C_1–C_6–C_5 angle and 83° was found for the C_1–C_7–C_5 angle. This agreement between calculated and experimentally determined values of η and γ lends credence, we believe, to the validity of our calculated δ and ω values, where comparison with experiment is not so straightforward. While the cyclobutyl ring parameters exhibit an expected uniformity, variations in the C_{10} methyl and hydroxyl configurations induce an interesting boat–chair variability in the calculated relative strain energy (cf. Table II), which energy increases in the order II < Ia < Ib ~ III < IVa < IVb. Except for *trans*-2-pinanol (I), the lowest energy conformations are (semi) boat, and all of the energy minima geometries exhibit an ω twist, to reduce the interactions between the *gem*-dimethyl bridge and the hydroxyl and C_{10} methyl groups.

The 2-pinanols have not been as widely studied as have the isopinocampheols. Our calculations suggest that I and II favor the chair (Ia) and boat conformations, respectively, which is in agreement with the favored conformations cited for *trans*- and *cis*-pinane.[1] The C_{10} methyl group is fixed in a pseudo-equatorial position in both the chair (Ia) and boat (II) conformations, and both the hydroxyl groups are therefore directed axially. Our calculated boat conformation II differs from the chair conformation suggested earlier,[3] where the hydroxyl group was equatorially projected. However, the axial and sterically least hindered projection of the hydroxyl group in II is fully consistent with II exhibiting a greater acetylation reactivity than in I[3] where the axial hydroxyl is somewhat sequestered.

Our calculations predict that isopinocampheol (III) is more stable than neoisopinocampheol (IV) and that the C_{10} methyl groups in both III and IV adopt equatorial positions in the ground-state conformations. These predictions are in full agreement with the analysis of Banthorpe and Whittaker,[12] which was based on varied esterification and deesterification rates. Zweifel and Brown[4] have predicted that the extreme boat and chair conformations for III and IV would not be favored, since the NMR data of Erskin and Knight[21] indicated that the C_{10} methyl protons in both compounds experience nearly identical chemical shifts and hence the relative positions of the C_{10} and C_9 methyl groups must be very similar in III and IV. It was suggested[4] that a planar, "cyclopentyl" conformation for the C_1–C_2–C_3–C_4–C_5 array could account for this invariance in the C_{10} methyl proton chemical shifts. As our calculations show (Table II), the semiboat conformation for III and IVa gives a reasonable account of the constancy in the C_{10}–C_9 spatial arrangement. We found that the strictly planar conformations were highly sterically excluded relative to the semiboat minima with barriers on the order of 83 (III) and 64 kcal/mol (IVa).

In summary, it appears that the configuration at C_2 of the C_{10} methyl group controls the conformation (semiboat or chair) of pinanols. The Monte Carlo empirical conformational energy algorithm we have here tested appears to give reliable results, at least for the cases studied here, in searching over multiple degrees of freedom. We reiterate that the sole use of primitive nonbonded atom interaction potentials is not a necessary feature of our algorithm. However, it has been demonstrated repeatedly[14] that such potentials often give results which are competitive with the most sophisticated computational schemes available.

Registry No. I, 35408-04-9; II, 35519-42-7; III, 24041-60-9; IV, 35998-01-7.

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Conformational Analysis of *N*-Acyl Derivatives of 1-Aza-3-cyclohexanone†

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Ground-state rotamer energy differences and amide rotation barriers are evaluated for a series of *N*-acyl-3-piperidones by using carbon-13 NMR. The effects of substituents in the six-membered ring and of the acyl group on these properties are considered. For a given acyl group, amide rotation barriers are in the order 4-piperidone < morpholine < piperidine < 3-piperidone. Use of chemical-shift data to evaluate preferred rotamers is probed, exposing anomalous behavior on the part of the ring carbonyl group and important acyl group influences. An electrostatic interaction is required to explain some of the experimental results.

Amide rotation barriers have been extensively studied,[1] yet there have been few attempts to systematically evaluate the various steric and electronic influences on the barrier heights. Reisse and co-workers[2] and Yoder's group[3] have presented evidence that electron-donating substituents attached to the amide carbonyl (or thiocarbonyl[2]) groups result in electrostatic lowering of the barrier to rotation. Direct resonance interactions[3] also play a role. Steric factors are also evident,[1,2] with larger substituents producing lower barriers because of ground-state repulsive forces.

In our previous study,[4] we utilized variable-temperature carbon-13 magnetic resonance (^{13}C DNMR) to investigate amide rotation barriers in a series of N-acylated six-membered nitrogen heterocycles (1–4), where steric factors

†Dedicated to Professor Egbert Havinga of the University of Leiden on the occasion of his retirement.

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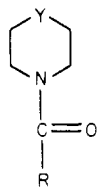
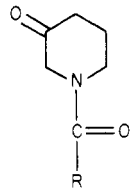


1, Y = CH_2
2, Y = O
3, Y = C=O
4, Y = NCH_3
5, Y = $CHCH_3$



6

a, R = C_6H_5; b, R = CH_3; c, R = OCH_3; d, R = OCH_2CH_3; e, R = $OCH_2C_6H_5$

can be essentially excluded from substituent effects in the heterocyclic ring on the barrier heights. At that time, we[4] concluded that the amide rotation barriers were "almost insensitive" to the nature of the substituent in the 4-position of the piperidine ring. Subsequent work by Reisse[2] and that reported herein require us to now conclude that the small differences previously observed[4] were indeed significant and that rotation barriers follow the order 4-piperidonide < morpholide < 4-methylpiperazide < piperidide for constant acyl groups under similar conditions (solvent and concentration). Reisse[2] has suggested that these barrier heights may be correlated with the availability of the nitrogen lone pair in these amides and has cited ionization potential data for morpholine (8.91 eV) and piperidine (8.66 eV) to support this hypothesis. He[2] has also suggested that the barrier heights might be interpreted in terms of the electron-donating properties of the amine group and the electron-withdrawing properties of the acyl group by using a HOMO–LUMO scheme, but details of this approach have not yet appeared.

Since we have available a series of N-acylated 3-piperidones[5] (**6a–e**) in connection with another study,[6] we herein report application of ^{13}C DNMR to these systems. These 3-piperidones differ from our previous systems in that the ground-state amide rotamers should be of different energies because of interactions between the amide carbonyl and the piperidone carbonyl. Data obtained at low temperatures under conditions of slow amide rotation will therefore be analyzed in order to assign the various ^{13}C chemical shifts to the major and minor conformers and to evaluate the magnitude of the presumably dipole–dipole terms. The use of carbon-13 NMR is again advantageous because the multitude of internally consistent values available for both the conformer energy differences and the rotation barrier heights in each molecular framework provide significant confidence in the results. In addition, it has been suggested[7] that carbons syn to the carbonyl oxygen of an amide are shielded relative to the corresponding carbon anti to the amide carbonyl oxygen, facilitating rotamer assignments.

Rotation Barriers

Few amide rotation barriers have been reported in systems where ground-state rotamers differ in energy[7-9] and where substituent effects do not have significant steric components. Analysis of barrier heights in such systems is complicated by these ground-state energy differences. The equation used to calculate free energies of activation at coalescence, $\Delta G^{\ddagger}_c = 4.58T_c(10.32 + \log (T_c/2.22\Delta\nu))$, assumes exchange between equally populated sites. Nevertheless, in order to facilitate comparison with previous work,[4] it is assumed that this equation will remain valid for exchange between unequal populations.[10] This assumption is also less drastic than it may appear to be because the experimental results in the 3-piperidones often were not compatible with accurate assignment of the coalescence temperature for a given exchange process. Since an error of 1 °C in T_c produces an error of about 50 cal/mol in $\Delta G^{\ddagger}_c$, an uncertainty of 5 °C in T_c is associated with an error in $\Delta G^{\ddagger}_c$ comparable to all but the largest ground-state energy differences actually observed (vide supra). This error in $\Delta G^{\ddagger}_c$, therefore, makes the value of $\Delta G°$ of little importance in most of our determinations of $\Delta G^{\ddagger}_c$.

Table I is a compilation of amide rotation barriers (from the literature and obtained in the present work with **6a–e**). As is evident from the data in Table I, the barrier heights in the 3-piperidone (**6**) are significantly greater than those in any of the piperidides with the same acyl group. In fact, it is somewhat surprising to find the highest barriers in the 3-piperidones and the lowest barriers in the 4-piperidones.

Some evidence for the nature of this substituent effect may be deduced from extrapolation of results reported by Pinto, Vyas, and Szarek.[13] These authors investigated several *N*-benzoyl-4-heterapiperidines, including unsubstituted and 3-substituted systems. Using their data,[13] which unfortunately is only given under conditions of "slow", "intermediate", and "fast" exchange, and assuming that the temperature of the "intermediate-exchange" results can be used as the coalescence temperature,[13] one can calculate the values of $\Delta G^{\ddagger}_c$ shown in Table II (ignoring ground-state rotamer energy differences where present). While the barrier height for 1-benzoylmorpholine in Table II is about 1 kcal/mol higher than that previously reported[4,11,16] and while the errors in the $\Delta G^{\ddagger}_c$ values must be significant and unknown, there is no doubt that the electron-withdrawing acetoxy groups in the amine moiety increase the barrier magnitude. Some or all of this barrier-increasing effect must be a ground-state phenomenon since the 4-piperidone system (**3**) exhibits significantly lower barriers than the 3-piperidone system (**6**). In these ketonic systems, ketone dipole–amide dipole interactions must also be considered, especially in the 3-piperidones (**6**). Such dipole–dipole interactions should be evident on changing the solvent. As shown in Table I, for 1-benzoyl-3-piperidone (**6a**), amide rotation barriers are lower in acetone than in chloroform.[17] Unfortunately, attempts to evaluate rotation barriers for this substrate in more polar solvents have failed because of inability to

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(14) For example, in Me_2SO-d_6 T_c values for C-2 and C-6 of **6a** are at 298–305 K. Assuming $\Delta\delta$ at slow exchange is an average of those values obtained in $CDCl_3$ and in $(CD_3)_2CO$, ΔG_c at 298 K would be 16.42–16.46 kcal/mol. These values would be comparable to those in $CDCl_3$ and higher than those in $(CD_3)_2CO$, suggesting no real trend.
(15) E. Wenkert, T. Hudlicky, and H. D. H. Showalter, *J. Am. Chem. Soc.*, **100**, 4893 (1978).
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(17) Similar behavior has been observed in *N*-acylazoles.[8,9]

Table I. Amide Rotation Barriers in Piperidides

compd	solvent	T_c, K	$\Delta G^{\ddagger}_c$, kcal/mol	NMR signal
1-benzoylpiperidine, 1a	$CDCl_3$[4]	292	14.82	α-^{1}H
	$CDCl_3$[4]	316	14.94	α-^{13}C
	$CDCl_3$[4]	289	14.75	β-^{13}C
	o-DCB[2]	281	14.1	not given[2]
	not given[16]	309	14.7	α-^{13}C
1-benzoyl-4-piperidone, 3a	$CDCl_3$[4]	273	13.97	α-^{1}H
	$CDCl_3$[4]	303[a]	14.32	α-^{13}C
1-benzoylmorpholine, 2a	$CHFCl_2$[11]	276	14.4	β-^{1}H
	$CHFCl_2$[11]	283	14.4	α-^{1}H
	$CDCl_3$[4]	305	14.39	α-^{13}C
	not given[16]	300	14.2	α-^{13}C
1-benzoyl-4-methylpiperazine, 4a	$CDCl_3$[4]	310[a]	14.64	α-^{13}C
	$CDCl_3$[4]	284	14.65	β-^{13}C
1-benzoyl-3-piperidone, 6a	$CDCl_3$	283	15.93	^{13}C-5
	$CDCl_3$	253	15.06	^{13}C-4
	$CDCl_3$	305[e]	16.42	^{13}C-6
	$CDCl_3$	299[e]	16.15	^{13}C-2
	$CDCl_3$	275	16.24	Ar-^{13}C
	$CDCl_3$	278	16.14	Ar-^{13}C
	$CDCl_3$	268	16.05	amide ^{13}C=O
	$CDCl_3$	253	15.42	ketone ^{13}C=O
	$(CD_3)_2CO$	280	15.78	^{13}C-5
	$(CD_3)_2CO$	263	15.42	^{13}C-4
	$(CD_3)_2CO$	290[a]	15.58	^{13}C-6
	$(CD_3)_2CO$	290[a]	15.60	^{13}C-2
	$(CD_3)_2CO$	259	15.26	Ar-^{13}C
	$(CD_3)_2CO$	268	15.68	Ar-^{13}C
	$(CD_3)_2CO$	263	15.68	amide ^{13}C=O
4-benzoyl-1-thia-4-azacyclohex-2-ene	CD_3CN[12]	255	14.79	α- and α′-^{1}H
	CD_3CN[12]	255	14.37	α- and α′-^{1}H
1-acetyl-4-methylpiperidine, 5b	$CDCl_3$[b]	330[b]	16.4	α-^{1}H
	$CDCl_3$[b]	330[b]	16.96	α-^{1}H
	$CDCl_3$[b]	343[b]	17.07	α-^{1}H
1-acetylmorpholine, 2b	$CHFCl_2$[11]	305	16.5	β-^{1}H
	$CHFCl_2$[11]	315	16.6	α-^{1}H
1-acetyl-3-piperidone, 6b	$CDCl_3$	309	18.52	amide ^{13}C=O
	$CDCl_3$	317	18.60	ketone ^{13}C=O
1-carbomethoxypiperidine, 1c	$CHFCl_2$[c,4]	223[d]	11.88	α- and β-^{13}C
1-carbomethoxy-3-piperidone, 6c	$CDCl_3$	273[f]	16.09	^{13}C-2
	$CDCl_3$	268	15.92	ketone ^{13}C=O
	$CDCl_3$	273	16.12	amide ^{13}C=O
1-carboethoxy-3-piperidone, 6d	$CDCl_3$	267	15.74	amide ^{13}C=O
	$CDCl_3$	267	15.97	^{13}C-6
	$CDCl_3$	267	15.99	ketone ^{13}C=O
	$CDCl_3$	276	16.08	^{13}C-2
1-carbobenzoxy-3-piperidone, 6e	$CDCl_3$	264	15.83	ketone ^{13}C=O
	$CDCl_3$	271	15.91	^{13}C-2
	$CDCl_3$	270	15.93	amide ^{13}C=O

[a] Not clearly defined coalescence, ±5 K. [b] Approximate coalescence temperature. See details in Table I of ref 4. [c] Containing a slight amount of CD_2Cl_2 for external lock. [d] Because of line broadening, T_c is between 215 and 235 K as outer limits. [e] Difficult to assess because of line broadening, so may be up to 10 K too high. [f] Coalescence difficult to assess because of overlap with $-OCH_3$ carbon, ±5 K.

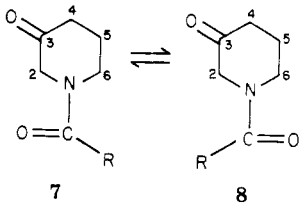
Table II. Amide Rotation Barriers Estimated from Ref 13

compd	T_c, K	$\Delta G^{\ddagger}_c$, kcal/mol	NMR signal
1-benzoylmorpholine, 2a	295	15.8	α-^{13}C
1-benzoyl-3-acetoxymorpholine	305	16.7	^{13}C-2
	305	16.8	^{13}C-6
4-benzoyl-1-thia-4-azacyclohexane	305	16.3	α-^{13}C
4-benzoyl-2-acetoxy-1-thia-4-azacyclohexane	305	16.5	^{13}C-3
	305	16.6	^{13}C-5

achieve conditions of slow exchange.[14]

Rotamer Energy Differences and Assignments

Under conditions of slow exchange, ground-state rotational isomers of unsymmetrical amides such as 6 differ in energy and, therefore, are present in unequal populations. Rotamer assignments can be made by using the previously suggested[7] ^{13}C NMR phenomenon that carbons syn to the amide carbonyl oxygen are shielded relative to the corresponding carbons anti to the amide carbonyl oxygen. The two rotamers in the 3-piperidone series are structures 7 and 8. In structure 7, carbon 2 is syn to the



7 8

amide carbonyl oxygen, while carbon 6 is syn in structure 8. Relevant chemical shifts, relevant signal intensities, assignment of major isomers (structures 7 or 8), and rotamer free-energy differences calculated from the experimental signal intensities are given in Table III. Intuitively, it might be expected that the preferred rotamer would be structure 8, in which the negative poles of the two carbonyl dipoles are as distant as possible.[9] For

Table III. Ground-State Rotamer Analysis

compd	solvent	T, K	carbon	chemical shifts[d] (rel intens)	major rotamer[a]	ΔG°, cal/mol
6a	$CDCl_3$	225	2	57.79 (13.73), 53.27 (19.94)	7	128
			3	205.34 (20.33), 205.13 (31.70)	7	198
			4	38.89 (19.28), 38.65 (16.97)		157
			5	23.48 (17.81), 22.11 (13.99)	7	108
			6	46.08 (18.08), 41.04 (13.75)	7	122
			amide CO	170.72 (29.80), 170.51 (22.36)		128
			Ar	134.60 (35.37), 134.05 (25.71)		143
			Ar	126.98 (49.51), 126.68 (70.61)		159
6a	$(CD_3)CO$	246	2	58.27 (13.78), 53.39 (30.03)	7	381
			4	39.19 (27.85), 38.80 (16.35)	*b*	260
			5	24.27 (28.36), 22.96 (14.15)	7	340
			6	46.44 (27.44), 41.32 (12.80)	7	373
			amide CO	170.18 (17.99), 169.94 (8.43)	*b*	370
			Ar	136.81 (22.27), 136.39 (10.50)	*b*	368
			Ar	127.95 (35.88), 127.62 (69.50)	*b*	323
6b	$CDCl_3$	249	2	56.15 (36.93), 51.72 (72.58)	7	334
			3	205.37 (51.53), 204.91 (25.07)	8	356
			6	44.41 (59.24), 40.28 (34.58)	7	266
			amide CO	169.51 (57.29), 169.27 (31.40)	*b*	298
6c	$CDCl_3$	249	3	205.58 (17.07), 205.31 (21.50)	7	114
			amide CO	155.74 (17.67), 155.40 (19.40)	*c*	46
6d	$CDCl_3$	249	2	54.00 (29.79), 53.51 (25.74)	8	73
			3	205.34 (20.62), 205.13 (23.43)	7	63
			6	42.29 (28.94), 42.07 (29.45)	8	9
			amide CO	155.22 (18.70), 154.89 (21.63)	*c*	72
6e	$CDCl_3$	249	2	53.78 (10.10), 53.39 (8.93)	8	61
			3	205.27 (5.46), 205.07 (6.76)	7	106
			amide CO	154.92 (6.78), 154.59 (7.65)	*c*	60

[a] Assigned as per ref 7. [b] Same major rotamer as in compound 6a. [c] Different major rotamer than in compound 6a suggested. [d] Given in ppm relative to Me_4Si.

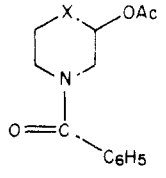
Table IV. Ground-State Rotamer Analysis of Data from Ref 13

compd	solvent	T, K	carbon	chemical shifts[b] (rel intens)	major rotamer[a]	ΔG°, cal/mol
1-benzoyl-3-acetoxymorpholine	$CDCl_3$	260	2	46.8 (1.0), 49.9 (3.1)	9	584
			6	41.5 (2.4), 44.2 (1.0)	9	452
4-benzoyl-2-acetoxy-1-thia-4-azacyclohexane	$CDCl_3$	260	3	53.1 (2.4), 48.8 (1.0)	9	407
			5	47.4 (1.0), 43.8 (4.2)	9	741
4-benzoyl-1-thia-4-azacyclohex-2-ene	$CDCl_3$	243	2	104.5 (1.0), 101.2 (2.2)	10	380
			3	124.5 (2.8), 121.5 (1.0)	10	497
			5	47.5 (1.0), 40.8 (2.3)	10	402

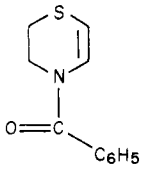
[a] Assigned as per ref 7 and 13. [b] Given in ppm relative to Me_4Si.

N-benzoyl-3-piperidone (**6a**), it is therefore surprising to note that every set of chemical shifts consistently indicates that presumed rotamer **7** is preferred under conditions of slow exchange. In the more polar solvent acetone, this preference for rotamer **7** is magnified, especially since the acetone data are at a higher temperature.

These results for *N*-benzoyl-3-piperidone may be contrasted with those of Pinto, Vyas, and Szarek.[13] Our calculations of their data are shown in Table IV. The major rotamer assigned[13] to both the acetoxymorpholine system and the thia analogue is **9**. In both acetoxy



9, X = O, S



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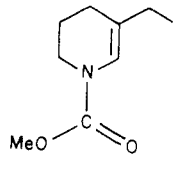
systems, the major rotamer appears to have the carbonyl oxygen anti to the carbon bearing the electron-withdrawing acetoxy group, while the rotamer syn to the electron-withdrawing ring carbonyl group (**7**) is preferred in our *N*-benzoyl-3-piperidone (**6a**). The major rotamer deduced[12,13] for the azacyclohexene compound is **10**.

It is also somewhat surprising to observe two signals under conditions of slow exchange (as well as a $\Delta G^{\ddagger}_c$ for amide rotation) for carbon 4 in **6a–e**. The latter clearly indicates an electrostatic (field and/or inductive) interaction between the amide carbonyl and its R group and carbon 4. Only an interaction which includes recognition of the position of the ring carbonyl as well as the amide carbonyl can cause carbon 4 in strucures **7** and **8** to be diastereotopic under conditions of slow exchange. An analogous result has recently been reported by Wenkert's group[15] for 1-carbomethoxy-3-ethylpiperideine and a carbene-addition adduct. Wenkert's azacyclohexene system appeared as an approximately 4:1 mixture in deuteriochloroform (temperature unspecified) favoring rotamer **11** (Table V). From the relationship of the amide



11

carbonyl oxygen relative to the vinyl group, this is the

Table V. Chemical Shifts[a] of Rotamers of 1-Carbomethoxy-3-ethyl-2-piperideine[15]

carbon	major rotamer	minor rotamer
2	118.4	118.9
3	119.9	119.9
4	24.4	24.8
5	21.4	21.4
6	41.4	38.1
OMe	52.1	51.9

[a] Given in ppm relative to Me_4Si.

opposite rotamer from that deduced by Grindley's group[12] for their N-benzoylazacyclohexene (**10**). Since the ethyl group in Wenkert's compound should not introduce a ground-state steric effect in the usual stereochemical sense, nor should the symmetrical sulfur replacement in Szarek's compound[12,13] be conformationally significant, this difference in conformational preference for an sp^2 carbon or an sp^3 carbon on changing the nitrogen substituent from a benzoyl group to a carbomethoxy group is puzzling (vide infra).

In N-acetyl-3-piperidone (**6b**), both ring carbons α to the nitrogen group suggest that rotamer **7** is again preferred. The larger signal for the amide carbonyl carbon is that with the greater chemical shift, paralleling the N-benzoyl system (**6a**) and thereby reinforcing the assignment of the major rotamer. However, data for the ring carbonyl carbon, carbon 3, suggest that rotamer **8** is preferred by an amount equal to that by which the other signals had suggested rotamer **7**. Clearly the quantitative agreement in rotamer preference for all of the signals available for **6b** (Table III) suggests that the ring carbonyl carbon must be anomalous or that the method of rotamer assignment must be questioned, but no reason for this behavior is apparent. In the urethanes **6c–e**, the ring carbons α to the nitrogen group consistently indicate small preferences for presumed rotamer **8**. The amide carbonyl carbon has relative intensities opposite to those of the analogous carbon in the N-benzoyl and N-acetyl systems, reinforcing the preference for presumed rotamer **8** in these urethanes. As for the acetyl analogue **6b** (vide supra), the ring carbonyl carbon is anomalous, suggesting a quantitatively similar preference for rotamer **7** in each urethane system. This consistent behavior of the ring carbonyl carbon (except in **6a**) engenders confidence that it truly cannot be used for such conformational assignments or that the method of rotamer assignment is in error.

Since N-benzoyl-**6a** seems to prefer rotamer **7** and urethanes **6c–e** seem to prefer rotamer **8**, our results parallel the different conformational preferences of Wenkert's[15] azacyclohexene urethane (**11**) and of Grindley's[12,13] N-benzoyl system (**10**). Both oxygens in the urethane groups are electronegative, which should reduce conformational energy differences between rotamers **7** and **8**, as observed. Another significant possibility is that the method of rotamer assignment[7] developed in the past is not applicable to urethanes and related amides not substituted on the carbonyl group by hydrogen or perhaps carbon.[3]

Regardless of the detailed interpretations which may evolve for some of the phenomena exposed herein, it is clear that our understanding of amide rotation barriers and of ground-state conformational preferences is far from complete and that ^{13}C NMR can be an extremely useful tool in unraveling the problems.

Experimental Section

All ^{13}C NMR spectra were recorded on a JEOL-PS-100 NMR spectrometer equipped with a JEOL-JNM-PFT-100 pulse unit and a JEOL-JEC-6 computer. Field-frequency stabilization was established by the deuterium signal of the solvent utilized. Chemical shifts are expressed in parts per million relative to internal Me_4Si and are believed to be accurate to 0.2 ppm. All solutions are 10–15%, so dilution effects should be minor. Experimental details, peak assignments, and spectral data under conditions of fast exchange were presented earlier.[6]

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Registry No. **1a**, 776-75-0; **1c**, 1796-27-6; **2a**, 1468-28-6; **2b**, 1696-20-4; **3a**, 24686-78-0; **4a**, 7556-56-1; **5b**, 4593-17-3; **6a**, 67452-85-1; **6b**, 34456-78-5; **6c**, 61995-18-4; **6d**, 61995-19-5; **6e**, 61995-20-8; **9** (X = S), 64918-18-9; **10**, 64416-12-2; **11**, 67708-23-0; **9** (X = O), 64918-12-3; 4-benzoyl-1-thia-4-azacyclohexane, 64918-16-7.