Registry No.—1, 7541-63-1; 1 DNPH, 7541-64-2; 2, 7541-65-3; 3, 7541-66-4; 3 DNPH, 7541-67-5; 4, 7541-68-6.

Hindered Rotation in N,N-Dimethylcarbamates

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Hindered rotation about the >N–C bond of various molecules was discovered and studied mostly by nmr methods.[1,2] In carbamates (R'R'') NCOOX hindered rotation has not been reported. In fact, Rogers and Woodbrey[2] observed no hindered rotation in two carbamates, $(CH_3)_2NCO_2CH_2CH_3$ and $(CF_3)_2NCO_2CH_3$, both as neat liquids at 25°. However, these authors did observe hindered rotation for carbamoyl chloride $(CH_3)_2NCOCl$.

The determination of the kinetic parameters of hindered rotation by nmr has been a controversial subject.[3] For instance, Whittaker and Siegel observed that the apparent activation energies (E_a) for hindered rotation in N,N-dimethylformamide[4] and in other amides[5] could be affected by a factor of up to 5, depending on the solvent used.

We studied a series of N,N-dimethylcarbamates in order to determine (a) whether hindered rotation is present in these molecules, (b) whether "true" kinetic parameters can be determined, and (c) whether these parameters can be correlated with carbamate structure and solvent interactions.

The results and conclusions of these studies are given below. The further application of these data to the calculation of the energy of activation (E_a) is now considered of doubtful value. Therefore, we are discontinuing these studies, but wished to report the findings which led us to this conclusion.

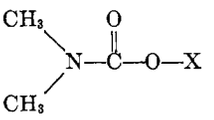
1. *All carbamates shown in the table exhibit hindered rotation about the carbonyl carbon–nitrogen bond,* as evidenced by doubling and/or broadening of the $(CH_3)_2N$ or $(CH_3CH_2)_2N$ signal at low temperatures and the coalescence of this signal at high temperatures.[6]

We also find that hindered rotation is present in $(CH_3)_2NCOF$, N,N-dimethylcarbamoyl fluoride; the $(CH_3)_2N$ proton pattern is complicated by the fact that the fluorine couples unequally to the *cis*- and *trans*-methyl protons.

2. *The parameters in the table show a strong dependence on solvent;* however, this dependence is unpredictable. For example, note that at 233°K, and for 10% solutions, $\Delta\omega$ increases in the sequence CS_2, $CHCl_3$, and $PhCH_3$ for ethyl N,N-diethylcarbamate, but increases in the sequence $CHCl_3$, CS_2, and $PhCH_3$ for cyclohexyl N,N-dimethylcarbamate.

3. *These parameters are also dependent on concentration;* note the data, for instance, in $CHCl_3$ solutions, for methyl N,N-dimethylcarbamate and cyclohexyl N,N-dimethylcarbamate (see Table I). Dipolar broadening owing to viscosity may also play a role.

TABLE I
NMR OF N,N-DIMETHYLCARBAMATES



Compd	X groups Aliphatic	Solvent	Parameters[a] t_s, °K	$\Delta\omega$	t_c, °K	t_m, °K
1	CH_3	60% in $CHCl_3$	248	0.75	260	303
		7% in $CHCl_3$	233	1.9		
2	$(CH_3)_3C$	40% in $CHCl_3$	233	B[b]		
		7% in $CHCl_3$	233	B		
3	CH_3CH_2	10% in CS_2	233	B		
	(N,N-Diethyl)[c]	10% in $CHCl_3$	233	3.4[c]		
		10% in $PhCH_3$	233	5.0		
4	Cyclohexyl	50% $CHCl_3$	233	B		313
		10% $CHCl_3$	233	0.7		
		10% CS_2	233	2.9	280	
		10% $PhCH_3$	233	5.9		
	p-(Y-Phenyl)					
5	Y = F	$CDCl_3$	281	3.05	304	336
6	Y = CH_3O[d]	$CDCl_3$	261	4.6	291	346
7	Y = NO_2	$CDCl_3$	281	5.3	312	357
8	Y = H	$CDCl_3$	260	3.0	292	333
9	Y = CH_3[d]	$CDCl_3$	260	2.2	278	348
	Others					
10	Naphthyl		281	11.35	315	373
11	6-Methyl-2-*n*-propyl-pyrimidin-4-yl (pyramat)		281	6.1	315	373
12	1-Isopropyl-3-methyl-pyrazol-5-yl (isolan)		281	5.1	311	383

[a] $\Delta\omega$ in Hz. t_s = highest temperature at which the maximum splitting of the above mentioned signal is observed; t_c = temperature of coalescence of a doublet; t_m = temperature at which no further narrowing of the coalesced line is observed; $\Delta\omega$ = peak separation at t_s. The splitting $\Delta\omega$ reflects the chemical-shift difference for the *cis*- and *trans*-methyl protons only if the t_s is higher than 233°K, the lowest temperature attainable with the equipment at hand. The line widths at t_s are made up by the natural line widths as well as by temperature-dependent contributions from coupling with N ($^2J_{HN}$) and field inhomogeneities owing to temperature gradients in the sample and the spectrometer. [b] B = broad single peak. [c] Doubling of CH_2 quartet. [d] No splitting observed at normal probe temperature (304°K).

No attempt should be made to correlate the electron-donating or -withdrawing power[7] of X groups in R_2NCOOX with t_s, t_c, t_m, or $\Delta\omega$. The only parameter suitable for such a correlation is the energy of activation (E_a). This could be obtained from Arrhenius plots. Our data could be used in principle for such a calculation of E_a. However, the results would be of little significance. Large corrections in the calculation of E_a are required when the contributions from (a) self-association in the case of neat liquids and (b) association with the solvent in the case of carbamate–solvent systems are considered. Simple inductive effects within the molecule alone are not sufficient to explain the observation that aliphatic and substituted aromatic N,N-dialkylcarbamates both exhibit hindered rotation.

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Experimental Section

All samples were run on a Varian A-60 spectrometer equipped with a variable-temperature probe. All carbamates were prepared in the same manner, and a typical preparation is given: *p*-Methoxyphenol (12.4 g) (0.1 m) was dissolved with 10.7 g (0.1 m) of dimethylcarbamoyl chloride in 30 ml of anhydrous pyridine. The solution was placed in a pressure-capped glass bottle. The bottle was heated for about 3 hr in a steam bath. The mixture was poured over ice and extracted with ether; the ether solution was washed with 10% HCl, then with $NaHCO_3$ solution, and dried for 1 hr with Na_2SO_4. Evaporation gave 12.5 g of crystalline material. Recrystallization from diethyl ether yielded *p*-methoxyphenyl N,N-dimethylcarbamate (**6**), mp 65–66° (lit.[7] mp 64–66°). In the case of *p*-fluorophenyl N,N-dimethylcarbamate (**5**), however, instead of aqueous $NaHCO_3$, 10% aqueous NaOH was necessary to wash the ethereal solution free of the phenol. After the solution was dried and evaporated with a flash evaporator, a gas chromatogram of the product showed only a trace of ether and no phenol, which would have appeared if present.

Anal. Calcd for $C_9H_{10}FNO_2$: C, 58.96; H, 5.50; N, 7.65. Found: C, 58.77; H, 5.61; N, 7.78.

p-Nitrophenyl N,N-dimethylcarbamate (**7**) was obtained in nearly 100% yield, mp 103° (lit.[8] mp 107–109°). Compounds **1**, **2**, **4**, **11**, and **12** were gas chromatographically pure. However, **12** was found to contain two products by tlc.[9]

Registry No.—**1**, 7541-16-4; **2**, 7541-17-5; **3**, 3553-80-8; **4**, 7541-19-7; **5**, 7541-20-0; **6**, 7305-10-4; **7**, 7244-70-4; **8**, 6969-90-0; **9**, 7305-08-0, **11**, 2532-49-2; **12**, 119-38-0.

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Homolytic Aromatic Substitution. VII. Phenylation of [2.2]Paracyclophane[1]

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During an extensive investigation of the chemistry of paracyclophanes Cram and co-workers observed that [2.2]paracylophane is considerably more reactive in acetylation than any of the larger members of the series.[2] Furthermore, the monoacetyl derivative of [2.2]paracyclophane is strongly deactivated toward further substitution in both rings.[3] These effects have been attributed to transannular delocalization in both types of cations, that is, to $\sigma-\pi$ overlap.[2] Since any rate enhancement in electrophilic aromatic substitution usually has a counterpart in homolytic aromatic substitution, the phenylation of [2.2]paracyclophane was studied to determine whether rate enhancement is observable in the latter type of reaction.

The required 4-phenyl[2.2]paracyclophane was prepared conveniently by direct phenylation of the parent hydrocarbon in pyridine with N-nitrosoacetanilide. Ring substitution was established by nmr spectroscopy and by comparison of retention times in glpc of a sample prepared, but not isolated in sufficient amounts to permit characterization, by treatment of 4-amino-[2.2]paracyclophane[3] with isoamyl nitrite in benzene.[4]

Quantitative measurements of reactivity were determined in the solvent pyridine–benzene using N-nitrosoacetanilide as the source of phenyl radicals.[5] We had hoped to compare N-nitrosoacetanilide and Meerwein phenylations of [2.2]paracyclophane but the insolubility of this arene in the usual solvent system, acetone–water, prevented use of the latter method of arylation. The pertinent data, determined by glpc, are given in Table I and reveal that the molecular reactivity of [2.2]paracyclophane is 33 times as great as that of benzene. In view of the fact that homolytic phenylation is one of the least selective substitution reactions known, a total rate factor of 33 is surprising. For example, both naphthalene[6] with eight and phenanthrene[7] with ten reaction sites, respectively, exhibit a total rate factor of only 16.

TABLE I

N-NITROSOACETANILIDE PHENYLATION OF [2.2]PARACYCLOPHANE

Run[a]	Biphenyl,[b] mmoles	4-Phenyl[2.2],[b] mmoles	TRF[c]	Yield, %	Recovery,[d] %
1	0.0154 ± 0.0008	0.00531 ± 0.0026	32.5 ± 2.8	4.4 ± 0.2	92 ± 1
2	0.0168 ± 0.0003	0.00594 ± 0.0009	33.2 ± 1.0	5.0 ± 0.1	89 ± 3

[a] The data for each run represent an average of three determinations. [b] Based on 0.120 mmole of [2.2]paracyclophane and 11.2 mmoles of benzene; see the Experimental Section for details. [c] Total rate factor. [d] Recovery of [2.2]paracyclophane including 4-phenyl[2.2]paracyclophane.

A total rate factor of 33 in the phenylation of [2.2]-paracyclophane is equivalent to a partial rate factor of 25; *i.e.*, each position in [2.2]paracyclophane is 25 times as reactive as a position in benzene. However, it can be argued that the usual concept of partial rate factor is not strictly applicable in assessing the reactivity of [2.2]paracyclophane. For example, there is compelling evidence that the transition state for radical addition to arenes is one in which the attacking radical is oriented essentially perpendicular to, rather than in, the nodal plane.[6,8,9] If the phenylation of [2.2]paracyclophane is mechanistically analogous, each position in this hydrocarbon is exposed to reaction at only one face of the nodal plane while each site in ordinary arenes is doubly exposed. Therefore, in homolytic phenylation the reactivity at each position in [2.2]paracyclophane

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