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Advantages of ^{15}N NMR in Studying Delocalization and Evaluating the Energy Barriers of C–N Rotation Process in Amides, Thioamides, and Related Compounds

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Abstract: Linear correlations are shown to exist between the activation energy E_a of the C–N rotation process and δ^{15}N in *N,N*-dimethylamino derivatives. The relations are applied to the prediction of E_a values related to high or low energy barriers, where the direct NMR methods of measurement are not applicable. The validity of the correlations is discussed on the basis of semiempirical calculations of the nitrogen chemical shifts.

The variation of ^{14}N chemical shifts in amides and thioamides was qualitatively explained by Hampson and Mathias[1] in terms of the delocalization of the nitrogen lone pair. Siddall et al.,[2] however, failed to observe the predicted correlation between ^{14}N downfield shifts and the increase of barrier heights to rotation in N-alkyl substituted amides and explained their results by the prominent role of steric effects. We wish to present here ^{15}N data which provide a good means of evaluating C–N bond rotation energy barriers in cases where conventional dynamic NMR methods (line shape analysis or Forsen–Hoffmann double resonance studies) are not applicable. Our results also indicate a striking difference in the behavior of ^{13}C and ^{15}N chemical shifts in a $>N{=}C<$ fragment, insofar as electronic delocalization is concerned.

Table I collects δ^{15}N and δ^{13}C values for the $>N{=}C<$ fragment of selected compounds for which good activation energy values are available. Amides, thioamides, and related compounds were considered and good correlations between E_a

Table I. Activation Energy Values, E_a, and ^{15}N, ^{13}C (sp^2 C_α of the Nitrogen Atom) Chemical Shifts of Various Dimethylamino Derivatives[a]

			Activation data		NMR results	
Series	No.	$(CH_3)_2N$-X X	E_a, kcal mol^{-1}	Ref	$\delta^{15}N$, ppm/NO_3^-	$\delta^{13}C$, ppm/TMS
I	**1**	CHO	20.6	18, 19, 20	−273.7	161.7
	2	$COCH_3$	18.5	21, 22, 23, 24	−280.2	169.6
	3	COC_6H_5	17.6	21, 25	−278.0	170.4
	4	COCl	17.4	19, 26, 27	−282.6	148.2
	5	$COCCl_3$	16.2	28, 29, 30	−285.8	159.7
	6	CH=CHCHO[b]	16.7	31	−287.5	160.7
	7	$CH{=}CHCOCH_3$[c]	14.5	31	−296.9	151.0
	8	$CH{=}NC_6H_5$	14.7	32	−298.1	153.0
	9	$CH{=}CHC_6H_5$	9.0	11	−322.5	139.7
II	**10**	CHS	22.0	2, 33	−224.1	186.6
	11	$CSCH_3$	20.7	22, 34	−233.4	198.5
	12	CSCl	19.0	27, 35	−232.3	173.1
	13	$CSSCH_3$	16.0	34, 36	−242.9	196.1
	14	$C(SCH_3)N(CH_3)_2^+$	9.5	37	−267.6	176.5

[a] The activation energies were averaged, when possible, from a selected set of homogeneous data corresponding to pure liquids or solutions in chlorinated solvents. It has been shown[38] that a slight decrease in E_a corresponds to a decrease in amide concentration in chlorinated solvents. [b] 95% s-trans conformation. [c] 65% s-cis conformation.

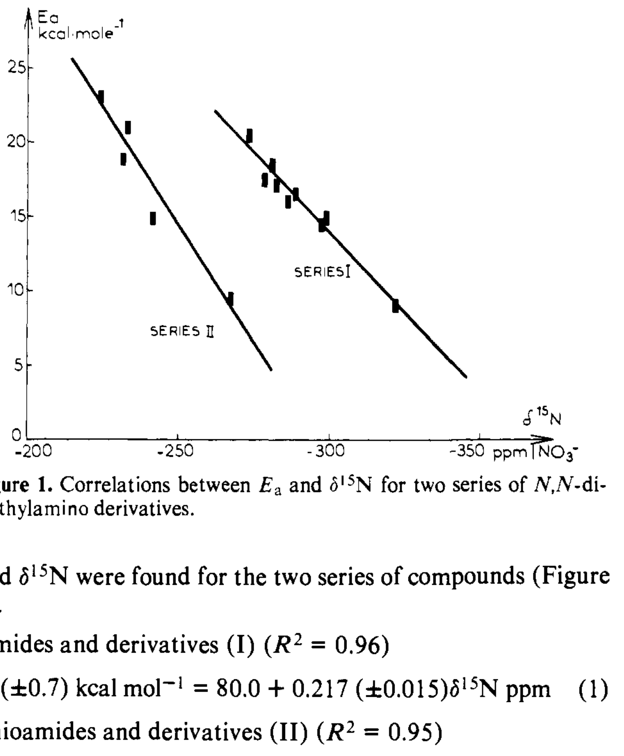


Figure 1. Correlations between E_a and $\delta^{15}N$ for two series of *N,N*-dimethylamino derivatives.

and $\delta^{15}N$ were found for the two series of compounds (Figure 1).

Amides and derivatives (I) ($R^2 = 0.96$)

$$E_a(\pm 0.7)\ \text{kcal mol}^{-1} = 80.0 + 0.217\ (\pm 0.015)\delta^{15}N\ \text{ppm} \quad (1)$$

Thioamides and derivatives (II) ($R^2 = 0.95$)

$$E_a(\pm 0.8)\ \text{kcal mol}^{-1} = 92.0 + 0.305\ (\pm 0.035)\delta^{15}N\ \text{ppm} \quad (2)$$

The constant parameters of eq 1 and 2 were computed with respect to reference E_a values: 20.6 (DMF, **1**) and 20.7 (DMTA, **11**) kcal mol^{-1}. Examination of Table I also shows that the shielding variations of the sp^2 carbon atom α to nitrogen are not related to $\delta^{15}N$ or E_a changes ($R^2 < 0.6$).

Using the above correlations, the heights of rotational barriers were predicted for various dimethylamino compounds for which activation energy data have not been published. The failure of DNMR methods to provide such data results from (i) the absence of nonequivalence between the diastereotopic sites (^1H, ^{13}C), (ii) the existence of high-energy barriers characterized by coalescence temperatures T_c greater than $\simeq$450 K or low-energy barriers ($T_c < 120$ K), and (iii) the occurrence of dynamic processes, such as intermolecular ligand exchanges, which mask the rotational phenomena. The predicted E_a values listed in Table II elicit the following comments.

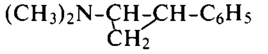
The computed E_a value for Mannich salt No. 15 agrees reasonably well with the results of ab initio and CNDO/2 calculations.[3] Second, the association of Lewis acids with amides has been known for some time[4] to significantly increase the height of the C-N rotational barriers although published activation energies are not very realistic. The E_a values predicted by eq 1 for the DMA-$AlCl_3$ complex (**18**) and the TMU-$SbCl_5$ adduct (**19**) appear to be reasonable.[5] It should be noted that these barriers cannot be measured accurately owing to intermolecular ligand exchange processes.[6,7] Iminium salts **16** and **17** are also characterized by high-energy barriers. The predicted values for these compounds correspond to the commonly accepted E_a values for the *Z/E* interconversion processes in disubstituted olefins[8] which is reasonable since it has been shown that a rotation mechanism exchanges N-alkyl groups in iminium derivatives.[9] It should also be noted that the above correlation enables the prediction of barrier heights in chloroamidinium salts for which intermolecular chlorine exchange precludes the observation of rotation processes.[10] Data are not available for compounds such as DMCE (**20**), TMU (**21**), or TMTU (**24**). Equation 1 gives realistic E_a values for **20** and **21** and interestingly, low activation energy is predicted for **24** from eq 2. Phenylcyclopropylamine (**22**) and propenylamine (**23**) are also characterized by a low-energy barrier and these results are consistent with previous DCMR measurements.[11]

The observed relationship between E_a and $\delta^{15}N$ may be rationalized in terms of the π electronic distribution in the $>N\overset{...}{=}C<$ fragment. The large range of ^{15}N shifts certainly results from the important variations in the nitrogen lone-pair configuration considered as a function of the substituents. A multilinear correlation between $\delta^{15}N$(exp), the π density on the nitrogen atom (Q_N^π), and the π bond order between N and the sp^2 α carbon atom ($P_{N\text{-}C}^\pi$) was computed from the data concerning the nonchlorinated oxo compounds of the series I.

$$\delta^{15}N(\text{exp})\ \text{ppm} = -2298 + 845Q_N^\pi + 1149P_{N\text{-}C}^\pi \quad (3)$$

Q_N^π and $P_{N\text{-}C}^\pi$ were obtained from a CNDO/2 calculation (Table III). Expression 3 satisfactorily matches the experimental data. The coefficient of the correlation between experimental and computed chemical shift values is 0.96. It turns

Table II. Predicted Values of Activation Energies, E_a, for the C-N Rotation in Dimethylamino Derivatives

		NMR results		
No.	Compd	$\delta^{15}N$, ppm/NO_3^-	$\delta^{13}C$, ppm/TMS	E_a (predicted), kcal mol^{-1}
15	$(CH_3)_2N{=}CH_2^+, CF_3COO^-$	−155.0	170.0	46.3[a]
16	$(CH_3)_2N{=}CH^+Cl, Cl^-$	−214.3	166.2	33.5[a]
17	$(CH_3)_2N{=}CHO^+CH_3, OSO_2^-F$	−234.4	168.6	29.1[a]
18	$(CH_3)_2NCOCH_3, AlCl_3$	−240.6	172.7	27.8[a]
19	$(CH_3)_2N_2CO, SbCl_5$	−304.8	161.6	13.9[a]
20	$(CH_3)_2N\text{-}CO\text{-}OCH_3$	−312.0	159.6	12.3[a]
21	$[(CH_3)_2N]_2CO$	−315.3	165.7	11.6[a]
22	 $(CH_3)_2N\text{-}\underset{CH_2}{CH\text{-}CH}\text{-}C_6H_5$	−344.2	50.1	5.3[a]
23	$(CH_3)_2N\text{-}CH{=}CH\text{-}CH_3$	−349.3	140.5	4.2[a]
24	$[(CH_3)_2N]_2CS$	−291.0	194.0	3.2[b]

[a] Computed from eq 1. The reported nitrogen shift for compound **15** was measured by ^{14}N spectroscopy.[39] [b] Computed from eq 2 (refer to the discussion in the text and ref 40).

Table III. Calculated Values of the Nitrogen and Carbon Paramagnetic Contribution Using the Karplus-Pople Scheme (eq 4) for the >N=C< Fragment[a]

	Nitrogen resonance					Carbon resonance		
Compd	Q_N^π	$P_{N\text{-}C}^\pi$	$\sum_B Q_{NB}$	$(Z_{2p})_N^3$	$-\sigma_{para}(N)$	$\sum_B Q_{CB}$	$(Z_{2p})_C^3$	$-\sigma_{para}(C)$
1	1.7559	0.4724	2.3177	38.5562	299.7	2.5139	24.8056	209.2
2	1.7631	0.4603	2.3105	38.3538	297.2	2.4145	25.077	203.1
3	1.7609	0.4616	2.3195	37.9334	295.1	2.6366	24.551	217.1
6	1.7682[b]	0.4498	2.3329	38.5046	301.3	2.4708	23.1635	192.0
7	1.7697[c]	0.4408	2.3304	38.9093	304.1	2.4872	23.3182	194.5
10	1.6043	0.6333	2.3755	39.9324	357.9	2.5617	22.6990	219.4
11	1.6279	0.6141	2.3696	39.6546	354.6	2.7051	23.1810	236.6

[a] $\Delta E = 9$ eV compounds **1, 2, 3, 6, 7** and $\Delta E = 8$ eV compounds **10, 11**. Q_N^π and $P_{N\text{-}C}^\pi$ are respectively the π density and the bond-order term used in eq 3. Bond distances and angles were taken from a compilation of structural data.[45] [b] s-trans conformation. [c] s-cis conformation.

out that, in the considered series, the activation energy E_a for the C-N rotation process can also be theoretically estimated from the π electron distribution. This simple treatment provides a good alternative to the more sophisticated ab initio calculations of the total electronic energy in both fundamental and transition states. By contrast, the carbon shift range is more restricted and the correlation between δCN and Q_C^π, $P_{N\text{-}C}^\pi$ is poor ($R^2 = 0.8$).

Nitrogen and carbon shifts were also estimated, according to Karplus and Pople,[12] from the CNDO/2 calculated electronic distribution. The paramagnetic term σ_{para} is obtained from the relationship[13]

$$\sigma_{para} = -\frac{30.1885}{\Delta E}(Z_{2p})^3 \sum_B Q_{AB} \qquad (4)$$

The ΔE values attributed to oxo and thio derivatives are 9 and 8 eV, respectively (Table III). Correspondence between experimental and calculated chemical shifts is poor ($R^2 < 0.8$ for ^{15}N and ^{13}C). It should also be noticed that, in the above treatment, the calculated changes in $Q_N^{\pi,\sigma}$, Q_{NN}, $Q_{N\text{-}CH_3}$, and $<r^{-3}>_{2p}$ do not exceed a few percent, whereas variations in $P_{N\text{-}C}^\pi$ and $Q_{N\text{-}CO}$ are of a higher order of magnitude.

The $\delta^{15}N$ values of thioamides and derivatives (II) show a paramagnetic shift with respect to the corresponding amides (I) as expected from the existence of low-lying excited states in the former.[14] A difference of about 45 ppm is estimated from the data relative to series I and II. In terms of the average excitation energy ΔE, such a change in shielding corresponds to a 1.5 eV variation in ΔE. In fact, photoelectron spectroscopy measurements[15] have shown that $\overline{N}_\pi$ transitions are situated ~1.2 eV higher in DMF (**1**) (9.3 eV) than in DMTF (**10**) (8.1 eV). Such a relationship for the ^{13}C shifts in amides and thioamides was recognized by Maciel[16] some time ago.

To conclude, it should be noted that $\delta^{15}N$ is a good expression of nitrogen lone pair delocalization in a homogeneous series of compounds and offers a simple and versatile way of evaluating the C-N rotational barriers in unhindered compounds. For conjugated and flat molecules, the breaking of the delocalized π bond between nitrogen and carbon atoms is the major contribution to the rotational activation energy. The case of TMTU (**24**) is an illustrative example of the information available from the proposed relationship. From the $\delta^{15}N$ data this compound may be ranged in a group of molecules characterized by a low degree of lone pair delocalization. This result may be explained by a gauche conformation of this crowded compound and is substantiated by the results of an electronic spectroscopy study.[17] Thus the failure to observe proton or carbon nonequivalence is related to the mean symmetry of the molecular ground state.

Experimental Section

NMR Spectroscopy. The carbon shifts were obtained with a Varian XL 100-12 spectrometer (SW = 5000 Hz, AT = 0.8 s, $\nu_0 = 25.2$ MHz, 30% v/v in $CDCl_3$, 305 K).

The nitrogen shifts were measured with a Bruker WP 60-DS spectrometer at natural abundance in pure liquids (303-350 K) or in $CHCl_2CHCl_2$ 50% v/v solutions, containing 0.1 M $Cr(AcAc)_3$. (SW = 3750 Hz, AT = 1 s, PW = 45°, $\nu_0 = 6.08$ MHz.) The spectra were obtained with the broad band decoupler on (2 w) and 10^3 to 10^5 scans were accumulated, depending on the nitrogen concentration. The shifts were referred to an external D_2O, D^+ (lock signal) solution of 30% enriched $^{15}NO_3Na$ contained in a coaxial 2-mm tube centered in a 10-mm sample tube.

The solvent effect on $\delta^{15}N$ did not exceed $\simeq$0.8 ppm upfield when going from pure liquid (DMF (**1**)) to a 30% solution in $CHCl_3$, $CHCl_2CHCl_2$, or CH_3CN. Fifty percent solutions of DMF in methanol or ethanol cause more important downfield shifts $\simeq$2 to 3 ppm. The influence of $Cr(AcAc)_3$ on $\delta^{15}N$ was checked by studying the ^{15}N resonance of enriched materials without using T_1 reagent. The addition of 0.1 M $Cr(AcAc)_3$ to DMF and DMA (**2**) brings about a small upfield shift ($\simeq$1.5 ppm) for $\delta^{15}N$.

Materials. Commercially produced amides, thioamides, and carbamoyl derivatives were carefully dried and distilled (**1-4**, **10-13**, **20**, **21**, **24**). The iminium salts and acceptor-donor complexes (**14-19**) were synthetized as previously described.[37] Vinylamides (**6**, **7**) and enamines (**8**, **9**, **22**, **23**) were prepared according to conventional procedures.[31,41,42]

Labeling experiments: 5% ^{15}N enriched DMA was synthetized by the reaction of acetyl chloride with a cold solution of 5% ^{15}N dimethylamine in hexamethylphosphoramide; 5% ^{15}N DMF was prepared from the reaction of CCl_3CHO with enriched dimethylamine dissolved in $CHCl_3$ (40% yield).[44] Five percent ^{15}N dimethylamine hydrochloride was prepared from 5% ^{15}N ammonium chloride (CEA, Paris) and a 30% aqueous solution of formaldehyde.[43] A solution of 5% ^{15}N $(CH_3)_2NH_2Cl$ in hot water is poured into 10 N NaOH and the gaseous enriched dimethylamine is collected in the appropriate solvent.

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Nitrogen-14 Nuclear Quadrupole Resonance Spectra of Coordinated Pyridine[1]

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Abstract: Nitrogen-14 nuclear quadrupole resonance (NQR) data have been obtained for several pyridine complexes with Zn(II) and Cd(II), $I(C_5H_5N)_2ClO_4$, $Br(C_5H_5N)_2ClO_4$, $HNC_5H_5NO_3$, and $4\text{-}CH_3C_5H_4NO$. The field gradient tensor is substantially altered upon coordination to a Lewis acid. Using a modification of the Townes-Dailey model it is possible to relate the field gradient parameters to the extent of charge transfer from nitrogen to the Lewis acid. ^{14}N NQR signals were also detected for the nitrato nitrogens in several cases and for the NCS^- ligand in $Zn(NCS)_2(C_5H_5N)_2$. The NQR data for this complex are consistent with coordination to Zn(II) through N.

During the past several years the number of reported ^{14}N nuclear quadrupole resonance (NQR) spectra has grown rapidly. Nevertheless, the number and variety of data available for compounds in which a nitrogen atom is coordinated directly to a metal ion or other Lewis acid is quite limited. We have indicated in another contribution the reasons why ^{14}N NQR spectra should be of interest in such systems.[4] The adiabatic demagnetization in the lab frame, double resonance level-crossing technique (drlc),[5-9] is of particular value in obtaining the desired data, because it is sensitive and capable of detecting resonances at frequencies too low for direct detection. The advantages and limitations of the technique have been described by Edmonds.[6,7]

In the present contribution we report the ^{14}N NQR spectra