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Hindered Internal Rotation and Dimerization of N,N-Dimethylformamide in Carbon Tetrachloride[1]

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Abstract: The well-known hindered internal rotation of N,N-dimethylformamide (DMF) is reinvestigated by a nmr total line-shape (TLS) treatment taking into account *both* the variance of $\Delta\nu$ (nonexchanging N-methyl doublet chemical shift) and the coupling between the formyl and N-methyl protons. The agreement between experimental and calculated spectra is excellent and the thermodynamic parameters derived are $E_a = 20.5 \pm 0.2$ kcal/mole, $\nu_0 = (5 \pm 3)10^{12}$ sec^{-1}, $\Delta G_{128°}{}^* = 21.0$ kcal/mole, $\Delta H^* = 20.2 \pm 0.2$ kcal/mole, and $\Delta S^* = -1.7$ eu, showing that DMF is not unexpectedly different from other amides. DMF in CCl_4 is examined and the rate of internal rotation (from TLS) at different concentrations is shown to correlate qualitatively with the extent of dimerization of DMF. The nature of the dimer is discussed briefly, and it is shown that there may be a contribution to the chemical shift behavior of DMF in solution by anisotropic shielding effects of the carbonyl groups in an oriented cyclic dimer.

Nmr spectroscopy is now well established as an everyday tool for the study of chemical rate processes.[2] There is little doubt that as a subject for the study of one such process, namely hindered internal molecular rotation, no compound has played a more dominant role than N,N-dimethylformamide (DMF).[3] Yet, the values reported for the Arrhenius activation parameters of internal rotation for this particular case have varied widely[1] (the activation energy increasing from 7 ± 3 to 26 kcal/mole and the frequency factor from 10^3–10^7 to 10^{16} sec^{-1}). All treatments to date have been based on one-parameter approximations (or combinations thereof)[2b,4] of the exchange equations derived[5] from the Bloch formulation,[6] and a review of most of the work done and the approximations used appears in ref 3e.

It is becoming increasingly apparent that accurate and reliable results for calculations such as these are of the utmost importance if any significance is to be attached to studies and comparisons of various types which are being undertaken, and which are of extreme interest to the theoretical and physical organic chemist.[7]

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[1] A preliminary communication of part of this study: A. Pines and M. Ravinovitz, *Tetrahedron Letters*, 3259 (1968).

[2] (a) C. S. Johnson, Jr., *Advan. Magn. Resonance*, **1**, 33 (1965); (b) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).

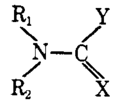
[3] (a) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956); (b) G. Fraenkel and C. Franconi, *J. Am. Chem. Soc.*, **82**, 4478 (1960); (c) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962); (d) A. G. Whittaker and S. Siegel, *J. Chem. Phys.*, **42**, 3320 (1965); (e) C. W. Fryer, F. Conti, and C. Franconi, *Ric. Sci. Rend.*, **A8**, 788 (1965); (f) F. Conti and W. von Phillipsborn, *Helv. Chim. Acta*, **50**, 603 (1967); (g) A. Mannschreck, *Tetrahedron Letters*, 1341 (1965); (h) A. Mannschreck, A. Mattheus, and G. Rissmann, *J. Mol. Spectry*, **23**, 15 (1967).

[4] See, however, Mannschreck, *et al.*,[3h] who did use a TLS analysis for DMF in chloronaphthalene, but again neglect spin coupling and report only on ΔG^* at coalescence temperature.

[5] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1965, Chapter 9.

[6] F. Bloch, *Phys. Rev.*, **70**, 460 (1946).

[7] To mention a few examples: the effects of protonation and complexation on the structure of DMF and other amides,[3b,e,f,8] the influence of substitution and functional groups (X) on the barriers for restricted rotation about C–N bonds in compounds of type **1**,[3c,h,9] comparisons



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between rates of rotation about different bonds in the same molecule,[6c,10] the effects of solvents on the internal rotation in these compounds,[3d,9a,11,12] comparisons between conjugated systems having similar structures, for example, DMF and 6-dimethylaminofulvene.[13]

[8] A. Fratiello, D. P. Miller, and R. Schuster, *Mol. Phys.*, **12**, 111 (1967).

The case of DMF has been complicated by the fact that (a) there exists a resolvable coupling between the N-methyl and formyl hydrogens[3b] and (b) the nonexchanging chemical shift[14] between the resonances of the two N-methyl group protons ($\Delta\nu$) is temperature and concentration dependent.[3d,e,15,16] Approximate allowance for the former[3b] as well as the latter[3d-f] phenomena has been made, but the results have not been consistent. The only criterion for precision of the results seems to have been linearity of Arrhenius plots, which is evidently insufficient as in all cases good linear plots were reported.

This Study. We have applied a total nmr line-shape (TLS) analysis[2] to the internal rotation of DMF in order to finally resolve this problem.[17] The treatment takes into account both the formyl N-methyl proton coupling and the temperature dependence of $\Delta\nu$ and further furnishes a direct check on the parameters derived by a visual or analytical comparison of experimental and calculated spectra.[9b,e,18,19]

Previously,[16] we saw that the temperature and concentration dependence of $\Delta\nu$ for DMF in CCl_4 could be accounted for *quantitatively* by assuming a dimeric association of DMF molecules in solution. The study was made at low temperatures where chemical shifts should be measured readily and accurately, and values for the dimerization thermodynamic parameters were estimated,[20] indicating strong interactions. One would expect such intermolecular attractions to have an appreciable influence on the internal rotation of the molecules, and using results derived by the TLS method we see here that this is indeed the case.

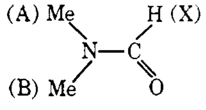
The nature of the dimer is also discussed briefly in terms of the thermodynamic parameters for its formation and the limiting chemical shifts.[20]

Experimental Section

Materials. DMF was analytical grade distilled twice immediately before use. The CCl_4 solutions were prepared with large volumes from which small samples were drawn and sealed in thick-walled high-precision nmr tubes from Varian Associates. The spectra were recorded on a Varian A-56/60 instrument.

Procedure. For the work on neat DMF special care was taken to obtain good symmetric spectra with constant temperature (±1°) and optimum *constant* homogeneity as determined by a small amount of internal TMS.[19] Temperature was measured using the Varian standard after precise adjustment and calibration of the spectrometer sweep width. Several measurements were made and the average taken as the representative value. Several spectra were recorded at each temperature, and the parameters were derived from that with the best experimental-theoretical fit of the TMS peak (for a single resonance with a Lorentzian line shape). For the solutions in CCl_4 this was not done, and the figures are less reliable; this is also due to the fact that (a) at low concentrations the noise increases and smooth lines must be drawn through the nmr curves, adding an additional source of error, and (b) the homogeneity was not held as constant as in the work with neat DMF and was systematically worse with increasing temperature. Care was taken to avoid saturation and ensuing distortion of signals.

Calculations. The exchange calculations were performed by a FORTRAN IV program MUTSIT[21] for the following case: the two N-methyl doublets of the proton magnetic resonance spectrum of DMF (**2**) were considered as arising from an equally populated four-site system (**3**) with all transition probabilities equal to $\tau^{-1}/2$ where τ^{-1} is the rotation rate constant.



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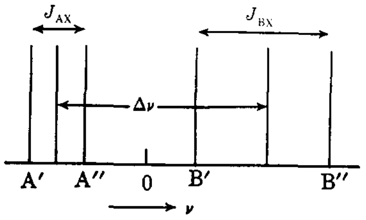

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Solving the Bloch equations[6] for this system modified by the method of McConnell[22] to include the above exchange we obtain for the absorption intensity at frequency ν (Hz) from the center (under the limiting conditions of slow passage and no saturation[22])

$$I(\nu) \sim \text{real}\left[\frac{\alpha_{A'}\alpha_{A''}(\alpha_{B'}+\alpha_{B''}) + \alpha_{B'}\alpha_{B''}(\alpha_{A'}+\alpha_{A''}) + \tau^{-1}(\alpha_{A'}+\alpha_{A''})(\alpha_{B'}+\alpha_{B''})}{\alpha_{A'}\alpha_{A''}\alpha_{B'}\alpha_{B''} - (\tau^{-1}/2)^2(\alpha_{A'}+\alpha_{A''})(\alpha_{B'}+\alpha_{B''})}\right] \quad (1)$$

where $\alpha_j = T_2^{*-1} + \tau'^{-1} - i(\nu - \nu_j)$; j = A′, A″, B′, B″; $\tau'^{-1} = \tau^{-1}/2\pi$; and T_2^{*-1} is an effective natural half line width.[23] The program calculates values of $\Delta\nu$ and τ^{-1} for each spectrum, leading to a best fit[24] between theoretical (1) and experimental normalized intensities at about 50 frequency points. Besides the intensities, the input consists of initial guesses for τ^{-1} and $\Delta\nu$ and values for T_2^{*-1}, J_{AX}, and J_{BX}. From a calculation at room temperature the best values for T_2^{*-1}, J_{AX}, and J_{BX} were found to be 0.3, 0.5, and 0.75 Hz, respectively,[25] and were used as constants throughout.

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[9] (a) J. Sandström, *J. Phys. Chem.*, **71**, 2318 (1967); (b) R. C. Neuman, Jr., D. N. Roark, and V. Jonas, *J. Am. Chem. Soc.*, **89**, 3412 (1967); (c) Y. Shvo, E. C. Taylor, and J. Bartulin, *Tetrahedron Letters*, 3259 (1967); (d) W. P. Purcell and J. A. Singer, *J. Phys. Chem.*, **71**, 4316 (1967); (e) R. C. Neuman, Jr., and V. Jonas, *J. Am. Chem. Soc.*, **90**, 1970 (1968).

[10] T. H. Siddall, III, and R. H. Garner, *Can. J. Chem.*, **44**, 2387 (1966).

[11] J. C. Woodbrey and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 13 (1962).

[12] R. C. Neuman, Jr., and L. B. Young, *J. Phys. Chem.*, **69**, 2570 (1965).

[13] J. H. Crabtree and D. J. Bertelli, *J. Am. Chem. Soc.*, **89**, 5384 (1967).

[14] By nonexchanging chemical shifts we mean those at low temperatures where the rate of internal rotation is negligible.

[15] J. V. Hatton and R. E. Richards, *Mol. Phys.*, **3**, 253 (1960).

[16] M. Rabinovitz and A. Pines, *J. Chem. Soc., B*, 1110 (1968).

[17] The nmr total line-shape analysis has recently been proved reliable by comparison with equilibration[3h,18] and double resonance[19] techniques.

[18] H. S. Gutowsky, J. Jonas, and T. H. Siddall, III, *J. Am. Chem. Soc.*, **89**, 4300 (1967).

[19] F. A. L. Anet and A. J. R. Bourn, *ibid.*, **89**, 760 (1967).

[20] The values obtained[16] were $\Delta H° \approx -6$ kcal/mole, $\Delta S° \approx -14$ eu. Also, the limiting $\Delta\nu$ for monomer and dimer were estimated: see Table III.

[21] We utilized an automatic search routine REEP (slightly modified here) for nonlinear estimations, obtained from Share Programme Library: SDA No. 3492. This routine was found to be extremely useful and we have used it on several other occasions.

[22] H. M. McConnell, *J. Chem. Phys.*, **28**, 430 (1958).

[23] (a) $T_2^{*-1} = T_2^{0-1} + T_2'^{-1}$, where $T_2'^{-1}$ is an inhomogeneity term.[2b,19] This procedure is valid if one ensures that the internal TMS peak is of Lorentzian shape.[19] (b) Also, T_2^{*-1} is considered constant which means that any change in T_2^{0-1} due to a temperature dependence of N^{14} coupling or coupling between the methyl group protons is not accounted for. However, such effects are important only at very high or very low exchange rates.[2b]

[24] (a) By "best fit" we mean in the least-squares sense. (b) M. R. Spiegel, "Theory and Problems of Statistics," Schaum Publishing Co., New York, N. Y., 1961.

[25] These coupling constants are identical with *one* set reported previously.[3b]

For the calculation of ΔG^*, the absolute rate equation of Eyring was used assuming a unit transmission coefficient.

The C=O magnetic anisotropy screening constants for DMF and the dimer were evaluated with the McConnell equation[26] using figures taken from a recent paper[27] (see Discussion). Dreiding angles and bond lengths were assumed, and the angle between the planar DMF molecules and the intermolecular bonds was taken as 90°.

All calculations were performed on the IBM 7040 digital computer of the Hebrew University.

Results and Discussion

Internal Rotation in Neat Dimethylformamide. Figure 1 shows the results obtained for DMF performing the calculations as discussed above. The agreement between experimental and calculated spectra is excellent (usually with less than 0.5% of the variation unexplained[24b]) over a temperature range of 48°, and Table I shows the ensuing rate constants. In Figure 2 we see the corresponding Arrhenius plot which gives the following activation parameters: E_a = 20.5 ± 0.2 kcal/mole, ν_0 = (5 ± 3)10^{12} sec^{-1}, $\Delta G^*_{128°}$ = 21.0 kcal/mole, ΔH^* = 20.2 ± 0.2 kcal/mole, ΔS^* = −1.7 eu. Thus, the Arrhenius activation energy is not unusually high or low compared with other amides,[3h,9e,18] and the "normal" frequency factor and small entropy of activation are also reasonable.[3h,9b]

Table I. Rate Constant for Hindered Internal Rotation in N,N-Dimethylformamide

No.	Temp, °C	k, sec^{-1}	No.	Temp, °C	k, sec^{-1}
1	80	0.94	7	107	6.91
2	85	1.21	8	111	9.61
3	90	2.32	9	114.5	11.99
4	94	2.70	10	119[a]	15.61
5	99	3.89	11	122	20.35
6	103	5.23	12	128	29.20

[a] Coalescence temperature.

Recently Neuman and Jonas[9e] obtained the following figures for dimethylacetamide-d_3 (DMA-d_3) using a two-site TLS analysis: E_a = 19.6 kcal/mole, log ν_0 = 13.8, ΔG^* = 18.2 kcal/mole, ΔH^* = 19.0 kcal/mole, ΔS^* = +2.7 eu. Using previous values for DMF and other amides from the literature, these authors discuss the factors influencing the rotation barrier in amides. There is a discrepancy between their positive entropy value for DMA-d_3 and our negative one for DMF; however, it is well known that the error range for ΔS^* is usually larger, and in our case at least, the error is probably as large as the value itself. In any case, as mentioned before, more accurate values are needed for other amides before any general discussion can be really meaningful.

This study again emphasizes the extreme importance of taking into account both the variance of $\Delta\nu$[18] and the significant fine structure exhibited by this particular compound. Unlike the report on N,N-dimethylcarbamoyl chloride by Neuman and co-workers,[9b] $\Delta\nu$ in this case as in that of the formyl proton resonance of N-methyl-N-benzylformamide[19] can on no account be taken as constant,[3e,f] probably because the changes in $\Delta\nu$ themselves are of greater magnitude. Thus, if a one-parameter study on systems of this type is to be

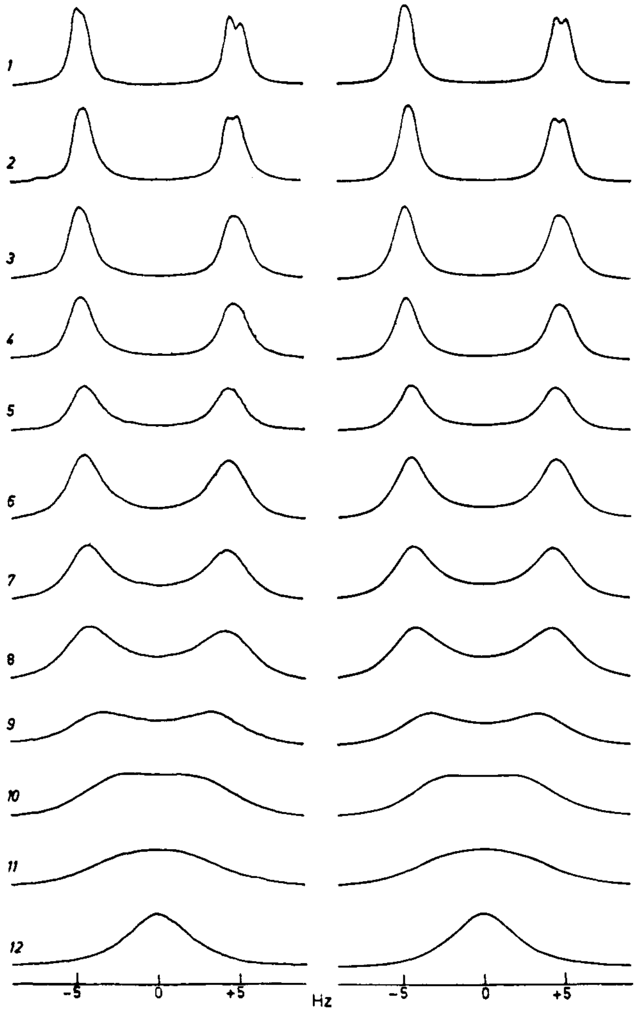

Figure 1. Experimental (left) and calculated (right) N-methyl 60-MHz proton magnetic resonance spectra of dimethylformamide at several temperatures (see Table I). The calculated spectra were obtained by a total line-shape analysis as explained in the Experimental Section.

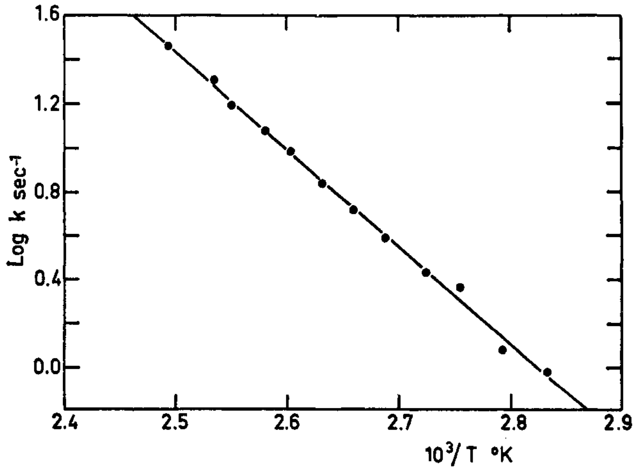

Figure 2. Arrhenius plot for the process of hindered internal rotation in neat dimethylformamide. The values of the activation parameters derived from this plot are E_a = 20.5 ± 0.2 kcal/mole, ν_0 = (5 ± 3)10^{12} sec^{-1}, $\Delta G_{128°}^*$ = 21.0 kcal/mole, ΔH^* = 20.3 ± 0.2 kcal/mole, ΔS^* = −1.7 eu.

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(26) H. M. McConnell, *J. Chem. Phys.*, 27, 226 (1957).

(27) J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, A. K. G. Nasser, L. Saunders, and W. B. Whalley, *Chem. Commun.*, 754 (1966).

Table II. Spectral and Kinetic Parameters for Dimethylformamide in Carbon Tetrachloride[a]

Temp, °C	Mole fraction of DMF															
	1.00		0.584		0.420		0.364		0.256		0.234		0.191		0.167	
	$\Delta\nu'$	k'	$\Delta\nu'$	k'	$\Delta\nu'$	k'	$\Delta\nu'$	k'	$\Delta\nu'$	k'	$\Delta\nu'$	k'	$\Delta\nu'$	k'	$\Delta\nu'$	k'
92	4.71	0.31	4.64	0.26	4.52	0.34	4.45	0.31	4.21	0.34	4.16	0.31	4.05	0.37	3.98	0.40
96	4.88	0.43	4.47	0.43	4.32	0.40	0.46	0.46	4.06	0.50	4.06	0.53	3.90	0.58	3.81	0.51
100	4.51	0.49	4.47	0.52	4.30	0.49	4.29	0.52	4.14	0.66	4.00	0.67	3.91	0.69	3.82	0.70
102	4.46	0.62	4.49	0.67	4.25	0.69	4.23	0.73	4.01	0.85	4.02	0.90	3.85	0.83	3.76	0.87
106	4.46	0.94	4.43	1.07	4.28	1.00	4.11	1.12	3.90	1.08	3.89	1.23	3.71	1.35	3.67	1.20
109	4.53	1.14	4.42	1.18	4.26	1.19	4.07	1.33	3.80	1.53	3.73	1.58	3.72	1.67	3.43	1.54
112.5	4.30	1.62	4.32	1.65	4.09	1.50	4.01	1.70	3.66	2.11	3.66	2.19	3.58	2.09	3.31	2.25

[a] The values given here are for $k' = k/2\pi$ and $\Delta\nu' = \Delta\nu/2$ which are from the direct output of the program.

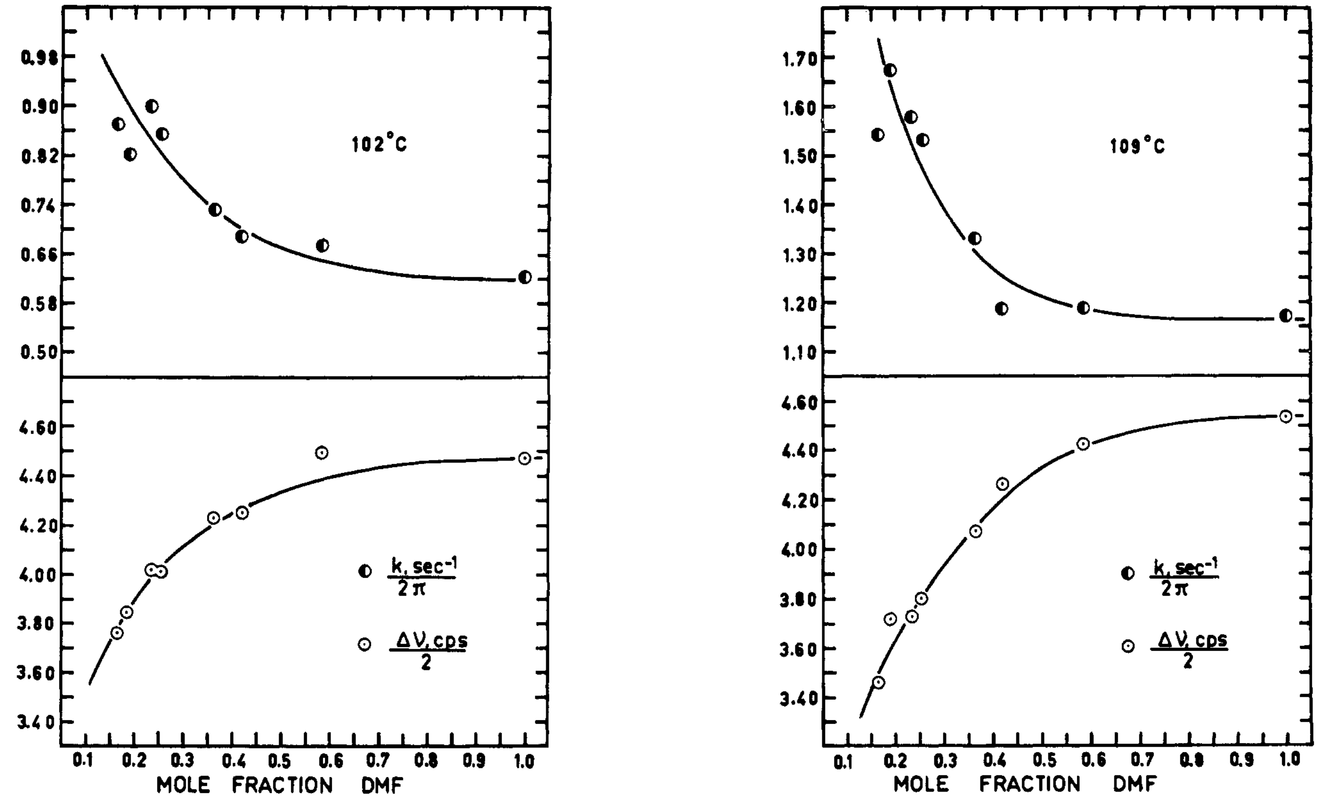


Figure 3. Concentration dependence of spectral and kinetic parameters for dimethylformamide in carbon tetrachloride. The figures are taken from Table II and are reproduced graphically here to show the qualitatively similar behavior of the rate constant of internal rotation and the N-methyl doublet chemical shift. The lines drawn through the points are arbitrary.

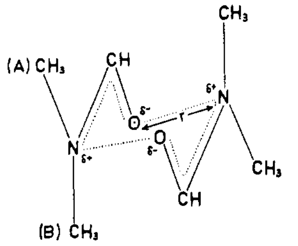
meaningful, it is imperative to establish whether the appropriate nonexchanging chemical shifts may indeed be considered constant and, if not, to take them explicitly into account. It appears therefore that the method applied to DMF by Fryer, *et al.*, and Conti and von Phillipsborn[3e,f] cannot be considered a rigorous TLS analysis, even for DMF-*d* (where the formyl-*d*–N-methyl proton coupling is negligible), since $\Delta\nu$ is taken as constant, and it is at best an improvement on simple one-parameter techniques. In fact, we suggest that one-parameter treatments would be more reliable in cases like this if the changes in $\Delta\nu$ could be incorporated explicitly in the calculations by some form of extrapolation from low temperatures. An approach to such an extrapolation can be derived if a suitable model for the chemical shift changes is found at low temperatures, *e.g.*, as described for DMF in CCl_4.[16]

Dimethylformamide in CCl_4. Elsewhere,[16] we have shown how the N-methyl doublet chemical shift ($\Delta\nu$) of DMF in CCl_4 could be accounted for quantitatively by assuming an equilibrium between monomeric and dimeric DMF molecules, the latter with a larger $\Delta\nu$.[20] The $\Delta\nu$ values were obtained at low temperatures by direct measurement, and the dependence should be the same as that obtained at higher temperatures from the TLS analysis.

Thus, Table II shows the rate constants for hindered internal rotation and the chemical shifts derived by the *TLS method* for DMF in CCl_4 at several temperatures and concentrations. The figures show significant scatter, and it may be seen that this is more serious the smaller the rate constant.[2b] In general, the values of the parameters are less reliable here, as explained in the Experimental Section, and for this reason they have not been used for calculating activation parameters. However, they are good enough for a discussion of the observed trends and, for illustration, Figure 3 depicts how these parameters change with concentration of

DMF at two temperatures. It may be seen that $\Delta\nu$ shows less scatter, and the calculations are therefore much more sensitive to this parameter (*vide infra*). As expected, the $\Delta\nu$ *vs.* concentration curves resemble those described previously.[16] More interesting, there is to our minds a noticeable similarity in the trends exhibited by the two types of curves, $\Delta\nu$ and k. We can see, at least qualitatively, that the rate of internal rotation is directly influenced by the extent of molecular association in this case and increases quite rapidly with dilution at low concentrations. This observation is in line with a small change of E_a with concentration in CCl_4 reported for other amides,[11] but a novelty here is the direct comparison with a parameter already related quantitatively to molecular association, and also the greater sensitivity of k to these changes. Evidently, in view of the above, k is not the true rate constant for DMF, and is probably an average for that in the monomer and dimer. A *quantitative* approach to the behavior of the rotation rate constant, and the manner in which this is brought about, using figures from a more extensive study, is the subject of present work being carried out in our laboratory.

Dimethylformamide Dimer. Woodbrey and Rogers[11] and Neuman and Young[12] suggested cyclic structures for amide dimers. Our figures[20] for $\Delta H°$ and $\Delta S°$ for the dimerization of DMF strengthen the assignment of a cyclic structure in this case.[28] If this is so, the question arises as to whether any preferred orientation of the participant molecules is involved, such as the oriented amide–solvent collision complexes proposed by Hatton and Richards[15] to explain chemical shift trends exhibited by amides in aromatic solvents. Examination of a model shows that a structure such as **4** has minimum steric interaction and could undoubtedly enhance charge delocalization and stability of the complex through formation of a chair-like six-membered ring.[29]



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If indeed there is a preferred cyclic orientation on the average such as **4** in the dimeric state, the magnetic anisotropy of each carbonyl bond should influence the N-methyl group protons in both molecules by direct shielding, and we expect this to explain the experimentally observed chemical shift trend between monomer and dimer. We have calculated the N-methyl doublet internal chemical shift in monomer (**2**) and dimer (**4** and see Experimental Section) using figures for the principal magnetic susceptibilities of the carbonyl bond[27] recently shown to be good for the prediction of qualitative trends in aldehydes.[30a, b] (χ_{xx} = 17.5, χ_{yy} = −10.5, χ_{zz} = −22.0 cm³/molecule). They are shown in Table III and correctly predict[31] that the resonance of B for the DMF molecule (**2**) occurs at higher field than that of A, in accordance with interpretations based on the magnitudes of the formyl-N-methyl hydrogen couplings,[15,32] and at variance with a previous model.[33] In the dimer, at any intermolecular distance, B is more shielded than A due to both C=O groups, and the chemical shift should therefore increase relative to monomer, as is borne out by experiment (Table III).[34]

Table III. Screening Constants (ppm) for N-Methyl Group Protons in DMF Monomer and Dimer

r, Å[a]	$(\sigma_B - \sigma_A)_{monomer}$, exptl	$\sigma_{A,monomer}$, calcd	$\sigma_{B,monomer}$, calcd	$(\sigma_B - \sigma_A)_{dimer}$, exptl	$\sigma_{A,dimer}$, calcd	$\sigma_{B,dimer}$, calcd
2					−0.41	0.41
2.5					−0.24	0.38
3	0.1	−0.29	0.10	0.2	−0.16	0.35
3.5					−0.18	0.29

[a] See Figure 3. [b] Taken from ref 16.

The change in internal chemical shift observed with concentration of DMF (and other amides) in nonaromatic solvents[3d–f, 15] has been attributed to a change in the magnetic anisotropy of the C=O bond with change in the polarity of the medium.[3d] In view of our work, however, it appears that a more satisfactory explanation lies in a contribution of the direct dimer shielding described in a monomer–dimer equilibrium. This point is being investigated further.

Acknowledgments. We are indebted to Professor J. Klein, Professor J. I. Musher, and Dr. T. H. Siddall, III, for helpful discussions, to Professor R. C. Neuman, Jr., for sending us a preprint of his paper (Concentration Dependence of the NMR of Some N,N-Dimethylamides and Thioamides), and to Mr. Rafi Malach for aiding with the calculations. The valuable and generous assistance of Mr. Michel Chekroun of the Computing Centre is also gratefully acknowledged.

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(28) The values are similar to those of cyclic hydrogen-bonded amide and lactam dimers and their thio analogs. For a recent paper with leading references, see N. Kulevsky and P. M. Froehlich, *J. Am. Chem. Soc.*, **89**, 4839 (1967).

(29) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

(30) (a) G. J. Karabatsos, G. C. Sonnichsen, N. Hsi, and D. J. Fenoglio, *J. Am. Chem. Soc.*, **89**, 5067 (1967); (b) J. I. Musher, *J. Chem. Phys.*, **35**, 1159 (1961).

(31) B. B. Wayland, R. S. Drago, and H. F. Henneike, *J. Am. Chem. Soc.*, **88**, 2455 (1966). These authors have shown unequivocally that the B signal appears at higher field than that of A.

(32) A. G. Whittaker, D. W. Moore, and S. Siegel, *J. Phys. Chem.*, **68**, 3431 (1964); these are based on *trans* coupling being larger than *cis* coupling across ethylenic double bonds: M. Karplus, *J. Chem. Phys.*, **36**, 540 (1962).

(33) P. T. Narasimhan and M. T. Rogers, *J. Phys. Chem.*, **63**, 1388 (1959).

(34) However, a shift of the center of absorption is also predicted, contrary to experiment,[3d,15] and therefore if a mechanism such as this is influencing the chemical shifts it must form part of a very complicated scheme.[18]