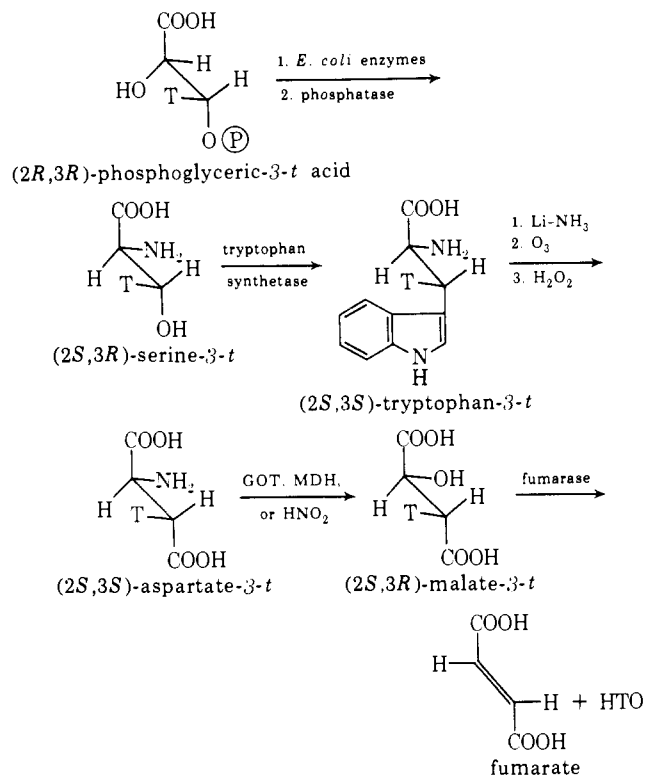


Scheme I



G. W. Kirby, University of Glasgow, for samples of (3R)- and (3S)-*D,L*-tryptophan-3-*t* and to Mr. Detlef Onderka, Purdue University, for the preparation of some of the tritiated phosphoglyceric acid samples. Financial support by the National Institutes of Health (Research Grant GM 18852 and Research Career Development Award GM 42389 to H. G. F.) is gratefully acknowledged.

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### Concerning the Carbon-13 Chemical Shifts of Benzocycloalkenes

Sir:

Recently Maciel and coworkers reported<sup>1</sup> carbon-13 chemical shift assignments for a number of benzocycloalkenes. The coherent <sup>1</sup>H spin decoupling technique was employed for assignments in indane, benzocyclobutene, benzocyclopropene, and *o*-di-*tert*-butylbenzene, but this necessitated acceptance of the previously reported <sup>1</sup>H aromatic assignments,<sup>2,3</sup> in no case established.<sup>4</sup> In view of the great interest in the effects of strain on spectroscopic (and other) properties<sup>5</sup> and

(1) E. L. Motell, D. Lauer, and G. E. Maciel, *J. Phys. Chem.*, **77**, 1865 (1973).

(2) M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, **92**, 1605 (1970).

(3) S. Castellano and R. Kostelnik, *Tetrahedron Lett.*, 5211 (1967).

(4) The main thrust of ref 2 and 3 concerned variations in <sup>1</sup>H-<sup>1</sup>H coupling with structural factors. Explicit assignment is not possible from an AA'BB' analysis, and in ref 2 the assignments were regarded as tentative, on the assumption of stronger coupling between methylene protons and H<sub>α</sub> (i.e., ortho protons).

(5) For leading references see (2) above.

the use of hydrocarbon data to test theories of nuclear shielding,<sup>6</sup> the need for reliable <sup>13</sup>C data is clear. We wish to report such data.

Previously we assigned<sup>7</sup> the aromatic carbons of indane and benzocyclobutene from data for 5-fluoroindane and 4-fluorobenzocyclobutene, readily understood by considerations of <sup>13</sup>C-<sup>19</sup>F couplings and fluorine contributions to carbon screenings in aryl systems.<sup>7,8</sup> These assignments have now been confirmed by tactical introduction of deuterium into the 5 position of indan<sup>9</sup> and the 4 (88%) and 3 (12%) positions of benzocyclobutene<sup>10</sup> by standard transformations of amino or halogeno precursors. 3-Fluorobenzocyclobutene<sup>11</sup> has also been synthesized and yields data completely concordant with our previous assignments.<sup>12</sup> Furthermore, our examination of the <sup>13</sup>C satellite patterns in the <sup>1</sup>H spectra of benzocyclobutene and *o*-di-*tert*-butylbenzene<sup>13</sup> demonstrates the previous order of <sup>1</sup>H chemical shifts should be reversed and *ipso facto* any experimentally sound <sup>13</sup>C assignments,<sup>14</sup> based on these previous assignments. (The <sup>1</sup>H spectra of the deuterated benzocyclobutene and indane confirm the assignments based on <sup>13</sup>C satellite patterns.)

Our <sup>13</sup>C spectrum of *o*-di-*tert*-butylbenzene, without <sup>1</sup>H decoupling,<sup>12</sup> confirms the order of chemical shifts reported,<sup>1</sup> despite the incorrect <sup>1</sup>H assignments. The fact that the <sup>13</sup>C assignments reported for indane<sup>1</sup> are in error, although the <sup>1</sup>H assignments on which they are

(6) J. B. Stothers, "Carbon-13 N.M.R. Spectroscopy," Academic Press, New York, N. Y., 1972, and ref 3-20 in ref 1.

(7) See S. Q. A. Rizvi, B. D. Gupta, W. Adcock, D. Doddrell, and W. Kitching, *J. Organometal. Chem.*, **63**, 67 (1973). Assignments for benzocyclobutene have appeared in the literature (A. J. Jones, P. J. Garratt, and K. P. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, **12**, 241 (1973)), apparently based on differential Overhauser effects. They agree with our rigorously established assignments.

(8) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 2361 (1971).

(9) The sequence was indan → 5-acetylindan → oxime → amide → 5-amino → 5-Br → 5-D. The constitution of the acetylindane has been demonstrated quite conclusively by synthesis to be the 5-isomer. See J. Vaughan, G. J. Welch, and G. J. Wright, *Tetrahedron* 1669 (1965); L. F. Fieser and A. M. Seligman, *J. Amer. Chem. Soc.*, **57**, 2174 (1935); **62**, 49 (1940). The aryl part of the <sup>1</sup>H nmr spectrum was typical of a 1,2,4-trisubstituted benzene with one proton quite prominent as a broadened "singlet."

(10) The iodination of benzocyclobutene was previously regarded to yield only the 4-iodo compound: L. Horner, P. V. Subramaniam, and K. Eiben, *Tetrahedron Lett.*, 247 (1965). Gas chromatography and mass spectral examination revealed two components in the ratio 6.67:1 (both with *m/e* 230), with the major one being the 4-isomer (87%) based on comparison of the physical and spectral properties of the derived acids. The mixture was converted to the deuterium derivative (Grignard) and a small amount of 3-deuteration was apparent also from the <sup>13</sup>C spectrum.

(11) Prepared from 3-fluoro-*o*-xylene (from 3-amino-*o*-xylene (Koch-Light) essentially by the procedure of J. A. Oliver and P. A. Ongley, *Chem. Ind. (London)*, 1024 (1965), for benzocyclobutene: bp 74° (100 mm) *n*<sub>D</sub><sup>20</sup> 1.5121. The synthesis of 4-fluorobenzocyclobutene will be reported in detail (W. Adcock, M. J. S. Dewar, R. Golden, and M. A. Zeb, *J. Amer. Chem. Soc.*, to be submitted).

(12) While this manuscript was in preparation, Professor Günther informed us of his studies of the uncoupled <sup>13</sup>C spectra of some symmetric ortho-disubstituted benzenes. The fine structure of the resonances is dissimilar for C<sub>α</sub> and C<sub>β</sub>. His assignments are in agreement with ours. See H. Günther, H. Schmickler, and G. Jikeli, *J. Magn. Resonance*, **11**, 344 (1973). Other data, apparently overlooked by Maciel and coworkers,<sup>1</sup> concerns comparisons of the spectra of indane and 1,3-dimethylindane discussed in ref 7.

(13) The value of this technique for symmetrical ortho-disubstituted benzenes was emphasized by Professor H. Günther (private communication). The overall width of the satellites must be larger for H<sub>β</sub> than H<sub>α</sub> since (2J<sub>o</sub> + J<sub>m</sub>) is larger than (J<sub>o</sub> + J<sub>m</sub> + J<sub>p</sub>).

(14) Because (δ<sub>H<sub>α</sub></sub> - δ<sub>H<sub>β</sub></sub>) is small in indan (~7 Hz at 100 MHz),<sup>2</sup> some overlapping of the <sup>13</sup>C satellite patterns occurred, but it was clear that the order was δ<sub>H<sub>α</sub></sub> > δ<sub>H<sub>β</sub></sub>, i.e., H<sub>β</sub> at higher field as suggested by Manatt and Cooper.<sup>2</sup> (Also confirmed by examination of 5-D-indan.)

Table I. Aromatic  $^{13}\text{C}$  Assignments<sup>a</sup> of Benzocycloalkenes and 1,2-Dialkylbenzenes

Entry	Compound <sup>b</sup>	Carbon					
		1	2	3	4	5	6
1 <sup>d</sup>		136.3	136.3	129.8	126.0	126.0	129.8
2		131.6 (2.5)	138.2 (7.2)	115.9 (21.2)	161.5 (244)	111.9 (20.3)	130.4 (7.4)
3		139.1 (4.6)	123.5 (16.0)	161.9 (245.0)	112.6 (24.0)	126.6 (9.1)	125.4 (3.10)
4		148.4	148.4	129.4	125.6	125.6	129.4
5 <sup>c</sup>		137.0	137.0	129.2	125.2	125.2	129.2
6		132.4 (2.3)	139.0 (7.0)	114.9 (20.3)	161.1 (245.9)	112.1 (20.9)	130.2 (7.6)
7 <sup>c</sup>		144.0	144.0	124.4	126.2	126.2	124.4
8		139.5 (2.11)	146.1 (8.3)	111.0 (22.1)	162.4 (244.2)	112.5 (23.0)	124.9 (8.6)
9 <sup>c</sup>		145.6	145.6	122.1	126.6	126.6	122.1
10		140.5 (2.0)	146.6 (7.5)	110.0 (22.2)	163.1 (245.3)	113.8 (23.6)	123.7 (8.2)
11		148.3 (9.5)	129.4 (15.6)	156.3 (257.8)	111.3 (21.2)	128.9 (5.6)	118.5 (4.6)

<sup>a</sup> Chemical shifts relative to TMS. More positive values correspond to lower shielding. Cyclohexane was used as internal reference, and data were converted to TMS scale by using  $\delta_C = 27.5 + \delta_{\text{wrt C}_6\text{H}_{12}}$ . Values in parentheses are  $^{13}\text{C}$ - $^{19}\text{F}$  couplings. The data for *o*-xylene (entry 1) and tetralin (entry 5) were confirmed by specific deuteration and are in close agreement with Maciel's data.<sup>1</sup> Aliphatic carbon assignments for the symmetrical cases (entries 1, 4, 5, 7, and 9) are straightforward on the bases of chemical shifts, relative intensities, and coherent decoupling.<sup>1,7b</sup> In the fluoro compounds, the  $\alpha$ - and  $\beta$ -aliphatic carbons can be distinguished on the basis of chemical shift, and a further decision within the groups, based on  $^{13}\text{C}$ - $^{19}\text{F}$  couplings.<sup>7b</sup> These data (for 10 and 11) will be reported in full at a later date. <sup>b</sup> Numbering system shown employed for convenience only. <sup>c</sup> Aromatic assignments confirmed by deuteration. <sup>d</sup> For *o*-diethylbenzene  $\delta_{\text{C}_3,6}$  128.46 and  $\delta_{\text{C}_4,5}$  126.21 ppm have been reported.<sup>1</sup>

based are correct, has serious implications regarding the applicability of the coherent decoupling technique to situations with strongly coupled nuclei where  $\Delta\delta$  is small.

Grave doubts also surround the  $^1\text{H}$  assignments reported<sup>2</sup> for benzocyclopropene, as the suggested  $^1\text{H}$  shifts<sup>2</sup> were based on the assumption that the broadened half of the AA'BB' pattern corresponded to  $\text{H}_\alpha$ . This, however, was apparently the basis also for the  $^1\text{H}$  assignments in benzocyclobutene,<sup>4</sup> now known to be incorrect by our  $^{13}\text{C}$  satellite and deuterium labeling studies, and the definite incorrectness of  $^{13}\text{C}$  assignments<sup>1</sup> based on these  $^1\text{H}$  shifts. Our data are collected in Table I.

The  $\text{C}_\alpha$  resonances (*i.e.*,  $\text{C}_{3,6}$ ) in tetralin, indan, and

benzocyclobutene (129.2, 124.4, 122.1, respectively) are more responsive to increasing strain than  $\text{C}_\beta$  (*i.e.*,  $\text{C}_{4,5}$ ) (125.2, 126.2, 126.6, respectively) and these trends suggest reversal<sup>15</sup> of Maciel's assignments<sup>1</sup> for benzocyclopropene to 116 for  $\text{C}_{3,6}$  and 130.30 for  $\text{C}_{4,5}$ . These trends (apparent also in the fluoro derivatives, entries 6, 8, and 10) may be associated with variations in total p bond order about the carbon.<sup>16</sup>

(15) The reported<sup>1</sup> assignments for  $\text{C}_{3,6}$  and  $\text{C}_{4,5}$  have in fact very recently been shown to require reversal, as suggested herein: H. Günther, G. Jikeli, H. Schmickler, and J. Prestien, *Angew. Chem., Int. Ed. Engl.*, **12**, 762 (1973).

(16) In this connection see J. A. Pople, *J. Chem. Phys.*, **37**, 53 (1962); T. D. Alger, D. M. Grant, and E. G. Paul, *J. Amer. Chem. Soc.*, **88**, 5397 (1966); J. D. Memory, "Quantum Theory of Magnetic Resonance Parameters," McGraw-Hill, New York, N. Y., 1968.

Strain in the fused ring has a definite influence on  $^{13}\text{C}$ – $^{19}\text{F}$  couplings<sup>17</sup> (e.g., cf.  $\text{C}_4$  and  $\text{C}_5$  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).

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## On the Degeneracy of the 260-m $\mu$ Band of the Uracils<sup>1</sup>

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.<sup>2</sup> 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 $\mu$  band of the uracils having associated with it two  $\pi \rightarrow \pi^*$  transitions,<sup>3</sup> polarized single-crystal studies have failed to reveal more than one transition in this region.<sup>4</sup> 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 $\mu$  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  $P_{2_1,2_1,2_1}$  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,<sup>5</sup> and a cylindrical absorption correction (maximum <5%) was made. Direct methods were utilized in determining the crystallographic structure.<sup>6,7</sup> 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<sup>a</sup>

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)

<sup>a</sup> 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 uracil<sup>8</sup> by at most several hundredths of an ångström unit and show similar agreement for several related compounds.<sup>9</sup> The bonding reported here thus appears to be that characteristic of the uracils, and the spectral results should consequently hold a measure of generality.<sup>10</sup>

(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. Carrabine and M. Sundaralingam, *Biochemistry*, **10**, 292 (1971); (e) T. Sakurai and M. Okunuki, *Acta Crystallogr.*, **27**, 1445 (1971).

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