"Solvent Friction" and the Entanglement of Long Hydrocarbon Chains

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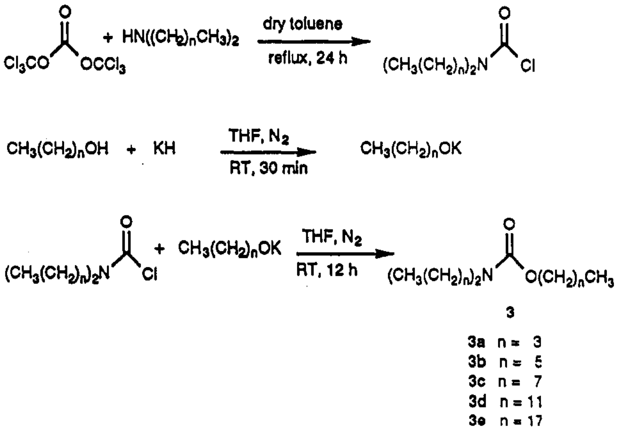
Summary: Rotation about the R_2N–COOR bond in carbamates with three alkyl chains (butyl through octadecyl) was investigated by NMR. Even solvents such as hexadecane and mineral oil did not substantially impede the rotation, revealing a surprising absence of "solvent friction" induced by chain entanglement. Possible explanations at the molecular level and the relevance to membrane systems are discussed.

Micelles and membrane bilayers adsorb and embed guest molecules within a sea of hydrocarbon chains.[1] It was natural to wonder if such an environment might provide a dynamic, solvent-induced impediment to internal rotation ("solvent friction").[2] One might expect that the guest molecules, particularly those which themselves possess long chains, would experience restricted motional freedom according to the extent of chain entanglement. A literature search revealed a surprisingly meager body of information on the subject. This led to our own experiments described herein.

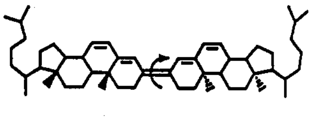
Molecular dynamics calculations on trans ⇌ gauche interconversions detected little rate difference between *n*-butane dissolved in a fluid solvent and in a solid matrix.[3] Similarly, rotation rates about an amide linkage or an azobenzene unit change little when the functionalities are incorporated into a polymer chain.[4,5] It was concluded from the polymer data that rotation about a bond involves many small oscillations in the internal angles of rotation; incorporation of the bond into a long chain retards equally both the approach to the transition state and return to the ground state.

Rotation of the vinyl group of 2-vinylanthracene was shown to have no dependency on solvent viscosity.[6] Propenyl- and butenylanthracenes displayed only a mild sensitivity to viscosity (rotation rates decreasing by a factor of less than 2 when the solvent was changed from heptane to hexadecane). The proton spin-lattice relaxations of poly(ethylene oxide), governed by segmental rotations, vary linearly with solvent viscosity.[7] The quantum yield of trans → cis photoisomerization of stilbene decreases with increasing viscosity, an effect ascribed to an expanded molecular volume somewhere along the photoconversion pathway.[8] The normally nonfluorescent *cis*-stilbene becomes strongly fluorescent in highly viscous media; it is claimed that viscous solvents reduce the probability and amplitude of the twisting and out-of-plane bending modes about the central double bond.[9,10]

Scheme I



Thermal syn–anti isomerization of 1 and 2 in benzene was shown to occur 78 times faster for the former polyene.[11] It is now believed that the difference lies in an alkyl substituent effect and that solvent friction plays little role here.[12]



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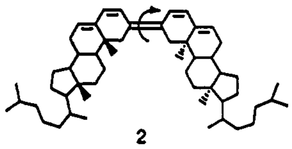

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None of the above examples addresses the situation where solvent friction is created by entangled chains as might occur within a micelle or membrane. We were, consequently, led to synthesize a series of carbamates each having three chains varying from 4 to 18 carbons in length (Scheme I).

The compounds were dissolved in one of four solvents (*n*-hexane, *n*-dodecane, *n*-hexadecane, or mineral oil with viscosities at 25 °C of 0.3, 1.4, 3.1, and ca. 40 cP, respectively) and examined, by dynamic NMR, for their rotational rates about the R_2N–COOR bond.[14] The question, then, was whether solvent friction, resulting from entanglement of carbamate and solvent chains, would inhibit (or prevent) rotational equilibration of the N-alkyl groups. 1-Adamantylethyl *N*,*N*-bis(1-adamantylethyl)carbamate 4 served as a control.[13]

^{1}H-NMR (500 MHz) of the two α-*N*-methylenes of 20 mM 3c in *n*-hexane at −15 to +50 °C are given in Figure 1. At −15 °C one sees two distinct triplets centered at 3.71 and 3.75 ppm. The methylene triplets coalesce into a broad single peak at +20 °C. Further warming to +50 °C renders

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[1] (a) Menger, F. M. *Acc. Chem. Res.* 1979, *12*, 111. (b) Menger, F. M. *Angew. Chem., Int. Ed. Engl.* 1991, *30*, 1086.

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[3] Rosenberg, R. O.; Berne, B. J.; Chandler, D. *Chem. Phys. Lett.* 1980, *75*, 162.

[4] Miron, Y.; McGarvey, B. R.; Morawetz, H. *Macromolecules* 1969, *2*, 154.

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[6] (a) Flom, S. R.; Nagarajan, V.; Barbara, P. F. *J. Phys. Chem.* 1986, *90*, 2085. (b) Barbara, P. F.; Jarzeba, W. *Acc. Chem. Res.* 1988, *21*, 195.

[7] Liu, K.-J.; Anderson, J. E. *Macromolecules* 1970, *3*, 163.

[8] Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* 1968, *90*, 12.

[9] Sharafy, S.; Muszkat, K. A. *J. Am. Chem. Soc.* 1971, *93*, 4119.

[10] For important recent papers on the intramolecular dynamics of stilbene see: Saltiel, J.; Sun, Y-P. *J. Phys. Chem.* 1989, *93*, 6246. Nikowa, L.; Schwarzer, D.; Troe, J.; Schroeder, J. *J. Chem. Phys.* 1992, *97*, 4827.

[11] Doering, W. von. E.; Birladeanu, L.; Cheng, X.; Kitagawa, T.; Sarma, K. *J. Am. Chem. Soc.* 1991, *113*, 4558.

[12] Doering, W. von E.; Shi, Y.; Zhao, D. *J. Am. Chem. Soc.* 1992, *114*, 10763.

[13] All compounds were purified by column chromatography and characterized by ^{1}H-NMR, ^{13}C-NMR, FAB-MS, and elemental analysis.

[14] Lustig, E.; Benson, W. R.; Duy, N. *J. Org. Chem.* 1967, *32*, 851.

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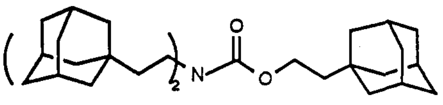

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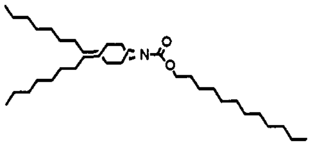
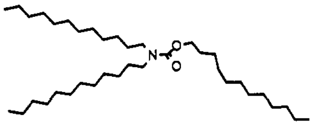
the methylenes equivalent so that the signal becomes a lone triplet.

The NMR data give no evidence for a significant solvent-friction effect even with the tri-C_{18}-carbamate dissolved in mineral oil! Thus, the four coalescence temperatures of **3a** and **3d** in *n*-hexane and *n*-dodecane are all identical (5–10 °C) and within 10 °C of **3d** in CCl_4. Broad singlets begin to show triplet fine structure[15] at 35 °C for the tri-C_4-carbamate as well as for the tri-C_{12}-carbamate in *n*-hexadecane. The corresponding value for the tri-C_{12}-carbamate in mineral oil is 55 °C, only 10 °C higher than the tri-C_6-carbamate in mineral oil. A difference between 45 and 55 °C corresponds, assuming a $\Delta G^* = 15$ kcal/mol,[16] to a rate difference of only 2. In summary, the data indicate that chain entanglements have only minor effects on R_2N–COOR rotation even under forcing conditions designed to maximize the effect.

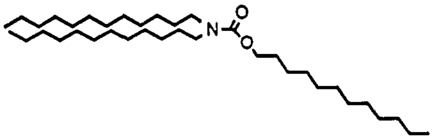
How might our results be interpreted on a molecular level? Three possibilities come to mind:

(a) Rotation about the R_2N–COOR bond could require only a "twisting" of short chain segments (a "crankshaft" motion[17]) rather than translation of entire chains.





(b) The two chains on nitrogen may form a cylindrical "bundle"; rotation would occur along the cylinder axis, possibly in concert with similarly aligned solvent molecules, thereby minimizing the viscous drag.



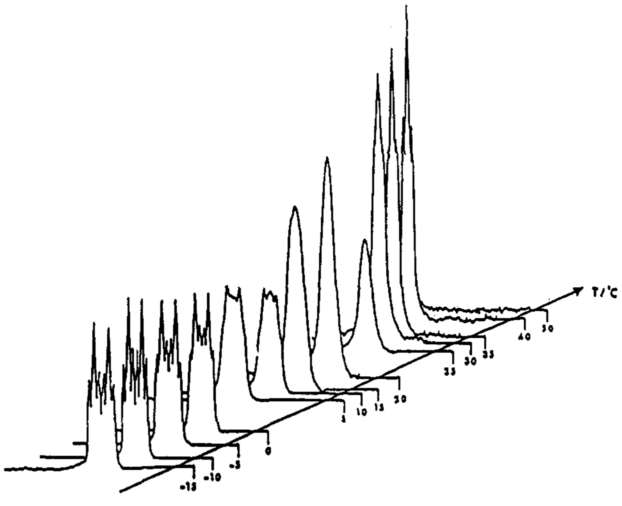


Figure 1. ^{1}H-NMR spectra (500 MHz) of the two α-*N*-methylenes of 20 mM octyl *N,N*-dioctylcarbamate in *n*-hexane at temperatures varying from −15 to +50 °C. Triplets at −15 °C are centered at 3.71 and 3.75 ppm.

(c) As previously proposed,[4,5] rotation may occur in finite steps whose forward progress and reverse "backpeddling" are equally impeded by dynamic solvent effects. In this connection, it was found that the triadamantylcarbamate rotates at a rate only slightly less rapid than the long-chained carbamates. Solvent friction seems to be a minor effect even when rotation must propel rigid and bulky substituents through a viscous solvent domain.

There is no doubt that manifestation of solvent-friction effects depends in part on the activation energy for the motion under scrutiny. In our case, the $\Delta G^* = 15.2$ kcal/mol for R_2N–COOR rotation (R = methyl).[16] It remains possible that solvent-friction effects, induced by long chains, would impede rotations of single bonds with much lower energy requirements.[18] This is however the first time, to our knowledge, that an upper limit has been established.

Acknowledgment. Work was supported by the National Science Foundation.

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(15) Singlet-to-triplet transitions were convenient to monitor since they occur at higher temperatures where solubility in mineral oil was less of a problem.

(16) Inglefield, P. T.; Kaplan, S. *Can. J. Chem.* **1972**, *50*, 1594.

(17) Helfand, E. *J. Chem. Phys.* **1971** *54*, 4651.

(18) An attempt to study tetraalkylureas, with lower rotational barriers, failed because the compounds precipitated at the lower temperatures necessary to observe the rotations by NMR.