationship and 3.2 for axial/equatorial. Since this latter value compares favorably with $J_{1,4'}$ in **5,** we suggest that the value of 1.8 Hz ($J_{1,4}$ in **5**) can be accepted as a reasonable estimate for equatorial/equatorial coupling in a boat-shaped[15] 1,4-dihydronaphthalene.

It is interesting to note that the vicinal coupling constants do not vary much in this series (in contrast to the homoallylic values), and appear not to be very sensitive to conformational

*Rabideau et al. / Conformational Analysis of 1,4-Dihydronaphthalenes*

**Table II.** General Values (in hertz) for Selected Coupling Constants in **1**, **2**, and **3** from Boat-Shaped Derivatives

| Geometric relationship | Ring system<br>1,4-Dihydrobenzene[a] | <br>1,4-Dihydronaphthalene[b] | <br>9,10-Dihydroanthracene |
|---|---|---|---|
| Pseudoaxial/ pseudoaxial | 12 | 8.5 | 4.8[c] |
| Pseudoaxial/ pseudoequatorial | 4.7 | 3.1[b] | 1.2[d] |
| Pseudoequatorial/ pseudoequatorial | | 1.8 | 0.4[d] |

[a] Data from ref 2. [b] Data from this study. [c] Estimated from $^{13}C$ satellites. See ref 18 and references cited therein. [d] An average value taken from ref 3b.

changes. In addition, the allylic coupling involving the more axial proton at C-4 (i.e., $J_{2,4'}$ in **2a**, **5**, and **7**; $J_{2,4}$ in **6**) changes very little, which is quite consistent with theoretical predictions from INDO calculations.[18] The allylic coupling involving the more equatorial proton ($J_{1,3}$ and $J_{2,4}$ in **2a**, **4**, and **5**; $J_{2,4'}$ in **6**, and $J_{2,4}$ in **7**) is predicted[18] to be more sensitive to conformational charges, but, unfortunately, is too small to be useful (or, in several cases, to be measured).

Thus, it appears that the homoallylic coupling constants are the most sensitive probe for conformational analysis in this system. However, the interpretation of these values is quite another matter. With the data of this study, we can now present a reasonably complete picture for the values of the homoallylic coupling constants in each of the three systems (i.e., **1**, **2**, and **3**), for several geometric relationships. As can be seen from this data in Table II, there is no simple correlation between these systems, and conclusions about conformational preferences will need to depend on comparison of values for a *particular relationship* within a *particular system.* Using this approach in summarizing our results for 1,4-dihydronaphthalenes, we conclude that a single large substituent such as $C(CH_3)_2OH$ forces a boat conformation (ca. 145° between planes[15]) to allow the pseudoaxial location for the substituent. On the other hand, smaller groups such as $CO_2H$ and $CD_2OH$ cause some degree of puckering, but certainly not to the same extent. We reject a nearly planar structure for these latter cases, however, since even though direct correlations of these numbers may not be possible, the theoretical prediction[12,13] that the cis homoallylic coupling will be larger than trans for planar geometries in 1,4-cyclohexadienes has received experimental verification[2] (theoretical ratio = 1.22–1.29, experimental = 1.1–1.16). This ratio is <1 for both **2a** and **4.**

## Experimental Section

**General.** NMR spectra were recorded with deoxygenated samples, with ca. 10% solution in $CDCl_3$, on a Varian HA 100 spectrometer. $Eu(fod)_3$ was added in small increments, and double or triple irradiation was employed to observe each signal as it became amenable to analysis. Typically no more than four or five additions of $Eu(fod)_3$ could be made, since line broadening hampered decoupling. Chemical shift assignments were based on the assumption that protons in nearest proximity to the coordination site for the $Eu(fod)_3$ would move downfield at the greatest rate with a series of shift reagent additions.

**1-Hydroxymethyl-*d*$_2$-1,4-dihydronaphthalene (4).** This compound (as well as the undeuterated material) was prepared from 1,4-dihydronaphthoic acid[5m,n] by the action of $LiAlD_4$ ($LiAlH_4$) according to the procedure previously described.[2] A nearly quantitative yield of **4** was obtained as a semisolid, and purification, where necessary, was accomplished by chromatography on a silica gel column: NMR ($CDCl_3$) $\delta$ 7.15 (m, 4 H), 6.0 (m, 2), 3.5 (m, 1), 3.35 (m, 2), 1.8 (s, 1).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.50; H, 7.50; O, 10.00. Found: C, 82.22; H, 7.61.

**1-Hydroxyisopropyl-1,4-dihydronaphthalene (5).** Naphthalene (9 g, 70 mmol) in 80 mL of anhydrous ether was added to 200 mL of anhydrous ammonia at −78 °C, followed by sodium metal (4 g, 170 mg-atoms) in pieces. After 10 min, 20 mL of dry acetone was added and stirring was continued for an additional 10 min, followed by the addition of water. Ether extraction afforded an oil which contained about 50% of the carbinol together with dihydro- and tetrahydronaphthalene (by GLC). An analytical sample was obtained by fractional distillation: bp 136 °C (7 mm); NMR ($CDCl_3$) $\delta$ 7.15 (m, 4 H), 6.1 (m, 2), 3.35 (m, 3), 1.6 (s, 1), 1.25 (s, 3), 1.03 (s, 3).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.70; H, 8.38.

***cis*-Methyl 2a,5-Dihydroacenaphthoate (6).** The *cis*-methyl-2a,5-dihydroacenaphthoic acid precursor was prepared by $Li/NH_3$ reduction, and during the course of our studies a similar report of its preparation has appeared.[18] The ester was prepared from boron trifluoride etherate/methanol[2] by overnight reflux to afford a nearly quantitative yield of white crystals. An analytical sample was obtained by recrystallization from petroleum ether: mp 70 °C; NMR ($CDCl_3$) $\delta$ 7.1 (m, 3) 6.19 (m, 1), 5.97 (m, 1), 4.29 (br d, 1), 3.78 (s, 3), 3.4 (m, 1), 2.9 (m, 2), 2.45 (m, 1), 1.72 (m, 1).

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 75.24; H, 6.13.

***trans*-5-(Hydroxyisopropyl)-2a,5-dihydroacenaphthene (7).** Acenaphthene (10 g, 64 mmol) was reacted with sodium metal (3.7 g, 160 mg-atoms) according to the procedure given for **5**, and afforded 9.1 g of an oil containing about 30% (by GLC) of the desired product. An analytical sample was obtained by fractional distillation: bp 129 °C (1 mm); mp 61–63 °C; NMR ($CDCl_3$) $\delta$ 7.2 (m, 3 H), 6.17 (d, 1), 6.02 (m, 1), 3.5 (m, 1), 3.39 (m, 1), 2.88 (m, 2), 2.45 (m, 1), 1.62 (m, 1), 1.72 (s, 1), 1.3 (s, 3), 1.17 (s, 3).

**Acknowledgment** is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support (to P.W.R.) of this research. We (P.W.R. and M.J.Y.) would also like to thank Professor James L. Marshall for his helpful interaction.

## References and Notes

(1) (a) Indiana-Purdue University; (b) Undergraduate Fellow of the Petroleum Research Fund; (c) Lilly Research Laboratories.
(2) P. W. Rabideau, J. W. Paschal, and L. E. Patterson, *J. Am. Chem. Soc.*, **97**, 5700 (1975), and references cited therein.
(3) (a) A. H. Beckett and B. A. Mulley, *Chem. Ind.* (*London*), 146 (1955); *J. Chem. Soc.*, 4159 (1955); W. Carruthers and G. E. Hall, *J. Chem. Soc. B*, 861 (1966); D. Nicholls and M. Szwarc, *J. Am. Chem. Soc.*, **88**, 5757 (1966); *Proc. R. Soc. London, Ser. A*, **301**, 231 (1967). (b) A. W. Brinkman, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay Jr., *J. Am. Chem. Soc.*, **92**, 5912 (1970). See also P. W. Rabideau and J. W. Paschal, *ibid.*, **94**, 5801 (1972).
(4) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Interscience, New York, N.Y., 1965, p 125.
(5) (a) H. Gerding and F. A. Haak, *Recl. Trav. Chim. Pays-Bas*, **68**, 293 (1949); (b) B. J. Monostori and A. Weber, *J. Mol. Spectrosc.*, **12**, 129 (1964); (c) H. D. Stidham, *Spectrochim. Acta*, 21 (1965); (d) G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, **1**, 117 (1967); (e) E. W. Garbisch Jr. and M. G. Griffith, *J. Am. Chem. Soc.*, **90**, 3590 (1968); (f) H. Oberhammer and S. H. Bauer, *ibid.*, **91**, 10 (1969); (g) L. J. Durham, J. Studebaker, and M. J. Perkins, *Chem. Commun.*, 456 (1965); (h) D. J. Atkinson and M. J. Perkins, *Tetrahedron Lett.*, 2335 (1969); (i) J. L. Marshall, K. C. Erickson, and T. K. Folsom, *J. Org. Chem.*, **35**, 2038 (1970); (j) J. Laane and R. C. Lord, *J. Mol. Spectrosc.*, **39**, 340 (1971); (k) N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.*, **94**, 5734 (1972); (l) J. L. Marshall and T. K. Folsom, *J. Org. Chem.*, **36**, 2011 (1971); (m) J. L. Marshall, A. M. Ihrig, and P. N. Jenkins, *J. Org. Chem.*, **37**, 1863 (1972).
(6) M. C. Grossel and M. J. Perkins, *J. Chem. Soc., Perkin Trans. 2*, 1544 (1975).
(7) Recent ab initio calculations indicate a planar geometry for 1,4-cyclohexadiene itself: G. Ahlgren, B. Akermark, and J. E. Backvall, *Tetrahedron Lett.*, 3501 (1975).
(8) D. J. Atkinson and M. J. Perkins, *Tetrahedron Lett.*, 2335 (1969).
(9) M. C. Grossel and M. J. Perkins, *J. Chem. Soc., Perkin Trans. 2*, 1544 (1975).
(10) M. C. Grossell and R. C. Hayward, *J. Chem. Soc., Perkin Trans. 2*, 851 (1976).
(11) J. L. Marshall, L. G. Faehl, A. M. Ihrig, and M. Barfield, *J. Am. Chem. Soc.*, **98**, 3406 (1976).
(12) J. L. Marshall, L. G. Faehl, C. R. McDaniel Jr., and N. D. Ledford, *J. Am. Chem. Soc.*, **99**, 321 (1977). We thank Dr. Marshall for sharing this manuscript with us.
(13) P. W. Rabideau, J. W. Paschal, and J. L. Marshall, *J. Chem. Soc., Perkin Trans. 2*, in press.
(14) We have described the details of these techniques previously.[2] As in our earlier studies, the measurement of at least one conformationally dependent

coupling constant or computer simulation of a segment of the spectrum was performed where possible to exclude the question of conformational changes caused by the shift reagent. As in our previous study, the vinyl proton most affected by shift reagent was assigned as $H_2$, and distinction was made between $H_4$ and $H_{4'}$ in a similar manner.

(15) We use the term highly puckered to mean a conformation which approximates the boat-shaped geometry that results when these ring systems are constructed with Dreiding models. This leads to an angle between planes[6] of approximately 145°, which is the exact angle found for 9,10-dihydroanthracene in the crystal.[16]

(16) W. G. Ferrier and J. Iball, *Chem. Ind.* (*London*), 1296 (1954).

(17) Since we completed our analysis of this compound, the corresponding carboxylic acid has been reported and NMR data furnished.[18]

(18) M. C. Grossel and R. C. Hayward, *J. Chem. Soc., Perkin Trans. 2*, 851 (1976).

(19) We were not able to obtain the trans isomer of **6**.

(20) A uniform numbering system is used throughout for purposes of comparison.

---

# The Mechanism of Chemical Ionization of *n*-Paraffins

**Raymond Houriet, Gérald Parisod, and Tino Gäumann***

*Contribution from the Department of Physical Chemistry, Ecole Polytechnique Fédérale, CH 1007 Lausanne, Switzerland.* *Received December 14, 1976*

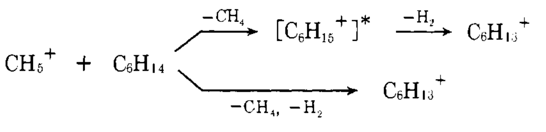
**Abstract:** An ion cyclotron resonance mass spectrometer has been used to study the mechanism of chemical ionization (CI) of *n*-hexane with methane as reagent gas. Extensive use of deuterium-labeled reactants was made. Double resonance techniques permit distinction between the different modes of reaction of hexane with the two major reactant ions in methane, $CH_5^+$ and $C_2H_5^+$. It is shown that the latter acts exclusively as a hydride acceptor to form the hexyl ion in which total scrambling of the hydrogen atoms takes place prior to further decomposition into butyl and propyl ion. $CH_5^+$ reacts as a proton donor to form a short-lived hexonium ion intermediate. This species decomposes by losing either an $H_2$ or an alkane molecule without prior rearrangement. This is interpreted in terms of C-H and C-C protonated hexane with possible equilibration between these two forms.

The chemical ionization (CI) of *n*-paraffins, $C_nH_{2n+2}$, using methane as reagent gas has been among the first class of compounds studied.[1] The CI ($CH_4$) mass spectra are characterized by the formation of an intense parent alkyl ion $C_nH_{2n+1}^+$, together with high abundances of fragment alkyl ions $C_mH_{2m+1}^+$ ($m < n$). Former studies by Hunt and McEwen[2] have established that the fragment alkyl ions are partly formed by olefin loss from the parent alkyl ion when $(n - m) \geqslant 2$, according to the reaction

$$C_nH_{2n+1}^+ \rightarrow C_mH_{2m+1}^+ + C_{n-m}H_{2(n-m)} \qquad (1)$$

On the other hand, Clow and Futrell using ion cyclotron resonance (ICR) techniques studied in more detail the relative rates of formation of the product ions in the CI ($CH_4$) mass spectra of the hexane isomers.[3] They show that the two main reagent ions in methane, i.e., $CH_5^+$ and $C_2H_5^+$, have similar reactivities, except for the formation of the pentyl ion that originates exclusively from $CH_5^+$.

$CH_5^+$ may react with *n*-hexane either according to reaction 2, the protonation reaction, or by the hydride transfer (eq 3),



$$CH_5^+ + C_6H_{14} \xrightarrow{-CH_4} [C_6H_{15}^+]^* \xrightarrow{-H_2} C_6H_{13}^+ \qquad (2)$$

$$CH_5^+ + C_6H_{14} \xrightarrow[-CH_4,\ -H_2]{} C_6H_{13}^+ \qquad (3)$$

while $C_2H_5^+$ transfers only a hydride from the hexane neutral.

$$C_2H_5^+ + C_6H_{14} \rightarrow C_6H_{13}^+ + C_2H_6 \qquad (4)$$

So far, there has been no experimental evidence for reaction 2 to occur (see, for instance, ref 2), although the intermediate hexonium ion has been proposed in order to account for the formation of the pentyl ion uniquely from $CH_5^+$ as precursor.[3]

Considering the differences in the mode of reaction of $CH_5^+$ and $C_2H_5^+$, we have investigated their reaction with a series of deuterium-labeled *n*-hexanes. The isotopically labeled distributions were determined for the alkyl ions containing from three to six carbon atoms. Experiments were also carried out using $CD_5^+$ and $C_2D_5^+$ precursors.

## Experimental Section

The ICR mass spectrometer with a four section cell used in this study has been described elsewhere.[4] The double resonance technique uses a continuous electron beam (accelerating voltage 25 eV) and the modulated frequency of ejection of the precursor ion piloted by the external sweep of the magnetic power unit. The marginal oscillator output is fed to a phase-sensitive detector which is triggered by the modulation frequency. For determination of the product distribution when using deuterated reactants, it was necessary to use a signal averaging technique. For this purpose, between 8 and 64 scans were accumulated on a Nicolet 1074 signal averager.

The following deuterated hexanes were synthesized by standard methods: hexane-*3-$d_2$*; *-2,5-$d_4$*; *-3,4-$d_4$*; *-1,6-$d_6$*; *-1,2,3-$d_7$*; *-1,3,4,6-$d_{10}$*; *-$d_{14}$*. The deuterium content of these samples was between 98 and 99.6%, as determined on a CEC-110B mass spectrometer.

Mixtures of 1% hexane into methane were used (total pressure = $2 \times 10^{-4}$ Torr).

## Results

The product distribution obtained in the 100/1 mixture of $CH_4/C_6H_{14}$ is reported in Table I. A fair agreement with the results of Clow and Futrell[3] is observed. In the forthcoming Tables II–V we present the isotopic distributions obtained with the different labeled reactants used in this study. The results reported were corrected for isotopic hexane impurities present in the samples. The absolute experimental error is within ±0.4% for the hexyl and pentyl ion intensities, while it is about ±1% for the other intensities reported.

**Hexyl Ion.** The distribution of D in the hexyl ion is reported in Table II. The hydride transfer reaction from $C_2H_5^+$ is characterized by two main features: (a) A slight isotope effect is noticed in the product distribution of hexane-*1,2,3-$d_7$*, favoring the transfer of a hydride as compared to a deuteride $k(H^-)/k(D^-) = 1.14$. This is compatible with the differences in zero-point energies of a C–H and a C–D bond. (b) A strong positional effect is present which favors the hydride transfer