this experiment as white, crystalline needles, mp 68–70° (lit.[19] mp 68–70°).

N-**(Diethylphosphonyl)succinimide.** This material separated from solution (92% N.A., 81% I.A.) during reaction as a white solid which was purified by recrystallization from methanol: mp 57–60° (lit.[2] mp 60–62°); ir ν_{max} (Nujol) 1730 (C=O), 1295, 1250, 1125, 1030, 815, 755, 665, 555 cm^{-1}; nmr δ_{TMS} ($CDCl_3$) 3.20 (triplet, J = 8 Hz, 6 H, CH_3's), 2.80 (singlet, 4 H, succinimidyl ring), 4.32 (quintet, J = 8 Hz; 4 H, ethyl CH_2's).

N-**(Diisopropylphosphonyl)succinimide** was obtained as a dark red oil from silica gel (56% N.A., 37% I.A.): ir ν_{max} (film) 1725 (C=O), 1280–1290, 1100–1140, 1000, 750, 650, 560 cm^{-1}; nmr δ_{TMS} ($CDCl_3$) 1.43 (doublet, J = 6 Hz, 12 H, isopropyl CH_3's), 2.80 (singlet, 4 H, succinimidyl ring), 4.85 (septet, J = 6 Hz, 2 H, isopropyl methines).

Anal. Calcd for $C_{10}H_{18}NO_5P$: C, 45.65; H, 6.85; N, 5.33; P, 11.78. Found: C, 45.57; H, 6.68; N, 4.96; P, 11.83.

N-**(Di-*n*-butylphosphonyl)succinimide.** This material was isolated from exhaustive stripping of product mix followed by recrystallization from chloroform. Melting point (45–47°) and spectral data were identical with those reported previously.[1]

N-**(Diisobutylphosphonyl)succinimide.** Solids (dark red) that separated from CS_2 solution during reaction at 5° were collected by suction filtration. Nmr (see below) indicated the crude material to be 90% of the title compound. Purification by recrystallization from ethyl ether (slow evaporation) yielded wheat-white needles: mp 94–97°; ir ν_{max} (Nujol) 1735 (C=O), 1275, 1130, 1030, 880, 820, 660, 545 cm^{-1}; nmr δ_{TMS} ($CDCl_3$) 0.98 (doublet, J = 6 Hz, 12 H, ester CH_3's), 2.0 (multiplet, broad, 2 H, butyl methine), 2.80 (singlet, 4 H, succinimidyl ring), 4.1 (doublet of doublets, J_{PCH_2} = 8 Hz, J_{CH_2CH} = 6 Hz, 4 H, $POCH_2$).

Anal. Calcd for $C_{12}H_{22}NO_5P$: C, 49.50; H, 7.56; N, 4.81; P, 10.65. Found: C, 49.36; H, 7.42; N, 4.54; P, 10.59.

N-**(Di-*sec*-butylphosphonyl)succinimide.** This material was obtained from silica gel chromatography as a light red oil not analytically pure. Spectral evidence is offered as proof of structure: ir ν_{max} (film) 1740 (C=O), 1280, 1180, 1120, 1040, 815, 770, 660, 550 cm^{-1}; nmr δ_{TMS} ($CDCl_3$) 0.95 (triplet, J = 8 Hz, 6 H, γ methyls on butyl group), 1.30 (doublet, J = 6 Hz, 6 H, α methyls on butyl group), 1.65 (multiplet, 4 H, butyl methylenes), 2.80 (singlet, 4 H, succinimidyl ring), 4.45 (sextet, J = 6 Hz, OCH methines).

Acknowledgment. Appreciation is afforded Hooker Chemical Corp. for permission to conduct and publish this work under its auspices.

Registry No.—1 (R = CH_3), 39843-52-2; 1 (R = C_2H_5), 2737-05-5; 1 (R = i-C_3H_7), 50599-95-6; 1 (R = i-C_4H_9), 50599-96-7; 1 (R = *sec*-C_4H_9), 50599-97-8; $P(OR)_3$ (R = CH_3), 121-45-9; $P(OR)_3$ (R = C_2H_5), 122-52-1; $P(OR)_3$ (R = n-C_4H_9), 102-85-2; $P(OR)_3$ (R = i-C_4H_9), 1606-96-8; $P(OR)_3$ (R = *sec*-C_4H_9), 7504-61-2; $P(OR)_3$ (R = t-C_4H_9), 15205-62-6; $P(OR)_3$ (R = i-C_3H_7), 116-17-6; *N*-bromosuccinimide, 128-08-5; *N*-chlorosuccinimide, 128-09-6.

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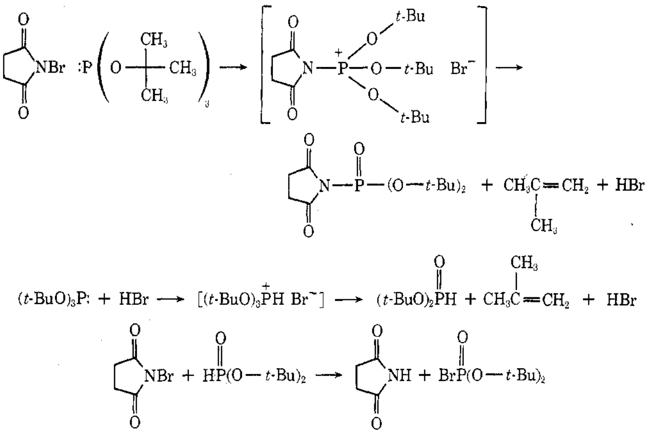

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Studies of Chemical Exchange by Nuclear Magnetic Resonance. IX. Rotation about the Amide Bond in *N*,*N*-Dimethylformamide[1,2]

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Received September 25, 1973

Activation parameters have been determined for rotation about the amide bond in pure *N*,*N*-dimethylformamide-d_1: E_a, 24.3 ± 0.2 kcal/mol; log A, 14.6 ± 0.1; ΔS^*, +6.3 ± 0.4 eu; ΔF^*_{298}, 21.8 kcal/mol. Kinetic data were obtained by total line shape analysis of the nmr spectra. The activation parameters are contrasted with previous values obtained using different techniques and a structure–reactivity correlation for amide rotation is discussed. These results are also compared with data for unsubstituted and *N*-methylformamide in an attempt to assess the importance of alkyl substitution on nitrogen on the C–N rotational barrier.

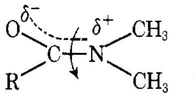
Rotation about the partial double bond of *N*,*N*-dimethylamides (1) has been extensively studied in part because these systems are the simplest models for the peptide bond in proteins.[1,3-10] Early studies gave inaccurate activation parameters for C–N rotation because approximate procedures were used to derive rate constants. Now

Table I
Kinetic Data for Rotation about the C–N Bond in *N,N*-Dimethylformamide-d_1 (3) in the Pure Liquid

Temp, °C	τ, sec[a]	$\delta\nu_\infty$, Hz[b]
107.3 ± 0.2	0.115	9.05
108.9 ± 0	0.0950	9.02
111.5 ± 0.2	0.0780	9.00
113.0 ± 0	0.0660	8.98
115.6 ± 0.2	0.0540	8.98
117.4 ± 0	0.0475	8.93
119.7 ± 0	0.0398	8.93
121.1 ± 0	0.0338	8.85
123.8 ± 0.2	0.0286	8.85
124.8 ± 0.1	0.0261	8.85
125.4 ± 0	0.0245	8.95
127.6 ± 0.2	0.0212	8.81
129.0 ± 0.2	0.0191	8.79
130.0 ± 0.1	0.0181	8.78
132.1 ± 0.1	0.0155	8.75
132.6 ± 0	0.0140	8.75
135.7 ± 0.2	0.0116	8.71
137.7 ± 0.2	0.0107	8.69
139.7 ± 0.1	0.00875	8.66
140.7 ± 0	0.00810	8.65
142.1 ± 0.3	0.00720	8.63
143.5 ± 0.2	0.00670	8.62
145.1 ± 0	0.00625	8.60

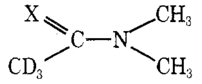
[a] The unimolecular rotational rate constant $k(\text{sec})^{-1}$ is equal to $1/(2\tau)$. [b] $\delta\nu_\infty$ is the chemical shift between the two NCH_3 groups which would exist in the absence of rotation about the C–N bond.

it is generally recognized that total analysis of the NCH_3 high-resolution pmr line shape is required to obtain the most accurate rate constants.[6-8,11,12]



1

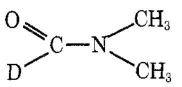
Spin coupling between R and the two NCH_3 groups must either be eliminated or taken into account in the line shape equations.[5,6,8] In our studies of amides and related derivatives of the general structure 2, we found that



2

the deuterium substitution shown minimized coupling to the extent that the complete two-site exchange equations of Gutowsky and Holm[13] could be successfully used to extract accurate rate constants.[1,3-6]

This approach has now been applied to the simplest member of the series, *N,N*-dimethylformamide-d_1 (3), and the data are presented here. At least 14 studies on DMF have been reported,[7,11,13,14] but their results have been inconsistent. Only two used reliable procedures for rate-constant determination and none of these included a total line shape study where spin coupling was eliminated by deuterium substitution.[11,14j] Several years ago we demonstrated that amide barriers appeared to be correlated by a linear free energy equation of the form $\rho^*\sigma^* + SE_S$ (Figure 1).[5,12] We hoped that new data might improve the correlation for the R = H system and this was a major motivation for the study of 3.



3

Experimental Section

N,N-Dimethylformamide-d_1 was synthesized by reaction of DCO_2H with dimethylamine in benzene.[15] Dimethylamine was bubbled into 95 ml of benzene for 45 min, during which time the solution volume increased to 110 ml. To this solution cooled in an ice bath were added dropwise 15 g of DCO_2H (Stohler Isotope Chemicals; 98% deuterium labeled). The resultant mixture was stirred for an additional 0.5 hr, removed from the ice bath, and refluxed. Water generated during the reflux was collected in a Dean-Stark trap. When no more water was produced, the benzene was evaporatively distilled and the crude $DCONMe_2$ was purified by vacuum distillation (74°, 65 mm). The second fraction, constituting the majority of the reaction product, shown to be pure and *ca.* 98% deuterated by nmr, was used for the variable-temperature experiments. Nmr of DMF-d_1 (neat, TMS internal reference) showed two equal-area singlets at δ 2.79 and 2.96 and a trace singlet visible at high amplitude at δ 8.03; commercial DMF (neat, TMS internal reference) showed two equal-area multiplets at δ 2.79 and 2.95 and a broad singlet at δ 8.02; relative areas 3:3:1.

Variable-temperature spectra were recorded for the NCH_3 doublet at a sweep width of 50 Hz using a Varian A-60D nmr spectrometer. Several spectra were recorded at each temperature to assure reproducibility. The sweep width was continuously calibrated and tuning of the spectrometer was checked before and after each spectrum using the signal of the internal standard hexamethyldisilane present in low concentration. The two NCH_3 peaks coalesced at 124.5° and the ambient temperature (41°) value of $\delta\nu_\infty$ was 9.85 Hz.[16]

Temperatures were determined before and after each spectrum using the Varian ethylene glycol standard and the equation $T(°C) = 193.5 - 1.693\ \delta\nu_e$ where $\delta\nu_e$ is the chemical shift in hertz between the CH_2 and OH protons.[16]

Line shape analyses were carried out using the complete Gutowsky–Holm equations modified for different T_2 values for the two NCH_3 signals.[14c] The T_2 values were different for each peak owing to the incomplete spin decoupling and were determined from the line widths of the NCH_3 signals. The best-fit analyses were carried out as previously described and the final step involved visual matching between the experimental and computer-generated spectra of the NCH_3 protons. The kinetic data are presented in Table I.[16]

Results and Discussion

Rotational Barrier for DMF. The ambient temperature NCH_3 spectrum of 3 is compared with its undeuterated analog in Figure 2. Most of the asymmetry arising from spin coupling has been eliminated. An Arrhenius plot of the rotational kinetic data (Table I) is shown in Figure 3 and gives the activation parameters E_a, 24.3 ± 0.2 kcal/mol; log *A*, 14.6 ± 0.1; ΔS^*, +6.3 ± 0.4 eu; ΔF^*_{298}, 21.8 kcal/mol.

Table II
Activation Parameters for C–N Rotation in Pure *N,N*-Dimethylformamide

Entry	Method	E_a, kcal/mol	Log *A*	ΔS^*, eu	ΔF_{25}^*, kcal/mol	Ref
1	TLS	24.3	14.6	+6.3	21.8	This work
2	TLS	20.5	12.7	−2.3	20.6	14j
3	TLS	20.8		0.0	20.2	11
4	SE	21.6		+1.0	20.7	11
5	COMB	22.0	13.0	−1.0	21.7	14i
6	COMB	26.0	15.0	+8.1	23.0	14k
7	COMB	26.0	16.0	+12.8	21.6	14d
8	COMB	27.4	16.0	+12.8	23.0	14i

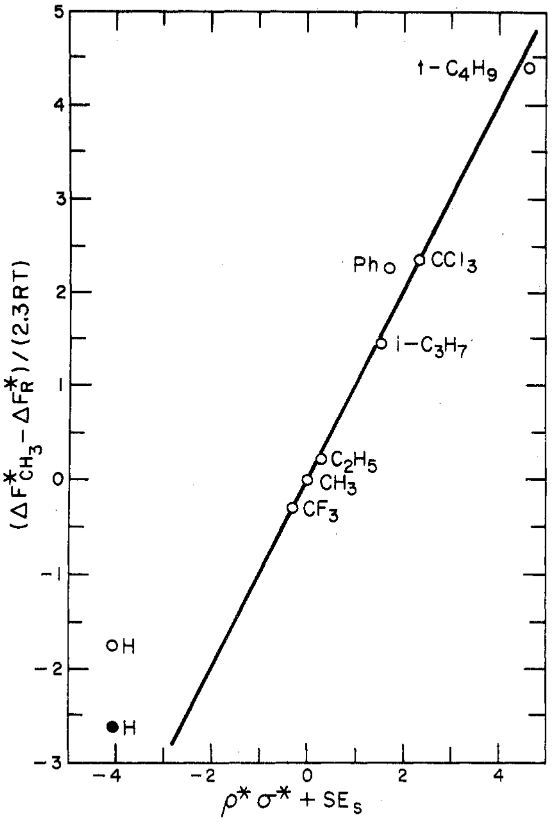


Figure 1. Linear free energy correlation for rotation about the central C-N bond for neat amides of the general structure $RC(O)NMe_2$; $\rho^* = -1.25$ and $S = -2.76$. The theoretical line has a slope of one and a zero intercept. Solid point for R = H represents new data from this study.

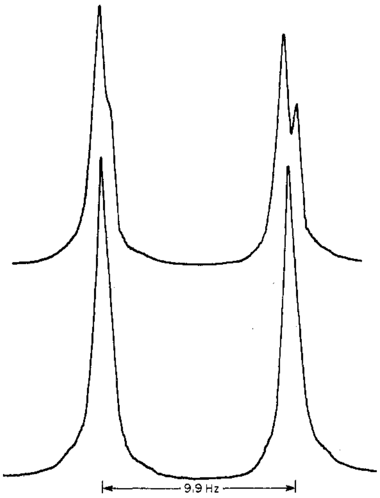


Figure 2. NMe_2 proton line shapes for neat *N,N*-dimethylformamide (top) and neat *N,N*-dimethylformamide-d_1 (bottom).

The most striking aspect of a comparison of these results with those from previous studies is that they are more similar to some of the data from studies using a combination of *approximate* methods (COMB) than to those obtained using the supposedly more reliable total line shape analysis (TLS) and spin-echo (SE) methods (Table II). Those listed as entries 2 and 3 were obtained using undeuterated DMF and it was necessary to try to correct for the spin coupling in the analysis equations. The data in the fourth entry were obtained using deuterated DMF (**3**), but there has been some indication that spin-echo studies lead to low activation parameters.

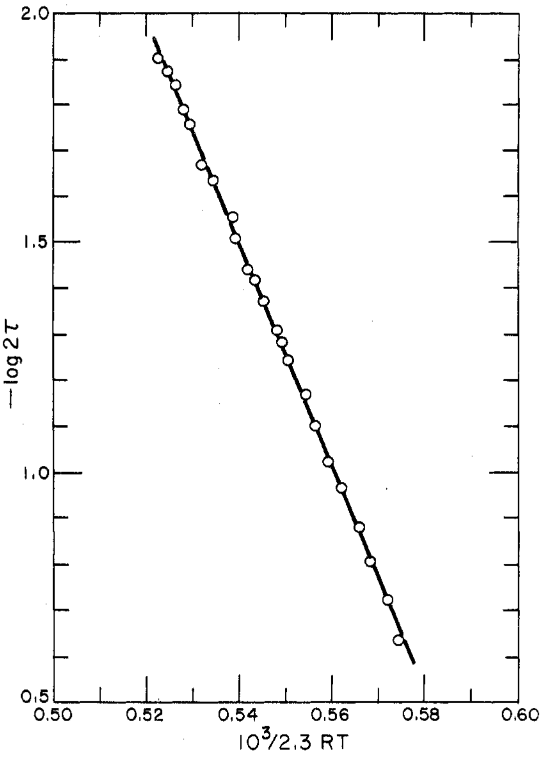


Figure 3. Arrhenius plot of the kinetic data for rotation about the central C-N bond in DMF-d_1.

Among the data in entries 5-8, only the latter set were obtained using deuterated DMF (**3**) to reduce asymmetry in the NCH_3 line shape. However, double irradiation of the formyl proton, an alternative way to eliminate the interfering coupling, was utilized to obtain the results listed as entry 5.

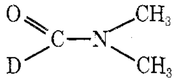
It seems unlikely that substitution of deuterium for protium on the formyl carbon of DMF would lead to a measurable change in the activation parameters. The linear free energy correlation for rotation in *N,N*-dimethylamides (Figure 1) shows that the barriers depend to similar extents on electronic and steric effects associated with R (1).[5,12] The difference in polar effects between H and D can be estimated from the relative ionization constants of DCO_2H and HCO_2H.[5,17,18] This difference is very small and is predicted to cause the rotational barrier for **3** to be 0.03 kcal/mol less than that for undeuterated DMF.[19]

The difference in steric effects could be calculated using data for the isotope effect on base-catalyzed hydrolysis of methyl or ethyl formate.[5,18] However, we have been unable to locate such data in the literature. It seems unlikely, however, that the "steric sizes" of H and D differ enough to have any significant effect on the rotational barrier. In particular it should be noted that the rotational process in DMF does not lead to rehybridization at the carbonyl carbon and that an isotope effect from rehybridization of the (D)H-CO bind is thus precluded.

From a parochial point of view we favor our data over the others in Table II. Care was taken to obtain many high-quality and reproducible spectra, to minimize asymmetry in the NCH_3 line shape, to accurately determine the temperatures at which spectra were recorded, and to obtain many data points over a reasonably large temperature range. The small positive entropy of activation (ΔS^*) is reasonable for C-N rotation of an *N,N*-dimethylamide in the pure liquid reflecting the expected increase in freedom owing to desolvation in the rotational transition state. Values of ΔS^* have often served as the primary gauge of the "goodness" of rotational barrier data because of the notorious insensitivity of values of ΔF^* to the experimental methods used to obtain the data.[1,3-6] In the case of DMF, however, the spread in values of ΔF^* seems unusually large and we do not have an explanation for this.

Our value of ΔF^* for DMF fits the linear free energy correlation[5] better than that[14j] previously used (Figure 1). However, a value above 23 kcal/mol would be required to obtain a perfect fit. While one or more of the other data points might be in error, it seems more likely that some special problem exists in fitting the R = H (1) substituent to the plot. We have noted that the chemical shift of the HCO proton for DMF remains relatively constant from below 0.1 *M* to almost 6 *M* DMF in carbon tetrachloride, but then it appears to shift downfield at higher concentrations.[20] No such change is observed for the CH_3CO protons in DMA.[20] This probably indicates some sort of special solvation interaction (perhaps hydrogen bonding) which would of course reach an extreme in the pure liquid. In this regard, it is perhaps fortuitous that any free-energy correlation exists for C–N rotation in the pure liquid *N,N*-dimethylamides. While the amide molecules are probably self-associated as dimers in each case,[20] the nature of this self-solvation cannot be identical.

A Comparison with Other Formamides. The formamide system is unique because rotational activation parameters are now available for the series of N-substituted compounds **3–6**. The data for isomers **4** and **5** were recently determined by us,[1a] while those for **6** were reported by another group.[21] However, these must be compared with care because major differences in intermolecular interactions must exist between these systems.



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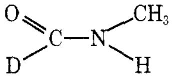
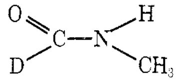


4

	3	4
E_a	24.3	23.6
Log *A*	14.6	14.0
ΔF^*	21.8	22.0



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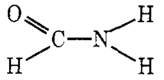
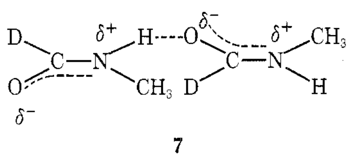


6

	5	6
E_a	23.7	19.2
Log *A*	15.0	13.9
ΔF^*	20.7	17.8

Dimethylformamide molecules probably exist mainly as dimers held together by dipolar attraction.[20] *N*-Methylformamide molecules are probably connected in short polymeric chains *via* hydrogen bonding as shown in **7**,[1]



7

and the formamide molecules are hydrogen bonded to 2-butanone, the solvent used in that study. It is possible that the extent of hydrogen bonding of **4** may be different from that of **5**; however, it should be noted that the effective solvent for both **4** and **5** is the same (90% **4** and 10% **5**).[1a]

We suggest that the NH hydrogen bonding of formamide (**6**) to 2-butanone has relatively little effect on the C–N rotational barrier because the carbonyl group of the amide is not involved. Thus the reported ΔF^* (*ca.* 18 kcal/mol) may be close to that of "monomeric" formamide. Studies carried out by us and others suggest that rotational ΔF^* values for self-associated amides (*e.g.*, neat DMF) are about 1 kcal/mol greater than those of the corresponding monomer,[14j,22] in which case the latter would be a little less than 21 kcal/mol. Finally, the interaction shown as **7** is similar to that proposed for *N,N*-dimethylacetamide in the solvent formamide, where we have estimated that the C–N rotational barrier is about 2 kcal/mol greater than that for monomeric DMA. This would indicate that monomeric **4** and **5** might have ΔF^* values of 20 and 19 kcal/mol, respectively. In summary, the inherent rotational barriers for **3–6** can be approximated as 21, 20, 19, and 18 kcal/mol, respectively.[23]

Registry No.—*N,N*-Dimethylformamide, 68-12-2.

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(16) Complete experimental details for studies of this sort have been described in detail.[1,3-6,12]

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(18) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 219–235.

(19) There is an error in the last paragraph of the discussion section of ref 5. The quantity σ_D^* should be 0.48 rather than −0.022. This gives $\Delta F_H^* - \Delta F_D^* = -2.3RT\rho^* (\sigma_D^* - \sigma_H^*) = 0.03$ kcal/mol where $\sigma_H^* = 0.50$ and $\rho^* = -1$.

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(22) R. C. Neuman, Jr., and V. Jonas, *J. Org. Chem.*, **39**, 929 (1974).

(23) We have learned from Professor A. Mannschreck that coalescence temperature studies on DMF and DMF-d_1 support our contention that deuterium substitution does not effect the C–N rotational activation parameters (E. Keck, Doctoral Dissertation, Universität, Heidelberg, 1970).