

**Table I.** Carbon-13 Spin-Lattice Relaxation Data for Poly(*n*-butyl methacrylate)<sup>a</sup>

Carbon <sup>c</sup>	$T_1$ , msec <sup>b</sup>	$\tau_c$ , sec
Chain CH <sub>3</sub> mr	31	$3 \times 10^{-10}$
rr	44	
Chain CH <sub>2</sub>	~75	
Chain CR <sub>4</sub> mr	~600	
rr		
C=O mr	1100	
rr		
		$\tau_c^{\text{eff}}$
$\alpha$ -CH <sub>2</sub>	120	$2 \times 10^{-10}$
$\beta$ -CH <sub>2</sub>	310	$8 \times 10^{-11}$
$\gamma$ -CH <sub>2</sub>	760	$3 \times 10^{-11}$
$\delta$ -CH <sub>3</sub>	1390	$1 \times 10^{-11}$

<sup>a</sup> Measured at 25.2 MHz and 35°. Sample: 25% (w/w) polymer in CCl<sub>2</sub>=CCl<sub>2</sub>. <sup>b</sup> The shorter  $T_1$  values are reported  $\pm 15$ –25%;  $T_1$  values longer than 500 msec,  $\pm 5$ –10%. <sup>c</sup> 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<sub>3</sub> groups.<sup>8,9</sup> 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  $\tau_c^{\text{eff}}$  (or  $\tau_i$  for "internal" rotational correlation time) can be defined. (Of course, calculations of  $\tau_c^{\text{eff}}$  for CH<sub>3</sub> carbons take into account three directly attached protons *vs.* two for CH<sub>2</sub> groups.) In the more easily defined spinning of CH<sub>3</sub><sup>8,9</sup> or phenyl groups<sup>10</sup> 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  $\tau_c^{\text{eff}}$  obtained from variations in the  $T_1$  values of linear chain carbons are compressed by some unknown factor, which can be as large as  $\sim 3$  (calculated from eq 27, ref 9,  $\theta = 109.5^\circ$ ). 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  $\sim 1.5$ <sup>1,2,5</sup> for adjacent CH<sub>2</sub> carbons near the free ends in aliphatic chains may correspond to internal rotational differentials intermediate

(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).

between 1.5 and 2.3 (from eq 27, ref 9). Likewise, the  $T_1$  differentials of *ca.* 3 observed for adjacent CH<sub>2</sub> carbons in the *n*-butyl side chain of PBMA may correspond with motional factors closer to 5–10.

We are currently examining the <sup>13</sup>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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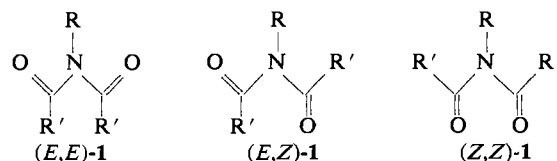
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### Conformational Analysis of Diformamide and Related Diacylamines<sup>1</sup>

Sir:

Although the conformational properties of simple amides have been extensively studied,<sup>2</sup> relatively little has been reported concerning the conformations of simple imides (diacylamines). The recent report<sup>3</sup> 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.



On the basis of a microwave spectroscopic investigation, Steinmetz<sup>3</sup> 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-<sup>15</sup>N), *viz.*, 1.7 and 13.5 Hz, respectively.<sup>4</sup> The difference is substantial enough that unequivocal assignments may be made in the present instance.

(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).

At  $-95^\circ$ , rotation about amide bonds and intermolecular N-H exchange are slow enough that spin-spin coupling is observed and the pmr spectrum of diformamide in acetone clearly reflects the presence of two of the possible isomers in a ratio of 87:13<sup>5</sup> (Figure 1).

The major isomer gives rise to a single doublet for the formyl protons at  $\delta$  9.13, while the minor isomer gives rise to two signals at  $\delta$  9.24 and 8.69. Unequivocal assignments are possible on the basis of symmetry arguments and amide coupling constants. The minor form clearly corresponds to the *E,Z* conformation. The two formyl resonances reflect a considerable difference in HNCH spin-spin coupling constants as anticipated based upon the known differences in formamide itself.<sup>4</sup> The coupling constant for the trans relationship in the *E,Z* isomer, *viz.* 10.0 Hz, is comparable to the large trans coupling observed in formamide, while the cis coupling constant is small enough that the separation between peaks is barely discernible ( $J \approx 0.7$  Hz). The major isomer is assigned the *E,E* configuration on the basis of the large coupling constant observed, *viz.* 10.2 Hz.

While the nmr results cited above provide unequivocal evidence for the preponderance of the *E,E* conformer in solution (acetone), Steinmetz has assigned the *E,Z* conformation to diformamide in the liquid state on the basis of the neat infrared spectrum.<sup>3</sup>

In order to assess the significance of the striking difference in conformational preference for the *E,E* isomer in solution, we have carried out CNDO/2 calculations on the three conformers of diformamide.<sup>6,7</sup> In all cases, we found that energy minimization is attained when the N-H proton lies in the CNC plane (planar nitrogen), in good accord with the microwave results. By contrast, formamide was found to prefer a pyramidal conformation with a small barrier to inversion at nitrogen (4 kcal/mol), also in reasonable agreement with the barrier obtained by microwave spectroscopy.<sup>8</sup> The calculations predict that the unsymmetrical *E,Z* conformation should be favored over the *E,E* conformation by about 0.9 kcal/mol and over the *Z,Z* conformation by about 1.4 kcal/mol.

Thus, the CNDO calculations are in qualitative accord with the gas-phase data but in sharp contrast with the solution results. It appears that there is a rather delicate balance in the factors responsible for the conformational preference. Indeed, the preference for the *E,E* isomer can be perturbed by *C*-methyl substitution. Thus, the low-temperature pmr spectrum of diacetamide (**1**, R = H; R' = CH<sub>3</sub>) exhibits two singlets for the acetyl methyl protons characteristic of the unsymmetrical *E,Z* isomer. The same behavior was observed for *N*-methyldiacetamide (**1**, R = R' = CH<sub>3</sub>).

(5) (a) The conformational equilibrium constant appears to be somewhat sensitive to solvent and concentration. (b) Diformamide was prepared as previously described (E. Allenstein and V. Beyl, *Chem. Ber.*, **100**, 3551 (1967)). Diacetamide and *N*-methyldiacetamide were obtained from commercial sources.

(6) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(7) Geometries used for these calculations were estimated on the basis of experimental geometries found for related compounds: formamide, C-N, 1.36 Å; C-O, 1.25 Å; C-H, 1.09 Å; N-H, 1.04 Å;  $\angle$ HCO, 119.3°;  $\angle$ NCO, 121.5°; diformamide, C-N, 1.36 Å; C-O, 1.25 Å; C-H, 1.09 Å; N-H, 1.04 Å;  $\angle$ HCO, 120°;  $\angle$ NCO, 120°;  $\angle$ CNC, 120°.

(8) C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).

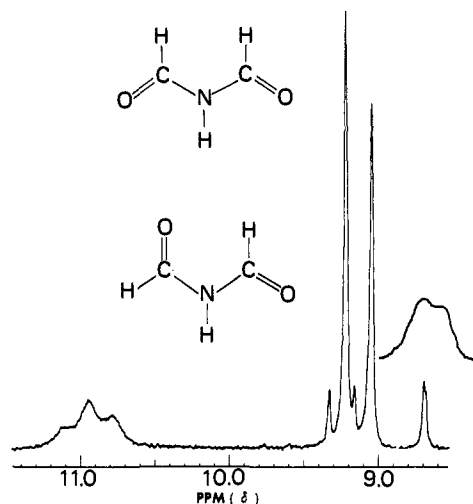


Figure 1. Low-temperature pmr spectrum of diformamide at  $-95^\circ$  in acetone solvent. The insert shows the upfield signal at 50-Hz sweep width.

There is no indication in either spectrum of the *E,E* or *Z,Z* conformer.

These results for diacetamide and *N*-methyldiacetamide are in accord with the evidence based on earlier infrared, dipole-moment, and X-ray diffraction studies.<sup>9-11</sup> Uno and coworkers<sup>9</sup> have isolated two crystalline forms of diacetamide and have assigned to them the *E,Z* and *Z,Z* conformations using infrared spectroscopy. They and others have concluded that the *E,Z* conformation is the more stable form in the crystal as well as in solution.<sup>9-11</sup> Dipole-moment data for *N*-methyldiacetamide have been interpreted in terms of the *E,Z* conformation.<sup>10</sup>

It may be noted that if diacylamines were to exist exclusively in the *E,E* or *Z,Z* form, it would not be possible to investigate their torsional barriers using nmr spectroscopy, since either of these isomers would be expected to exhibit chemical-shift equivalence of the R' groups when rotation of the amide bond is slow on the nmr time scale, as well as when rotation is rapid. Indeed, it is fortunate that for the three simple diacylamines whose conformational properties are reported here, the *E,Z* conformation is either the exclusive conformer observed or has a significant population.

The free energies of activation for topomerization in diacetamide and *N*-methyldiacetamide were determined at the coalescence point<sup>12</sup> (at 60 MHz) for the diastereotopic acetyl methyl groups (diacetamide,  $\Delta\nu = 17.7$  Hz,  $T_c = -60^\circ$ ,  $\Delta G^* = 10.8$  kcal/mol; *N*-methyldiacetamide,  $\Delta\nu = 9.2$  Hz,  $T_c = -113^\circ$ ,  $\Delta G^* = 8.2$  kcal/mol).

Two exchange processes are evident in the variable temperature nmr spectra of diformamide. Intramolecular exchange of the formyl protons occurs as the result of torsion about amide bonds, while intermolecular exchange of N-H protons leads to decoupling

(9) T. Uno and K. Machida, *Bull. Chem. Soc. Jap.*, **34**, 545, 551 (1961); **35**, 1226 (1962); **36**, 427 (1963); (b) Y. Kurodu, Y. Saito, K. Machida, and T. Uno, *Spectrochim. Acta, Part A*, **27**, 1481 (1971); (c) Y. Kurodu, Y. Saito, K. Machida, and T. Uno, *Bull. Chem. Soc. Jap.*, **45**, 2413 (1972).

(10) C. M. Lee and W. D. Kumler, *J. Org. Chem.*, **27**, 2055 (1962); *J. Amer. Chem. Soc.*, **83**, 4586 (1961); **84**, 565, 571 (1962).

(11) G. Toth, *Acta Chim. Sci. Hung.*, **64**, 101 (1970).

(12) D. Kost, E. H. Carlson, and M. Raban, *J. Chem. Soc., Chem. Commun.*, 656 (1971).

of the formyl and amide protons. In an effort to simplify the spectra so that the rate constant for intermolecular exchange could be more conveniently determined, the N-H proton was replaced with deuterium. The rate constant at the coalescence point for *N*-deuteriodiformamide was determined using complete line-shape analysis<sup>13</sup> ( $k_o(EZ \rightarrow EE) = 45 \text{ sec}^{-1}$ ,  $T_c = -23^\circ$ ,  $\Delta G^\ddagger(EZ \rightarrow EE) = 12.6 \text{ kcal/mol}$ ). It is interesting to note the fairly wide range of barriers (8.2–12.6 kcal/mol) that is evident even within this small group of compounds.

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### 9-Thiabicyclo[3.3.1]non-1-ene<sup>1,2</sup>

Sir:

Previous studies of bridgehead alkenes have resulted in the synthesis of several representatives of this class of compounds.<sup>3,4</sup> We have initiated a program for the study of the chemical properties of some bridgehead alkenes substituted with heteroatoms within the bicyclic framework,<sup>5</sup> and we recently reported the synthesis of the unusual enol ether **1**. We now report of synthesis of the sulfur congener, 9-thiabicyclo[3.3.1]non-1-ene (**2**).



An acid-catalyzed reaction of hemiketal **3** with hydrogen sulfide in aqueous solution at  $100^\circ$  for 3 days in an autoclave produced 45% of 9-thiabicyclo[3.3.1]nonan-1-ol (**4**), mp  $151\text{--}152^\circ$ , and 45% of 9-thiabicyclo-

(1) Paper VII in the Bredt's rule series. For previous papers see ref 3 and 5.

(2) From the Ph.D. dissertation of C. B. Quinn, University of Michigan, 1973.

(3) (a) J. A. Chong and J. R. Wiseman, *J. Amer. Chem. Soc.*, **94**, 8627 (1972); (b) J. R. Wiseman and J. A. Chong, *ibid.*, **91**, 7775 (1969); (c) N. M. Weinshenker and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 506 (1968); (d) G. J. Buchanan and G. Jamieson, *Tetrahedron*, **28**, 1123, 1129 (1972); (e) R. Keese and E. P. Krebs, *Angew. Chem., Int. Ed. Engl.*, **10**, 262 (1971); R. Keese and E. P. Krebs, *ibid.*, **11**, 518 (1972); (f) P. Warner, R. LaRose, C. M. Lee, and J. C. Clardy, *J. Amer. Chem. Soc.*, **94**, 7607 (1972); (g) J. E. Gano and L. Eisenberg, *ibid.*, **95**, 972 (1973); D. Lenoir, *Tetrahedron Lett.*, 4049 (1972); D. Grant, M. A. McKervey, J. J. Rooney, N. G. Samman, and G. Step, *J. Chem. Soc., Chem. Commun.*, 1186 (1972).

(4) (a) J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **92**, 948 (1970); (b) W. Carruthers and M. I. Qureshi, *Chem. Commun.*, 832 (1969); (c) N. M. Weinshenker and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 506 (1968); (d) G. J. Buchanan and G. Jamieson, *Tetrahedron*, **28**, 1123, 1129 (1972); (e) R. Keese and E. P. Krebs, *Angew. Chem., Int. Ed. Engl.*, **10**, 262 (1971); R. Keese and E. P. Krebs, *ibid.*, **11**, 518 (1972); (f) P. Warner, R. LaRose, C. M. Lee, and J. C. Clardy, *J. Amer. Chem. Soc.*, **94**, 7607 (1972); (g) J. E. Gano and L. Eisenberg, *ibid.*, **95**, 972 (1973); D. Lenoir, *Tetrahedron Lett.*, 4049 (1972); D. Grant, M. A. McKervey, J. J. Rooney, N. G. Samman, and G. Step, *J. Chem. Soc., Chem. Commun.*, 1186 (1972).

(5) (a) C. B. Quinn and J. R. Wiseman, *J. Amer. Chem. Soc.*, **95**, 1342 (1973); see also (b) P. D. Bartlett and J. L. Kice, *ibid.*, **75**, 5591 (1953); (c) E. Vogel, M. Biskup, W. Pretzer, and W. A. Böll, *Angew. Chem., Int. Ed. Engl.*, **3**, 642 (1964); (d) F. Sondheimer and A. Shani, *J. Amer. Chem. Soc.*, **86**, 3168 (1964).

[3.3.1]nonane-1-thiol (**5**),<sup>6</sup> mp  $83\text{--}85^\circ$ . Reaction of



3, X=O; Y=OH

4, X=S; Y=OH

5, X=S; Y=SH

6, X=S; Y=OSO<sub>2</sub>CH<sub>3</sub>

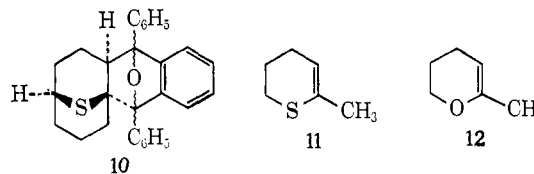
9, X=S; Y=H

hydroxy sulfide **4** with methanesulfonyl chloride and triethylamine in benzene-petroleum ether yielded 60% of methanesulfonate **6**, a stable white crystalline compound melting sharply at  $66.5\text{--}68^\circ$ . Elimination of methanesulfonic acid from **6** occurred smoothly with potassium *tert*-butoxide to give olefins **2** (65%) and **7** (1%). Evidently **7** is formed from **2** since the amount of **7** produced is proportional to the reaction time. The isomerization possibly proceeds through the allylic anion **8**.<sup>7</sup> Distillation attempts resulted in decomposi-



tion of **2**, and pure samples were obtained by preparative vpc.<sup>6</sup> Olefin **2** is a colorless liquid with a powerful penetrating odor. It is stable at ordinary temperatures in the absence of oxygen with which it reacts slowly.

Reduction of **2** with aluminum hydride<sup>8</sup> produced known **9**<sup>9</sup> in 52% yield along with four unidentified products, and hydrogenation of **2** using a large excess of 5% palladium on carbon<sup>10</sup> gave **9** in 85% yield. Reaction of **2** with 1,3-diphenylisobenzofuran produces the adduct **10**, mp  $225\text{--}228^\circ$ . Since **2** is a stable entity we assign it the *zusammen*<sup>11</sup> stereochemistry.<sup>3d</sup> Consequently we assign partial stereochemistry to Diels-Alder adduct **10** as shown. The orientation of the



oxygen bridge with respect to the sulfur bridge is presently unknown.

The spectroscopic properties of **2** provide some interesting comparisons. The infrared frequency for stretching of the carbon double bond occurs at  $1600 \text{ cm}^{-1}$ , whereas the band for 6-methyl-2,3-dihydrothiapyran (**11**) falls at  $1640 \text{ cm}^{-1}$ . Both bands are weak, as is typical of vinyl sulfides.

Table I lists the nmr chemical shifts of the vinyl protons of several vinyl sulfides. Some vinyl ethers and cyclohexene are included for comparison.

In normal untwisted vinyl ethers mixing of the non-bonding orbitals of oxygen with the  $\pi$  and  $\pi^*$  orbitals results in increased electron density at the  $\beta$  carbon and

(6) All new compounds reported gave satisfactory ir, nmr, and mass spectra and acceptable elemental analyses.

(7) A similar isomerization is observed during the addition of methyl-lithium to bicyclo[3.3.1]non-1-ene.<sup>4b</sup>

(8) J. M. Coulter and J. M. Leurs, *Tetrahedron Lett.*, 3715 (1966).

(9) (a) E. J. Corey and E. Block, *J. Org. Chem.*, **31**, 1663 (1966); (b) E. D. Weil, K. J. Smith, and R. J. Gruber, *ibid.*, **31**, 1669 (1966).

(10) L. Bateman and F. W. Shipley, *J. Chem. Soc.*, 2888 (1958).

(11) See IUPAC Tentative Rules for Nomenclature in Organic Chemistry, Section E-2, *J. Org. Chem.*, **35**, 2849 (1970).