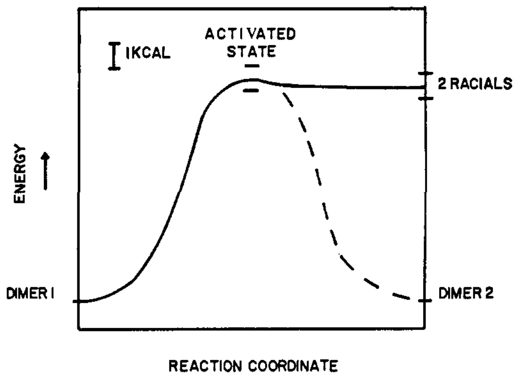

Figure 5. Reaction coordinate *vs.* energy for the two processes.

pendent of concentration in both cases (eq 7). We have conducted experiments in which the dimer concentration was varied incrementally by a factor of 6 (six samples). The line broadening was found to be completely independent of concentration.

A plot of the log of the rate constants *vs.* $1/T$ is given in Figure 4. Data for a series of different concentrations are included in this plot. The rate constant for process I is about a factor of 2 greater than that for process II over the entire temperature region. The two lines are parallel, within experimental error, showing that the activation energies are almost the same.

Table I. Rate Constants and Thermodynamic Data at 243°K

Rate constants and equilibrium constant	Activation energies and standard enthalpy change
$k_1 = 7.6 \pm 0.8\ \text{sec}^{-1}$	$\Delta H_1 = 9.1 \pm 0.5$ kcal/mole
$k_2 = (2.5 \pm 0.05) \times 10^5\ M^{-1}\ \text{sec}^{-1}$	$\Delta H_2^{\ddagger} < 1$ kcal/mole
$k_3 = (2.0 \pm 0.1) \times 10^2\ \text{sec}^{-1}$	$\Delta H_3^{\ddagger} = 9.1 \pm 0.5$ kcal/mole
$K = (3.1 \pm 1.0) \times 10^{-5}\ M$	$\Delta H^{\circ} = 9.1 \pm 0.5$ kcal/mole

The equivalence of the activation energies might have been anticipated, as the same carbon–oxygen bond is being broken in both reactions. The difference in rates is apparently due to either differences in preexponential factors and/or activation entropies. A plot of the reaction coordinate *vs.* energy, for both reactions, is given in Figure 5. The value of the standard enthalpy change for the dissociation reaction is identical with that of the activation energy within experimental error. Thermodynamic data and rate constants are given in Table I.

Conclusions

It has been possible to determine rate constants for the dissociation of a dimer into two free radicals with nmr techniques. A second reaction involving rearrangement of the two halves of the dimer was also observed and rate constants were determined. The two processes were found to have the same activation energies but different rate constants.

Studies of Chemical Exchange by Nuclear Magnetic Resonance. II. Hindered Rotation in Amides and Thioamides[1]

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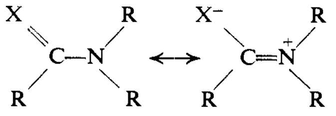
Abstract: A detailed kinetic study of rotation about the central carbon–nitrogen bond in N,N-dimethylcarbamoyl chloride (DMCC) and N,N-dimethylthiocarbamoyl chloride (DMTCC) using *total* nmr line-shape analyses has been carried out. Comparative rotational barriers for amides and analogous thioamides are discussed and the literature is reviewed. Results for DMCC are compared with other available data for this amide and discussed in the light of recent controversy about the significance of chemical exchange studies by nmr. Temperature and concentration dependences of the nmr spectra of DMTCC in carbon tetrachloride indicate significant association of DMTCC into polymeric aggregates. Activation parameters obtained in this study are: DMCC (neat), $E_a = 16.9 \pm 0.5$ kcal/mole, log $A = 12.9 \pm 0.4$, $\Delta F^*_{298.2} = 16.8$ kcal/mole; DMCC (10.4 mole % in CCl_4), $E_a = 17.7 \pm 0.9$ kcal/mole, log $A = 13.8 \pm 0.7$, $\Delta F^*_{298.2} = 16.3$ kcal/mole; DMTCC (CCl_4 solvent), $\Delta F^*_{298.2} \simeq 19$ kcal/mole.

Electron delocalization in amides (I, X = O) and thioamides (I, X = S) causes the rotational barrier about the central C–N bond to be significantly higher



I

than that for a normal single C–N bond.[1,3–5] Comparative nmr studies have indicated that these rotational barriers are consistently higher for the thioamides, and this is not unexpected.[1a,5–8]

Interconversion rates of geometrical isomers of unsymmetrically N,N-disubstituted amides[7,9] and thio-

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[1] (a) Part I: R. C. Neuman, Jr., and L. B. Young, *J. Phys. Chem.*, **69**, 2570 (1965). (b) Support by the U. S. Public Health Service (National Institute of General Medical Sciences) through Grant GM-13342 is gratefully acknowledged.

[2] National Science Foundation Undergraduate Research Participant, academic year 1965–1966 and summer 1966.

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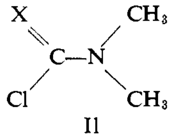
amides[7,8] have been measured by nmr by monitoring the increase or decrease in signal areas corresponding to the two different isomers. Such studies are relatively unambiguous but are limited to small temperature ranges and unusual compounds. Studies of simple symmetrically N,N-disubstituted amides[1a,4,10–19] and thioamides[1a,5] have required the use of nmr methods which are much more difficult to perform and give results which are much less easily interpreted. High-resolution line-shape studies were the first type employed in the study of amides[4] and have continued to be the most frequently used. Careful analyses of all of the possible difficulties associated with this method have only recently been outlined, and it seems likely that many studies have given erroneous results.[14,15,20] Spin-echo nmr methods have been recently employed in studies of amides.[14,18] Although this technique is experimentally difficult, somewhat restricted in application, and may lead to significant interpretational errors,[14,20] these problems were carefully considered and avoided as much as possible, giving the few available results a high level of credance. Unfortunately, the relative nonavailability of spin-echo instrumentation has so far precluded its extensive utilization in studies of chemical exchange processes. However, if proper precautions are taken in high-resolution line-shape studies, the results obtained should be at least as valid as those from other methods.[15,20]

Comparisons of rotational barriers in amides (I, X = O), thioamides (I, X = S), amidines (I, X = NH), and amidinium ions (I, X = NH_2^+) were undertaken[1a] in order to obtain information about the electronic properties of the heteroatoms O, S, and N which might find application in other studies of molecular structure. Our first results,[1a] although of qualitative significance, most likely fall into the great mass of high-resolution studies whose quantitative interpretations are uncertain. As a result, we decided to choose a system for a careful high-resolution study which could give information both about the fundamental questions associated with high-resolution line-shape methods and the effects of heteroatom substitution discussed above.

Gutowsky, *et al.*, have studied N,N-dimethylcarbamoyl chloride (II, X = O) by the spin-echo method,[14] and the corresponding thioamide, N,N-dimethylthiocarbamoyl chloride (II, X = S), is also a known compound. The results of our kinetic studies on these two compounds using the *total line-shape* comparison method[20] are reported here.



II

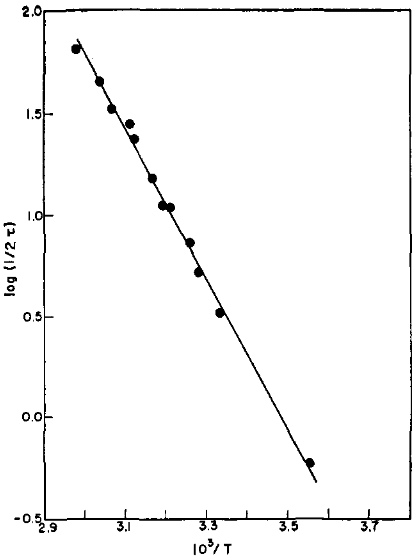


Figure 1. Arrhenius plot of the kinetic data for hindered rotation about the central C–N bond in a neat sample of DMCC. Kinetic data are given in Table IV (Experimental Section). E_a = 16.9 ± 0.5 kcal/mole, log A = 12.9 ± 0.4, $\Delta F^*_{298.2}$ = 16.8 kcal/mole.

Results

N,N-Dimethylcarbamoyl Chloride (DMCC). Kinetic studies of DMCC neat and in carbon tetrachloride (10.4 mole %) have been carried out. The kinetic data obtained by comparison of experimental and computer-generated spectra are given in Table IV in the Experimental Section.[21] The usual Arrhenius plots[4,11,14] (*e.g.*, Figure 1) of these data gave the following activation parameters: DMCC (neat), E_a = 16.9 ± 0.5 kcal/mole, log A = 12.9 ± 0.4, $\Delta F^*_{298.2}$ = 16.8 kcal/mole; DMCC (10.4 mole % in CCl_4), E_a = 17.7 ± 0.9 kcal/mole, log A = 13.8 ± 0.7, $\Delta F^*_{298.2}$ = 16.3 kcal/mole. These activation parameters represent temperature ranges of 54° for neat DMCC and 40° for 10.4 mole % DMCC in carbon tetrachloride. These values and all of the previously available data for DMCC have been included in Table I.

The nonexchanging chemical shift of 6.33 cps was used for neat DMCC, and variable nonexchanging shifts of 7.20–7.05 cps (see Table IV) were used for 10.4 mole % DMCC in CCl_4. However, *the choice of the exactly correct nonexchanging chemical shift is apparently not important when total line-shape analysis is used.* There was virtually no difference in the activation parameters calculated for 10.4 mole % DMCC in CCl_4 when rate constants were obtained using the $\delta\nu_\infty$ values of 7.20 or 7.05 cps to generate the best-fit spectra, since very little difference in the resulting best-fit values of 2τ occurred.

N,N-Dimethylthiocarbamoyl Chloride (DMTCC). The solid thioamide DMTCC was studied using carbon

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(21) Correspondence between the experimental and best-fit calculated spectra was excellent. Pictures of these spectra have not been included because of space limitations but can be obtained from the authors on request.

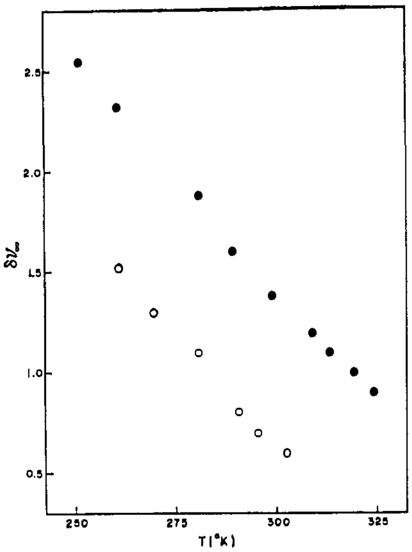

Figure 2. The temperature dependence of the nonexchanging chemical shift ($\delta\nu_\infty$) between the two N-CH$_3$ proton resonances of DMTCC in carbon tetrachloride solution: 2.1 *M* (solid circles), 0.062 *M* (open circles).

tetrachloride as solvent. On calculation of theoretical spectra corresponding to the experimental spectra, we found that the nonexchanging chemical shifts necessary to bring about the best fit were both temperature and concentration dependent. The resultant nonexchanging chemical shift values are plotted *vs.* temperature in Figure 2. Because the chemical shifts were very small and since they varied markedly with temperature, the resulting kinetic data (Table II) are not as reliable as those obtained for DMCC. An Arrhenius plot of these rate data showed significant scatter; however, the majority of the points lay on a line corresponding to the values E_a = 19.5 kcal/mole and log A = 13.2. Since it is not clear that a single line should fit the data for both concentrations (*vide infra*), we place little reliance in these activation parameters. However, free energies of activation (ΔF^*_T) appear to be much less sensitive to inaccuracies in kinetic data (*vide infra*), and these are given in Table II as calculated for each kinetic point.

Table I. Activation Parameters for Hindered Internal Rotation in N,N-Dimethylcarbamoyl Chloride

Solvent (mole %)	E_a, kcal/mole[a]	Log A[a]	$\Delta F_{298.2}$, kcal/mole[a]	Method[b]
Neat	16.9 ± 0.5[c]	12.9 ± 0.4	16.8	HR, TLS
	14.0 ± 0.9[d]	10.9 ± 0.6	16.6	SE
	9.7 ± 0.5[d]	7.7 ± 0.4	16.6	HR, IR
	8.6 ± 1.7[d]	6.9 ± 1.2	16.6	HR, PS
	7.3 ± 0.5[e]	6.1 ± 0.3	16.4	HR, IR
CCl$_4$ (10.4)[g]	17.7 ± 0.9[c]	13.8 ± 0.7	16.3	HR, TLS
(11.0)	6.8 ± 0.2[f]	5.9 ± 0.2	16.2	HR, IR

[a] Calculated using the usual equations previously outlined (ref 11). [b] HR, high-resolution, steady-state nmr spectroscopy; SE, spin-echo nmr spectroscopy; TLS, total line-shape analysis; IR, intensity-ratio method; PS, peak-separation method. [c] Our results. [d] Reference 14. [e] Reference 11. [f] Reference 12. [g] Approximately 1.2 moles/l.

Table II. Kinetic Data and Free Energies of Activation for Internal Rotation in DMTCC

Concn, *M*[a]	Temp, °K	2τ, sec	ΔF^*_T, kcal/mole[b]
2.1	324.2	0.8820	19.0
	319.2	1.8958	19.1
	313.2	2.3753	18.9
	309.2	66.135	20.7
0.062	302.6	1.7515	18.1
	295.6	17.568	19.0
	290.7	32.536	19.0
	280.7	13.449	17.9

[a] Formal concentration (*vide infra*) of DMTCC in carbon tetrachloride. [b] Calculated using the usual equation (ref 11).

Discussion

Rotational Barrier for DMCC. Activation parameters for amides determined by nmr methods have been characterized by their lack of reproducibility and unreasonably low frequency factors.[1a,4,10-19] However, it has been previously noted that, in spite of major discrepancies in the values of E_a and log A obtained by different groups for the same reaction, the values of the free energy of activation (ΔF^*_T) have been found to be remarkably constant.[14,20] This is evident from an inspection of the data for DMCC in Table I. It also seems to be generally observed that, as increasing care has been taken in carrying out the kinetic experiments and in analyzing the experimental results, the values of E_a and log A have tended to increase. In the case of internal rotation in amides and related molecules, this is particularly satisfying since no reasonable explanations for frequency factors significantly less than 10^{13} sec^{-1} (log A = 13.0) have been proposed.[15] This value of a frequency factor for a unimolecular process has enjoyed somewhat magical status which is undeserved for reactions in condensed phases due to probable differences in solvation of ground and transition states.[1a,15] However, low frequency factors reflect a loss of entropy in proceeding to the transition state, and this is very difficult to rationalize for internal rotation in amides where the ground state should be more polar than the transition state. This suggests, on the contrary, that frequency factors higher than 10^{13} should not be unexpected, and recent studies on several N,N-dimethylamides tend to support this.[1a,15,19]

Although we are gratified by our kinetic data (*e.g.*, Figure 1)[21] and the resultant frequency factors (Table I), we would be presumptuous to claim that our activation parameters are the true values for DMCC. Further checks by other laboratories would certainly be desirable. However, we do feel that our data more closely correspond to the true activation parameters than those recently obtained by the spin-echo method.[15] These latter kinetic data give an entropy of activation of approximately −10.7 eu, while our data for neat DMCC give the more reasonable value −1.6 eu.[22]

In passing it should be noted that the observed correspondence[21] between the theoretical and experimental spectra lends strong support to the adequacy of the model which was used (see Experimental Section). This correspondence was achieved using only two adjustable parameters (τ, $\delta\nu_\infty$) since the value of T_2 for each

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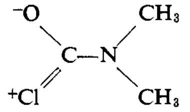
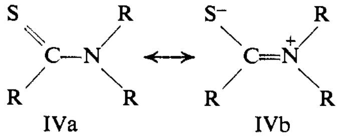
[22] Also see F. A. L. Anet and A. J. R. Bourn, *J. Am. Chem. Soc.*, **89**, 760 (1967).

spectrum was experimentally determined and not varied in seeking the best fit (see Experimental Section).

The rotational barrier for DMCC is significantly lower than those of other simple N,N-dimethylamides. For example, recent reliable data[15] for dimethylacetamide (DMA) and dimethylformamide (DMF) give the values $E_a = 23$ kcal/mole, $\log A = 16$, and $\Delta F_{298.2} = 19$ kcal/mole, and $E_a = 26$ kcal/mole, $\log A = 16$, and $\Delta F_{298.2} = 22$ kcal/mole, respectively. This has been attributed to electron delocalization involving chlorine as shown in III which should decrease the partial double-bond character about the C–N bond.[11] It is also informative to compare the frequency factors obtained for DMA and DMF with the value $\log A \simeq 13$ obtained for DMCC in this study. These data were obtained using neat samples of the amides, and the frequency factors should reflect the effects of solvation by the amide molecules themselves. Since charge delocalization may be more extensive in DMCC because of the additional canonical structure III, differences in the extent of solvation of the ground and transition states of DMCC should be less pronounced than in the case of DMA and DMF. This would agree with the differences in the frequency factors for these compounds.


III

Temperature Dependence of the DMTCC Spectra. Although the temperature dependence of nonexchanging chemical shifts is not unexpected, the magnitude of this effect for DMTCC was surprising (Figure 2). In addition the absolute magnitudes of the values $\delta\nu_\infty$ (Figure 2) are low compared to amides and other thioamides which have been examined.[23] Microanalytical data for DMTCC support the empirical formula $(C_3H_6ClNS)_x$, and its physical properties (mp 35–37°; bp 55° (0.8 mm)) suggest a monomeric structure ($x = 1$).[24] Acid hydrolysis gave N,N-dimethylammonium ion as the only organic product, ruling out other isomers. The infrared spectrum is also consistent with a thioamide. However, molecular weight determinations (vapor pressure osmometry) on carbon tetrachloride solutions of DMTCC gave results intermediate between the molecular weight of the monomer and a dimer (see Experimental Section). Ultraviolet spectral data, rotational barriers, and ^{13}C–H coupling constants for other N,N-dimethylthioamides suggest that the canonical structure IVb contributes more to the ground state of a thioamide than the analogous structure does to the ground state of an amide.[1a] This in turn suggests that dimeric (or higher) association of DMTCC in carbon tetrachloride might be expected. Since only two N–CH$_3$ resonance lines of equal intensity were observed at both concentrations, and over the temperature ranges studied, it seems reasonable to assume that the various molecular aggregates of DMTCC (monomer, dimer, etc.) are in rapid equilibrium. If this is true the value $\delta\nu_\infty$ (Figure 2) should be described by eq 1, where δ_M, δ_D, and δ_T are the


IVa IVb

$$\delta\nu_\infty = \delta_M\delta\nu_M + \delta_D\delta\nu_D + \delta_T\delta\nu_T + \ldots \qquad (1)$$

mole fractions of monomer, dimer, and trimer, respectively, and $\delta\nu_M$, $\delta\nu_D$, and $\delta\nu_T$ are the nonexchanging chemical shift differences between the two N–CH$_3$ groups in DMTCC in the monomer, dimer, and trimer, respectively.[25] In such an association equilibrium, the relative amount of monomer to higher aggregates will increase as the concentration is lowered. Thus, the fact that $\delta\nu_\infty$ decreases as concentration is lowered (Figure 2) implies that $\delta\nu_M$ is less than $\delta\nu_D$, $\delta\nu_T$, and the values for higher aggregates ($\delta\nu_P$). Similarly, the decrease in $\delta\nu_\infty$ with increasing temperature suggests an increasing relative amount of monomer to that of higher aggregates. Since the values of $\delta\nu_\infty$ approach zero in the high-temperature region of Figure 2, it may be that the *sign* of the value $\delta\nu_M$ is *opposite* that of the values of $\delta\nu_D$, $\delta\nu_T$, etc. That is, the relative *shielding of the two N–CH$_3$ groups may be different in the monomer compared to the higher aggregates.* Unusual results previously reported for dimethylthioacetamide seem to confirm the possibility of such an occurrence.[26]

This analysis predicts that the *absolute* value of $\delta\nu_\infty$ should decrease to zero as temperature is increased and then begin to increase again. This has not been observed. However, an inspection of the kinetic data in Table II indicates a probable reason. At the high-temperature end of the data (Figure 2), coalescence apparently occurs, not only because the nonexchanging chemical shift is decreasing, but also because the rate of rotation is increasing (Table II). Thus the observation that reseparation of the two components does not occur at high temperatures may be explained by an increasing rotational rate compensating for an increasing nonexchanging chemical shift.

The values of ΔF^*_T given in Table II are probably a reasonable representation of the free-energy barrier to rotation in DMTCC. The differences in the rotational barriers of DMTCC in the monomeric form and in higher aggregates are probably not large, and, since the doublets observed represent an average of doublet structures corresponding to the various states of association, the values of ΔF^*_T should represent some intermediate value for DMTCC in these various states of aggregation.

Rotational barriers for thioamides appear to be larger than those for the corresponding amides (see introductory section). Measured values of $\Delta F^*_{298.2}$ for dimethylacetamide[1a,5,15] and dimethylthioacet-

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[23] Values of $\delta\nu_\infty$ in the range of 5–10 cps are generally encountered.

[24] (a) Some boiling points[24b] for amides and thioamides are: dimethylformamide, 153° (760 mm); dimethylthioformamide, 97° (12 mm); dimethylcarbamoyl chloride, 167° (755 mm); dimethylthiocarbamoyl chloride, 98° (10 mm) and 55° (0.8 mm)[24c]. (b) Obtained from various supplements of Beilstein. (c) Our data.

[25] This equation arises from the often-used equation describing the observed position of a resonance signal for a proton or group of equivalent protons exchanging rapidly between two or more sites which are magnetically different; for example, see J. W. Emsley, J. Feeny, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press Ltd., Oxford, England, pp 539–540.

[26] (a) R. C. Neuman, Jr., and L. B. Young, *J. Phys. Chem.*, **69**, 1777 (1965). (b) To our knowledge, anistropy studies for the system N—C═S have not been reported. In the case of amides, however, the values of $\delta\nu_m$ do appear to be less than the values of $\delta\nu$ for the higher aggregates.[16]

amide[1a] are ~19 and ~30 kcal/mole, respectively; for dimethylformamide[1a,15] and dimethylthioformamide,[5] ~22 and ~27 kcal/mole, respectively; and for the *cis* (*trans*) isomers of N-methyl-N-benzyl mesitylenecarboxylic acid amide and N-methyl-N-benzyl mesitylenecarboxylic acid thioamide, 22.3 (22.9) and 26.8 kcal/mole (27.3 kcal/mole), respectively.[7] A comparison of the data in Tables I and II shows the same trend; however, the difference is somewhat smaller. This is expected, however, if chlorine participates as in III. The additional electron demand in changing oxygen to sulfur will be partially taken up by an increased response from chlorine, and thus the full effect will not be felt by the nitrogen atom.

Experimental Section

N,N-Dimethylcarbamoyl chloride (DMCC), obtained from Matheson Coleman and Bell, was purified by vacuum distillation and stored over molecular sieves.

N,N-Dimethylthiocarbamoyl chloride (DMTCC) was prepared by the reaction[27] of chlorine with tetramethylthiuram disulfide (Aldrich) and purified by vacuum distillation, bp 55° (0.8 mm); mp 35–37°.[28] *Anal.* Calcd for C_3H_6ClNS: C, 29.15; H, 4.89; Cl, 28.68; N, 11.33; S, 25.94. Found: C, 29.35, 29.17; H, 5.50, 5.06; Cl, 28.65, 28.75; N, 10.95, 10.91; S, 24.75, 24.74. Nmr (see text): center of $N-CH_3$ doublet at ambient temperature, 210.5 cps (TMS internal reference).

The white solid thioamide was very sensitive to water and oxygen and was stored under nitrogen over a drying agent. It was repurified by distillation prior to its use in these studies.

Hydrolysis of DMTCC in aqueous hydrochloric acid solution gave a single solid product on evaporation of the water. This was identified as N,N-dimethylammonium chloride by infrared and nmr spectroscopic analyses.

Molecular Weight Determinations on DMTCC in Carbon Tetrachloride. Molecular weight determinations were performed at 37° using a vapor pressure osmometer (Mechrolab, Inc.). Calibration was accomplished using carbon tetrachloride solutions of benzil. Results on solutions of DMTCC in carbon tetrachloride and on control solutions of biphenyl in carbon tetrachloride are given in Table III.

Table III. Molecular Weight Determinations on Carbon Tetrachloride Solutions of DMTCC and Biphenyl

Compound	Concn, M^a	Molecular weight Theor	Molecular weight Obsd
Biphenyl	0.0325	154.2	156.3
	0.0556		152.5
	0.0955		148.1
DMTCC	0.0331	123.6	178.9
	0.0572		172.4
	0.0955		171.9

[a] Based on theoretical molecular weight.

Variable-Temperature Spectra. Spectra were recorded using a Varian A-60 nmr spectrometer equipped with a Varian V-6040 variable-temperature accessory. Care was taken to maintain the spectrometer in peak-operating condition. Homogeneity, curvature, and resolution adjustments were done at each temperature, and final adjustments were performed using the line of an internal TMS sample. Values of T_2 for each spectrum were determined from the TMS line width.

Temperatures were monitored using the methanol and ethylene glycol standards supplied by Varian. Experimental spectra were rejected unless temperature readings, before and after each spectrum was recorded, were the same. Experimental spectra which were not reproducible were not used in the calculations. The specific machine settings used in these studies were for DMCC (neat): filter band width, 4 or 2 cps; radiofrequency field, 0.04 mgauss; sweep width, 50 cps; sweep time, 250 sec (sweep rate, 0.2 cps/sec); for DMCC (CCl_4): same as DMCC (neat); for DMTCC (CCl_4), filter band width, 4 cps (occasionally 1 cps); radiofrequency field, 0.04 mgauss (occasionally 0.06 mgauss); sweep width, 50 cps; sweep time, 500 sec (sweep rate, 0.1 cps/sec).

Calculations of Theoretical Spectra. The complete line-shape equation of Gutowsky and Holm[4] for an uncoupled two-site exchange was programmed in FORTRAN IV. Intensity values were calculated as a function of frequency (500 frequency values used) over the narrow spectral range of interest (22 cps or less) using the following input data: transverse relaxation time (T_2) (determined for each spectrum); nonexchanging chemical shift ($\delta\nu_\infty$, cps) (chosen for best spectral fit); and mean lifetime (2τ). This program also calculated the exchanging peak separation (cps) and the intensity ratio (or the signal half-width for a coalesced doublet) in order to facilitate preliminary choices of the correct values of τ. These calculations were performed on an IBM 7040 digital computer. When a nearly correct τ has been obtained, the intensity frequency data were plotted using a California Computer Co. plotter in conjunction with an IBM 1620 digital computer. The theoretical plots were normalized to the experimental spectra to facilitate visual comparison. Final values of τ were chosen as those giving the best superposition of calculated and experimental spectra. All kinetic data are given in Tables II and IV.

Table IV. Kinetic and Spectral Data for DMCC

Solvent	Temp, °K	$\delta\nu_\infty$, cps^a	2τ, sec
Neat	335.9	6.33	0.0154
	329.4		0.0221
	326.3		0.0302
	321.5		0.0357
	320.4		0.0427
	315.9		0.0655
	313.3		0.0896
	311.6		0.0913
	307.1		0.1355
	305.0		0.1900
	300.2		0.3040
	281.4		1.6650
CCl_4 (10.4 mole %)	318.4	7.05	0.0226
	315.6		0.0344
	312.2		0.0518
	307.2		0.0819
	304.5		0.0986
	301.5		0.1265
	298.5		0.1675
	294.5	7.10	0.2445
	292.0	7.05	0.3044
	288.7	7.20	0.4662
	284.5	7.20	0.8860

[a] Nonexchanging chemical shift used in the calculations. Each value equal to immediately preceding value unless shown otherwise.

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(27) R. H. Goshorn, W. W. Levis, E. Jaul, and E. J. Ritter, *Org. Syn.*, **35**, 55 (1955).

(28) A discrepancy in the boiling point for DMTCC exists in the literature. Goshorn, *et al.*, report bp 90–95° (0.5 mm) and mp 42.5–43.5° for DMTCC. Beilstein lists bp 98° (10 mm) (4, II, 576) and although Beilstein lists the melting point reported by Goshorn[27] (4, III 147) it does not list his boiling point. The boiling point for the diethyl derivative reported by Goshorn[27] is 80–85° (1 mm). It seems unreasonable to us that the diethyl compound should boil lower than the dimethyl compound, and we believe Goshorn's reported boiling point for DMTCC to be in error for some unknown reason.