within this range. Wilcox and Leung[30] have suggested that an attenuation factor of 1/2.7 is most reasonable. Using this value, the predicted inductive slope falls very close to both the experimental and field slopes in the comparison of systems I and II. This same attenuation factor, however, predicts a slope for systems I and III which is far from the field and experimental slopes. These results suggest that the cavity model is a more useful approach in predicting the relative magnitude of substituent effects.

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Carbon-13 Nmr Study of Aliphatic Amides and Oximes. Spin–Lattice Relaxation Times and Fast Internal Motions

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Abstract: ^{13}C Fourier transform nmr spectra and *partially relaxed Fourier transform* (PRFT) cmr spectra of aliphatic amides and oximes yield insight into intramolecular interactions in these molecules. *N,N*-Dimethylformamide, *N,N*-di-*n*-butylformamide, *N,N*-di-*n*-butylacetamide, acetone oxime, and methyl ethyl ketone oxime have been studied. Significant carbon steric compression shifts are reported for the four aliphatic carbons transoid to the formyl hydrogen and eclipsing the carbonyl oxygen in *N,N*-di-*n*-butylformamide (DBF). These steric shifts range from over 5 ppm for the α-CH$_2$ carbon to *ca.* 0.1 ppm for the δ-CH$_3$ carbon on the same chain. Carbon spin–lattice relaxation behavior in DBF indicates that the ends of both butyl chains have significantly increased motional freedom. PRFT studies also yield insight into intramolecular steric interactions. For example in methyl ethyl ketone oxime the 1-CH$_3$ carbons in the two isomers (syn and anti to the NOH group) have very different T_1 values (6.1 and 2.8 sec, respectively).

The ability of ^{13}C nmr to resolve small differences in molecular environment has been well documented in recent years. Chemical shifts arising from steric perturbations of carbon nuclei, known as *steric compression shifts*, have been utilized in studies of diverse organic compounds.[1,2] The experimental result of steric compression is an upfield shift for carbons experiencing the interaction. For example, in methyl cyclohexanes the upfield shift due to an axial CH$_3$ group at C$_1$ is over 5 ppm experienced by both the C$_3$ and C$_5$ ring carbons.[1] Evaluation of steric compression shifts is facilitated where conformations can be "locked" and where model compounds are available to allow determination of ^{13}C chemical shifts in the absence of steric compression. Amides and oximes are particularly suited and of particular interest for such studies.

In the present work we have examined the cmr (carbon magnetic resonance) spectra of *N,N*-dimethylformamide (DMF) and *N,N*-di-*n*-butylformamide (DBF), plus several other amides and oximes. All spectra were obtained by pulsed Fourier transform (FT) nmr methods. In several cases, the spin–lattice relaxation behavior of each carbon was investigated in order to gain insight into the fast, internal motions $\gtrsim 10^{11}$/sec) of the different aliphatic groups. No attempt was made to study rotation around the amide C–N bond.[3] At the temperatures of observation, rotation around that bond was slow enough to freeze out conformers and yield separate resonances for aliphatic peaks cisoid and transoid to the formyl hydrogen.

In amides having two different N substituents and in oximes with different derivatized carbonyl substituents, the two conformers or isomers are not of equal energy; the equilibrium populations can be very different. Using steric compression shifts to facilitate ^{13}C spectral assignments allows rapid determination of isomer ratios for many amides and oximes. It is necessary to have some knowledge of the carbon spin–lattice relaxation times (T_1) and nuclear Overhauser enhancements (NOE) in order to obtain quantitative or near quantitative results. The spin relaxation and NOE behavior of these compounds is also of interest because it probes molecular geometry and intramolecular interactions.

Experimental Section

^{13}C Nmr Spectra. All ^{13}C nmr spectra were recorded on a Varian XL-100-15 spectrometer equipped for both frequency sweep and pulsed Fourier transform (FT) operation. In all cases, the FT mode was utilized. Chemical shifts are reported in ppm downfield from the internal standard TMS. The accuracy of chemical shifts determined in 5000-Hz spectra is better than 0.1 ppm; for 1000 Hz spectra, the maximum error is <0.02 ppm. The system computer (Varian 620-i, 16K core) allowed acquisition of 8K data points, thus yielding 4K (4096) output data points in the transformed, phase corrected real spectrum ($\sim$1.3 Hz per data point in a 5000 Hz spectrum). ^{13}C spectra were obtained with complete proton decoupling utilizing the pseudorandom noise modulation mode of the Gyrocode decoupler. Off resonance, partial decoupling to differentiate nonprotonated carbons, CH, CH$_2$, and CH$_3$ carbons, was effected by offsetting the ^{1}H irradiation frequency 0.5–1.0 kHz and turning off the noise modulation. In both wide-

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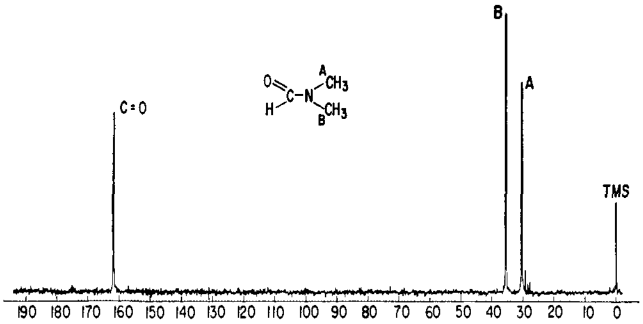

Figure 1. Cmr spectrum of *N,N*-dimethylformamide.

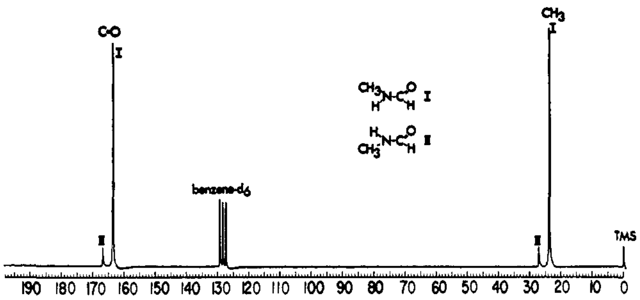

Figure 2. Cmr spectrum of *N*-methylformamide.

band and off-resonance decoupled experiments the high power heteronuclear decoupling mode was utilized (≈ 10 W of rf power).

Spin–Lattice Relaxation Measurements. Spin-lattice relaxation times (T_1) for carbons were determined simultaneously by the inversion–recovery pulse method,[4] modified by Freeman and Hill (Varian Associates). Two sets of partially relaxed Fourier transform (PRFT) spectra are given in Figures 4 and 7. The pulse sequence utilized in these measurements was

$$(T - 90°_\infty - T - 180° - t - 90°_t)_x$$

where t is experimentally varied and T is set greater than three times the longest T_1 to be measured.

In the Freeman–Hill modified program, the log of ($S_\infty - S_t$) is plotted against t where S_∞ and S_t are the transformed signals from the $90_\infty°$ and $90_t°$ pulses, thus yielding only positive peaks in the spectral display. T_1 is the time, t, at which $S_\infty - S_t$ reaches 0.368 ($\equiv 1/e$) of $S_\infty - S_t$ for $t = 0$ ($\equiv 2S_\infty$) (see Figure 5). Because the effective ^{13}C rf field for the XL-100-15 is under 2 kHz (90° pulse = $\sim$140 μsec), spin-lattice relaxation experiments were restricted to spectral widths <1500 Hz. When larger widths were required, separate experiments were run on each spectral region. For each determination 6–10 sets of measurements were taken. Some determinations were repeated on different samples of the same compound. Reproducibility of T_1 values was better than $\pm 10\%$.

NOE Measurements. The absolute nuclear Overhauser enhancement for each measured carbon was recorded by determining individual integrated peak intensities in ^{1}H decoupled cmr spectra and dividing these values by the total integrated band intensities in the coupled cmr spectra. In cases of band overlap in the coupled spectra appropriate integration assignments were made. In all cases, the pulse interval was longer than $5T_1$ for the slowest relaxing carbon being measured. This ensured complete relaxation of all nuclei between pulses. 4–16 free induction decays were accumulated for ^{1}H decoupled spectra while 32–256 free induction decays were accumulated for the coupled spectra. No internal integration standard was required, as the data acquisition computer program (Varian Associates) automatically scales the data to the same basis. In some cases experiments were repeated three-four times. Reproducibility of both decoupled and coupled peak integrations was generally ± 5 and always better than $\pm 15\%$. The accuracy obtained in this study was largely due to the very high signal:noise ratios obtained with concentrated solutions of low molecular weight materials.

Materials. All compounds were reagent grade and were used without further purification. Samples were run neat or concentrated (>70%) in acetone-d_6 or benzene-d_6 (utilized for field/frequency control). Samples were not degassed unless noted. When degassing was required, N_2 was bubbled through the solution for *ca.* 1 min.

Results and Discussion

Spectral features common to homologous aliphatic amides and oximes can be demonstrated with the spectrum of DMF.

***N,N*-Dimethylformamide (DMF).** The proton decoupled cmr spectrum of DMF shown in Figure 1 clearly shows separate resonances for the two CH_3 groups. The chemical shift difference ($\Delta\delta$) between the two CH_3 resonances is 5.1 ppm.[5a,b] Assignment of the two resonances was based on an expected upfield steric shift for the CH_3 group transoid to the formyl proton and eclipsing the carbonyl oxygen. This assignment was confirmed by running the cmr spectrum of *N*-methylformamide (Figure 2) and noting that the known "conformer" ratio[5c] (10:1, transoid:cisoid) was observed with the CH_3 group eclipsing the carbonyl oxygen being 3.4 ppm upfield from the CH_3 group cisoid to the formyl hydrogen.

In suitable molecules, spin–lattice (longitudinal) relaxation times determined by FT techniques may be utilized to give effective rotational correlation times for individual protonated carbons (carbons with directly attached protons) in a molecule.[6,7] This allows estimation of rapid internal reorientation of the individual groups and gives insight into various stereochemical interactions. In particular, when dipole–dipole (DD) relaxation is dominant, internal motions at frequencies comparable to or faster than the rate of overall molecular reorientation ($\approx \tau_c$, the molecular correlation time) may have a significant effect on relaxation rates (relaxation rate, $R_1 = 1/T_1$) for those carbon nuclei that are involved. Dipole–dipole relaxation is dominant for most hydrogen bearing (protonated) carbons;[6,8] where other relaxation mechanisms contribute to the relaxation of a given nucleus, the DD contribution may be calculated if the nuclear Overhauser enhancement (NOE) for that nucleus is determined.[9] The experimentally observed NOE, expressed as $(I_D/I_O) - 1$ or η (where I_D/I_O is the integrated ^{13}C peak intensity with ^{1}H saturation divided by the integrated intensity of the undecoupled ^{13}C resonance band), divided by the theoretical maximum NOE ($\eta = 1.99$) is a direct measure of the contribution of DD relaxation for individual carbons.[10] The spin-lattice relaxation behavior of the two CH_3 carbons and the carbonyl carbon in DMF illustrates the utility of these measurements in studies of molecular structure and motion.

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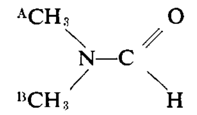
(10) The contributions to total relaxation are calculated as reciprocals of T_1 (or relaxation rates, R_1).

In general, the evaluation of internal rotational motion in molecules requires the assumption of overall isotropic molecular tumbling (*i.e.*, no mode of rotation being favored over another). In small unsymmetrical polar molecules such as DMF tumbling is generally more or less anisotropic (*i.e.*, *not* isotropic). The motional anisotropy of liquid DMF was examined by Wallach and Huntress.[11] Rotational diffusion constants reported in that work indicated that the tumbling of DMF molecules in the pure liquid was highly anisotropic. However, the diffusional rotational axes were found to be noncoincident with the principal inertial axes. Therefore, the effect of overall motional anisotropy on the relaxation behavior of the three carbons in DMF may be reduced.

T_1 values can also be affected by rotation about principal bonds where such rotation leads to exchange of equivalent carbons. The T_1 values for the two N–CH_3 carbons may thus be affected by rotation about the C–N amide bond even if the rotation is slow enough to give separate, narrow lines. This is true *only* if the lifetime of the CH_3 groups between bond rotations (the exchange lifetime) is not *much longer* than T_1. If the T_1 values for the two CH_3 carbons are different in the absence of exchange, then the observed T_1 values will tend to become averaged as the T_1's become significant relative to the exchange lifetime. Recent nmr kinetic data[12a,b] indicate that the rate of C–N amide bond rotation in DMF at 38° would result in an exchange lifetime of 10^2–10^3 sec ($E_a \gtrsim 20$ kcal[12a,b]). For DMF at 38° the exchange lifetime is long enough to allow determination of separate T_1 values for the two CH_3 carbons, within the stated limits of experimental accuracy.

Table I lists the experimental T_1 and NOE values and calculated T_1^{DD} values for the two CH_3 carbons and the carbonyl carbon in DMF (data at 25, 38, and 72°).

Table I. T_1 and NOE Data[a] for



Temp, °C	Carbon	T_1, sec[b]	NOE, η[c]	NOE, % theoretical max	T_1^{DD}, sec[d]
38	A	18.6	1.3	65	28.6
	B	11.1	1.7	85	13.1
	C=O	20.2	1.4	70	28.9
25	A	17.8			
	B	10.5			
	C=O	19.5			
72	A	19	1.2	60	32
	B	18	1.3	65	28

[a] At 25.2 MHz; 70% DMF, 30% benzene-d_6; sample degassed. [b] Estimated maximum error ±10%. [c] Estimated maximum error ±0.2. $\eta = I_D/I_O - 1$. [d] Estimated maximum error ±20%.

At 25° where the exchange lifetime is $>10^3$ sec, observed CH_3 T_1's are somewhat shorter than at 38° as a result of slightly more efficient dipole–dipole relaxation.

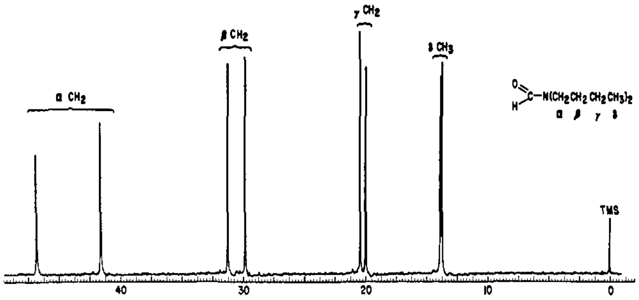


Figure 3. Cmr spectrum of *N*,*N*-di-*n*-butylformamide, aliphatic region (spectral width = 1,250 Hz).

No evidence for partial averaging of the relaxation data at 38° is indicated. At 72° on the other hand, the N–CH_3 relaxation times (Table I) are largely averaged (the exchange lifetime at 72° is *ca.* 10^1 sec). NOE determinations at 72° also appear to be averaged, as expected when the N–CH_3 carbons are able to exchange molecular environments through C–N amide bond rotation during relaxation.[12c]

The significantly longer T_1^{DD} (38°) for the CH_3 carbon eclipsing the carbonyl oxygen (carbon A) indicates that this CH_3 group may be able to spin more rapidly than CH_3 group B. In the absence of anisotropic molecular tumbling, if both CH_3 groups were rotating slowly relative to the overall molecular tumbling, then the CH_3 carbons would have the same relaxation times, and T_1^{DD} for both CH_3 carbons would be $^1/_3T_1^{DD}$ for the carbonyl carbon.[6,13] If the rotations of A and B were *very fast* relative to overall molecular motion (isotropic) then T_1^{DD} for A and B would be approximately three times longer than T_1^{DD} for the carbonyl carbon.[6] The experimental data for DMF (Table I) are not typical of either extreme noted above. T_1^{DD} for CH_3 carbon A is over twice as long as T_1^{DD} for CH_3 carbon B and approximately the same as T_1^{DD} for the carbonyl carbon.

In the absence of anisotropic overall molecular tumbling, these differences in relaxation times would allow calculation of approximate rates of rotation for the two CH_3 carbons. It is not known how much the anisotropy of overall molecular tumbling and rapid CH_3 group internal rotations contribute to the observed relaxation behavior for DMF. Further experiments will be required to assess these contributions. It does seem likely from the analogous behavior observed for the two oximes discussed below that rapid A-CH_3 group rotation contributes at least in part to the observed behavior.

Fast rotation of CH_3 group A relative to CH_3 group B can be explained in terms of available rotomeric conformations. Because of *opposing* unfavorable interactions with CH_3 group B and the carbonyl oxygen there are no favored rotomeric conformations for A whereas CH_3 group B is able to minimize unfavorable interaction with A without incurring a strong unfavorable interaction with the formyl hydrogen.

***N*,*N*-Di-*n*-butylformamide (DBF).** The cmr spectrum of DBF (Figure 3) shows four resolved pairs of aliphatic resonances corresponding to α-, β-, and γ-CH_2 carbons, and terminal δ-CH_3 carbons cisoid and transoid to the formyl hydrogen. The observed chemical

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(11) D. Wallach and W. T. Huntress, *J. Chem. Phys.*, **50**, 1219 (1969).

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Table II. Cmr Data for *N,N*-Di-*n*-butylformamide (DBF) and *N,N*-Di-*n*-butylacetamide (DBA)[a]

DBF	δ, cisoid[b]		δ, transoid[b]	$\Delta\delta$	T_1, cisoid, sec[c]	T_1, transoid, sec[c]
α-CH$_2$	46.95		41.71	5.24	1.0	1.2
β-CH$_2$	31.42		30.02	1.40	1.5	1.7
γ-CH$_2$	20.52		20.06	0.46	2.4	2.3
δ-CH$_3$	13.98		13.85	0.13	3.1	3.1
C=O		162.34				
DBA						
α-CH$_2$	48.65		45.39	3.26		
β-CH$_2$	31.75		30.52	1.22		
γ-CH$_2$	20.62		20.46	0.16		
δ-CH$_3$	14.09		14.06	0.03		
C=O		169.05				
COCH$_3$		21.39[d]				

[a] 38°, 25.2 MHz; solutions in acetone-d_6, chemical shifts in ppm downfield from TMS. [b] Cisoid and transoid to the formyl hydrogen. Assignments for DBA are tentative. [c] Neat solution, estimated maximum error ±10%. [d] Assignment confirmed by off-resonance ^{1}H decoupling.

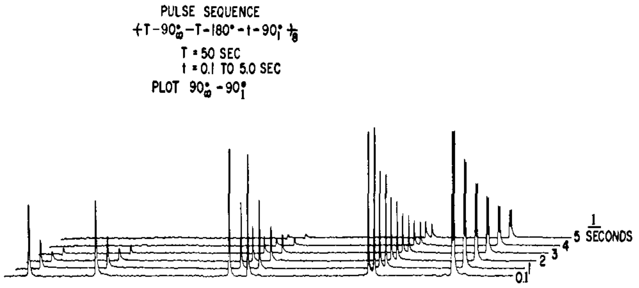

Figure 4. PRFT spectral set for *N,N*-di-*n*-butylformamide, aliphatic region.

shift difference ($\Delta\delta$) for the two α-CH$_2$ groups is 5.24 ppm (see Table II) in close agreement with the steric shift observed in DMF (5.1 ppm, Figure 1). As expected, differences between cisoid and transoid aliphatic carbon chemical shifts get smaller farther away from the carbonyl group. The fact that $\Delta\delta$ decreases in a regular way by *ca.* 70% with each intervening carbon (bond) suggests that all upfield resonances belong to the carbons transoid to the formyl hydrogen and cisoid to the oxygen, and that the upfield shifts are long distance steric compression shifts. In *N,N*-di-*n*-butylacetamide (DBA) the differences between cisoid and transoid groups are smaller. For the α-CH$_2$ groups that difference is 3.26 ppm. Also, cisoid–transoid $\Delta\delta$ values in the acetamide are not as linearly attenuated as in the formamide (see Table II). Presumably, the smaller $\Delta\delta$ values for the acetamide reflect the fact that both the cisoid and transoid chains are subject to steric compression shifts (from the carbonyl oxygen or the acetyl CH$_3$ group). The small chemical shift differences between the formamide and acetamide do not allow positive assignment of cisoid and transoid chains in the acetamide; however probable assignments are given in Table II.

The relaxation behavior of the aliphatic carbons in DBF (shown in Figures 4 and 5 and summarized in Table II) is quite analogous to that reported by Allerhand[7] for the end-of-chain carbons in 1-decanol. In Allerhand's paper, the T_1 values reported for the 7, 8, 9, and 10 carbons were nearly identical with the T_1 values of the *n*-butyl fragments in DBF.

$$\overset{10}{C}H_3(CH_2)_8\overset{1}{C}H_2OH$$

Carbon	10	9	8	7	6
T_1, sec[7]	3.1	2.2	1.6	1.1	0.84
Carbon	5	4	3	2	1
T_1, sec[7]	0.84	0.84	0.77	0.77	0.65

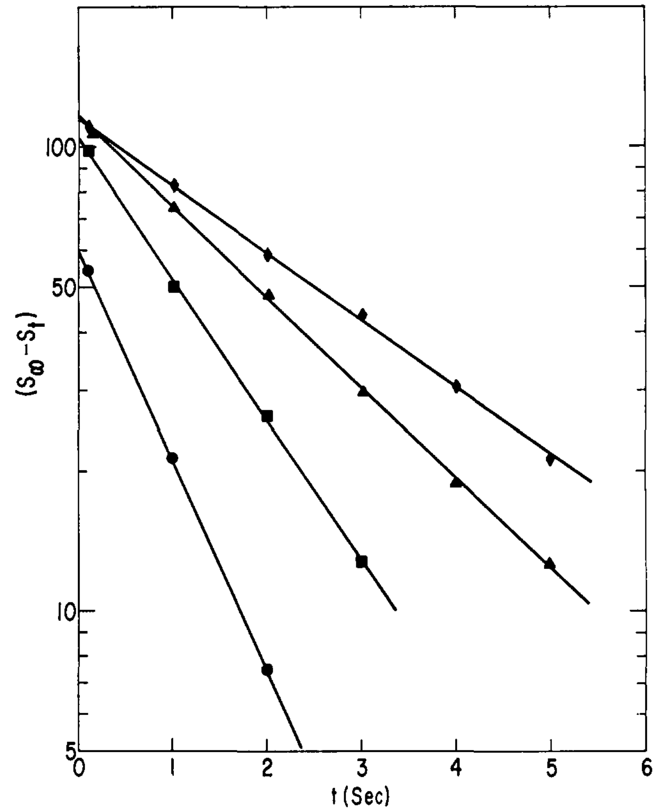

Figure 5. T_1 Determinations for *N,N*-di-*n*-butylformamide. Data points are from Figure 4. Cisoid carbon data plotted: ● = α-CH$_2$; ■ = β-CH$_2$; ▲ = γ-CH$_2$; ◆ = δ-CH$_3$.

The longer T_1 values for the carbons near the end of the ten carbon chain in *n*-decanol and for the β, γ, and δ carbons in DBF result from segmental motion at and near the "free" ends of these molecules.[7] In order to observe this type of behavior, motion at one part of the chain must be restricted. Allerhand noted that in 1-decanol, intermolecular hydrogen bonding effectively anchored the CH$_2$OH group. In DBF there is no possibility for strong hydrogen bonding effects, and subsequent restriction of molecular motion. On the other

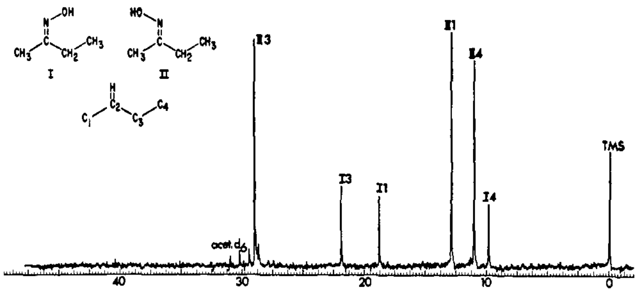

Figure 6. Cmr spectrum of methyl ethyl ketone oxime isomers, aliphatic region.

hand, the *n*-butyl chain is effectively anchored at the amide nitrogen since translational or rotational movement at that nucleus also requires moving parts of two aliphatic chains and a carbonyl group.

The restriction on internal motion near the nitrogen in DBF suggests that H bonding is not a requirement for anchoring relatively small molecules in solution. In order to assess the ability of H bonding to anchor butyl chains, the T_1 values for the four carbons in neat 1-butanol were determined. The T_1 values for carbons 1–4 were 3.0, 3.9, 3.6, and 4.2 sec, respectively. Although some degree of segmental motion is evident in 1-butanol, it is clear that intermolecular hydrogen bonding is not restricting CH_2OH motion as much as it does in 1-decanol. It appears that molecular geometry or size and H bonding may be of comparable importance for imposition of restrictions on molecular motion in solution.

It was hoped that some difference in relaxation behavior for cisoid and transoid chains in DBF would be evident; however none was noted witnin experimental error limitations (see Table II).

Acetone and Methyl Ethyl Ketone Oximes. Differences in relaxation behavior between conformational isomers for the oximes of acetone and methyl ethyl ketone, however, were observed. The cmr spectrum of acetone oxime has three resonances, the derivatized carbonyl carbon at 154.5 ppm, and the two nonequivalent CH_3 groups at 21.5 and 14.7 ppm. The difference between the chemical shifts of the two CH_3 groups, 6.8 ppm, is primarily a steric compression shift. This is clearly indicated in the cmr spectrum of methyl ethyl ketone (MEK) oxime (Figure 6) where the two oxime substituents are not sterically identical and thus the isomers are not present in equal amounts. In MEK oxime the observed isomer ratio is ~77 :23 in favor of the isomer with the N–OH group facing the CH_3 group. This isomer ratio is comparable to that found for protonated MEK observed in FSO_3H-SbF_5-SO_2.[14] It is also in agreement with recently determined values for MEK oxime from europium chemical shift reagent–proton nmr studies by Berlin.[15]

The carbon resonance assignments for MEK oxime are given in Table III. In the predominant isomer, the 1-CH_3 carbon exhibits a steric compression shift (6.1 ppm) while C_3 and C_4 are unperturbed. In the other isomer both C_3 and C_4 exhibit steric compression shifts (5.9 and 1.2 ppm, respectively). Both α carbon steric shifts are comparable to the steric shift in acetone oxime (6.8 ppm). The 4-CH_3 carbon steric shift is comparable to the steric shift observed for β-CH_2 carbons in DBF and DBA.

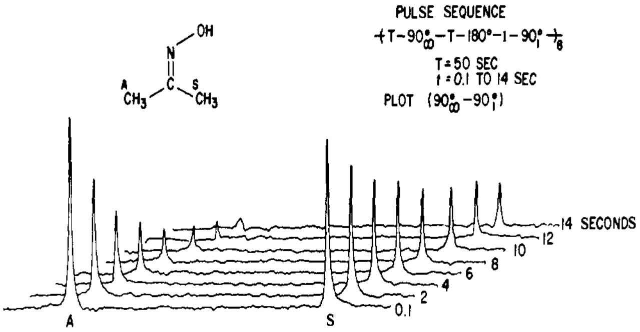

Figure 7. Set of PRFT spectra for acetone oxime.

Table III. Cmr Data for Methyl Ethyl Ketone Oxime Isomers

		δ^a	T_1, sec^b
I	1-CH_3	18.97	2.8
(NO*H* anti to	2-C=N	159.17	
CH_3 group)	3-CH_2	23.30	1.9
~23%	4-CH_3	9.95	3.6
II	1-CH_3	12.97	6.1
(NO*H* syn to	2-C=N	158.70	
CH_3 group)	3-CH_2	29.20	1.9
~77%	4-CH_3	11.12	3.4

[a] In acetone-d_6; chemical shifts downfield from internal TMS. [b] Run neat; T_1 values ±10–15%. T_1^{DD} not calculated.

Relaxation behavior in acetone oxime is analogous to the behavior noted for the CH_3 groups in DMF. Figure 7 shows the partially relaxed FT spectra of the two CH_3 groups in acetone oxime. The T_1 values corresponding to these data are 10.0 and 4.5 sec for the CH_3 groups syn and anti to NOH, respectively. The measured NOE for the syn and anti CH_3 groups are (η) 1.4 and 1.9. T_1^{DD} values calculated for syn and anti CH_3 groups are 14.3 and 5.0 sec, respectively. The increased group rotation indicated by the longer T_1^{DD} (and lower NOE) for the CH_3 group syn to the NOH group demonstrates that 1,3 methyl–methyl steric interactions are significant in acetone oxime. The CH_3 group anti to the NOH group has a conformational (rotomeric) energy well available to it, thereby reducing its tendency to freely rotate, whereas the CH_3 group syn to the NOH group has opposing steric interactions and cannot achieve a favorable conformation. Thus it is able to rotate more freely. In MEK oxime, similar behavior is noted for carbon 1 (Table III).

The additional degree of internal motional freedom in MEK oxime can be indirectly observed by noting the differences in T_1 values for C_1, C_3, and C_4 in each isomer (Table III). In both isomers the 4-CH_3 group has a longer T_1 than the 3-CH_2 group. Because there is more than one available mode of internal motion, it is not possible to exactly correlate τ_c with T_1 for C_4. Nevertheless, the longer T_1 values for the 4-CH_3 carbons are qualitative indications of free internal motion for those groups relative to the internal CH_2 group.

Acknowledgments. The authors thank Professor F. A. L. Anet for helpful discussions and Mr. Joseph D. Cargioli for assistance in the experimental work.

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