

Strain in the fused ring has a definite influence on ^{13}C - ^{19}F couplings¹⁷ (e.g., cf. C_4 and C_3 in entries 10 and 11), but these and related results will be discussed fully at a later date.

Acknowledgments. The authors are grateful to the Australian Research Grants Committee for funding parts of this research and spectrometer components. The sample of *o*-di-*tert*-butylbenzene was kindly provided by Professor E. M. Arnett, University of Pittsburgh. We thank Professor H. Günther for some unpublished information.

(17) For a discussion of steric influences on these couplings see S. L. Manatt, M. A. Cooper, C. W. Mallory, and F. B. Mallory, *J. Amer. Chem. Soc.*, **95**, 975 (1973).

(18) Queen Elizabeth II Research Fellow at University of New England 1973-1974.

(19) Address correspondence to this author at the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

William Adcock, B. D. Gupta, T. C. Khor
School of Physical Sciences, Flinders University
Adelaide, South Australia, Australia

David Doddrell,¹⁸ David Jordan
Department of Organic Chemistry, University of New England
Armidale, New South Wales, Australia

William Kitching*¹⁹
Department of Chemistry, University of Queensland
St. Lucia, 4067, Queensland, Australia

Received October 27, 1973

On the Degeneracy of the 260-m μ Band of the Uracils¹

Sir:

Energy-transfer processes and optical properties of DNA and RNA are intimately related to the interactions among their constituent purine and pyrimidine bases. Theoretical treatments of these interactions in turn typically require a knowledge of the energies of the electronic transitions of the individual bases and the associated transition moments.² Although considerable effort has been directed toward the determination of these latter quantities, the picture is not entirely clear concerning even the lowest energy allowed transitions for some of the bases. In particular, although theoretical and experimental studies have pointed to the 260-m μ band of the uracils having associated with it two $\pi \rightarrow \pi^*$ transitions,³ polarized single-crystal studies have failed to reveal more than one transition in this region.⁴ With this situation in mind, a comprehensive X-ray crystallographic and single-crystal spectral investigation of 6-azauracil has been undertaken. We here report a summary of the crystallographic work coupled with preliminary reflection spectra that contain important evidence concerning the 260-m μ band.

6-Azauracil was obtained from Nutritional Biochem-

(1) This work has been in part supported by grants from the National Institutes of Health and the Warner-Lambert Pharmaceutical Co.

(2) For instance: (a) E. Brown and E. S. Pysh, *J. Chem. Phys.*, **56**, 31 (1972); (b) H. DeVoe and I. Tinoco, Jr., *J. Mol. Biol.*, **4**, 518 (1962).

(3) (a) D. W. Miles, R. K. Robins, and H. Eyring, *Proc. Nat. Acad. Sci. U. S.*, **57**, 1138 (1967); (b) W. Voelter, R. Records, E. Bunnenberg, and C. Djerassi, *J. Amer. Chem. Soc.*, **90**, 6163 (1968); (c) D. W. Miles, M. J. Robins, R. K. Robins, M. W. Winkley, and H. Eyring, *ibid.*, **91**, 824 (1969); (d) L. B. Clark and I. Tinoco, Jr., *ibid.*, **87**, 11 (1965); (e) H. Berthod, C. Giessner-Prettre, and A. Pullman, *Theor. Chim. Acta*, **5**, 53 (1966); (f) H. Berthod, C. Giessner-Prettre, and A. Pullman, *Int. J. Quantum Chem.*, **1**, 123 (1967).

(4) (a) R. F. Stewart and N. Davidson, *J. Chem. Phys.*, **39**, 255 (1963); (b) W. A. Eaton and T. P. Lewis, *ibid.*, **53**, 2164 (1970).

icals Corporation (Cleveland, Ohio). Suitable crystals were prepared through slow evaporation of aqueous solutions. The compound crystallizes in the orthorhombic space group P_{212121} with cell dimensions (and estimated standard deviations) as follows: $a = 5.027$ (1), $b = 17.570$ (2), and $c = 4.867$ (1) Å. The crystals are plates elongated along c with (010), (100), (120), and (021) as prominent faces.

A total of 608 reflections were measured on a General Electric XRD-490 system using filtered Cu $K\alpha$ radiation. In addition to the usual Lorentz-polarization and scaling corrections an $\alpha_1 - \alpha_2$ splitting correction was applied,⁵ and a cylindrical absorption correction (maximum <5%) was made. Direct methods were utilized in determining the crystallographic structure.^{6,7} Additional least-squares refinement with all atoms using $1/\sigma^2$ weights ultimately converged to an R value of 0.046.

Table I reports the atomic coordinates obtained for

Table I. Final Positional Parameters for 6-Azauracil^a

Atom	x	y	z
N(1)	0.8097 (6)	0.1906 (1)	0.2361 (6)
C(2)	1.0290 (6)	0.1507 (2)	0.3141 (7)
N(3)	1.0772 (5)	0.0857 (1)	0.1643 (6)
C(4)	0.9275 (6)	0.0629 (2)	-0.0567 (6)
C(5)	0.7039 (6)	0.1122 (2)	-0.1146 (7)
N(6)	0.6476 (5)	0.1727 (1)	0.0226 (6)
O(2)	1.1736 (5)	0.1692 (1)	0.5067 (5)
O(4)	0.9804 (4)	0.0051 (1)	-0.1870 (5)
H(1)	0.7802 (81)	0.2394 (19)	0.3286 (75)
H(3)	1.2217 (64)	0.0562 (17)	0.2181 (78)
H(5)	0.5798 (61)	0.0970 (17)	-0.2546 (71)

^a The numbering scheme followed here for the ring atoms is given in ref 4a, and the indices for the oxygen and hydrogen atoms are the same as the ring atoms to which they are bonded.

6-azauracil. These data lead to interatomic distances and angles involving nonhydrogen atoms that possess estimated standard deviations of less than 0.004 Å and 0.3°, respectively. Analogous esd values for the hydrogen atoms are 0.03 Å and 2.0°, respectively. The molecule is planar, showing an average esd value of 0.008 Å from the best least-squares plane for the eight carbons, nitrogens, and oxygens and 0.07 Å for the hydrogens.

The bond lengths derived from the data of Table I differ from those most recently reported for uracil⁸ by at most several hundredths of an ångström unit and show similar agreement for several related compounds.⁹ The bonding reported here thus appears to be that characteristic of the uracils, and the spectral results should consequently hold a measure of generality.¹⁰

(5) A. Tulinsky, C. R. Worthington, and E. Pignataro, *Acta Crystallogr.*, **12**, 623 (1959).

(6) J. Karle, H. Hauptman, and C. L. Christ, *Acta Crystallogr.*, **11**, 757 (1958).

(7) Program MULTAN, P. Main and M. M. Woolfson, Department of Physics, University of York, England, and G. Germain, Laboratoire de Chimie Physique, Université de Louvain, Leuven, Belgium, May 1971.

(8) R. F. Stewart and L. H. Jensen, *Acta Crystallogr.*, **23**, 1102 (1967).

(9) (a) K. Hoogsteen, *Acta Crystallogr.*, **16**, 907 (1963); (b) K. Hoogsteen, *ibid.*, **16**, 28 (1963); (c) R. Gerdil, *ibid.*, **14**, 333 (1961); (d) J. A. Carrabai and M. Sundaralingam, *Biochemistry*, **10**, 292 (1971); (e) T. Sakurai and M. Okunuki, *Acta Crystallogr.*, **Secr. B**, **27**, 1445 (1971).

(10) In this respect, the similarity of the spectra of 6-azauracil and uracil itself should be noted (ref 3d).

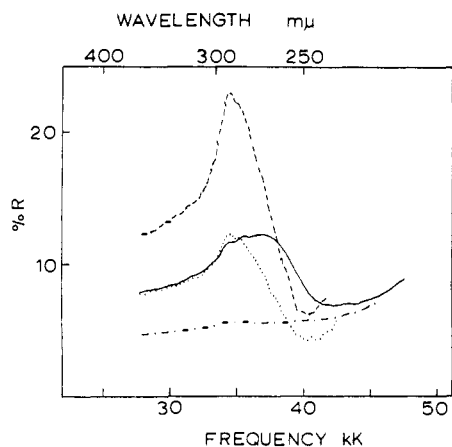


Figure 1. Polarized single-crystal reflection spectra of 6-azauracil obtained with light whose electric vector vibrates parallel to a (---), b (- - -), c (—), and a direction in the ab plane 60° from the a axis (····). These spectra were measured on the (010), (100), and (120) faces, and the c -axis 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 $6500 M^{-1} cm^{-1}$ and that for b peaking at 36 kK with $\epsilon_{crystal} = 11,700 M^{-1} cm^{-1}$. 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 μ band in the uracils as such and the biologically significant compounds of which they are components.

Joe N. Brown, Louis M. Trefonas
Anthony F. Fucaloro, Basil G. Anex*

Department of Chemistry, Louisiana State University in New Orleans
New Orleans, Louisiana 70122

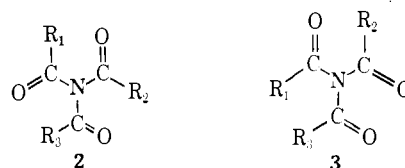
Received July 9, 1973

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., $R_1CONCOR_2$. 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 ($R_1CONCOR_2$), E,E ($R_1CONCOR_3$), and Z,Z ($R_2CONCOR_3$). 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)