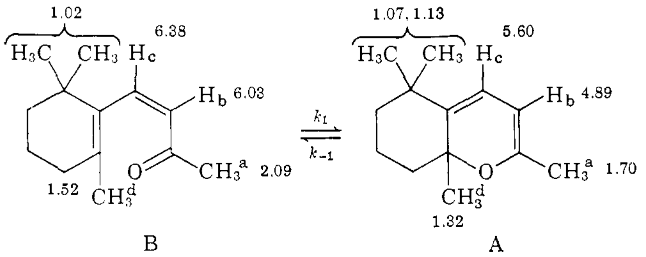

Figure 1. Nmr spectral data for *cis*-β-ionone and the corresponding α-pyran.

explain certain otherwise enigmatic results. We wish to report the first clear-cut example of such a valence isomerization. A sample of 1-oxa-2,5,5,9-tetramethyl-1,5,6,7,8,10-hexahydronaphthalene (A) was obtained by irradiation of *trans*-β-ionone according to the procedure of Büchi and Yang.[1a] As Figure 1 shows, the nmr spectrum of A is in complete accord with the α-pyran structure assigned this substance by Büchi and Yang. However, there appeared in the spectrum, in addition to the bands attributed to the α-pyran, the following series of weak bands: singlet at δ 1.02 another at 2.09, and a modified AB pattern at 6.03 and 6.38 (J_{AB} = 12.5 cps). Two features of these extraneous bands were striking. They were not removed by further purification of the pyran, and they were a part of the series of bands expected for the unknown *cis*-β-ionone (B).

If *cis*-β-ionone were responsible for these bands and were also in mobile equilibrium with the α-pyran, it seemed reasonable to expect the equilibrium content of the less stable isomer to be increased with increasing temperature. The predicted change can indeed be observed; the spectrum of B (Figure 1) shows an increase in intensity with a compensating decrease in that due to A as the temperature of the nmr probe is increased. The total spectrum reverts to its original form when the temperature is returned to normal. This process has been repeated a number of times with a single sample with no apparent decomposition. On the basis of the nmr spectrum, and the complete reversibility of the process, we have assigned B the *cis*-β-ionone structure.

Since the AB patterns for the C-3 and C-4 protons in A and B are separated cleanly from each other and from all other bands in the spectrum, the equilibrium constant for the valence isomerization can be measured conveniently. At 327°K it is 4.61 and at 386°K it is 1.52. The α-pyran is more stable than *cis*-β-ionone, $\Delta H^\circ = 5.5$ kcal/mole, but the thermodynamic stability is largely compensated by the entropy change (−14 eu) in going from the monocyclic to the bicyclic molecule. The rigidity of the bicyclic α-pyran is reflected in the separate resonance peaks for the two methyls of the geminal methyl grouping.

The rate of the valence isomerization was determined by perturbing the equilibrium and measuring the rate of reversion. An nmr tube containing 150 mg of the pyran in 500 mg of tetrachloroethylene was heated to 120° for 10 min and quenched in a Dry Ice bath. The tube was then placed in the probe and allowed to reach thermal equilibrium. The rate was followed by measuring the decrease in the peak height of the larger peak in the doublet at δ 6.03. Using the rate equation

$$2.3 \log \frac{x_0 - x_e}{x_t - x_e} = (k_1 + k_{-1})t$$

where x = peak height,[2] and values of the equilibrium constant calculated from the data obtained at higher temperatures, both k_1 and k_{-1} were obtained. At 18° $k_1 = 1.4 \times 10^{-3}$ sec^{-1} while $k_{-1} = 1.3 \times 10^{-4}$ sec^{-1}. Measurements at several temperatures between 0 and 18° gave E_a = 20 kcal/mole for the *cis*-dienone to α-pyran reaction and E_a = 27 kcal/mole for the reverse process.

The magnitude of the rate difference for the valence isomerization of the *cis*-dienone to pyran compared with that of *cis*-2-*cis*-4-*trans*-6-octatriene to *trans*-5,6-dimethyl-1,3-cyclohexadiene[3] seems surprisingly large. A factor of between five and six powers of ten can be estimated from the reported data. In view of the high rate of the dienone to pyran isomerization the failure of previous investigators[1] to isolate both valence isomers seems reasonable.[4]

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[2] A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms of Homogeneous Chemical Reactions," John Wiley and Sons, Inc., New York, N. Y., 2nd ed, 1961, p 186.

[3] E. N. Marvell, G. Caple, and B. Schatz, *Tetrahedron Letters*, 385 (1965).

[4] We are pleased to acknowledge the generous support provided for this work by the National Science Foundation through Grants G-23702 and GP 4985. Financial assistance from the National Science Foundation for the purchase of the Varian A-60 nmr spectrometer used in this study is also gratefully acknowledged.

Elliot N. Marvell, Gerald Caple
Thomas A. Gosink, Gerald Zimmer
Department of Chemistry, Oregon State University
Corvallis, Oregon
Received November 8 1965

The Conformational Preference of the Nonbonding Electron Pair in Piperidine

Sir:

Central to the problem of the spatial requirements of nonbonding electrons has been the determination of the conformational preference of the nitrogen lone pair in piperidine. Aroney and LeFèvre[1] reported that the sign and magnitude of the molar Kerr constants of piperidine and N-methylpiperidine require the electron lone pair to be larger[2] than hydrogen, and, in fact, approximately equivalent in size to the methyl group. These conclusions have been criticized by several groups.[3–5] Thus, Allinger and co-workers[5] have presented arguments that the methyl group is considerably larger,[2] and hydrogen somewhat larger, than the lone pair. From the low-temperature nmr spectra of N-substituted and unsubstituted piperidines, we have obtained evidence which corroborates portions of the conclusions of both groups. Our evidence indicates that the lone pair in N-substituted piperidines is indeed axially oriented,[5] but that the

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[1] M. Aroney and R. J. W. LeFèvre, *J. Chem. Soc.*, 3002 (1958); M. J. Aroney, C.-Y. Chen, R. J. W. LeFèvre, and J. D. Saxby, *ibid.*, 4269 (1964).

[2] The "larger" of two groups is operationally defined in this context as that group which preferentially assumes the equatorial position.

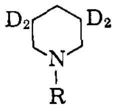
[3] T. M. Moynehan, K. Schofield, R. A. Y. Jones, and A. R. Katritzky, *Proc. Chem. Soc.*, 218 (1961); *J. Chem. Soc.*, 2637 (1962).

[4] N. W. J. Pumphrey and M. J. T. Robinson, *Chem. Ind.* (London), 1903 (1963).

[5] N. L. Allinger, J. G. D. Carpenter, and F. M. Karkowski, *Tetrahedron Letters*, No. 45, 3345 (1964); *J. Am. Chem. Soc.*, **87**, 1232 (1965).

lone pair in piperidine itself assumes the equatorial position[1] in both polar and nonpolar solvents.

Hamlow,[6] Bohlmann,[7] and their respective coworkers have demonstrated from studies of quinolizidine systems that the axial protons that are on the α-carbon atoms and are *anti*-coplanar to the nitrogen lone pair are shifted upfield with respect to the positions of axial protons of model systems which lack these characteristics. This shift, possibly caused by bonding of the lone pair with the *anti*-coplanar σ^* (C–H$_{\text{axial}}$) orbital,[6] gives rise to a considerable enhancement of the axial–equatorial chemical shift difference between the α-protons (0.80–0.93 ppm in quinolizidine,[6,7] as compared to 0.40–0.50 ppm in cyclohexane,[8,9] cyclohexene,[10] and protonated quinolizidine,[6] all of which lack nonbonding electrons). With this precedent in mind, we have examined the chemical shift differences between the axial and equatorial protons at the α positions of piperidine (I), N-methylpiperidine (II), N-*t*-butylpiperidine (III), and their respective hydrochlorides. Observation of an enhanced chemical shift difference would establish the *anti*-coplanar geometry, which is possible only when the lone pair is axial.



I, R = H
II, R = CH_3
III, R = *t*-C_4H_9

For the sake of facility in the analysis of the nmr spectra, we have placed deuterium in the β positions of I–III. Dimethyl glutarate was subjected to conditions suitable for exchange (CH_3OD–CH_3ONa) and reduced to the diol, which was converted to the piperidine by way of the dibromide. Two processes may be operative in piperidine systems: ring inversion and inversion of configuration of nitrogen. Since, at temperatures above −10°, the spectra of the ring protons of I–III consist of two fairly sharp peaks, both processes must be fast on the nmr time scale.[11] As the tempeature is decreased, slowing of ring inversion brings about the formation of two AB spectra associated with the α and the γ protons. Since only one AB pattern is observed for each of the geminal proton pairs, nitrogen inversion and/or chemical exchange of the proton on nitrogen in I must still be fast. As predicted from the model described above, the chemical shift difference, $\delta_{ae}(\alpha)$, between the protons adjacent to nitrogen in N-substituted piperidines is exceptionally large (0.942 ± 0.014 ppm for II and 0.997 for III in methanol-d_4, 1.057 for III in cyclopropane), whereas $\delta_{ae}(\gamma)$ for the protons further removed from the nitrogen atom is quite normal (0.518 ± 0.012 ppm for II and 0.528 for III in methanol-d_4). The predominant species in solution therefore possesses an axial lone pair and an equatorial substituent. The situation is reversed, however, in the case of piperidine. The observed normal chemical shift differences [$\delta_{ae}(\alpha) = 0.436 \pm 0.004$ ppm in methanol-d_4 and 0.458 in cyclopropane; $\delta_{ae}(\gamma) = 0.414 \pm 0.006$ ppm in methanol-d_4] indicate that the axial α-protons are not *anti*-coplanar with the lone pair. Thus, the predominant though not necessarily sole species in solution possesses an equatorial lone pair and an axial hydrogen. These conclusions, although qualitative, appear to be independent of whether a polar, hydroxylic solvent (methanol) or a nonpolar, nonhydroxylic solvent (cyclopropane) is used.[12] Furthermore, protonation of II and III in methanol-d_4, with concomitant removal of the lone pair, brings the values of $\delta_{ae}(\alpha)$ close to that of piperidine. All the above-mentioned compounds that lack an axial lone pair therefore share a nearly common value of $\delta_{ae}(\alpha)$. The spectral differences of these structurally similar compounds are clearly demonstrated in Figure 1.

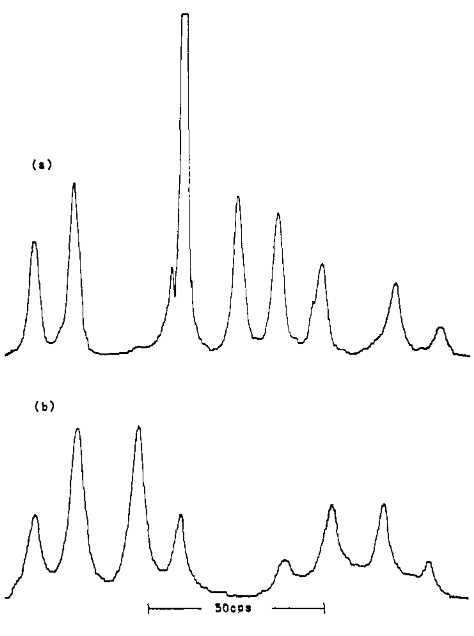


Figure 1. The low-temperature nmr spectra of N-methylpiperidine-d_4 (a, −60°) and piperidine-d_4 (b, −85°) in methanol-d_4 at the slow-exchange limit of ring inversion. The α-protons give rise to the low-field quartet in both cases. The resonances in (a) of the methyl group and of an impurity fall between the α-axial and α-equatorial protons. The large upfield shift of the α-axial protons in (a), caused by the axial lone pair, produces an overlapping with the first peak of the γ-equatorial protons. The field increases from left to right. The spectra in cyclopropane were almost identical with those shown here.

These investigations suggest the following steric order:[2] CH_3 > lone pair > H. The relative orientation of the proton and the lone pair in piperidine may not in fact be a function of size alone. Claxton[13] has suggested that an equatorial preference may occur because this orientation is spatially favorable for delocalization of the lone pair into the ring. There may still be rather serious solvent effects.[12] The

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(6) H. P. Hamlow, S. Okuda, and N. Nakagawa, *Tetrahedron Letters*, No. 37, 2553 (1964).

(7) F. Bohlmann, D. Schumann, and H. Schulz, *ibid.*, **No. 3**, 173 (1965); F. Bohlmann, D. Schumann, and C. Arndt, *ibid.*, **No. 31**, 2705 (1965); however, see C.-Y. Chen and R. J. W. LeFèvre, *ibid.*, **No. 21**, 1611 (1965).

(8) F. A. L. Anet, M. Ahmad, and L. D. Hall, *Proc. Chem. Soc.*, 145 (1964).

(9) F. A. Bovey, F. P. Hood, III, E. W. Anderson, and R. L. Kornegay, *ibid.*, 146 (1964); *J. Chem. Phys.*, **41**, 2041 (1964).

(10) F. A. L. Anet and M. Z. Haq, *J. Am. Chem. Soc.*, **87**, 3147 (1965).

(11) All spectra were taken with a Varian Associates A-60 spectrometer, equipped with a temperature probe. The recorder was calibrated prior to these experiments. The full range of temperatures was calibrated with a methanol sample, thus assuring an accuracy of at least ±1°.

(12) However, see E. L. Eliel, E. W. Della, and T. H. Williams, *Tetrahedron Letters*, **No. 13**, 831 (1963), and K. Brown, A. R. Katritzky, and A. J. Waring, *Proc. Chem. Soc.*, 257 (1964).

(13) T. A. Claxton, *Chem. Ind.* (London), 1713 (1964).

present results do not constitute a direct contradiction[5] or corroboration[1] of the work of previous authors, since identical conditions of solvent (benzene) and concentration (infinite dilution) can never be attained. Experiments with other aromatic solvents are being undertaken with the hope of resolving this discrepancy.

We have analyzed the temperature dependence of the nmr spectra of I–III according to the method of Alexander.[14] The ring-inversion processes of I–III were characterized by activation energies on the order of 15 kcal/mole. Detailed consideration of the rate processes will be deferred to the complete paper. This work is being expanded to include the oxygen, sulfur, sulfoxide, silicon, and remaining group V heterocycles.

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(14) S. Alexander, *J. Chem. Phys.*, **37**, 967, 974 (1962); **38**, 1787 (1963); 40, 2741 (1964).

(15) The authors wish to express thanks to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this research.

(16) National Science Foundation Undergraduate Fellow, summer 1965.

Joseph B. Lambert,[15] Robert G. Keske[16]
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

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(p → d)–π Interactions in the Silicon–Nitrogen Bond. An Experimental Test

Sir:

We have tested the hypothesis of (p → d)–π interaction in the silicon–nitrogen bond by the synthesis and study of systems suitable for the application of nmr techniques. It has been shown recently that nitrogen–proton coupling constants are useful parameters for the examination of nitrogen atom hybridization, provided the dominant coupling mechanism is by the Fermi contact term (other necessary conditions have been discussed).[1,2] In this event the magnitude of the coupling J(N–H) between directly bonded atoms is proportional to the s character of the nitrogen orbital directed toward the hydrogen. The amount of s character in the nitrogen hybrid should increase with (p → d)–π bonding between nitrogen and silicon since this interaction requires the use of a nitrogen orbital with large, perhaps pure, p character. Thus the N–H coupling should provide a measure of this interaction in Si–N–H systems.

We have accordingly synthesized the isotopic isomers (for which we have coined the word "isotopomers"[3]) N-trimethylsilylaniline-N^{14} and -N^{15}, the isotopic substitution being effected because of the more favorable nmr spectral behavior of N^{15} compared with quadrupolar N^{14}. N-Trimethylsilylaniline[4] (I) was obtained by the action of trimethylchlorosilane on the yellow monolithio salt of aniline in benzene–hexane solution. This novel route, although requiring first the *in situ* preparation of the lithium salt from *n*-butyllithium, gave I in better yield (80%) than previously reported for the one-step synthesis[5] since no aniline hydrochloride is produced.

The nmr spectral parameters measured on a Varian A-60 using audio side-band calibration are: J(N^{15}–H) = 76.0 ± 0.2 cps; τ(N^{15}–H) 6.853 ± 0.003 cps; J(CH$_3$–N^{15}) = 1.0 ± 0.1 cps; τ(CH$_3$) 8.567 ± 0.003 cps.

The bonding situation at the nitrogen apparently differs little from (I)-N^{15} to the sp^3-hybridized ammonium-N^{15} ion [J(N^{15}–H) = 73.7 cps;[6] 73.2 cps[2]], whereas the results for both of these compounds differ markedly from the values of 98.7[1] and 90.5[2] cps for the sp^2-hybridized pyridinium ion. We deduce on the hypothesis outlined above that there is little (p → d)–π interaction in I.

We have observed the N^{15}–H coupling in aniline-N^{15} [J(N^{15}–H) = 78.5 ± 0.2 cps] in solutions of I, where the silicon compound acts as a drying agent, releasing aniline-N^{15} on hydrolysis. The observation of this coupling indicates lack of the proton exchange which is normally found in insufficiently dried samples of aniline-N^{15} and which causes collapse of the N^{15}–H doublet.[7] The magnitude of this coupling is consistent with a pyramidal stereochemical arrangement around nitrogen in aniline as deduced from dipole moment studies.[8]

These results clearly show that the hypothesis outlined above for coupling constants is incompatible with the hypothesis that there is considerable π interaction either in I or in aniline. The coupling constant hypothesis has ignored the effect of variations in the radial portions of the wave functions which may change according to the effective nuclear charge on nitrogen. Grant and Lichtman have recently cautioned use of directly bonded C^{13}–H couplings to deduce s character on the grounds that J(C^{13}–H) depends on the effective nuclear charge of carbon.[9] Use of this factor alone for the N–H systems cannot explain the differences between NH$_4^+$ and pyridinium ion without recourse to the other factors previously enumerated.[1,2]

The observation of J(CH$_3$–N^{15}) in (I)-N^{15} and of separate resonances for aniline-N^{15} (τ 6.947 ± 0.002 cps) and (I)-N^{15} in mixtures of the two shows that any exchange of trimethylsilyl group occurs at a rate slower than about 1 sec^{-1}, despite the ease of transamination reactions involving silicon.[10] No change in the spectrum of (I)-N^{15} was observed on heating to 120°.

Experiments are in progress to test the (p → d)–π bonding hypothesis in other group IV–nitrogen bonds.

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E. W. Randall
Department of Chemistry, Queen Mary College
University of London, London, E.1, England

J. J. Ellner, J. J. Zuckerman
Baker Laboratory, Cornell University
Ithaca, New York

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