*J. Am. Chem. Soc.* **1983**, *105*, 3568-3571

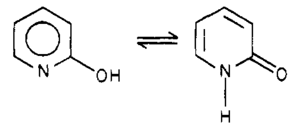
# Theoretical Studies of the Tautomeric Equilibria and Isomer Energetics of 2-, 3-, and 4-Hydroxypyridine

**Martin J. Scanlan, Ian H. Hillier,* and Alastair A. MacDowell**

*Contribution from the Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.* *Received October 25, 1982*

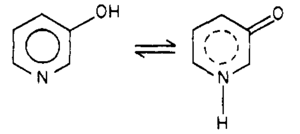
**Abstract:** Fully optimized geometries for 2-, 3-, and 4-hydroxypyridine and the corresponding pyridone tautomers have been determined with a split 3-21G basis set and a gradient procedure. At the optimized geometries, the relative stabilities of the three hydroxypyridines are predicted with an accuracy of 10 kJ mol$^{-1}$. With a 3-21G basis the energy difference between 2-hydroxypyridine and 2-pyridone is predicted to a similar accuracy. A 6-31G** basis yields this energy difference to within 1 kJ mol$^{-1}$ of the experimental value. The nitrogen and oxygen 1s ionization energies, also reported herein, are discussed with the aid of these calculations.

Tautomeric equilibria of heterocycles, especially those of the lactam–lactim type

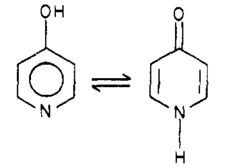


(I)

are of considerable interest, being representative of a large number of equilibria that are relevant to studies of thermodynamic stabilities, particularly of biological systems.[1-3] The equilibria involving the isomeric hydroxypyridines and corresponding pyridones (I, II, and III) have been extensively studied, both theoretically and experimentally. Beak et al.[4] studied the gaseous equilibrium (eq I) with IR and UV spectroscopy, while Guimon et al.[5] used photoelectron spectroscopy with similar results. A value of $\Delta H°$(tautomerization) = (2.6 ± 1.2) kJ mol$^{-1}$ is obtained[6] from the data of Beak et al. Cook et al.,[7] from photoelectron spectroscopy, showed that 4-hydroxypyridine is at least 95% in the hydroxypyridine form in the gaseous state, suggesting a value of $\Delta H°$(tautomerization) for (III), rather greater than that for (I). Suradi et al.[6] measured the enthalpies of combustion of the three isomeric hydroxypyridines and obtained values of $\Delta H_f°$(g) for these molecules, their relative values being listed in Table I.



(II)



(III)

Theoretical studies at varying levels of approximation have been carried out in order to predict $\Delta H°$(tautomerization) for reactions I–III, with special emphasis on (I) for which experimental data are available. Results using CNDO/2, NDDO, MINDO/2, MINDO/3, MNDO, and STO-3G methods have been reported,[8] some coupled with a complete geometry optimization procedure, while others have used standard geometries. In all cases the stability of the hydroxy form is strongly overestimated, the energy differences for (I) ranging from 15.7 kJ mol$^{-1}$ given by MINDO/3 to 145.0 kJ mol$^{-1}$ from the CNDO/2 method, to be compared with the experimental value of (2.6 ± 1.2) kJ mol$^{-1}$. A more recent STO-3G calculation employing a very limited geometry optimization procedure led to an energy difference for (I) of 51 kJ mol$^{-1}$, again grossly overestimating the stability of the hydroxy form.[9]

Table I. Total Energies (hartrees) and Relative Energies (kJ mol$^{-1}$) of Hydroxypyridines and Pyridones[a]

| | total energies | | relative energies | | |
|---|---|---|---|---|---|
| molecule | 3-21G | 6-31G** | 3-21G | 6-31G** | exptl |
| 2-hydroxypyridine | −319.76794 | −321.57838 | −44.0 | −49.2 | −36.0 |
| 2-pyridone | −319.77072 | −321.57680 | | | |
| 3-hydroxypyridine | −319.75117 | −321.55964 | 0 | 0 | 0 |
| 3-pyridone | −319.71415 | | | | |
| 4-hydroxypyridine | −319.75507 | −321.56550 | −10.2 | −15.4 | +2.9 |
| 4-pyridone | −319.75389 | −321.55984 | | | |

[a] All calculations were carried out at the optimized 3-21G geometries.

In view of the importance of such tautomeric equilibria, there is a need for the accurate theoretical prediction of the energy differences between the tautomeric forms, which calculations reported to date have failed to provide. Such accurate predictions are a prerequisite for the determination of macroscopic properties such as equilibrium constants and the inclusion of solvent effects. Previous calculations suggest that only ab initio calculations of suitable quality can accurately provide such predictions. In view of the lack of experimental geometries for the molecules under investigation, a *full* geometry optimization is required. Previous studies on simpler molecules[10] and other heterocycles[11] have shown that to obtain accurate geometries, a double-$\zeta$ quality basis is a minimum standard.

In this paper we describe the results of such calculations on the six molecules involved in equilibria I, II, and III. We also present measurements of the core electron ionization energies (IE) of the three isomeric hydroxypyridines, and the interpretation of

---

(1) Pullman, B. *Int. J. Quantum Chem., Symp.* **1969**, *3*, 83.

(2) Pullman, B.; Pullman, A. *Adv. Heterocycl. Chem.* **1971**, *13*, 77.

(3) Kwiatkowski, J. S.; Pullman, B. *Adv. Heterocycl. Chem.* **1975**, *18*, 199.

(4) Beak, P.; Fry, F. S.; Lee, J.; Steele, F. *J. Am. Chem. Soc.* **1976**, *98*, 171.

(5) Guimon, C.; Garrabe, G.; Pfister-Guillouzo, G. *Tetrahedron Lett.* **1979**, *28*, 2585.

(6) Suradi, S.; El Saiad, N.; Pilcher, G.; Skinner, H. A. *J. Chem. Thermodyn.* **1982**, *14*, 45.

(7) Cook, M. J.; El-Abbady, S.; Katritzky, A. R.; Guimon, C.; Pfister-Guillouzo, G. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1652.

(8) Krebs, C.; Hofmann, H. J.; Kohler, M. J.; Weiss, C. *Chem. Phys. Lett.* **1980**, *69*, 537.

(9) La Manna, G. *J. Mol. Struct.* (*Theochem.*) **1981**, *85*, 389.

(10) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(11) Patterson, A. J.; Hillier, I. H.; Davies, R. H., unpublished results.

0002-7863/83/1505-3568$01.50/0 © 1983 American Chemical Society

Table II. Optimized Bond Lengths (Å)

| | bond | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| molecule | N1C2 | C2C3 | C3C4 | C4C5 | C5C6 | C6N1 | N1H | C2H | C3H | C4H | C5H | C6H | CO | OH |
| pyridine | 1.331 | 1.382 | 1.383 | 1.383 | 1.382 | 1.331 | | 1.070 | 1.070 | 1.071 | 1.070 | 1.070 | | |
| pyridine exptl[17] | 1.3402 | 1.3945 | 1.3944 | 1.3944 | 1.3945 | 1.3402 | | 1.0843 | 1.0805 | 1.0773 | 1.0805 | 1.0843 | | |
| 2-hydroxypyridine | 1.312 | 1.392 | 1.375 | 1.393 | 1.374 | 1.334 | | | 1.069 | 1.071 | 1.068 | 1.069 | 1.359 | 0.969 |
| 2-pyridone | 1.390 | 1.449 | 1.339 | 1.437 | 1.340 | 1.368 | 0.999 | | 1.066 | 1.075 | 1.068 | 1.072 | 1.220 | |
| 3-hydroxypyridine | 1.329 | 1.380 | 1.384 | 1.381 | 1.388 | 1.329 | | 1.070 | | 1.071 | 1.072 | 1.072 | 1.374 | 0.965 |
| 3-pyridone | 1.329 | 1.435 | 1.438 | 1.366 | 1.382 | 1.341 | 1.003 | 1.068 | | 1.069 | 1.070 | 1.065 | 1.241 | |
| 4-hydroxypyridine | 1.327 | 1.382 | 1.383 | 1.386 | 1.378 | 1.335 | | 1.071 | 1.070 | | 1.067 | 1.071 | 1.369 | 0.967 |
| 4-pyridone | 1.372 | 1.334 | 1.460 | 1.460 | 1.334 | 1.372 | 0.996 | 1.070 | 1.067 | | 1.067 | 1.070 | 1.225 | |
| 2-pyridone exptl[18] | 1.401 | 1.444 | 1.334 | 1.421 | 1.371 | 1.335 | | | | | | | 1.236 | |

these data, as a further aid in the study of the differences in the electronic structure of these molecules.

## Theoretical Methods

Optimized geometries were determined for the six molecules, assuming $C_s$ symmetry and employing a 3-21G split valence basis,[10] successfully used in previous optimization studies. The calculations were carried out with the program HONDO, using analytic gradient techniques.[12] Full geometry optimization was carried out until the largest component of the energy gradient was less than 0.0026 au, yielding bond lengths and angles converged to better than 0.005 Å and 0.5°, respectively. Further optimization of 2-hydroxypyridine and 2-pyridone until this figure was reduced to 0.001 au led to an energy lowering of only 0.5 kJ mol$^{-1}$. We therefore estimate that the energy differences quoted in this paper are accurate to better than 1 kJ mol$^{-1}$. The calculations for 2- and 3-hydroxypyridine were carried out with the hydroxy hydrogen being cis to the nitrogen atom. Further calculations at these optimized geometries were carried out with a basis having a better s, p basis, together with p and d polarization functions on the hydrogen and first-row atoms, respectively. For these calculations we use the 6-31G** basis described by Pople.[13] The calculations were carried out on the CDC 7600 of the University of Manchester Regional Computer Center and the CRAY 1 computer of the S.E.R.C. Daresbury Laboratory.

## Experimental Details

Commerical samples (Aldrich Chemical Co.) of the hydroxypyridines were employed. Gas-phase X-ray photoelectron spectra (XPES) were measured with Al Kα radiation. The spectrometer described earlier[14] was modified[15] to obtain XPES. The spectra were calibrated with $CO_2$, $C_6H_6$, and $N_2$ which have IEs close to those being measured.[16]

## Theoretical Results

In the discussion of the molecular geometries, the atoms are numbered starting at the nitrogen atom, with the oxygen atom being bonded to C2, C3, and C4 in 2-, 3-, and 4-hydroxypyridine, respectively. The optimized bond lengths and angles for the six molecules studied here are given in Tables II and III, respectively. For pyridine, also optimized in a 3-21G basis, the agreement with the experimental microwave data of Bak et al.[17] is to within 0.02 Å and 2° for bond lengths and angles, respectively. In general it can be seen that OH substitution has very little effect on the ring geometry, compared to that of pyridine, except that for 2-hydroxypyridine the N1C2 bond length is shortened by 0.02 Å. For 2- and 4-pyridone, the optimized structures conform closely to those expected from classical valence structures. For 3-pyridone, however, for which no classical valence structure can be written, N–C bond lengths close to those of pyridine are found, showing the importance of those structures involving a positively charged nitrogen atom. For 2-pyridone, our optimized gas-phase structure yields bond lengths which differ by up to 0.03 Å from those found in previously reported solid-state crystallographic studies,[18] where considerable intermolecular hydrogen bonding occurs.

We turn now to the relative energies of the isomeric hydroxypyridines and to the tautomeric equilibria. The calculations using both basis sets correctly predict that 2-hydroxypyridine is the most stable isomer. The stabilities of the other two isomers are the same within experimental error, while our calculations predict 3-hydroxypyridine to be the least stable. At the 3-21G level, the relative energies, when compared with the experimental values,[6] are seen to be accurate to 10 kJ mol$^{-1}$ (Table I). Expansion of the basis to the 6-31G** level alters the relative stabilities by approximately 5 kJ mol$^{-1}$ and does not lead to a better correlation between theory and experiment. The stabilizing effect of the intramolecular hydrogen bonding in 2-hydroxypyridine was investigated by calculating the energies of the three hydroxypyridines following rotation about the C–O(H) bond by 90°, thus moving the C–OH hydrogen atom out of the plane of the ring. In a 3-21G basis, using optimized geometries, the planar forms were more stable by 39.4, 10.6, and 17.1 kJ mol$^{-1}$ for the 2-, 3-, and 4-hydroxypyridines, respectively, indicating a considerable contribution to the stability of 2-hydroxypyridine from intramolecular hydrogen bonding.

In the following discussion, we neglect contributions to $\Delta H^\circ$ arising from the temperature dependence of the enthalpy, which have been estimated to be less than 1 kJ mol$^{-1}$.[8] The use of the 3-21G basis predicts 2-pyridone to be more stable than 2-hydroxypyridine, in disagreement with the experimental result, although the calculated energy difference (7 kJ mol$^{-1}$) is small (Table IV). However, the 6-31G** basis reverses the relative stabilities found with the 3-21G basis and yields a calculated relative stability that is essentially in agreement with the experimental data (Table IV). Both basis sets predict 4-hydroxypyridine to be more stable than 4-pyridone, the stabilities being ~10 kJ mol$^{-1}$ greater than those calculated for reaction I, in line with the experimental results of Cook et al.[7] The 3-21G basis predicts 3-hydroxypyridine to be considerably more stable (by 97 kJ mol$^{-1}$) than 3-pyridone, which may be associated with the lack of a classical valence structure for the latter molecule.

## Core Ionization Energies and Molecular Charge Distributions

The measured core IEs are shown in Table V. For the 3- and 4-hydroxypyridines the XPES shows a single N 1s and O 1s line. However, in the case of 2-hydroxypyridine, the XPES, measured at 68 °C, shows two well-resolved peaks in the O 1s spectrum, the N 1s peak having a shoulder to high IE. These features are clearly due to both tautomers being present in the gas phase. The pyridone form, having a higher N 1s and lower O 1s IE than the hydroxy tautomer, being the minor component, in agreement with previous studies employing low-energy photoelectron spectroscopy.[5] We discussed only the O 1s and N 1s IEs, the C 1s peaks being too broad to allow a detailed interpretation. A comparison of the experimental IEs, with those given by Koopmans' theorem (Table V), shows that for oxygen, but not for nitrogen, observed changes in the IEs are accurately given by the calculations, although, as expected, the calculated values are some 20 eV too large, due to the lack of electron reorganization effects. The origin of the rather small chemical shifts may be sought from a consideration of the

---

(12) Dupuis, M.; Rys, J.; King, H. F. Quantum Chemistry Program Exchange, University of Indiana. Bloomington, Indiana 47401; HONDO 76, Programs 338 and 336.

(13) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(14) Considine, M.; Connor, J. A.; Hillier, I. H. *Inorg. Chem.* **1977**, *16*, 1392.

(15) Atha, P. M.; Hillier, I. H.; MacDowell, A. A.; Guest, M. F. *J. Chem. Phys.* **1982**, *77*, 195.

(16) Thomas, T. D.; Shaw, R. W. *J. Electron Spectrosc. Relat. Phenom.* **1974**, *5*, 1081.

(17) Bak, B.; Hansen-Nygaard, L.; Rastrup-Andersen, J. *J. Mol. Spectrosc.* **1958**, *2*, 361.

(18) Penfold, B. R. *Acta Crystallogr.* **1953**, *6*, 591.

**Table III.** Calculated Bond Angles (deg)

| molecule | bond angle | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | N1C2C3 | C2C3C4 | C3C4C5 | C4C5C6 | C5C6N1 | C6N1C2 | N1C2H | C2C3H | C3C4H | C4C5H | C5C6H | C6N1H | $C_{(x-1)}C_xO$ | $C_xOH$ |
| pyridine | 122.6 | 118.5 | 119.0 | 118.5 | 122.6 | 118.8 | 116.8 | 120.4 | 120.5 | 121.0 | 120.7 | | | |
| pyridine exptl[17] | 123.9 | 118.5 | 118.3 | 118.5 | 123.9 | 116.8 | 115.9 | 120.2 | 120.8 | 121.3 | 120.2 | | | |
| 2-hydroxypyridine | 122.9 | 117.3 | 120.1 | 117.9 | 122.3 | 119.5 | | 120.3 | 120.0 | 121.4 | 121.6 | | 117.0 | 108.7 |
| 2-pyridone | 113.5 | 122.1 | 120.9 | 117.9 | 120.9 | 124.6 | | 114.9 | 120.5 | 121.0 | 122.7 | 119.9 | 120.7 | |
| 3-hydroxypyridine | 122.7 | 118.5 | 118.6 | 119.4 | 121.5 | 119.3 | 117.6 | | 119.3 | 120.6 | 121.0 | | 122.9 | 113.5 |
| 3-pyridone | 122.4 | 112.0 | 123.1 | 120.9 | 117.1 | 124.5 | 118.0 | | 116.6 | 120.8 | 124.8 | 117.9 | 122.6 | |
| 4-hydroxypyridine | 123.0 | 118.9 | 118.4 | 118.7 | 123.2 | 117.9 | 116.8 | 120.0 | | 119.8 | 119.9 | | 123.4 | 113.3 |
| 4-pyridone | 121.7 | 121.9 | 113.2 | 121.9 | 121.7 | 119.5 | 115.9 | 121.1 | | 117.0 | 122.4 | 120.2 | 123.4 | |
| 2-pyridone exptl[18] | 112.7 | 122.3 | 122.2 | 116.0 | 121.8 | 125.1 | | | | | | | 121.3 | |

Table IV. Calculated Enthalpies (kJ mol$^{-1}$) of the Reactions Hydroxypyridine → Pyridone[a]

| reaction no.[b] | calcd $\Delta H°$ | | exptl $\Delta H°$ |
|---|---|---|---|
| | 3-21G | 6-31G** | |
| I | −7.4 | 4.2 | 2.6 ± 1.2 |
| II | 97.1 | | |
| III | 3.2 | 14.9 | |

[a] All calculations were carried out at the optimized 3-21G geometries. [b] The reactions are: (I) 2-hydroxypyridine → 2-pyridone; (II) 3-hydroxypyridine → 3-pyridone; (III) 4-hydroxypyridine → 4-pyridone.

Table V. Experimental[a] and Calculated Core Ionization Energies (eV) of Hydroxypyridines

| molecule | O 1s | | N 1s | | |
|---|---|---|---|---|---|
| | exptl | calcd[b] | exptl | calcd[b] | ΔSCF[c] |
| 2-hydroxypyridine | 539.3 | 560.3 (557.3) | 404.9 | 423.37 (421.5) | 406.55 |
| 2-pyridone | 536.6 | 558.1 (555.2) | 406.0 | 425.0 (423.0) | |
| 3-hydroxypyridine | 539.6 | 560.5 (557.5) | 404.9 | 423.68 (421.8) | 406.76 |
| 4-hydroxypyridine | 539.7 | 560.7 (557.8) | 404.6 | 423.26 (421.4) | 406.34 |

[a] Estimated uncertainty ±0.1 eV, relative to calibrant. [b] Calculated with Koopmans' theorem; values obtained from the 6-31G** basis are given first, the values in parentheses are from the 3-21G basis. [c] 6-31G** basis.

Table VI. Calculated Atomic Charges (6-31G** Basis)

| atom | molecule | | | |
|---|---|---|---|---|
| | 2-hydroxypyridine | 2-pyridone | 3-hydroxypyridine | 4-hydroxypyridine |
| C2 | 0.68 | 0.80 | 0.06 | 0.15 |
| C3 | −0.23 | −0.29 | 0.37 | −0.28 |
| C4 | −0.07 | −0.06 | −0.12 | 0.48 |
| C5 | −0.23 | −0.27 | −0.19 | −0.24 |
| C6 | 0.14 | 0.21 | 0.11 | 0.14 |
| N | −0.63 | −0.77 | −0.53 | −0.56 |
| O | −0.68 | −0.65 | −0.70 | −0.69 |

formal Mulliken atomic charges summarized in Table VI. We report those from the 6-31G** basis; those from the 3-21G basis follow a similar trend. The core IEs may be related to the atomic charges via the point-charge potential model[19] in which the core IE ($E_i$) associated with atom $i$ is given as

$$E_i = Aq_i + \sum_{i \neq j} q_j/R_{ij} \qquad (1)$$

Here $q_i$ is the charge on atom $i$, $R_{ij}$ is the separation of atoms $i$ and $j$, and $A$ is a constant. Of the three isomers, 3-hydroxypyridine has the smallest nitrogen electron density and also the smallest nitrogen π density, in line with the contribution of structures having a negatively charged nitrogen atom to the ortho- and para-substituted pyridines. This result correlates with the observation that Koopmans' theorem predicts 3-hydroxypyridine to have the largest N 1s IE of the isomers. In spite of differences in the nitrogen atomic charges, Koopmans' theorem predicts that both 2- and 4-hydroxypyridine have the same N 1s IEs. This is due to the larger carbon (C2) charge in 2- than in 4-hydroxypyridine arising from the electron withdrawing effect of the oxygen atom attached to C2 in the former molecule (Table VI). However, these predictions from Koopmans' theorem, which correlate with the formal atomic charges, disagree with the experimental observation that 2- and 3-hydroxypyridine have the same N 1s IE, that of 4-hydroxypyridine being somewhat smaller. SCF calculations of the N 1s hole states of the three isomers were carried out in the 6-31G** basis and yielded the ΔSCF IEs shown in Table V. It

---

(19) Gelius, U.; Roos, B.; Siegbahn, P. *Chem. Phys. Lett.* **1970**, *4*, 471.

can be seen that small differences in the relaxation energies for the three core hole states has yielded IE differences which agree with experiment, within the experimental uncertainty.

The shifts in the O 1s IEs are well reproduced by Koopmans' theorem and are determined to a large extent by the Coulombic potential arising from neighboring atoms, being the second term in eq 1. Thus, the oxygen charges for all three isomers are very similar, although the meta-substituted molecule has the greatest oxygen electron density in line with the smallest nitrogen density found for this molecule. The similar O 1s IEs in 3- and 4-hydroxypyridine and the smaller value found for 2-hydroxypyridine may be attributed to the Coulombic effect of neighboring atoms. Thus, in 2-hydroxypyridine, although C2 is more positively charged than the corresponding atoms (C3, C4) in 3- and 4-hydroxypyridine, the O 1s IE in 2-hydroxypyridine is reduced, due in part to the neighboring nitrogen atom having a large negative charge, an effect absent for the other two isomers. For these latter two molecules, the effective atomic charges suggest that the Coulombic effect of the neighboring atoms is approximately the same, leading to similar O 1s IEs. the measured and calculated O 1s and N 1s IEs for 2-hydroxypyridine and 2-pyridone correlate well, but are not in line with the respective atomic charges. This may be attributed to the Coulombic effect of the positively charged hydrogen atom bonded respectively to the oxygen and nitrogen atoms, leading to an increased IE from that expected from self-charges alone.

## Conclusions

With the higher level of theory reported in this paper, we have achieved an energy difference for the tautomers involved in equilibrium I close to the experimental value, and far better than that previously reported. The energy differences between the three isomeric hydroxypyridines studied here are within 10 kJ mol$^{-1}$ of the experimental values. The effect of correlation on these energetics remains to be studied. For oxygen the measured core electron IEs are found to reflect the small changes in the charge distributions of the three isomers, and to be interpreted by calculations at the Koopmans' theorem level of approximation. For nitrogen, $\Delta$SCF calculations are needed to predict the correct ordering of the core electron IEs.

**Acknowledgment.** We thank the Science and Engineering Research Council and the Royal Society for financial support and Professor H. A. Skinner and Dr. R. H. Davies for helpful discussions.

**Registry No.** 2-Hydroxypyridine, 72762-00-6; 2-pyridine, 142-08-5; 3-hydroxypyridine, 109-00-2; 3-pyridone, 58064-43-0; 4-hydroxypyridine, 626-64-2; 4-pyridine, 108-96-3.

---

# Isotopic Perturbation Effects on a Single Averaged NMR Peak: Norbornyl Cation

**Martin Saunders* and Mandes R. Kates**

*Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. Received December 14, 1982*

**Abstract:** A variant of the isotopic perturbation method for investigating questions of whether molecules are rapidly equilibrating over low barriers or have symmetric, single-minimum surfaces is reported. To apply it, the $^1$H NMR spectrum of monodeuterated norbornyl cation was examined over a higher temperature range than that used previously. It shows an additional peak on the high-field side of the averaged 1,2,6 signal due to perturbation of the average shift of the remaining three protons by an equilibrium isotope effect in the fraction of molecules containing deuterium on carbons 1, 2, or 6. $K_{iso}$ was found to vary from 1.66 to 2.14 over the temperature range from −105 to −43 °C, yielding a value for $\Delta H$ of 310 ± 20 cal/mol. Using a model of the equilibrating classical ions and the reported kinetic isotope effects on solvolysis leads to a prediction of a *downfield* shift for this peak, while the nonclassical ion structure readily accommodates an upfield shift.

The isotopic perturbation method for investigating questions of whether molecules are rapidly equilibrating over low barriers or have symmetric, single-minimum surfaces has yielded valuable information in carbonium ion and noncarbonium ion cases. In the applications reported,[1,2] asymmetric introduction of an isotope has resulted in the splitting of peaks in the NMR spectrum, the magnitude of the splitting values being compared with splittings in reference compounds known to have single- and double-minimum energy surfaces. Cases involving rapid equilibrium (double-minimum cases) have shown large values of splitting in the $^{13}$C NMR in contrast with nonequilibrating systems (single-minimum cases).

It is our present purpose to report a case where a rapid rearrangement process completely scrambles a group of protons among a group of carbons, producing all possible permutations of the hydrogens. Introduction of deuterium, in such a molecule, cannot cause splitting of the corresponding carbon NMR signal since the rapid rearrangements of deuterium and hydrogen give each carbon the same averaged environment and frequency. Nevertheless, introduction of deuterium can cause a *shift* in the single averaged peak of the remaining *protons*, compared with its position in the nondeuterated material. Since the frequency of any peak in a system undergoing rapid rearrangement is the weighted average of the separate frequencies being averaged, the magnitude and direction of this shift can be used to decide among various structural possibilities by comparison with the predicted shifts for the different possibilities.

We report the application of this variant of the isotopic perturbation method to the case of the stable norbornyl cation. This ion was previously investigated by isotopic perturbation through investigating the *low-temperature* $^{13}$C NMR spectra of species where deuterium was introduced to break the symmetry.[2] We concluded from the results that the ion has the nonclassical, bridged, protonated-cyclopropane structure with high likelihood.

---

(1) (a) M. Saunders, M. R. Kates, K. B. Wiberg, and W Pratt, *J. Am. Chem. Soc.*, **99**, 8072 (1977); (b) M. Saunders in "Stereodynamics of Molecular Systemsrqt, R. Sarma, Ed., Pergamon Press: New York 1979, p 171; (c) L. R Schmitz and T. S. Sorensen, *J. Am. Chem. Soc.*, **102**, 1645 (1980); (d) M. Saunders and H.-U. Siehl, *ibid.*, **102**, 6868 (1980); (e) P. Ahlberg, C. Engdahl, and G. Jonsall, *ibid.*, **103**, 1583 (1981); (f) H. Hogeveen and E. M. G. A. van Kruchten, *J. Org. Chem.* **46**, 1350 (1981); (g) R. P. Kirchen, K. Ranganayakula, A. Rauk, B. P. Singh, and T. S. Sorensen. *J. Am. Chem. Soc.*, *103*, 588 (1981).

(2) M. Saunders and M. R. Kates, *J. Am. Chem. Soc.*, **102**, 6867 (1980).

0002-7863/83/1505-3571$01.50/0 © 1983 American Chemical Society