disproportionation reactions of *cis*-diimide (**1**) with itself and with *trans*-diimide (**2**) are lower than that for reduction of ethene by **1**.

There essentially remains only one aspect of the diimide reduction reaction that still requires clarification. From a realistic point of view the reduction of a C=C or C≡C by N_2H_2 involves transfer of hydrogen only from *cis*-diimide (**1**). This demands that the less thermodynamically stable cis isomer be formed preferentially in order to attain the efficiencies in reductions that are observed. Only the thermal cycloreversion of the *cis*-diimide–anthracene adduct,[7] pyrolysis of *p*-toluenesulfonylhydrazine,[8] and the microwave discharge decomposition of hydrazine[9] are demanded to produce *cis*-diimide, and of these three processes only the second is adaptable to preparative-scale reactions. However, the most commonly used experimental procedures for the generation of diimide involve the oxidation of hydrazine[10] and the hydrolysis of azodicarboxylic acid[8,10,11] in which one would anticipate that the trans isomer should be preferentially formed. Thermal equilibration of the trans to the cis isomer is energetically precluded[1] under the normal experimental conditions. The only way in which to rationalize the efficiency of such reductions is to invoke a rapid, acid-catalyzed equilibration in aqueous or alcoholic solvents to continuously replenish the supply of the active reducing agent *cis*-diimide. Only experimental studies can resolve this aspect of the problem.

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On the Question of the Relationship of Nitrogen-15 Chemical Shifts to Barriers to C–N Internal Rotation. Dynamic Nuclear Magnetic Resonance of Urea and Aniline Derivatives

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Abstract: Dynamic ^1H and ^{13}C NMR effects resulting from restricted internal rotation about C–N bonds are observed in tetramethylurea (**1**), tetramethylthiourea (**2**), *N*-methylaniline (**3**), and *p*-nitro-*N*-methylaniline (**4**) in the temperature range 0 to −150 °C. The free-energy barriers for C(=X)–N internal rotation in **1** and **2** are both 6.3 kcal/mol and do not agree with barriers recently predicted for these compounds from ^{15}N chemical shift data. The barrier found for **1** by means of line-shape measurements agrees with a previously determined value obtained by a $T_{1\rho}$ technique. A reason for the failure of the predictions based on chemical shifts is presented. The barrier to C–N internal rotation in **3** is 6.1 kcal/mol, and is in reasonable agreement with barriers predicted from ^{15}N chemical shifts and from a Hammett relationship. The barrier to internal rotation in **4** is distinctly solvent dependent, being larger in acetone-d_6 (11 kcal/mol) than in CD_2Cl_2 (10.2 kcal/mol). The barriers predicted for **4** on the bases of ^{15}N chemical shifts and of the Hammett relationship are in fair agreement with the experimental value.

The chemical shift of ^{15}N is known to be dominated by the paramagnetic term in the usual expression for the chemical shift of a nucleus in a molecule.[1] The paramagnetic term is strongly dependent on the amount of π bonding at the nitrogen atom.[1] Since barriers to internal rotation about C–N bonds in many compounds are also strongly dependent on π bonding, it is understable that there should be a correlation between free-energy barriers for C–N internal rotation and ^{15}N chemical shifts.[2] Clearly, molecules where the origin of the barrier is steric have to be excluded. Even then, different classes of compounds, e.g., amides, thioamides, and anilines, give separate correlation lines. It has been suggested[2] that ^{15}N chemical shifts provide a way of evaluating C–N bond rotational barriers in molecules where conventional dynamic NMR techniques may not be applicable. That such predictions may not be entirely reliable is indicated by the recent report[3] that the barrier to rotation in tetramethylurea (**1**), as obtained from $T_{1\rho}$ measurements at −115 to −120 °C, is only 6.1 kcal/mol, compared to a predicted value of 11.6 kcal/mol.[2a] In view of the somewhat indirect nature of $T_{1\rho}$ measurements, we have made direct dynamic NMR measurements on **1**, and also on tetramethylthiourea (**2**), *N*-methylaniline (**3**), and *p*-nitro-*N*-methylaniline (**4**), compounds whose barriers have not previously been measured directly, although the barriers have

Table I. Barriers to C–N Rotation

compd[a]	nucleus	chemical shift difference, Hz[b]	coalescence temp T_c, °C	obsd barrier[c] ($\Delta G^{\ddagger}$ at T_c), kcal/mol	predicted barrier, kcal/mol
1	^{13}C	157[d]	−133	6.3	11.6,[e] 5.2[f]
1[g]	^{1}H	25	−141	6.4	
2	^{13}C	55	−139	6.3	3.2[e]
3	^{13}C	278	−135	6.1	5.3,[h] 5.1[i]
4[j]	^{13}C	320	−30	10.9	*f*
4[j]	^{1}H	31	−48	11.0	
4[k]	^{1}H	34	−65	10.2	

[a] The solvent is $CHFCl_2$–CHF_2Cl (1:4) unless stated otherwise. [b] At 200 MHz for ^{1}H and 50.3 MHz for ^{13}C (Bruker WP-200 spectrometer); the chemical shift differences were used for calculating $\Delta G^{\ddagger}$'s and are for the methyl groups in **1** and **2**, and for the ortho CH groups in **3** and **4**, and were measured at 20 °C or more below T_c. [c] Estimated error is ±0.1 kcal/mol. [d] The chemical shift difference is 3.1 ppm (cf. 3.7 ppm in 2:1:2 $CDCl_3$–acetone-d_6–CHF_2Cl as obtained in $T_{1\rho}$ measurements, ref 3). [e] Reference 2a. [f] See text. [g] In $CDFCl_2 + CF_2Cl_2$ (1:3). [h] Reference 2b. [i] Reference 10. [j] In acetone-d_6. [k] In CD_2Cl_2.

Table II. ^{1}H and ^{13}C Chemical Shifts of Ureas and Anilines Derivatives

compd	nucleus	temp, °C	chemical shifts, δ ppm				
			CH_3		C=O or C=S		
1	^{13}C[a]	−105	39.0		166.5		
		−150	40.5, 37.5		166.5		
1	^{1}H[b]	−100	2.8				
		−150	2.92, 2.68				
2	^{13}C[a]	−90	43.8		192		
		−150	44.9, 42.7		192		
			Me	C_1	C_2H	C_3H	C_4H
3	^{13}C[a]	−110	30.5	150.2	112.2	129.8	117.5
		−150	30.5	150.2	115, 109.5	129.5, 130.2	117.5
4	^{13}C[c]	0.0	31	158	110.5	126.5	137.7
		−60	31	158	113.6, 107.4	127.2, 125.8	137.7
4[d]	^{1}H[c]	0.0	2.95		8.1	6.65	
		−60	2.95		8.12, 8.03	6.76, 6.61	
4[d]	^{1}H[e]	−10	2.95		8.1	6.55	
		−80	2.95		8.13, 7.93	6.53, 6.47	

[a] The solvent is $CHFCl_2$–CF_2Cl_2 (1:3). [b] The solvent is $CDFCl_2$–CF_2Cl_2 (1:3). [c] The solvent is acetone-d_6. [d] All the aromatic proton resonances of **4** were split into doublets (J = 10 Hz) by mutual vicinal couplings. [e] The solvent is CD_2Cl_2.

been predicted on the basis of ^{15}N chemical shift correlations (Table I).[2]

Experimental Section

All compounds were commercial samples and, with the exception of *N*-methylaniline, which was distilled, were used without purification.

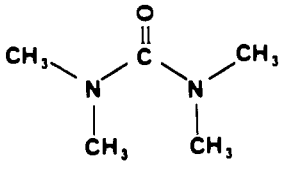
^{13}C and ^{1}H NMR spectra were recorded on a Bruker WP-200 spectrometer at 50.3 and 200 MHz operating in the Fourier transform mode. Typical spectrometer settings follow: spectral widths, 2000 (^{1}H) and 12 500 Hz (^{13}C); number of data points, 16K; pulse angle, 30°. The spectrometer was locked on a deuterium signal from $CDFCl_2$, CD_2Cl_2, or acetone-d_6. Temperatures were measured by means of a thermocouple situated in the cooling gas a few centimeters below the sample.

Free energies of activation were obtained at the coalescence temperature of doublets by means of the Eyring equation and the expression $k = \pi\Delta\nu/\sqrt{2}$, where k is the rate constant (s^{-1}) for internal rotation and $\Delta\nu$ is the chemical shift difference in hertz. In the aniline derivatives, the dynamic ^{1}H NMR effects involve spin-coupled nuclei, but, because $|\Delta\nu| \gg |J|$ for all J_{HH}'s, the simple expression given above should be an excellent approximation. We have not tried to obtain values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, since these quantities, unlike $\Delta G^{\ddagger}$, are very prone to systematic errors.[4] The free-energy barriers in the present compounds, with the possible exception of **4**, should be dominated by energy rather than entropy effects, and thus $\Delta H^{\ddagger}$ should be approximately the same as $\Delta G^{\ddagger}$.[5] No statistical correction was applied to $\Delta G^{\ddagger}$ to take into account the fact that internal rotation can take place in one of two directions.

Results and Discussion

Ureas. The barrier in **1** was determined from both the ^{1}H and ^{13}C resonances of the methyl groups, while in **2** only the ^{13}C spectrum was examined. Free-energy barriers and chemical shifts are given in Tables I and II, respectively. Our data for **1** is in satisfactory agreement with that obtained by the $T_{1\rho}$ method,[3] especially since the solvents used in that investigation and in the present work are different.

The observed barriers in both **1** and **2** do not agree with the barriers predicted from ^{15}N chemical shifts (Table I), but there is, in our view, a good reason for this apparent disagreement, and this lies in the fact that ureas are cross-conjugated systems. As a result, the rotation of one nitrogen moiety will cause the second nitrogen atom to conjugate more strongly with the carbonyl group, thus lowering the energy of the transition state



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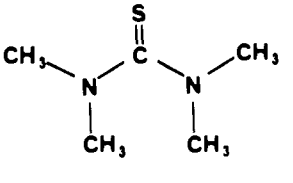

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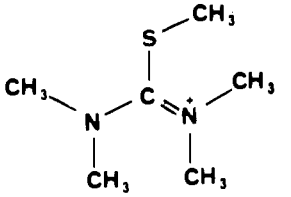

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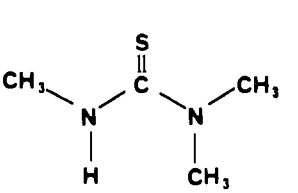


6

as compared to that predicted from a simple correlation based on amides, which contain only a single nitrogen atom. A more correct analysis can be carried out as follows. The ^{15}N chemical shift correlation can be used to predict the energy required to make *both* nitrogens in **1** perpendicular to the carbonyl group, as in **1a** (Figure 1); this should be twice the barrier (Table I) given by Martin et al.,[2a] i.e., 23.2 kcal/mol. The energy of the transition state (**1b**) in the dynamic NMR work differs from the energy of **1a** by just the resonance energy of a simple amide system, and this is known from the barriers to rotation in acetamides to be of the order of 18 kcal/mol.[6] From the formal cycle shown in Figure 1, it follows that the barrier to rotation about one C–N bond in **1** should be about 5 kcal/mol, in reasonable agreement with the experimental value. The above argument seems to fail with **2**, since a similar calculation gives a strongly negative barrier. However, Martin's predicted barrier (Table I) for **2** is very dependent on one value in the correlation line for thiocarbonyl compounds, and this point corresponds to the thiomethyltetramethylamidinium ion (**5**). Since **5** is a symmetrical cross-conjugated system, it cannot be incorporated in a simple correlation with thioamides, but should be treated as described above for **1**. Furthermore, **5** does not contain a simple thiocarbonyl group, and thus may not lie on the correlation line of thioamides. Thus a prediction, based on ^{15}N chemical shifts, of the barrier to internal rotation in **2** cannot easily be made at present, in our opinion.

Both **1** and **2** are quite strained compounds because the nonbonded repulsions of the endo methyl groups force these molecules to be significantly nonplanar.[7] This accounts for the much lower barrier to internal rotation in **2** than in trimethylthiourea (**6**), which does not have such a repulsion, and where the barrier is 10.6 kcal/mol.[8,9] From the comparison of **2** and **6**, the strain in **2** can be calculated to be about 4 kcal/mol.

Anilines. Although barriers to C–N rotation in aniline and its *N,N*-dimethyl derivative cannot be measured by dynamic NMR methods because of the symmetry of these molecules, *N*-methylaniline (**3**) presents no such difficulty. In fact, **3** gives two different resonances for both the ortho and meta carbons at low temperatures (Table I). The barrier to C–N rotation is 6.1 kcal/mol, which is in reasonable agreement with the barriers predicted from ^{15}N chemical shifts (5.3 kcal/mol)[2b] and from a Hammett treatment of the known barriers in *p*-formyl-, *p*-acetyl-, and *p*-nitroso-*N,N*-dimethylaniline (5.1 ± 1.0 kcal/mol for *N,N*-dimethylaniline).[10] The nitrogen atom in aniline is distinctly pyramidal[11,12] and from an infrared analysis a barrier to C–N rotation of 3.5 kcal/mol has been deduced.[11] From the NMR data on **3**, a barrier of at least 5 kcal/mol is expected for aniline and thus the infrared and NMR values do not agree.[13]

The barrier to internal rotation in aniline (or its simple derivatives) is a measure of the resonance interaction of the nitrogen lone pair with the aromatic π electrons. This interaction also makes aniline a weaker base than aliphatic amines. It has been estimated that one-half of the six-unit difference in pK_a between aliphatic and aromatic amines results from the above resonance interaction, the other half being due to an inductive effect of the phenyl group.[14] This means that the resonance interaction in aniline amounts to about 4 kcal/mol.[14] This value is somewhat lower than the barrier to internal rotation in *N*-methylaniline, but a precise agreement cannot be really expected, because of the greatly different solvents used in the NMR and pK_a measurements, and because of the assumptions made in choosing appropriate model compounds for the pK_a deductions.

The barrier to rotation in *p*-nitro-*N*-methylaniline (**4**) (Table I) is distinctly solvent dependent, as might be expected from the large dipole moment of the compound and the presence of a fairly acidic NH group which can partake in hydrogen bonding with the solvent (e.g., with the carbonyl group in

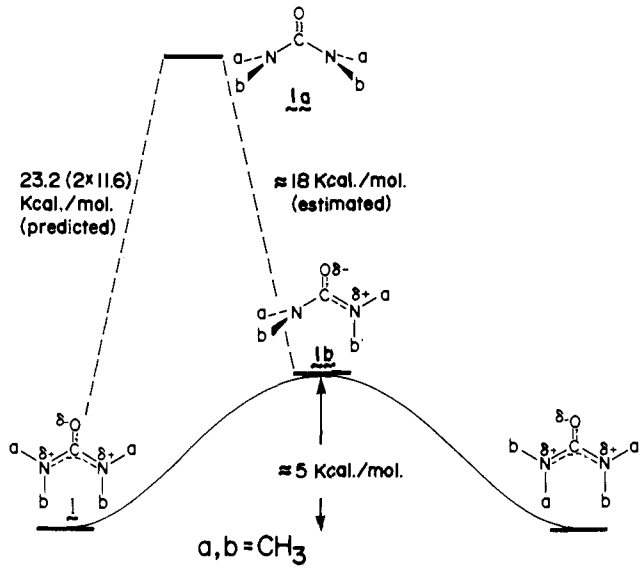
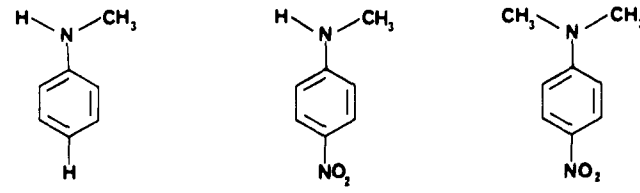


Figure 1. Restricted rotation about the C(=O)—N bond in tetramethylurea (**1**) and the formal realtionship of **1a** to **1** and **1b**.



3 **4** **7**

acetone). The predicted barrier in this case is 8.7 kcal/mol and is based on the ^{15}N chemical shift of *p*-nitro-*N,N*-dimethylaniline (**7**) in dimethyl sulfoxide as the solvent.[2b] Despite the different solvent and the different substituents on nitrogen, the predicted barrier for **7** is not in as good agreement with the observed barrier in **4** as might have been expected. Another predicted value (7.9 kcal/mol) for the barrier in **7** has been obtained from the previously mentioned Hammett treatment.[10] The solvent used in that work was toluene-d_8–vinyl chloride, whose dielectric constant is low. The barrier for **7** in a solvent of high dielectric constant should be considerably greater than 8 kcal/mol, and thus the barrier predicted from the Hammett treatment is not necessarily in bad disagreement with the observed barrier in **4**.

Chemical shifts for the substituted anilines **3** and **4** are given in Table II. The differences in ^1H shifts for the aromatic protons in **4** at low temperatures show a strong solvent dependence. In acetone-d_6, the protons meta to the *N*-methyl group in **4** are actually split more than are the ortho protons. In CD_2Cl_2, however, the expected order ($\Delta\delta_{ortho} > \Delta\delta_{meta}$) is observed. Such solvent effects are presumably the result of weak association of the solute and solvent molecules or of "collision complexes".[15]

Conclusions

Dynamic NMR spectroscopy of urea and aniline derivatives gives direct measurements of barriers to internal rotation. The correlations which have been made between these barriers and ^{15}N chemical shifts require different correlation lines for different classes of compounds, and as a result it may not always be obvious whether a particular compound belongs to a known correlation or whether it should be placed on a new correlation line. There is a further difficulty in interpreting the data in the case of more or less strongly cross-conjugated systems. For these reasons, caution should be exercised in accepting barriers

obtained on the basis of ^{15}N chemical shifts correlations, and we recommend that barriers be determined by more direct methods, whenever possible.

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^{13}C Magnetic Relaxation in Micellar Solutions. Influence of Aggregate Motion on T_1

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Abstract: The ^{13}C T_1 NMR relaxation times of the carbon atoms in the alkyl chains of a micelle-forming amphiphile are discussed. A theoretical model for the relaxation process is developed. The relaxation in a $^{13}C^1H_2$ methylene group is treated in detail using a density matrix formalism. In modeling the molecular dynamics of the system the emphasis is placed on a separation between a fast local motion within the micelles and a slower overall motion associated with the aggregate itself. In applying the model to octanoate micelles it is shown that, using previously determined structural parameters, it is possible to obtain an a priori estimate of the contribution from the slow motion to T_1 of the individual carbons. Particularly for the carbons close to the polar group, the overall motion gives a substantial, and probably dominating, contribution to T_1. It also emerges that the T_1's should be frequency dependent. The predictions of the model are tested against experimentally determined T_1 values for four carbons in sodium octanoate micelles and a surprisingly good agreement is found. Particularly the observed frequency dependence of T_1 shows unequivocally that the slow micellar motion contributes to the spin–lattice relaxation. It also follows that the alkyl chain motion within the micelles is very rapid. The interior of the micelle is thus even more liquid-like than has been inferred previously from ^{13}C T_1 measurements.

In studying the properties of micellar solutions on a molecular level, nuclear magnetic resonance has proved to be one of the most versatile experimental techniques.[2a] The chemical shift and relaxation parameters of different magnetic nuclei in a micellar system are sensitive to different molecular properties and by a careful choice of method one is able to study a particular aspect of the problem of the molecular organization. For example, the size of micellar aggregates can be determined using ^1H[2b,3] and ^{14}N[4] NMR. By using ^{19}F chemical shifts one can accurately determine cmc values;[5] ^{23}Na, ^{35}Cl, and ^{81}Br NMR provide information on counterion binding.[6]

^{13}C T_1 measurements are particularly well suited for the study of alkyl chain motions.[7] In micellar systems the ^{13}C relaxation times give a picture of the dynamics of the (unperturbed) micellar interior. It was originally concluded from thermodynamic arguments[8,9] that the micellar interior is similar to a liquid hydrocarbon and the validity of these conclusions was later established through spectroscopic studies directly probing the molecular motion.[10,11] However, several problems regarding the details of the alkyl chain motions within the micelle are still unsolved. Are the motional time scales quite similar to those in a corresponding hydrocarbon system or are they an order of magnitude larger? How does the fact that the polar head is more or less fixed at the micelle surface influence the motional properties? The ^{13}C T_1 values of micellar systems are often significantly shorter than those characteristic of the monomer state.[12-18] This has usually been

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