Conformational equilibria in some cyclic imines: NH and CH stretching vibrations and the axial lone pair

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The fundamental NH and CH stretching vibrations of a number of cyclic imines have been examined in dilute CCl_4 solution. A *trans* orientation of the N lone pair orbital and one or more hydrogen atoms on adjacent carbons lowers the relevant ν_{CH} ("Bohlmann" bands) and raises ν_{NH}, reflecting an increase in the s-character of the CH bond(s), consistent with a partial delocalization of the lone pair electrons into the CN bond. Conformations in which this interaction occurs are thermodynamically favored, and the ΔH values for the lone pair axial–equatorial equilibrium in piperidine, pyrrolidine, and indolene are estimated to be 0.4, 0.2, and 0.1 kcal/mole, respectively, in dilute CCl_4 solution.

The effects of hetero ring size, *N*-substitution, α-methyl substitution, and the solvent environment are investigated.

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Introduction

Conformational problems which arise from different orientations of the nitrogen atom lone pair orbital in heterocyclic compounds (1*a*) have received much attention in the case of six-membered rings like piperidine or morpholine, and a variety of methods like i.r. spectroscopy (2–12), n.m.r. spectroscopy (12–22), microwave spectroscopy (23), and dipole moment measurements (24–30) have been employed. The results of these studies have not been uniformly consistent. A comparative review has appeared recently (31), and there has been a full discussion of the question of the "size" of the lone pair on N with respect to other substituents (32, 33). A simple quantitative approach to intramolecular interactions in saturated heterocycles has been achieved (34, 35), from which axial–equatorial equilibria can be predicted.

This investigation shows that the low frequency CH stretching vibrations identified by Bohlmann in some cyclic imines (36) arise in conjunction with a secondary *increase* in the NH stretching frequency, supporting a decrease in the N atom charge density and a partial delocalization of charge into the CN bond (37, 38) when one or more α-CH bonds are *trans* to the lone pair. The hybridization of N in this molecular conformation therefore differs from the hybridization in conformations where no α-CH bond(s) bear this geometrical relation to the lone pair.

It has been possible to assess the spectral changes arising when the electron density on N is altered, and to make some specific vibrational assignments concerning the origin of CH absorption bands below ~2850 cm^{-1} through the use of specifically deuterated species.

Experimental

Except where otherwise noted, all the compounds used were commercial products which were purified prior to use and had acceptable physical constants, or they were prepared by standard methods. The deuterated materials α-d_2-piperidine, α-d_2-pyrrolidine, and α,α′-d_4-pyrrolidine were prepared by $LiAlD_4$ reduction of α-piperidone, α-pyrrolidone, and succinimide respectively. A deuteration level of 95% or better was indicated by n.m.r. spectra.

Spectroscopic measurements were made with a Perkin–Elmer Model 621 i.r. spectrophotometer, and a few spectra were obtained with a Cary Model 81 laser Raman spectrometer. Commercial "spectroquality" CCl_4 was used as a solvent for i.r. measurements at path lengths from 2.0–10.0 cm, except in the CD stretching region where shorter path lengths are required. Spectra in deuterated solvents were also obtained at shorter path-lengths.

A complete list of absorption frequencies is filed in the Depository of Unpublished Data, National Science Library, NRCC, Ottawa, Canada.

Results and Discussion

Piperidine

Figure 1 shows the spectrum of piperidine and α-d_2-piperidine in the CH and CD stretching regions. Piperidine exhibits normal ν_{asym} and ν_{sym} CH_2 stretching vibrations[2] at 2933 and 2850

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[2] The α-, β-, and γ-methylene vibrations in the lone pair equatorial form and the β- and γ-methylene vibrations in the lone pair axial form are likely superimposed to a high degree, leading to relatively broad bands.

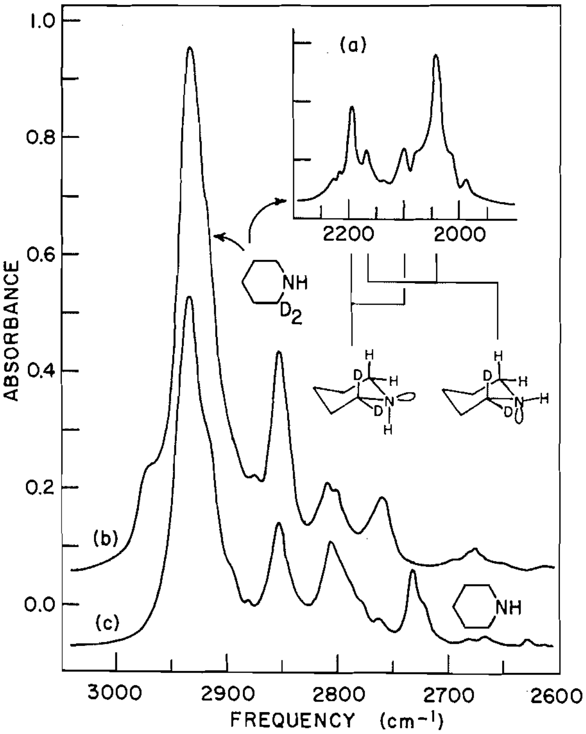

FIG. 1. Methylene stretching vibrations in the i.r. spectra of (*a*), (*b*) α-d_2-piperidine, and (*c*) piperidine (CCl_4 solutions; 2 cm cells in CH stretching region and 0.1 cm cells in CD stretching region).

cm^{-1} respectively, and all other piperidines investigated show similar absorptions. Deuteration of one α-methylene group removes the shoulders at 2915 and 2895 cm^{-1} from ν_{asym}, and replaces the low frequency bands at 2730 and 2803 cm^{-1} with an intermediate band at 2760 cm^{-1}.

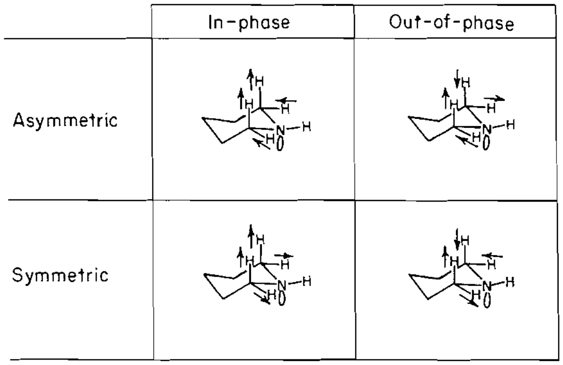

FIG. 2. Projected coupling of asymmetric and symmetric CH stretching vibrations in piperidine conformation with axial lone pair.

These spectral features can be accounted for in terms of a *trans* diaxial lone pair/α-CH interaction, and consequent coupling of the two α-CH_2 group vibrations in the piperidine conformation with an axial lone pair. Figure 2 shows the vibrations that might be expected. The bands at 2915 and 2895 cm^{-1} can be explained as the two components of ν_{asym}, and the bands at 2803 and 2730 cm^{-1} as the two ν_{sym} components.[3] Insertion of one α-CD_2 group breaks the coupling and accounts for the appearance of the 2760 cm^{-1} band, while the shoulders at 2915 and 2895 cm^{-1} also become less marked.

In the CD stretching region the interpretation is guided by spectroscopic studies of $CH_3CD_2NH_2$ (38) which show that "normal" ν_{asym} and ν_{sym} frequencies arise from the conformation which does not have a *trans* lone pair/α-CD interaction, while the CD_2 frequencies are lowered by 32 and 39 cm^{-1} respectively if such an interaction is present. This is in agreement with calculations for an XH_2 group showing that ν_{sym} is lowered by more than ν_{asym} if one of the HX force constants is progressively reduced (39). The four main CD bands in α-d_2-piperidine are therefore interpreted as shown in Table 1.[4]

The shifted ν_{sym} band at 2043 cm^{-1} is unusually intense, which may reflect the high degree of interaction between the axial lone pair on N and the axial α-CD bond, and the greater involvement of the lone pair in ν_{sym} relative to ν_{asym} (40). No quantitative conclusions can be based on the CH and CD stretching frequencies regarding the relative proportions of lone pair axial and lone pair equatorial conformers, but it is clear that both exist in piperidine in CCl_4 solution.

Measurements in the NH stretching region are collected in Fig. 3. Piperidine (curve *e*, at concentration 3×10^{-3} moles/l) has a main NH band at 3343 cm^{-1} with a shoulder at 3315 cm^{-1}. The dominant high frequency component is assigned to the NH equatorial (lone pair axial) conforma-

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[3] The band at 2803 cm^{-1} appears to be overlapped with other absorptions and therefore does not disappear entirely on deuteration but is only reduced in intensity relative to the main CH bands. Both the 2803 and the 2730 cm^{-1} bands were noted in the Raman spectrum of piperidine. The appearance of "Bohlmann bands" in Raman spectra has not been reported to date.

[4] It is recognized that equatorial CD bonds of —CHD groups absorb about 30 cm^{-1} higher than axial CD bonds in cyclohexanes (1*c*), reflecting slight non-equivalence of the two bonds of CH_2 (or CD_2) groups.

TABLE 1

Main CD bands in α-d_2-piperidine

	ν_{asym} (cm^{-1})	(ν_{CH}/ν_{CD})	ν_{sym} (cm^{-1})	(ν_{CH}/ν_{CD})
Lone pair equatorial	2194	1.337	2100	1.358
Lone pair axial	2164	1.347	2043	1.346

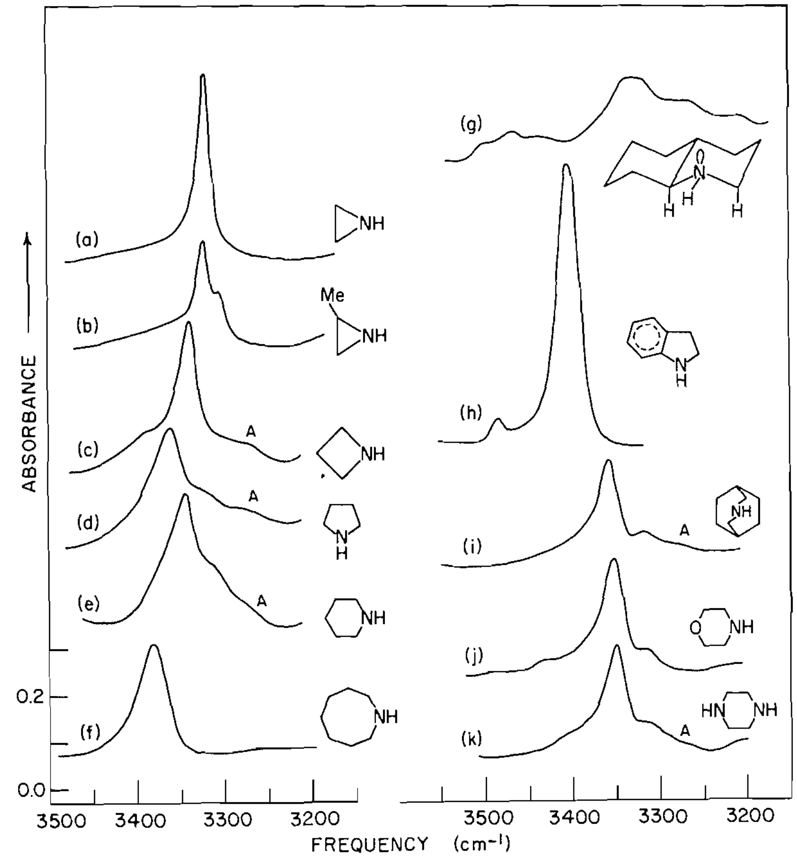

FIG. 3. Infrared spectra in the NH stretching region: (*a*) aziridine, (*b*) propyleneimine, (*c*) azetidine, (*d*) pyrrolidine, (*e*) piperidine, (*f*) heptamethyleneimine, (*g*) *trans*-decahydroquinoline, (*h*) indoline, (*i*) 3-azabicyclo[3.2.2]nonane, (*j*) morpholine and (*k*) piperazine (A = association bands; measurements in dilute CCl_4 solution at 5 or 10 cm path length).

tion, and the increase in frequency ascribed to the partial loss of charge from the N atom. The low frequency component is assigned to the NH axial form. Baldock and Katritzky (5, 6) have recently made similar assignments for piperidine based on gas phase and CCl_4 solution spectra in the first overtone NH region. In the gas phase they conclude that the NH equatorial form of piperidine predominates (*ca.* 60%) with $\Delta H = 0.53 \pm 0.13$ kcal/mole, and that the same holds for CCl_4 solutions with $\Delta H = 0.6 \pm 0.2$ kcal/mole. Our own estimate of ΔH based on badly overlapped NH bands in solution is 0.4 kcal/mole, with the lone pair axial form being the more stable form.

Alkyl Piperidines

The spectrum of 2,2,6,6-tetramethylpiperidine has only CH_3 and normal CH_2 stretching vibrations, the lowest of which lies at 2840 cm^{-1}, in marked contrast to the 2803 and 2730 cm^{-1}

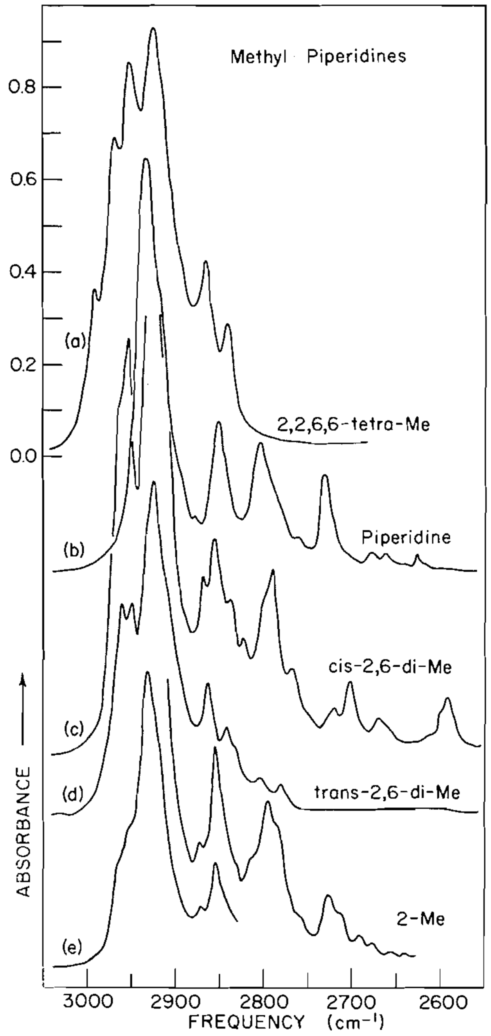

FIG. 4. Infrared spectra of α-methyl piperidines in the CH stretching region: (*a*) 2,2,6,6-tetramethylpiperidine, (*b*) piperidine, (*c*) *cis*-2,6-dimethylpiperidine, (*d*) *trans*-2,6-dimethylpiperidine, (*e*) 2-methylpiperidine.

bands of piperidine (Fig. 4*a* and *b*). Booth *et al.* (18) have recently shown from n.m.r. measurements that *cis*-2,6-dimethylpiperidine has its two methyl groups in the equatorial conformation. Shifted CH absorption at 2790 and 2701 cm^{-1} confirms that the α-CH bonds are axial[5] (Fig. 4*c*), particularly when compared with the corresponding *trans*-2,6-dimethylpiperidine (Fig. 4*d*) which only has weak CH absorption below 2840 cm^{-1} consistent with one axial tertiary α-CH group.[6] 2-Methylpiperidine exhibits absorption similar to that of piperidine, which would be expected with the methyl group in an equatorial position.

Measurements in the fundamental NH stretching region were in general agreement with those reported by Baldock and Katritzky (6) for the first overtones. Because the interpretation of the fundamental region is complicated by the presence of combination bands no such data are reported here. Only a single ν_{NH} band at 3312 cm^{-1} was observed in 2,2,6,6-tetramethylpiperidine; this corresponds to the low frequency component in those cases with α-CH groups, as expected.

N-Substituent Effects

The effect of substitution on N is summarized in Fig. 5 and in Table 2, which also gives some tentative assignments. In *N*-benzoylpiperidine the lone pair on N is withdrawn and no absorption occurs below 2855 cm^{-1} (Fig. 5*j*). The *N*-*p*-tolyl group does not withdraw charge from N as effectively, and weak absorption below 2855 cm^{-1} remains (Fig. 5*h*). Although piperidine-*N*-oxide is held to exist as the *N*-hydroxypiperidine, its spectrum also shows only very weak absorption below 2855 cm^{-1} (Fig. 5*i*).

On the other hand, electron-donating substituents enhance the perturbed in-phase and out-of-phase α-CH$_2$ bands near 2780 and 2730 cm^{-1}, relative to the normal CH bands. The particular compounds investigated were *N*-amino-, *N*-*t*-butyl-, *N*-methyl-, and *N*-methyl-4-hydroxypiperidine (Fig. 5*a*–*d*).[7]

N-Chloropiperidine is a special case with a relatively intense CH band at 2830 cm^{-1}; in view of the absence of absorption near 2730 cm^{-1}, its assignment to "perturbed" α-CH$_2$ groups is uncertain.

trans-Decahydroquinoline

According to Booth and Bostock (16) this compound is expected to exist entirely in the conformation shown in Fig. 5*f*. The perturbed CH bands at 2794 and 2740 cm^{-1} are consistent with this conformation and an appreciable proportion of axially oriented lone pairs on N.

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[5] In-phase and out-of-phase coupling in the lone pair axial conformation.

[6] We thank Dr. H. Booth for making samples of *cis*- and *trans*-2,6-dimethylpiperidine available.

[7] In *N*-methylpiperidines the band at 2780 cm^{-1} is enhanced by ν_{sym} of the CH$_3$ group, which is expected to have one CH bond *trans* to the lone pair.

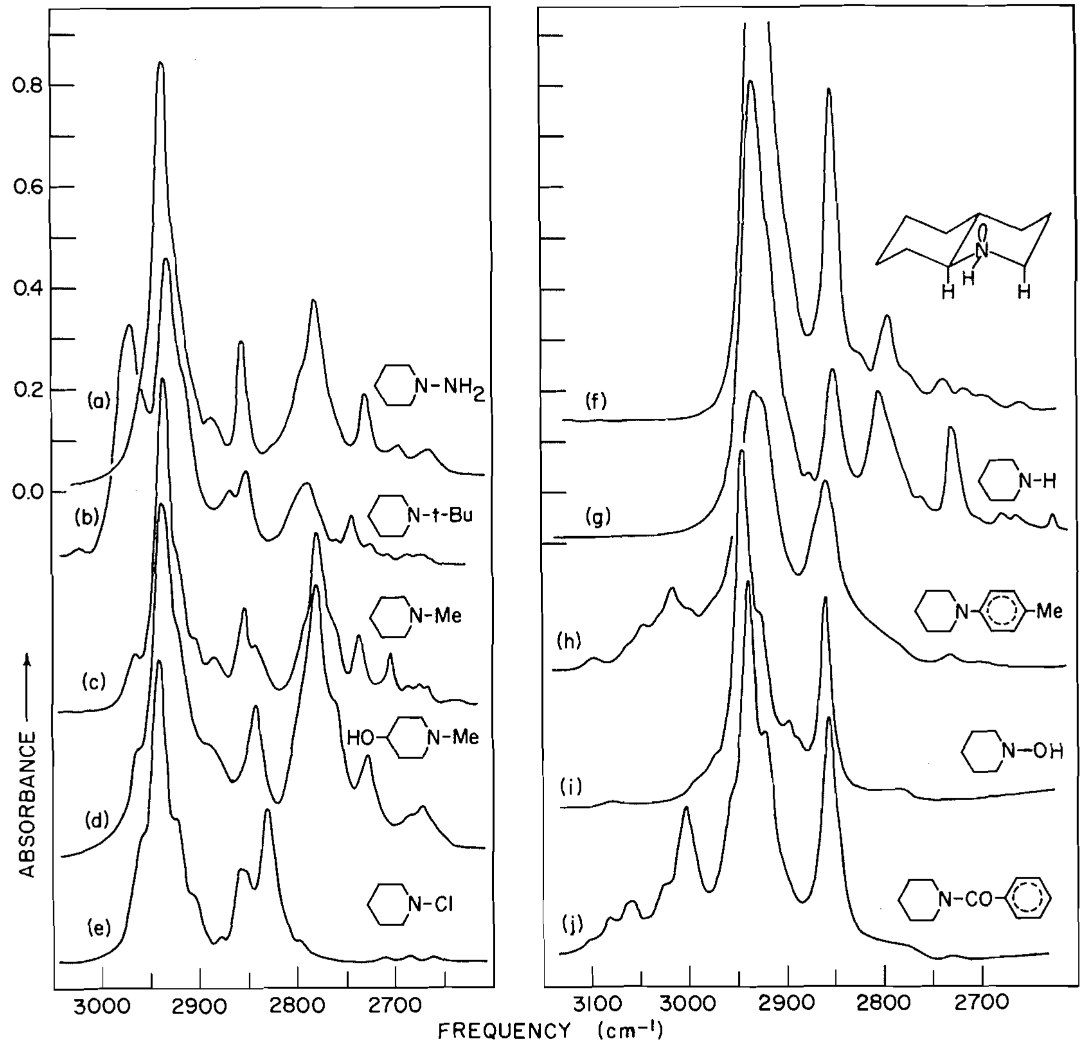

FIG. 5. Infrared spectra of *N*-substituted piperidines in the CH stretching region: (*a*) *N*-aminopiperidine, (*b*) *N*-*t*-butylpiperidine, (*c*) *N*-methylpiperidine, (*d*) *N*-methyl-4-piperidinol, (*e*) *N*-chloropiperidine, (*f*) *trans*-decahydroquinoline, (*g*) piperidine, (*h*) *N*-*p*-tolylpiperidine, (*i*) *N*-nitrosopiperidine, (*j*) *N*-benzoylpiperidine.

However, from Fig. 3*c* it appears that the NH band is a doublet (~3336 and ~3316 cm^{-1}), which indicates equatorial as well as axial lone pair orientation.

Piperazines

Relative to piperidines the piperazines exhibit more intense perturbed CH bands, which in some cases are stronger than the normal CH bands (Fig. 6). *N*,*N*-Diamino-piperazine and *N*-amino-*N*′-methylpiperazine fall into the latter category. This is expected since the substituents are strong electron donors, and all the CH_2 groups are adjacent to a N atom.

The CH absorption of piperazine is undoubtedly complicated by the existence of conformers with axial–axial, axial–equatorial, and equatorial–equatorial lone pair combinations (25). The spectrum of *N*,*N*′-diaminopiperidine is simpler than that of piperidine, since the substituents are probably largely in equatorial orientations, yielding a conformer with two intensified axial lone pairs. Nevertheless, the presence of a ν_{asym} CH_2 stretching band in the normal position

TABLE 2

Methylene stretching vibrations of some six-membered *N*-heterocycles (in cm^{-1}; measurements in dilute CCl_4 solution)

Compound	Asymmetric mode		Symmetric mode	
	Normal	Perturbed*	Normal	Perturbed*
Piperidine (P)	2933	2915 sh, 2895 sh	2850	2803, 2730
2-Methyl P	2930	2915 sh	2855	2795, 2728
trans-2,6-Dimethyl P	2925	~2895 sh†	2842	2803†
cis-2,6-Dimethyl P	2925	2910 sh	2855	2790, 2701
2,2,6,6-Tetramethyl P	2925	—	2840	—
N-Amino P	2937	2920 sh, 2887	2855	2781, 2729
N-*t*-Butyl P	2932	2915 sh	2850	2787, 2743
N-Methyl P	2935	2920 sh, 2903 sh	2852	(2779)‡, 2735, 2709
N-Methyl-4-piperidinol	2939	2920 sh, 2889 sh	2842	(2780)‡, 2728
N-Chloro P	2941	2925 sh, 2905 sh	2855	2830 (?)
N-*p*-Tolyl P	2932	—	2859	—
Piperidine-*N*-oxide	2944	—	2859	—
N-Benzoyl P	2938	—	2855	—
Piperazine (Pz)	2944	2918, 2911, 2883	2855 sh	2825, 2812, 2749, 2733, 2723
N-Methyl-*N'*-amino Pz	2938	2912, 2877	2842	2810, (2796)‡, 2766, 2738
1,4-Diamino Pz	2938	2911, 2877	2828	2809, 2737
N,*N'*,*N''*-Trimethylhexahydro-*s*-triazine	2940	2892	2841	2787, 2772, 2724

*Belonging to α-CH_2 groups in lone pair axial conformer.
†Tertiary α-CH group(s) only.
‡ν_{sym} of *N*-CH_3 group.

(2938 cm^{-1}) indicates that at least some molecules have an axial substituent (equatorial lone pair).

The NH stretching region, with a main band at 3351 cm^{-1} and a shoulder at 3314 cm^{-1}, shows strong preference for the axial orientation of lone pairs in piperazine (Fig. 3*k*).

1,3,5-Trimethylhexahydro-*s*-triazine is expected to show a conformational preference for equatorial substituents (41). Again the CH region is complicated because each methylene is adjacent to two N atoms, of which a significant number must have axial substituents to account for the normal ν_{asym} CH_2 intensity at 2940 cm^{-1}. However, *trans* diaxial lone pair/α-CH interactions (plus vibrational coupling) account for the intense and complicated absorption below 2835 cm^{-1}.

Pyrrolidines

By analogy with tetrahydrofuran (42) the nonplanar semi-chair conformation appears most reasonable for pyrrolidine (Fig. 7). In conformation (**1**) an α-CH bond at C-1 is *trans* to the N lone pair while none of the hydrogens at C-4 are *trans*. With inversion at N to form conformer **2**, none of the α-CH bonds are *trans* to the lone pair. A principal difference between piperidine and pyrrolidine should therefore be the absence of coupling between α-CH_2 groups in the latter.

The relevant frequencies and assignments are tabulated in Table 3. Pyrrolidine exhibits a shoulder at 2930 and a band at 2821 cm^{-1} corresponding to ν_{asym} and ν_{sym} of a "perturbed" α-CH_2 group. In the α-CD_2 compound the 2930 cm^{-1} is largely gone (leading to resolution of an underlying weak band at 2911 cm^{-1}), and the 2821 cm^{-1} band is reduced to a shoulder. In the α,α'-di-CD_2 compound both bands are eliminated.

In the CD stretching region pyrrolidine-α-d_2 has "normal" CD_2 stretching frequencies at 2215 and 2110 cm^{-1} (ν_{asym} and ν_{sym}, respectively) arising from **2** with the CD_2 group at either C-1 or C-4, and from **1** with the CD_2 group at C-4. "Perturbed" ν_{asym} and ν_{sym} CD_2 frequencies at 2195 and 2088 cm^{-1}, respectively, must arise from **1** with a 1-CD_2 group; since these bands are relatively more intense conformer **1** with the *trans* lone pair/α-CH interaction seems to be favored over **2**. The weak CD absorption at 2137 cm^{-1} is probably due to —CHD impurity.

TABLE 3

Methylene stretching frequencies in pyrrolidines (cm^{-1})

	CH_2				CD_2			
	Asymmetric		Symmetric		Asymmetric		Symmetric	
Compound	Normal	Perturbed	Normal	Perturbed	Normal	Perturbed	Normal	Perturbed
Pyrrolidine	2962	2930 sh	2872	2821	—	—	—	—
Pyrrolidine-α-d_2	2960	?	2874	2820 sh	2215	2195	2110	2088
(ν_{CH}/ν_{CD})					(1.336)	(1.335)	(1.361)	(1.351)
Pyrrolidine-α,α′-d_4	2956	—	2873	—	2215	2195	2110	2087
(ν_{CH}/ν_{CD})					(1.336)	(1.335)	(1.361)	(1.352)
N-Aminopyrrolidine	2957	2928	2875	2789	—	—	—	—

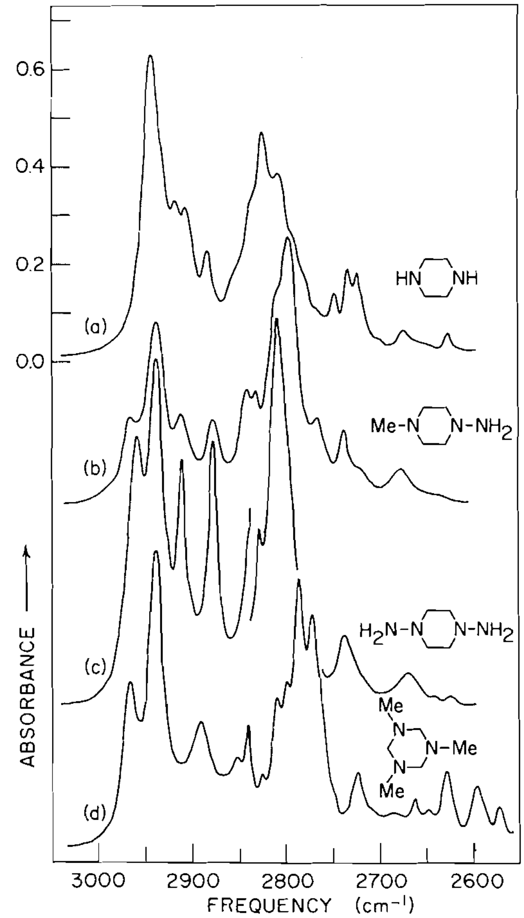

FIG. 6. Infrared spectra in the CH stretching region: (*a*) piperazine, (*b*) 1-amino-4-methylpiperazine, (*c*) 1,4-diaminopiperazine, (*d*) 1,3,5-trimethyltriazine.

In pyrrolidine-α,α′-d_4 the same four bands appear, with no new features such as would be expected if two α-CD bonds were *trans* to the lone pair. Although the asymmetric CD_2 band was more difficult to resolve, the apparent peak at 2207 cm^{-1} shows both high and low frequency shoulders consistent with the spectrum of the α-CD_2 compound.

In the NH stretching region pyrrolidine has a main band at 3362 cm^{-1} with a shoulder at 3320 cm^{-1} (Fig. 3*c*), confirming that **1** is favored over **2**. From the temperature dependence of these bands the enthalpy difference is estimated as ~ 0.2 kcal/mole.

The intensity of the perturbed ν_{sym} CH_2 stretching vibration at 2789 cm^{-1} in *N*-aminopyrrolidine is almost equal to that of the normal ν_{asym} CH_2 band (Fig. 8*e*). This spectrum provides further evidence that only one "Bohlmann band" is induced below 2850 cm^{-1} in pyrrolidine, even if the electron density on N is increased. The perturbed ν_{asym} CH_2 stretching vibration is tentatively assigned to the band at 2928 cm^{-1} in the *N*-amino compound.

If the electron density is removed from N, as in indoline (Fig. 8*b*), the CH absorption below 2850 cm^{-1} is reduced to two very weak bands at 2796 and 2708 cm^{-1}. Figure 3*h* shows that in the NH stretching region the conformer with the pyrrolidine ring of type **1** and having the aromatic ring fused on the C-4 side now absorbs only very weakly at 3483 cm^{-1}, while the conformer with the pyrrolidine ring of the type **2** having the lone pair delocalized into the fused aromatic ring is much more abundant and absorbs strongly at 3403 cm^{-1}. Both bands can be shifted by deuteration. Conformer **1** is more stable than conformer **2** by ~ 0.1 kcal/mole in dilute CCl_4 solution.

Morpholine

The CH stretching region of morpholine (Fig. 8*a*) is surprisingly like that of piperazine, with the exception of changes in relative intensities. This suggests that the lone pair orbitals on oxygen may play a similar role to those on nitrogen in shifting certain CH bands. This effect has been investigated further in this laboratory, using simpler model compounds (43).

In the NH stretching region (Fig. 3*j*) morpholine shows the same strong preference for axial orientation of the lone pair as piperazine.[8]

3-Azabicyclo[3.2.2]nonane

The weak CH absorption below 2850 cm^{-1} (Fig. 8*c*) suggests that some molecules exist in a conformation where *trans* N lone pair/α-CH_2 interaction is possible. This is consistent with molecular models. In the NH region the spectrum resembles that of morpholine (Fig. 3*j*).

Effect of Heterocyclic Ring Size

The i.r. spectra of cyclic imines of ring size 3–7 have been investigated (44), and the increase in ν_{CH} as ring size decreases is well known. The frequency assignments for 3-membered hetero-

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[8] In agreement with recent conclusions by Baldock and Katritzky (6) for morpholine in the gas phase and in dilute CCl_4 solution.

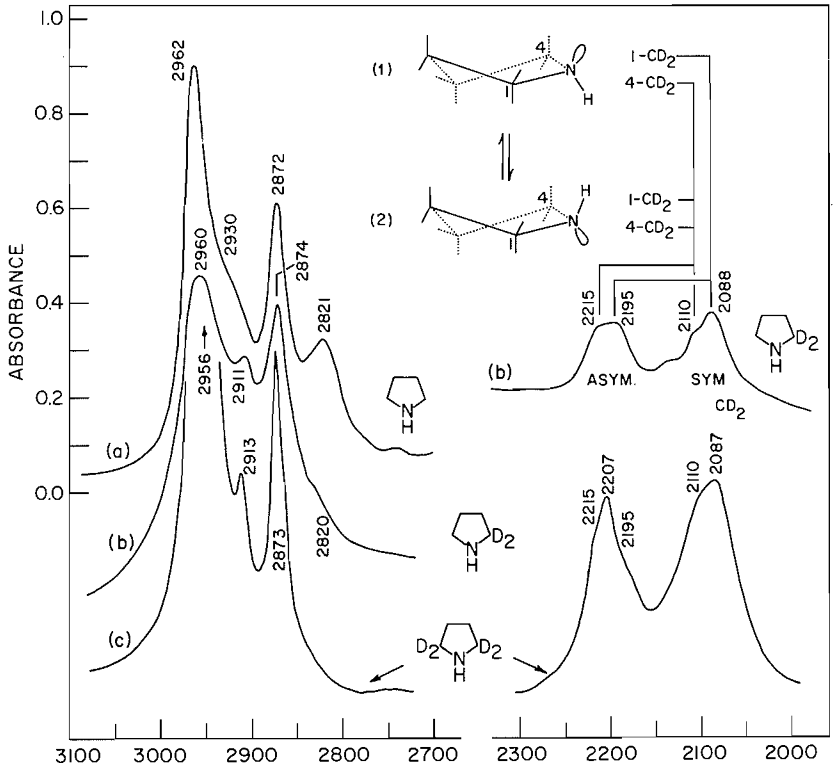
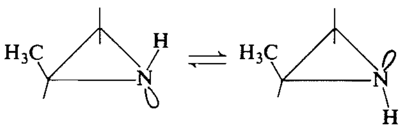


FIG. 7. Methylene stretching vibrations in the i.r. spectra of (*a*) pyrrolidine, (*b*) α-d_2-pyrrolidine, and (*c*) α,α'-d_4-pyrrolidine.

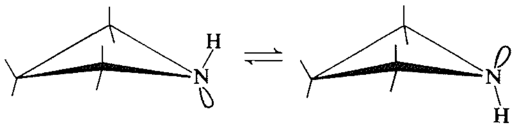
cyclic rings are firmly based (45), and the bands at 2935, 2903, and 2896 cm^{-1} in ethyleneimine (aziridine) must be overtones and/or combination bands (Fig. 9*a*). Similar absorptions are observed in 2-methylaziridine (Fig. 9*b*), although a doublet ν_{NH} is observed for the latter (Fig. 3*a* and *b*) because of *cis–trans* isomerism of the CH_3 group and the NH (46). The ν_{NH} components at 3322 and 3305 cm^{-1} are shifted to 2465 and 2453 cm^{-1} on deuteration.



3
CH_3/NH *cis*
(Low frequency ν_{NH})

4
CH_3/NH *trans*
(High frequency ν_{NH})

By analogy with mono-substituted cyclobutanes (47), azetidine should exist in two conformations with lone pair orientations that are essentially "axial" and "equatorial" and this is borne out by NH and CH frequencies (Figs. 3*c* and 9*c*).



5
Lone pair "axial"
(two *trans* CH/lone pair interactions)
high frequency ν_{NH}(3387 cm^{-1})

6
Lone pair "equatorial"
(no *trans* CH/lone pair interaction)
low frequency ν_{NH}(3339 cm^{-1})

The lowest CH frequency (2859 cm^{-1}) has the highest intensity, and this band is tentatively related to the quasi-*trans* orientation of α-CH bonds to the lone pair in **5**. It should be noted that the electron donor ability of N in cyclic imines is

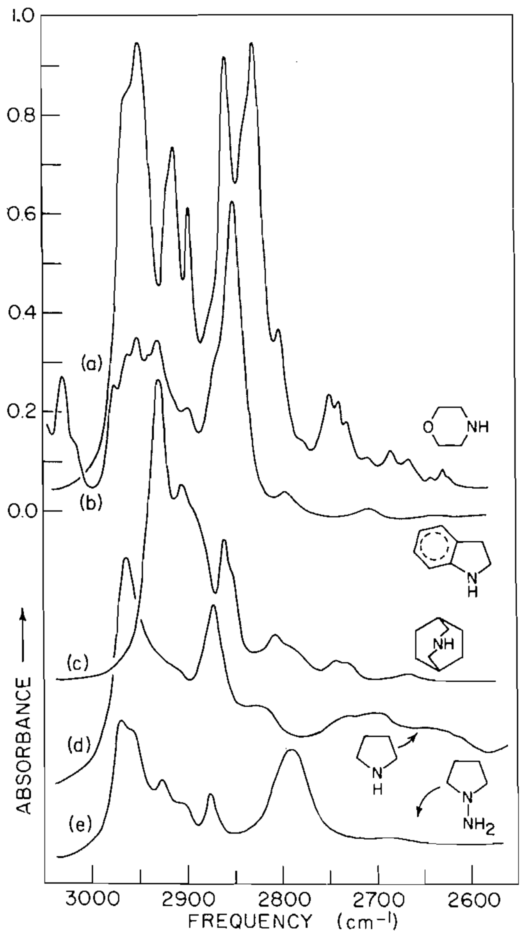


FIG. 8. Infrared spectra in the CH stretching region: (*a*) morpholine, (*b*) indoline, (*c*) 3-azabicyclo[3.2.2] nonane, (*d*) pyrrolidine, (*e*) *N*-aminopyrrolidine.

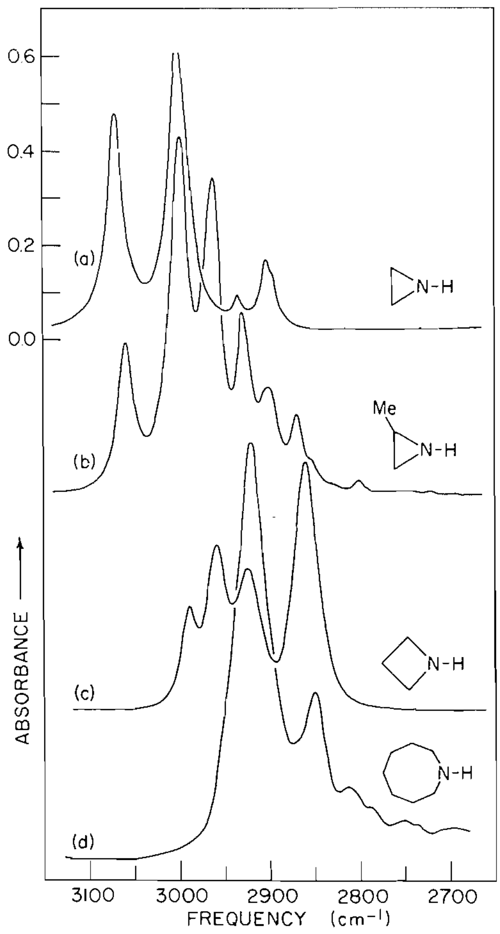


FIG. 9. Infrared spectra in the CH stretching region: (*a*) aziridine, (*b*) 2-methylaziridine, (*c*) azetidine, (*d*) heptamethyleneimine.

known to follow the ring size order 4 > 5 > 6 > 7 > 3 (48). In *N*-benzoyl azetidine where the lone pair has been delocalized the lowest frequency CH band is found at 2885 cm^{-1}.

The only large ring imine investigated was heptamethyleneimine, which has normal ν_{asym} and ν_{sym} CH_2 modes at 2920 and 2850 cm^{-1}, respectively, and weak absorption below 2850 cm^{-1} (Fig. 9*d*). In the NH region the main band at 3381 cm^{-1} shows some asymmetry on the high frequency side.

Solvent Effect Studies

The ν_{CD} shift of $CDCl_3$ when amines are added to it until the "free" CD band at 2252 cm^{-1} disappears (49) shows a dual basicity for piperidine and *N*-alkylpiperidines (Fig. 10). Similar spectra are obtained if CCl_4 is used as a ternary solvent. The relative intensities for the two CD···N bands do not, however, represent the relative proportions of the less basic (lone pair axial, $\Delta\nu_{CD} \approx 33\ \text{cm}^{-1}$) and more basic (lone pair equatorial, $\Delta\nu_{CD} \approx 75\ \text{cm}^{-1}$) forms under these conditions. Lord *et al.* (50) have shown that the integrated ν_{CD} intensity of $CDCl_3$ increases dramatically on hydrogen bond formation, e.g. for $\Delta\nu_{CD} = 36\ \text{cm}^{-1}$ on hydrogen bond formation with pyridine the CD band intensity increases more than 20-fold. Thus Fig. 10 grossly accentuates the low frequency CD···N band (lone pair

TABLE 4

Peak intensities of CH bands in piperidines* relative to 2935 cm^{-1} (normal asymmetric CH_2 stretch) set at 1.00

	Piperidine			*N*-Methylpiperidine			
Solvent	2850 cm^{-1}†	2803 cm^{-1}	2730 cm^{-1}	2852 cm^{-1}†	2779 cm^{-1}‡	2735 cm^{-1}	2709 cm^{-1}
CCl_4	0.37	0.31	0.24	0.30	0.53	0.22	0.16
Pure liquid	0.56	0.42	0.32	0.45	0.68	0.37	0.28
Solid film (−135 °C)	0.31	0.32	0.32	—	—	—	—
$CDCl_3$	0.38	0.28	0.12	0.37	0.51	0.17	0.13
$(CD_3)_2C{=}O$	0.44	0.27	0.07	0.34	0.48	0.20	0.09
$CD_3C{\equiv}N$	0.44	0.27	0.16	0.36	0.52	0.23	0.17
$(CD_3)_2S{=}O$	0.48	0.28	0.20	0.39	0.53	0.27	0.19
CD_3OD§	0.45	≪0.28	0.09	0.48	0.45	0.16	0.07
	(2856)	(2833 broad, overlapped)	(2747)	(2857)	(2803)	(2741)	(2710)

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*Frequencies slightly solvent dependent; values cited in dilute CCl_4 solution.

†Normal symmetric CH_2 stretching vibration of N lone pair equatorial conformer.

‡ν_{sym} of N-CH_3 group.

§Reference bands shifted very little, other bands moved to higher frequencies as indicated.

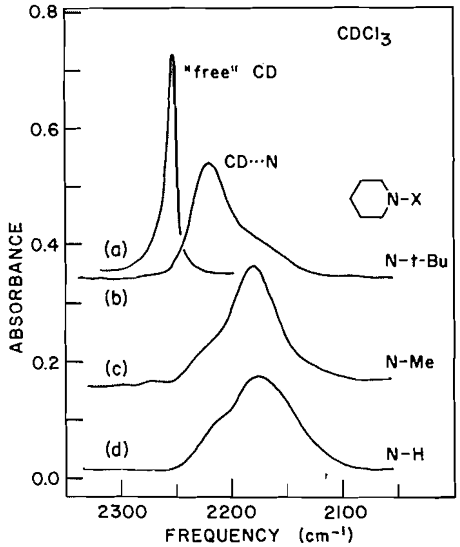


FIG. 10. Fundamental CD stretching vibrations of $CDCl_3$: (*a*) in dilute CCl_4, (*b*) in *N*-*t*-butylpiperidine, (*c*) in *N*-methylpiperidine, and (*d*) in piperidine.

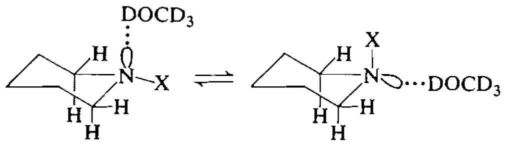
equatorial form). Nevertheless it provides some further evidence that the lone pair axial conformer is *less* basic than the lone pair equatorial conformer.

While the concentration of axially oriented *t*-butyl groups is normally considered to be negligible (1*b*), *N*-*t*-butylpiperidine appears to have some, although if $\varepsilon_{CD\cdots N}{}^{axial}$ (2170 cm^{-1}) > $\varepsilon_{CD\cdots N}{}^{equatorial}$ (2219 cm^{-1}) a very small percentage of axial *t*-butyl groups could account for the observed spectrum.

For piperidine and *N*-methylpiperidine in which *ca.* 60 and 66%, respectively, of the *N*-substituent are now deemed to be equatorial in benzene solution (6), the low frequency CD···N chloroform complex band predominates, but probably only because of its intrinsically greater extinction coefficient.

The axial–equatorial equilibrium in piperidines is expected to show some solvent sensitivity, and CH spectra were obtained for piperidine and *N*-methylpiperidine in a variety of deuterated solvents (Table 4). The projected properties of the two conformers are summarized in Fig. 11.

Since only peak height ratios for these overlapped bands are readily obtained, the data can only be interpreted qualitatively. The 2730 cm^{-1} band in piperidine assigned to the lone pair axial form has the highest relative intensity in the pure liquid and in low temperature solid film spectra. In the glassy film spectrum, where the resolution is improved, the 2850 cm^{-1} normal ν_{asym} CH_2 band has the lowest relative intensity. In the crystalline state the concentration of the lone pair axial form has previously been held to increase (3). In dimethyl sulfoxide-d_6, acetonitrile-d_3, chloroform-*d*, acetone-d_6, and methanol-d_4 the 2730 cm^{-1} piperidine band is relatively less intense than in CCl_4 solution, and decreases in the order given. In all cases except the low temperature solid film the 2850 cm^{-1} band is relatively more intense than in CCl_4 solution. These changes can be explained by increased stabilization of the more polar conformer (N lone pair equatorial) in polar solvents, and in the case of $CDCl_3$ and CD_3OD, also by preferential stabilization of the lone pair equatorial form by hydrogen bonding. Obviously a number of factors must be involved, some of which are mentioned in Fig. 11.



7 8

$X = H, D, \text{or } CH_3$

Basicity of N: 7 < 8
Acidity of NH: 7 > 8
Steric hindrance of $N—CH_3$: 7 > 8
Steric hindrance to solvent attack on lone pair: 7 > 8
Polarity of conformer: 7 < 8
Thermodynamic stability: 7 > 8

FIG. 11. Projected properties of N lone pair axial and equatorial conformers in piperidine and *N*-methylpiperidine.

While the CH frequencies are not markedly solvent dependent, the CD_3OD solution appears exceptional. The frequency of the normal ν_{asym} CH_2 reference band is hardly altered but all the others are shifted to higher frequencies (Table 4). This is consistent with hydrogen bonding in the lone pair axial form, thereby reducing the effective charge on N and in turn making the α-CH_2 bands in this conformer more normal.

N-Methylpiperidine shows roughly similar behavior in deuterated solvents, although the relative decrease in the 2709 cm^{-1} band with respect to the value in CCl_4 solution is not as great. In CD_3CN no significant change in the low frequency band is noted, and in $(CD_3)_2SO$ a small increase is observed. The lower solvent sensitivity of the conformational equilibrium in *M*-methylpiperidine may arise from the fact that the N lone pair can always be *trans* to at least one CH bond (of the methyl group) in both conformations, plus the greater steric hindrance in the *N*-methyl axial position.

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