

Figure 1. Polarized single-crystal reflection spectra of 6-azauracil obtained with light whose electric vector vibrates parallel to *a* (---), *b* (- - -), *c* (—), and a direction in the *ab* plane 60° from the *a* axis (····). These spectra were measured on the (010), (100), and (120) faces, and the *c*-axis curve is that obtained on all three of these faces. The (····) curve is referred to in the text as the *ab* spectrum.

Preliminary¹¹ polarized reflection spectra of the three well-developed faces that occur in the zone containing *c* have been obtained using a microspectrophotometer described elsewhere.¹² Figure 1 shows the spectra obtained with the incident radiation polarized along the four distinct principal directions available in these faces. The *ab* spectrum is expected to be an admixture of the *a*-axis and *b*-axis spectra, and, since the *a*-axis curve shows essentially no absorption, the *ab* spectrum should be an attenuated *b*-axis spectrum. This expectation is fulfilled, attesting to the consistency of the data presented here.

The *c*-axis spectrum contains considerable intensity to the blue of the *b*-axis band (compare *ab* and *c* spectra). This observation is consistent with a distinctly new band appearing in *c* (hereafter called band II) and another band (band I) appearing predominantly in the *b*-axis spectrum but also along *c*. That the *c*-axis spectrum gives evidence of a second transition in this region is supported even more strongly by the absorption curves provided by the Kramers–Kronig transformation¹² of the reflection spectra. One thus finds the *c* absorption peaking at 39 kK with a crystal epsilon of 6500 $M^{-1} \text{ cm}^{-1}$ and that for *b* peaking at 36 kK with $\epsilon_{\text{crystal}} = 11,700 M^{-1} \text{ cm}^{-1}$. Both curves appear composite and can be resolved into consistent I and II bands. Relating the intensities of these bands and the detailed molecular orientations in the crystal gives, in terms of DeVoe and Tinoco's convention,¹³ preliminary transition moment directions of 9° for band I and -35° for band II.

The present results raise the question of why one does not find evidence for the composite nature of the low-energy uracil band in previous crystal studies. The answer could lie in the removal of an angular or energetic degeneracy, the intensification of a weak band, or a combination of these factors occurring in 6-azauracil.

(11) Refinement of these spectra will primarily consist of extension to both longer and shorter wavelengths and studies on several additional crystals.

(12) (a) B. G. Anex, *Mol. Cryst.*, **1**, 1 (1966); (b) L. J. Parkhurst and B. G. Anex, *J. Chem. Phys.*, **45**, 862 (1966).

(13) H. DeVoe and I. Tinoco, Jr., *J. Mol. Biol.*, **4**, 500 (1962).

In any event, the sensitivity of transition moment direction to molecular structure in the uracils⁴ and the general sensitivity of the purine and pyrimidine spectra to environment would indicate that one should be alert to other manifestations of the complexity of the 260- $m\mu$ band in the uracils as such and the biologically significant compounds of which they are components.

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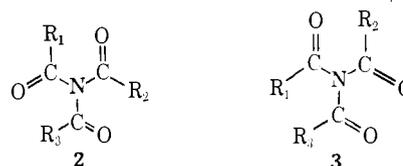
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Stereochemistry in Trivalent Nitrogen Compounds. XXIII. Restricted Rotation in a Triamide (Triacylamine)¹

Sir:

While nmr spectroscopy has long been used to study torsional barriers in simple amides,² only recently have barriers to conformational interchange in representative imides been reported.¹ We now wish to describe the results of an nmr study of *N*-acetylformimide (*N,N*-di-formylacetamide) (**1**), the first triamide in which the barrier to torsion about amide bonds has been measured using nuclear magnetic resonance spectroscopy.

Two planar conformations, **2** and **3**, are possible for



an acyclic triamide in which the three acyl groups are identical ($R_1 = R_2 = R_3$). The more symmetrical conformation, **2**, has the symmetry of a triskelion (C_{3h}), while the other is less symmetrical (C_s). The symmetry of the triskelion conformation assures that the nmr spectrum would exhibit only a single resonance for the three R groups, even under conditions of slow rotation about the amide groups, while all three R groups in the C_s conformation are diastereotopic, and three resonances would be expected if rotation about amide bonds were slow on the nmr time scale.

Conformation **2** appears to be more probable on several grounds. We may view pairs of acyl groups in **2** and **3** as imide fragments, e.g., $R_1\text{CONCOR}_2$. Three imide fragments can be constructed from the acyl groups of the triamide, and, for **2**, each of the fragments has the *E,Z* relationship. In contrast, the pairwise relationships of **3** are *E,Z* ($R_1\text{CONCOR}_2$), *E,E* ($R_1\text{CONCOR}_3$), and *Z,Z* ($R_2\text{CONCOR}_3$). Significantly, the *E,Z* relationship is generally favored in imides. Formimide itself exhibits both *E,E* and *E,Z* conformations in solution, with a preponderance of the former.¹ The *Z,Z* conformation, on the other hand, seems to be significantly destabilized by dipole–dipole interactions and has been assigned to diacylamines in solution only in

(1) For part XXII see E. A. Noe and M. Raban, *J. Amer. Chem. Soc.*, **95**, 6118 (1973).

(2) W. E. Stewart and T. H. Siddall, III, *Chem. Rev.*, **70**, 517 (1970)

Table I. Barriers and Related Parameters for Amides Containing One, Two, and Three Acyl Groups

Compound	Solvent	T_0 , °C	k_c , sec ⁻¹	ΔG^\ddagger , kcal/mol (kJ/mol)	Ref
HCONH ₂	Diglyme			17.8 (77)	5
(HCO) ₂ NH	Acetone	-23	45	12.6 (53)	1
(HCO) ₂ NCOCH ₃	CHClF ₂	-126 ^a	20	7.5 (31) ^a	This work

^a We regard ΔG^\ddagger as accurate to ± 0.2 kcal/mol (± 1 kJ/mol). The main source of error in the free energy of activation derives from the uncertainty in the sample temperature. Temperatures were measured with a copper-constantan thermocouple and are estimated to be accurate to $\pm 2^\circ$.

the case of dipivalamide),³ in which nonbonded (steric) interactions are expected to make the *E,E* and *E,Z* conformations unfavorable. In triformamide ($R_1 = R_2 = R_3 = H$), the existence of the *Z,Z* relationship in **3** is expected to cause this form to be of higher energy than **2**. Indeed, Allenstein⁴ has assigned the triskelion conformation to this compound in the solid state on the basis of its infrared and Raman spectra. For triamides with groups larger than hydrogen, the conformations in which the larger groups are components of imide segments having the *E,E* configuration are likely to be further destabilized because of steric interactions between the R groups of these segments.

If triformamide were to adopt conformation **2** in solution, it would exhibit an nmr spectrum invariant with respect to the rate of torsion about amide bonds. As a consequence, we chose the less symmetrical compound, *N*-acetylformimide (**1**), for our nmr study. Allenstein, *et al.*,⁴ have suggested that **1** adopts conformation **2** ($R_1 = CH_3$, $R_2 = R_3 = H$) on the basis of the similarity between its infrared and Raman spectra and those of triformamide. In addition to the single triskelion conformation, three conformations of type **3** are possible, corresponding to the replacement of R_1 , R_2 , or R_3 by CH_3 . Inspection of all four possible conformations of **1** shows that the formyl protons in each form are diastereotopic and would be expected to exhibit chemical shift nonequivalence at temperatures where torsion about amide bonds is slow on the nmr time scale.

The pmr spectrum of **1** in chlorodifluoromethane at -84° consists of two singlets at δ 9.45 and 2.61 for the formyl and methyl protons, respectively, indicating rapid conformational interchange at this temperature. On cooling, torsion about amide bonds becomes slow on the nmr time scale, and the resonance at lower field broadens and splits by -142° into two peaks of equal intensity centered at δ 9.47 and separated by 10.0 Hz at 60 MHz (Figure 1). The rate constant at the coalescence point was determined using complete line shape analysis (Table I).

The slow-exchange spectrum is consistent with the sole presence of the triskelion conformation suggested by the infrared and Raman studies⁴ but would not rule out the sole presence of a single nontriskelion conformation. If conformation **2** is, in fact, the correct conformation, then topomerization requires rotation about all three amide bonds. Based on the behavior of amides and imides, it seems likely that the transition state involves torsion about a formyl group, since acetamides and diacetamides generally exhibit lower barriers than the corresponding formyl compounds.^{1,2}

Comparison of the barrier in **1** with those in form-

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(4) E. Allenstein, V. Beyl, and W. Eitel, *Chem. Ber.*, **102**, 4089 (1969).

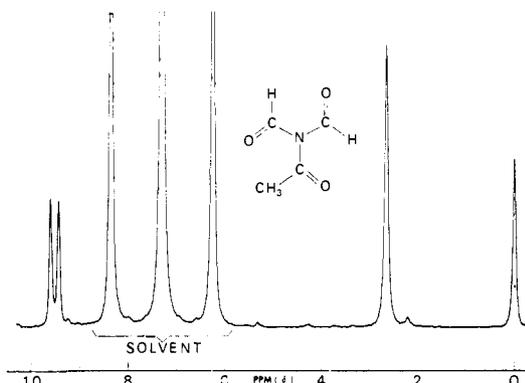


Figure 1. Pmr spectrum of *N*-acetylformimide (**1**) at -142° in chlorodifluoromethane solution (60 MHz). A small peak at δ 2.2 is due to acetic anhydride, which is present as an impurity.

amide⁵ and formimide¹ affords a measure of the effect of successive replacement of formamide hydrogens by acyl groups (Table I). Although increased conjugation attenuates the amide barrier, it is noteworthy that a substantial barrier, well within the range amenable to determination by nmr spectroscopy, remains even with three carbonyl groups in conjugation with the nitrogen lone pair.

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(5) T. Drakenberg and S. Forsen, *J. Phys. Chem.*, **74**, 1 (1970).

(6) A. P. Sloan Fellow, 1972-1974.

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On the Use of Tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium(III) as a Shift Reagent for Carboxylic Acids and Phenols

Sir:

Since the initial application of the lanthanide shift reagent europium(III) dipivaloylmethanoate ($Eu(dpm)_3$) to organic compounds by Hinckley,¹ numerous applications to structural problems of this class of compounds in organic chemistry have been found.

In an early study on the range of applicability of the reagent, it was stated that $Eu(dpm)_3$ was unsuited for use with carboxylic acids and phenols because it was slowly decomposed by these classes of compounds.² This statement seems to have been taken as a general

(1) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

(2) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).