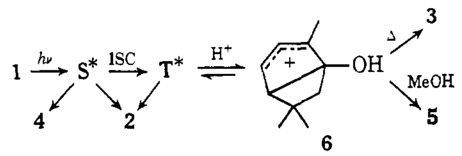
3.[9,11] Moreover, these results show that the formation of **3** and **5** with increasing acid concentration occurs solely at the expense of **2**. It would appear that the protonation of a precursor of **2** is giving rise eventually to **6** and thence **3** and **5**. A very close parallel exists between the relative geometry changes and bonding required to form **2** and **6**. Formation of **2** must arise from a disrotatory motion resulting in bonding between C_5 and C_2 in an excited state of **1**, while bonding between C_5 and C_1 is required for the formation of **6**. Unless a proton is available, it would seem that this latter bonding is either of prohibitively high energy to effectively compete, or very rapidly reverts to C_5–C_2 bonding. A possible reaction sequence is shown.



On the basis of quenching studies, Schuster[3e] has suggested that the formation of **2** in benzene occurs from both singlet (n,π^*), 60%, and triplet (π,π^*), 40%, states of **1**. Analogous results have been obtained by us in 96% dioxane–4% H_2O, although no quenching of **2** and **3** could be detected in acidic solutions.[12] Since under no conditions where unprotonated eucarvone is absorbing energy can all of **2** be diverted to **3** and **5**, it is attractive to consider that in acidic solvents these products derive from protonation of the triplet state of **1**.[14] While the exact timing of this protonation is not known,[15] it is interesting to note that the corresponding hydroxy dienylic cations undergo an exactly comparable C_5–C_1 bonding upon π,π^* excitation.[3d,4b]

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[11] It is quite possible that **6** is a ground state, ionic intermediate. *Cf.* H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962), and subsequent papers.

[12] The rate of protonation of a triplet state of **1** is expected to be sufficiently fast to effectively compete with the rate of quenching by piperylene or 1,3-cyclohexadiene.[3d,13]

[13] *Cf.* A. Weller, *Progr. React. Kinet.*, **1**, 187 (1961); E. Vander Donckt, *ibid.*, **5**, 273 (1970); M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).

[14] Hart[3c] has provided strong evidence that **4** comes from a π,π^* singlet state of **1**.

[15] Alternatively protonation may occur after formation of the ground-state zwitterion corresponding to **6**.[16] This seems less likely as the results in Table I would then demand that in the absence of a proton this zwitterion rearranges exclusively to give 2.

[16] H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966).

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On Segmental Motion in Short Aliphatic Chains

Sir:

Segmental motions along short (*e.g.*, four-carbon) aliphatic chains, as observed from ^{13}C spin-lattice relaxation (T_1) measurements, are generally not as marked as are analogous motions along linear aliphatic chains containing ≳eight carbons.[1-5] With four-carbon chains rapid overall molecular reorientation masks the internal motions. However, in cases where an *n*-butyl group is effectively anchored at one end, segmental motion can result in observed ^{13}C T_1 ratios of 3–4 between the CH_3 carbon farthest from the anchored end (the δ-CH_3 group, or in general the ω carbon) and the CH_2 carbon α to the site of restriction. Two such instances are the *n*-butylammonium ion in nonpolar solvents[3] and the butyl groups in *N*,*N*-di-*n*-butylformamide.[4]

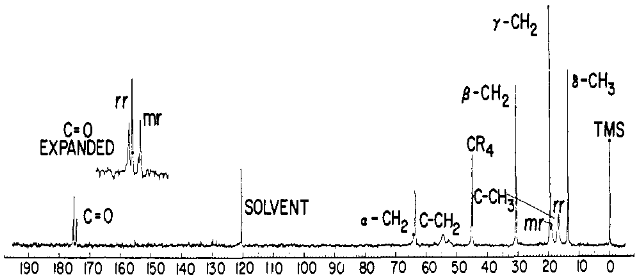

Figure 1. ^{13}C FT nmr spectrum of PBMA. Assignments noted; C–CH_3 and C–CH_2 represent main chain groups. Tacticity assignments are based on analogies with PMMA (tacticity assignments from poly(methyl methacrylate): I. R. Peat and W. F. Reynolds, *Tetrahedron Lett.*, 1359 (1972); J. Schaefer, *Macromolecules*, **4**, 99 (1971); L. F. Johnson, F. Heatley, and F. A. Bovey, *ibid.*, **3**, 175 (1970)); mr and rr refer to meso–racemic and racemic–racemic triads, respectively.

In order to further examine segmental motion along *n*-butyl chains, particularly at the limits of maximum observable internal motion, we have examined the ^{13}C relaxation behavior of a synthetic high polymer, poly(*n*-butyl methacrylate) (PBMA). The ^{13}C Fourier transform (FT) nmr spectrum of PBMA is given in Figure 1. ^{13}C relaxation data for a 25% (w/w) solution of PBMA [mol wt 143,000 by intrinsic viscosity (≡0.583) in $CCl_2{=}CCl_2$] are given in Table I. The T_1 values for the protonated main chain carbons in PBMA are very short, indicative of highly restricted overall and main-chain segmental motions. The overall molecular correlation time for this polymer, $\tau_c \simeq 3 \times 10^{-10}$ sec, is similar to τ_c for synthetic polymer systems previously studied.[6,7] The longer T_1 values for the *n*-butyl chain carbons indicate that each carbon is able to introduce substantial "rotational" contributions to butyl chain segmental motions.

In spite of the large macroscopic viscosity of this solution (~150 cP) the free ends of the short side chains in PBMA have (effective) correlation times more typical of low molecular weight (mol wt 200–400) molecules in mobile solutions (≲1 cP).

The ω/α ratio (defined as the T_1 for the terminal CH_3 carbon divided by T_1 for the α-CH_2 carbon in the chain) for this four-carbon chain is >11 with adjacent CH_2 carbons having *ca. threefold* T_1 differentials!

In the much longer 10-carbon chain of 1-decanol[1] an ω/α ^{13}C T_1 ratio of ~5 was observed while in the 15-carbon chains of sonicated dipalmitoyllecithin the ω/α ratio was *ca.* 30.[2] In these as well as other previous cases the T_1 differentials for adjacent CH_2 carbons were always ≲1.5, considerably smaller than observed in PBMA.

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[1] D. Doddrell and A. Allerhand, *J. Amer. Chem. Soc.*, **93**, 1558 (1971).

[2] Y. K. Levine, N. J. M. Birdsall, A. G. Lee, and J. C. Metcalfe, *Biochemistry*, **11**, 1416 (1972).

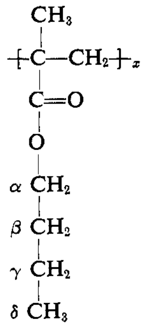
[3] G. C. Levy, *J. Chem. Soc., Chem. Commun.*, 768 (1972).

[4] G. C. Levy and G. L. Nelson, *J. Amer. Chem. Soc.*, **94**, 4897 (1972).

[5] G. C. Levy, *Accounts Chem. Res.*, **6**, 161 (1973).

[6] J. Schaefer and D. F. S. Natusch, *Macromolecules*, **5**. 416 (1972).

[7] Note that τ_c is outside of the so-called region of extreme spectral narrowing.[6]



$$-\!\!\left[C(CH_3)(C{=}O\text{–}O\text{–}CH_2CH_2CH_2CH_3)\text{–}CH_2\right]\!\!-_x$$

PBMA

Table I. Carbon-13 Spin–Lattice Relaxation Data for Poly(n-butyl methacrylate)[a]

Carbon[c]	T_1, msec[b]	τ_c, sec
Chain CH_3 mr	31	3×10^{-10}
rr	44	
Chain CH_2	~75	
Chain CR_4 mr rr	~600	
C=O mr rr	1100	
		τ_c^{eff}
α-CH_2	120	2×10^{-10}
β-CH_2	310	8×10^{-11}
γ-CH_2	760	3×10^{-11}
δ-CH_3	1390	1×10^{-11}

[a] Measured at 25.2 MHz and 35°. Sample: 25% (w/w) polymer in $CCl_2{=}CCl_2$. [b] The shorter T_1 values are reported ±15–25%; T_1 values longer than 500 msec, ±5–10%. [c] mr, meso-racemic; rr, racemic–racemic.

In principle, T_1 values resulting largely from segmental motions should be convertible directly into group rotational correlation times as in the case of rapidly rotating CH_3 groups.[8,9] However, because of the multiple degrees of freedom inherent in these motions it is not practical to calculate actual rotational rates. Usually these motions are represented as inversely proportional to the segmental motion contribution to T_1. Thus the parameter τ_c^{eff} (or τ_i for "internal" rotational correlation time) can be defined. (Of course, calculations of τ_c^{eff} for CH_3 carbons take into account three directly attached protons *vs.* two for CH_2 groups.) In the more easily defined spinning of CH_3[8,9] or phenyl groups[10] a factor of 2 in observed T_1 values for off- and on-axis C–H dipole pairs corresponds with group rotational rates 4–5 times faster than overall molecular reorientation. By analogy, values of τ_c^{eff} obtained from variations in the T_1 values of linear chain carbons are compressed by some unknown factor, which can be as large as ~3 (calculated from eq 27, ref 9, $\theta = 109.5°$). The multiple degrees of freedom inherent in the segmental motion case will tend to lower the compression factor to something intermediate between that indicated from simple internal rotation theory and the factor 1 corresponding to direct proportionality to $1/T_1$. Thus, previously reported T_1 differentials of ~1.5[1,2,5] for adjacent CH_2 carbons near the free ends in aliphatic chains may correspond to internal rotational differentials intermediate between 1.5 and 2.3 (from eq 27, ref 9). Likewise, the T_1 differentials of *ca.* 3 observed for adjacent CH_2 carbons in the n-butyl side chain of PBMA may correspond with motional factors closer to 5–10.

We are currently examining the ^{13}C T_1 behavior of this polymer as a function of concentration, solvent, and temperature in order to learn more about the phenomenon of segmental motion along short aliphatic chains. Studies of related molecular systems along with the development of new theoretical models should allow closer evaluation of the relationship between observed relaxation behavior and complex group segmental motions.

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[8] T. D. Alger, D. M. Grant, and R. K. Harris, *J. Phys. Chem.*, 76, 281 (1972), and earlier papers.

[9] A. Allerhand, R. Komoroski, and D. Doddrell, *J. Chem. Phys.*, **55**, 189 (1971).

[10] G. C. Levy, J. D. Cargioli, and F. A. L. Anet, *J. Amer. Chem. Soc.*, **95**, 1527 (1973).

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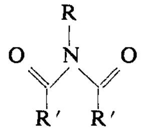
Conformational Analysis of Diformamide and Related Diacylamines[1]

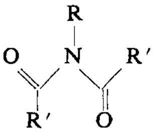
Sir:

Although the conformational properties of simple amides have been extensively studied,[2] relatively little has been reported concerning the conformations of simple imides (diacylamines). The recent report[3] on the conformation of diformamide (formimide) in the gas phase as studied by microwave spectroscopy prompts us to disclose nmr evidence we have obtained for a different conformational preference in solution.

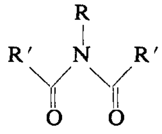
Three possible conformers are conceivable for simple symmetrical imides, (*E*,*E*)-**1**, (*E*,*Z*)-**1**, and (*Z*,*Z*)-**1**.



(*E*,*E*)-**1**



(*E*,*Z*)-**1**



(*Z*,*Z*)-**1**

On the basis of a microwave spectroscopic investigation, Steinmetz[3] has concluded that diformamide exists predominantly (if not exclusively) in the planar *E*,*Z* conformation. Nmr spectroscopy is an especially useful probe for the conformation of symmetrical imides in the solution phase since an unequivocal identification of the *E*,*Z* isomer can be made on symmetry arguments alone. While the *E*,*E* and *Z*,*Z* conformers should each exhibit single resonances for the R′ groups, the *E*,*Z* form should exhibit two resonances for the two diastereotopic R′ groups. In addition, assignments in diformamide (**1**, R = R′ = H) can be made on the basis of H–H coupling constants. The magnitudes of the cis and trans couplings across the amide bond have been measured for formamide itself (using formamide-^{15}N), *viz.*, 1.7 and 13.5 Hz, respectively.[4] The difference is substantial enough that unequivocal assignments may be made in the present instance.

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[1] Stereochemistry in Trivalent Nitrogen Compounds. XXII. Part XXI: E. H. Carlson, A. P. Schaap, and M. Raban, *J. Org. Chem.*, **38**, 1605 (1973).

[2] W. E. Stewart and T. H. Siddall, III, *Chem. Rev.*, **70**, 517 (1970); G. Binsch, *Top. Stereochem.*, 3, 97 (1968).

[3] W. E. Steinmetz, *J. Amer. Chem. Soc.*, **95**, 2777 (1973).

[4] B. Sunners, L. H. Piette, and W. G. Schneider, *Can. J. Chem.*, **38**, 681 (1960).