

directions. Similarly negligible interactions were observed for 5-methyl-1,4-hexadiene and, by Schäfer and Schweig, for allylmethyl sulfide.^{19b} These results should be contrasted to the 2.2-eV interaction observed in allyltrimethyltin²² where σ - π conjugation has been demonstrated.^{5a, 19a}

We therefore agree with the original postulates^{2, 3b, c, d} and most current interpretations^{3a} that β -aryl group participation leads to a transition state *cis*ely resembling a symmetrical phenonium ion as depicted in eq 1. That is, the stabilizations are: for k_1 , principally distortional stabilization, and for k_2 mostly vertical stabilization. Both transition states 1^\ddagger and 3^\ddagger , being similar to 2, probably derive stabilization from cyclopropyl σ - π conjugation.²⁴

The results with the very nucleophilic neighboring group, MeS, when compared to our previous studies of neighboring C-metal bonds,⁵ suggest the following generalization for the neighboring group B: in eq 6. If the G: lone pair has a much lower ionization potential than does an orbital associated with the G-C σ bond, then the stabilization will require distortion to increase 13 overlap, whereas a lower "G-C σ bond ionization potential"¹⁹ results in dominant stabilization by σ - π conjugation which does not require such distortion.

Acknowledgment. We wish to acknowledge the assistance of Dr. Robert S. Brown and Dr. John Wright in the construction of the instrument and determination of photoelectron spectra.

(24) This development of σ - π conjugation at the transition state 1^\ddagger could explain both the facts that Ar_3 is faster than Ar_5 participation and the failure of Ar_5 participation to accurately follow σ^+ values.²⁵

(25) F. L. Schadt and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 7860 (1973).

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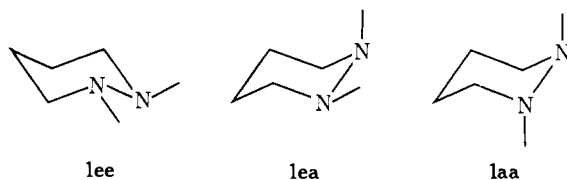
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Received April 11, 1973

1,2-Dimethylhexahydropyridazine Conformations by Carbon-13 Nuclear Magnetic Resonance

Sir:

The conformations of 1,2-dimethylhexahydropyridazine (1) have been the cause of some discussion. Anderson¹ concluded that it existed solely in the equatorial, equatorial *N*-methyl conformation **1ee** because the



proton nmr spectrum of the *N*-methyl groups remained a singlet at low temperature, where he assumed both ring flipping and nitrogen inversion to be slow. Katritzky and coworkers² then showed that the dipole

(1) J. E. Anderson, *J. Amer. Chem. Soc.*, **91**, 6374 (1969), and references therein.

moment of **1** was too high for **1ee** to be the sole conformation and, by using low temperature nmr studies of derivatives in conjunction with dipole moment studies, came to the striking conclusion that **1** exists as a 36:34:30 mixture,^{2b} later revised to a 62:20:18 mixture^{2d} of **1aa**:**1ea**:**1ee** at room temperature. Using a diagram topologically similar to Figure 1,^{2b} they made the important point that different ring flips and nitrogen inversions ought to have different activation energies, pointing out that all of the processes which cross the heavy vertical line of Figure 1 will be relatively slow because they force methyl groups to pass each other. They subsequently realized^{2d} that even ring flips, which do not force methyl groups past each other, should have substantially higher activation energies than nitrogen inversions which do not force methyl groups past each other, leading to three types of barriers for **1**.

We report ¹³C nmr data for **1** which illustrate freezing out of the two lower energy barriers, and which allow a more accurate estimation of the conformational population of **1**, by direct observation of the conformers.

The ¹³C nmr spectrum of **1**³ shows three sharp lines at ambient temperature, as expected when rapid conformational interconversion occurs. These lines broaden below about -20°, and, by -53°, six lines can be observed: a set of three lines (set A) which remain sharp as the temperature is lowered further, and a second set of three lines (set B). The lines of set B sharpen until about -85°, but then broaden substantially and disappear into the base line near -100°. At still lower temperatures, a new set of five lines (set C) appears. The positions of the lines together with assignments to the three types of carbons (verified by using undecoupled spectra for the ambient temperature spectrum and set A) appear as shown in Table I.

Because steric compression will certainly cause upfield cmr shifts for any conformation containing axial *N*-methyl substituents, set A, which has the farthest downfield carbon signals for each type of carbon present can be confidently assigned to **1ee**. By -53°, **1ee** is already interconverting slowly enough with the other conformations to allow resolution of the mixture of interconverting conformations **1ae**, **1aa**, and **1ea** as a second set of signals (set B). Thus the "easy" ring flip marked with dotted lines in Figure 1 is frozen out by -53°. A rough estimate of ΔG^\ddagger for this process gives *ca.* 10 kcal/mol, but line shape analysis for a more accurate figure remains to be carried out. This "easy" ring flip is thus not very much lower in energy than the processes marked by the center line in Figure 1, for which Anderson found a ΔG^\ddagger of about 12 kcal/mol.¹

The only rate processes left to freeze out are those of "easy" nitrogen inversion, the unmarked equilibria of Figure 1. We attribute the five observed lines of set C, the result of freezing out these equilibria, to conformation **1ae** (= **1ea**) and note that the average of each set of two lines is close to the positions for set B (and the

(2) (a) R. A. Y. Jones, A. R. Katritzky, D. L. Ostercamp, K. A. F. Record, and A. C. Richards, *Chem. Commun.*, 644 (1971); (b) R. A. Y. Jones, A. R. Katritzky, and R. Scattergood, *Chem. Commun.*, 644 (1971); (c) R. A. Y. Jones, A. R. Katritzky, D. L. Ostercamp, K. A. F. Record, and A. C. Richards, *J. Chem. Soc., Perkin Trans. 2*, 34 (1972); (d) R. A. Y. Jones, A. R. Katritzky, K. A. F. Record, and R. Scattergood, *ibid.*, 406 (1974).

(3) Data were collected on a Varian XL 100 instrument equipped for Fourier transform, using internal deuterium lock, and are reported in parts per million downfield from TMS.

Table I. Line Positions for the ^{13}C Nmr Spectrum of **1** (ppm from TMS)

Solvent	Temp., °C		CCH ₂	NCH ₃	NCH ₂
(CD ₃) ₂ CO	Ambient		23.4	40.9	54.1
(CD ₃) ₂ CO	-87	Set A	25.5	44.7	58.3
		Set B	20.0	35.4	48.0
1:1 (CD ₃) ₂ CO-CF ₂ Cl ₂	-88	Set A	25.6	44.8	58.5
		Set B	20.4	35.8	48.4
1:1 (CD ₃) ₂ CO-CF ₂ Cl ₂	-121	Set A	25.4	44.7	58.2
		Set C	15.6, 25.4 ^a	26.5, 43.5 ^b	43.0, ^b 54.2

^a This line was not observed, and presumably is obscured by the "set A" line at this position. ^b The assignments of these two lines may be inverted.

unobserved sixth line must then fall under a **1ee** line and remain unobserved), the averages being 20.5, 35.0, and 48.6 (at -121°), and set B coming at 20.4, 35.8, and 48.4 (at -88°). We observed no lines attributable to **1aa**, and, since substantial upfield shifts would be sure to result from the presence of two axial N-methyl groups, we doubt that a substantial amount of this conformation can be present at low temperature. Although line shape analysis remains to be carried out, ΔG^\ddagger will probably not turn out to be far from the 7–7.5 kcal/mol estimated from the temperature of maximum broadening.

It is interesting to compare the observed shifts for **1ea** with those expected for the effect of having an axial methyl group replace an equatorial one (Table II).

Table II. Comparison of Chemical Shifts for **1ee** and **1ea** at -121.3° (ppm from TMS)

Position	1ee	1ea	Shift difference	Predicted ^a
Me-1	44.7	43.5 ^b	-1.2	0
Me-2	44.7	26.5	-18.2	-8.5
C-3	58.2	54.2	-4.0	-2.6
C-4	25.4	15.6	-9.7	-5.5
C-5	25.4	Unobsd	~ 0	0
C-6	58.2	43.0 ^b	-15.2	-5.5

^a Using Grant's parameters derived for cyclohexane rings.

^b These assignments are rather arbitrary and might well be reversed.

We used the parameters derived by Grant's group for methyl substituents on cyclohexane rings.⁴ It may be seen that Grant's $\gamma_{2\text{HH}}$ and γ_{HH} parameters are too small for the hexahydropyridazine ring, and furthermore, that a higher γ_{HH} parameter would be necessary for C₄ than for C₆. Both of these effects are expected because of the shorter C–N and N–N bond lengths present in **1**, compared to the uniform C–C bond lengths in the cyclohexanes studied by Grant.

Another point of interest is the ratio of **1ee**:**1ae**:**1aa**. As stated before, no evidence for the presence of **1aa** is in hand. By comparing the peak positions for the three-line spectrum at -15° with those of set A and set B, and attempting to correct for the temperature dependence of the peak positions, a crude estimate of 56% **1ee** at -15° was obtained. By comparison of areas of the set A and set B peaks in the -53 to -68° region, estimates between 60 and 70% **1ee** were obtained, with an apparent increase as the temperature was lowered. From vapor phase photoelectron spectroscopy work, the ratio of **1ee**:other conformations ap-

(4) D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **96**, 1874 (1974), and references therein.

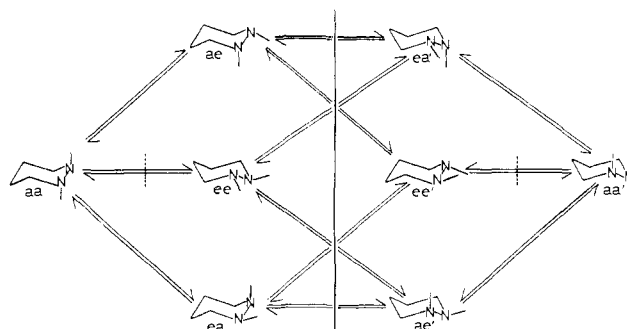


Figure 1. A diagram showing the possible interconversions between the isomers possible for **1**, assuming double nitrogen inversions and nitrogen inversions simultaneous with ring flips will be too slow to need consideration.

peared to be significantly higher, approximately 3:1.⁵ Although we consider it reasonable that the lowest dipole moment **1ee** conformation would be relatively more favored in the vapor phase than in solution, this conclusion must remain tentative until more extensive work is done.

Variable temperature ^{13}C nmr has been shown to be an extremely useful technique for conformational studies of cyclic hydrazines, which are being actively pursued in this laboratory.⁶

(5) (a) S. F. Nelsen, J. M. Buschek, and P. J. Hintz, *J. Amer. Chem. Soc.*, **95**, 2013 (1973); (b) S. F. Nelsen and J. M. Buschek, *ibid.*, **96**, 2392 (1974).

(6) We thank the National Science Foundation for support of this work, including the Major Instrument program for funds used in purchasing the spectrometer employed.

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Received June 22, 1974

The Three-Phase Test for Reactive Intermediates. Cyclobutadiene

Sir:

Previous applications of reactions on polymeric supports have emphasized either the ease of phase separations (ion exchange, affinity chromatography, peptide synthesis) or the benefits of matrix isolation (mono-functionalization,¹ Dieckmann cyclization²) available for reagents bound to insoluble supports. We now report the use of solid phase chemistry as a mechanistic probe for the detection of reactive intermediates.

(1) J. Y. Wong and C. C. Leznoff, *Can. J. Chem.*, **51**, 2452 (1973).

(2) J. I. Crowley and H. Rapoport, *J. Amer. Chem. Soc.*, **92**, 6363 (1970).