ide was then added, and the tube was isolated from the vacuum line and heated at 150° until a faint opalescence was apparent. Success of the procedure was determined by placing a drop of distilled water in the tube. If any surface was wetted, the process was repeated.

For the "salty" crystals, ca. 0.1 mg of reagent grade NaCl was placed in each side of the crystallizer.

Conductivity measurements were performed using standard four-probe techniques.[30]

Acknowledgments. This work was supported by a grant from the Materials Science Office, Advanced Research Projects Agency, Department of Defense. We wish to thank Dr. John P. Ferraris for the preparation of the TTF used in this work.

Registry No.—TTF-TCNQ, 40210-84-2; tetrathiafulvalene, 31366-25-3; tetracyanoquinodimethane, 1518-16-7.

Supplementary Material Available Figures 1–5, the HPLC traces, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-3544.

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Barriers to Amide Rotation in Piperidides and Related Systems. Unambiguous Assignments Using Carbon-13 Magnetic Resonance

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Received June 6, 1975

Variable-temperature carbon-13 magnetic resonance is used to investigate barriers to amide rotation in a series of benzoyl- and carboethoxy-substituted six-membered nitrogen heterocycles. Observed barriers are unambiguously assigned to amide rotation (as opposed to ring reversal or nitrogen inversion) because of the symmetry properties inherent in the carbon-13 technique. Barriers are compared with those obtained by variable-temperature proton magnetic resonance. The amide rotation barriers are relatively insensitive to changes in the nature of the ring substituent γ to the nitrogen, thereby supporting earlier results which suggested little or no 1,4-transannular interaction in six-membered heterocycles.

Application of carbon-13 magnetic resonance spectroscopy (^{13}C NMR)[2] to temperature-dependent phenomena (^{13}C DNMR) is still in its infancy.[2,3] It is the intention herein to use ^{13}C DNMR to provide unambiguous assignment of the nature of a dynamic process in a situation where several processes may occur. Variable-temperature proton magnetic resonance spectroscopy (^{1}H DNMR)[4] will be used to support[5] ^{13}C DNMR studies[6] in two examples.

Table I
Amide Rotation Barriers in Piperidides

Compd	Solvent	T_c, K	$\Delta G^{\ddagger}$, NMR method	Ref
1-Acetyl-4-methylpiperidine	$CDCl_3$	~330	16.4 α-^{1}H	Calcd by ref 9 from ref 8
	$CDCl_3$	~330	16.96 α-^{1}H	Calcd by ref 11a from ref 8
	$CDCl_3$	~343	17.07 α-^{1}H	Calcd here from ref 10
1-Acetyl-4-phenylpiperidine	Toluene-d_8	357	16.96 α-^{1}H	11a
1-Acetyl-2-methylpiperidine	Neat	288	15.3 CH_3-^{1}H	9
	Toluene-d_8	279	15.03 CH_3CO-^{1}H	11a
	Toluene-d_8	290.5	15.09 CH_3-^{1}H	11a
Acetamidomonosaccharides	C_2Cl_4	~360	17.4 α-^{1}H	9
	D_2O	303	16.1 α-^{1}H	9
	D_2O	278	15.7 CH_3CO-^{1}H	9
1-Acetylmorpholine	$CHFCl_2$	305	16.5 β-^{1}H	12
	$CHFCl_2$	315	16.6 α-^{1}H	12
1-Benzoyl-4-methylpiperidine	$CDCl_3$	~285	14.77 axial α-^{1}H	Calcd here from ref 10
	$CDCl_3$	~308	15.07 equat α-^{1}H	Calcd here from ref 10
1-Benzoyl-3-methylpiperidine	$CDCl_3$	~308	15.09 α-^{1}H	Calcd here from ref 10
1-Benzoyl-*cis*-2,6-dimethylpiperidine	$CDCl_3$	~253	12.30 α-^{1}H	Calcd here from ref 10
	CCl_4	~242	12.1 α-^{1}H	11b
	CH_3OH	247	12.5 α-CH_3-^{1}H	11b
	$CDCl_3$	~263	13.16 α-^{1}H	Here
1-Benzoylpiperidine (**1a**)	$CDCl_3$	292	14.82 α-^{1}H	Here
	$CDCl_3$	316	14.94 α-^{13}C	Here
	$CDCl_3$	289	14.75 β-^{13}C	Here
1-Benzoyl-4-piperidone (**1b**)	$CDCl_3$	273	13.97 α-^{1}H	Here
	$CDCl_3$	303[a]	14.32 α-^{13}C	Here
1-Benzoylmorpholine (**1c**)	$CHFCl_2$	276	14.4 β-^{1}H	12
	$CHFCl_2$	283	14.4 α-^{1}H	12
	$CDCl_3$	305	14.39 α-^{13}C	Here
1-Benzoyl-4-methylpiperazine (**1d**)	$CDCl_3$	310[a]	14.64 α-^{13}C	Here
	$CDCl_3$	284	14.65 β-^{13}C	Here
1-Carbomethoxypiperidine (**1e**)	$CHFCl_2$[b]	223[c]	11.88[c] α- and β-^{13}C	Here

[a] Not clearly defined coalescence because of overlapping signals; ±5°. [b] Containing a slight amount of CD_2Cl_2 for external lock. [c] Because of line broadening, the coalescence temperatures are somewhat indefinite here. The T_c's definitely lie between 215 and 235 K, corresponding to $\Delta G^{\ddagger}$ of 11.86 and 12.54, respectively, as outer limits.

Piperidides (**1**) were chosen for investigation since three dynamic processes are possible—amide rotation[4,7-12] (eq 1), ring reversal[4,12-14] (eq 2), and nitrogen inversion[4,14-16] (eq 3). Conformational isomers related by amide rotation (eq 1) should exhibit different ^{13}C NMR chemical shifts for the ring carbons α to the nitrogen, and possibly for the ring carbons β to the nitrogen, under conditions of slow interconversion.[3] Preliminary ^{13}C NMR studies[17] indicated that such conformational equilibria were occurring slowly at room temperature for **1a** and **1b**, but not slowly for **1e** and **1f**. Unless nitrogen inversion has a higher energy requirement than ring reversal, the latter (eq 2) will not be observable by ^{13}C DNMR. Similarly, ^{13}C DNMR will only be useful for nitrogen inversion barriers (eq 3) if ring reversal has a higher barrier. In summary, ^{13}C DNMR can be used to detect amide rotation in **1**, but cannot discriminate between ring reversal and nitrogen inversion.

Examination of the literature suggests that amide rotation should have the highest barrier of the three possible processes in **1**. While solvent, concentration, and method of data analysis are all found to be critical,[4,7,18,19] the overall results indicate free energies of activation at the appropriate coalescence temperatures[20] [$\Delta G^{\ddagger}(T_c)$] in the range of 15–16 kcal/mol for *N,N*-dimethylbenzamides and *N,N*-dimethylcarbamates using ^{1}H DNMR techniques. Available ^{1}H DNMR data in the 1-acylpiperidines[8-11] (Table I) suggest an amide rotation barrier around 16.5 kcal/mol for the 1-acetylpiperidines and a lower barrier for the 1-benzoylpiperidines (although actual barriers were not calculated for the latter compounds[10,21]). LeCam and Sandström's results[12] for partially deuterated acylmorpholines (Table I) support these conclusions and suggest that the nature of the ring substituent in a 1,4 relationship to the nitrogen may be of little significance.

Ring reversal barriers in piperidines, morpholines, and piperazines are observed with $\Delta G^{\ddagger}(T_c)$ of 10–13 kcal/mol,[4,12-14] and should be considerably lower (by 4–5 kcal/mol) in the 4-piperidones.[14,23] Nitrogen inversion barriers in acylpiperidines[15,16,24] should be below the range detectable by ^{1}H DNMR and ^{13}C DNMR studies. Nevertheless, as pointed out by Lambert,[15a] almost all of the ^{1}H DNMR studies of piperidines and piperidides are ambiguous as to the nature of the specific dynamic process being observed. However, as indicated previously, ^{13}C DNMR studies of piperidides (**1**) will provide unambiguous evidence whether a given dynamic process is amide rotation or not. In addition, because of the simplicity of the observed exchange process in the proton-decoupled spectra, the $\Delta G^{\ddagger}(T_c)$ should be obtained with reasonable accuracy.[20,22]

The results for compounds **1** are presented in Table I. In each instance, the benzamides (**1a–d**) exhibit amide rotation barriers of 14–15 kcal/mol under conditions of ^{1}H DNMR and ^{13}C DNMR analysis in $CDCl_3$ solutions. The ^{13}C DNMR method is especially useful for 1-benzoylmorpholine[26] (**1c**), a compound whose ^{1}H NMR spectrum appears as a slightly broadened singlet at both 60 and 100 MHz and is, therefore, not amenable to ^{1}H DNMR analysis without the preparation of deuterated derivatives.[12] On the other hand, ^{1}H DNMR is more useful than ^{13}C DNMR for 1-benzoyl-4-piperidone (**1b**), since overlapping signals in

Table II
^{13}C NMR Data in $CDCl_3$

Compd	Temp, K	α to N[a]	β to N[a]
1a[c]	249	48.5 (524), 42.8 (534)	26.3 (478), 25.5 (475)
	275	48.5 (370), 42.8 (323)	26.4 (443), 25.5 (418)
	287	48.4 (190), 42.9 (186)	26.3 (257), 25.6 (270)
	291	48.4 (152), 42.9 (148)	26.0 (124)
	299	48.4 (118), 42.8 (119)	26.0 (361)
	303	Broad d	26.0 (424)
	315	Coalescence	26.0 (611)
	317	Broad s	26.0 (702)
	321	Broad s	26.1 (822)
	329	45.8 (401)	26.1 (872)
1b[d]	248	46.1 (211), 40.6 (286)	41.3 (475)
	273	46.0 (220), 40.7 (346)	41.1 (516)
	299	Broad d	40.9 (521)
	306	Broad s	40.9 (582)
	311	Broad s	41.0 (712)
	322	43.8 (249)	41.1 (811)
	332	43.9 (237)	41.0 (732)
1c[e]	248	47.9 (383), 42.2 (401)	66.6 (760)
	273	48.0 (92), 42.3 (88)	66.6 (611)
	300	Broad d	66.6 (797)
	305	Coalescence	66.6 (654)
	309	Broad s	66.6 (717)
	333	45.4 (212)	66.7 (816)
1d[f]	248	47.3 (261), 41.6 (246)[b]	54.8 (264), 54.3 (256)[b]
	273	47.4 (165), 41.9 (173)	54.6 (280) d
	281	47.4 (227), 41.7 (247)	54.9 (292), 54.5 (306)
	286	47.3 (182), 41.8 (235)	54.7 (418) broad
	299	47.4 (50), 42.0 (58)	54.9 (412)
	305	Broad d	54.9 (810)
	310	Coalescence	54.9 (1036)
	323	Broad s	54.9 (475)
	331	44.8 (210)	54.8 (1050)
1e[g]	248	44.6 (921)	25.7 (889), 25.5 (879)
	299	44.8 (1893)	25.8 (1814)
1f[h]	248	42.8 (941)	41.1 (783)
	299	43.0 (981)	40.9 (876)
	303	43.0 (233)	41.0 (263)

[a] Relative peak intensities indicated in parentheses where relevant. [b] Signals α and β to the amide nitrogen, respectively, in the columns. [c] Amide CO, 169.8–170.0; γ to N, 24.4–24.5; Ar, 136.2–136.8, 129.2–129.3, 128.2–128.3, 126.6–126.8. [d] Amide CO, 170.3–170.6; ring CO, 206.0–206.9; Ar, 134.8–135.5, 129.9–130.0, 128.4–128.5, 126.8–127.0. [e] Amide CO, 170.0; Ar, 134.9–135.7, 129.6–129.7, 128.4–128.5, 126.9–127.0. [f] Amide CO, 169.5–169.9; NCH_3, 45.7–46.0; Ar, 135.2–136.1, 129.3–129.5; 128.1–128.3; 126.8–127.0. [g] Amide CO, 155.4; γ to N, 24.4–24.6; OCH_2, 60.9–61.1; CH_3, 14.7–14.8. [h] Amide CO, 155.1–155.3; ring CO, 207.2; OCH_2, 61.6–61.7; CH_3, 14.7.

the ^{13}C NMR spectrum interfere with accurate assignment of the coalescence temperature. Neither technique provides an advantage for 1-benzoyl-4-methylpiperazine (**1d**), since overlapping signals are a problem in both approaches.

The urethanes **1e** and **1f** behave somewhat strangely. No change is observed in the ^{13}C NMR spectrum of 1-carboethoxy-4-piperidone (**1f**) on cooling to 248 K in $CDCl_3$ or to 181 K in $CHFCl_2$, at which temperature precipitation begins to occur from each solvent. The behavior of 1-carboethoxypiperidine (**1e**) in $CDCl_3$ is somewhat puzzling. The signal attributed[17] to the ring carbons α to the nitrogen becomes less intense relative to the other signals on cooling, but does not obviously broaden or split. However, a small splitting (5 Hz) is observed at 248 K for the signal of the ring carbons β to the nitrogen. An accurate coalescence temperature could not be obtained but the $\Delta G^{\ddagger}$ at 270 K would be 14.47 kcal/mol. On switching to $CHFCl_2$ as the solvent, splittings of 4.9 Hz are observed for the ring carbons both α and β to the nitrogen. Because of problems caused by line broadenings, coalescence is estimated to occur at 223 K (outer limits are 215 and 235 K), corresponding to $\Delta G^{\ddagger}(T_c)$ of 11.88 kcal/mol (outer limits of 11.86 and 12.54 kcal/mol, respectively). This large solvent effect using quite similar solvents has no obvious explanation.

As previously noted,[7,10] the barriers to rotation are lower in the carbamates than in the benzamides, a result which differs from that observed in the acyclic analogues. The piperidide system differs from the acyclic case in that the six-membered ring minimizes rotation of the nitrogen end of the amide group, leaving C=O rotation as the major isomerization pathway. In addition, as pointed out by LeCam and Sandström,[12] repulsions between the *N*-acyl group and the vicinal equatorial hydrogens would cause more sp^3 character on nitrogen in the piperidides than in the acyclic analogues, leading to a lower barrier to amide rotation in the piperidides than in the *N,N*-dimethylamides, as observed in this work.

It is also apparent that the amide rotation barriers are almost insensitive to the nature of the substituent in the 4 position of the piperidine ring. All of these systems exist in chair conformations;[17] however, changing the atom in the 4 position would change the bond lengths, bond angles, and dihedral angles in the ring, as well as changing the electron

Table III
^{13}C NMR Data in $CHFCl_2$[a]

Compd	Temp, K	α to N[b]	β to N[b]
1e[c]	194	44.9 (280), 44.7 (320)	26.1 (392), 25.9 (348)
	211	45.1 (1726), 44.9 (1899)	26.2 (2070), 26.0 (2071)
	215	45.1 (116), 44.9 (120)	26.2 (144), 26.0 (140)
	223	Multiplicity?	Multiplicity?
	240	45.1 (553)	26.2 (591)
	253	45.3 (509)	26.2 (455)
1f[d]	182	43.1 (283)	41.4 (256)
	211	43.3 (462)	41.4 (443)

[a] Containing a trace of CD_2Cl_2 for field-frequency stabilization. [b] Signals in the ring α and β to the amide nitrogen, respectively. [c] Amide CO, 156.1–156.2; γ to N, 24.7–25.0; OCH_2, 61.6; CH_3, 14.8–14.9. [d] Amide CO, 155.4–155.6; OCH_2, 62.0; CH_3, 14.7–14.8.

distribution. The amide rotation barriers in **1** appear to be insensitive to such changes. The results, therefore, corroborate those determined earlier[17] in that no significant transannular electronic effects are observed between γ positions[28] in saturated six-membered heterocycles by ^{13}C NMR methods.

Experimental Section

All compounds were commercially available or prepared as previously reported[17] except for 1-benzoyl-4-methylpiperazine (**1d**), which was prepared from 1-methylpiperazine and benzoyl chloride by the method of Harfenist.[29]

^1H NMR spectra were recorded on a Varian A-60A spectrometer using deuteriochloroform or 1,1,2,2-tetrachloroethane solutions. Variable-temperature studies were performed with the aid of a Varian 6040 temperature controller. The temperature was calibrated by the peak separation of ethylene glycol,[30] and the instrument was retuned at each temperature by optimization of the aromatic singlet.

^{13}C NMR spectra were recorded on a JEOL PS-100 NMR spectrometer equipped with a JEOL JNM-PFT-100 pulse unit, a JEOL JEC-6 computer, and a JEOL VT-3C temperature controller. Field frequency stabilization was established by the deuterium signal of solvent deuteriochloroform or by the deuterium signal of a trace amount of dideuteriodichloromethane in solvent fluorodichloromethane (Matheson Genetron 21). The chemical shifts are expressed in parts per million relative to internal Me_4Si, and are believed to be accurate to 0.2 ppm. Relative peak intensities are indicated in parentheses after chemical shift values. Temperatures are accurate to ±2°. Results are shown in Tables II and III.

Acknowledgments. We wish to thank Mr. C. Erkelens for operating the JEOL spectrometer and Drs. F. J. Koer and C. Altona for helpful discussions. J.A.H. is especially grateful to Seton Hall University for a sabbatical leave and to Professor E. Havinga for his generous hospitality in Leiden.

Registry No.—**1a**, 776-75-0; **1b**, 24686-78-0; **1c**, 1468-28-6; **1d**, 7556-56-1; **1e**, 5325-94-0; **1f**, 29976-53-2.

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