

## THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF BICYCLO[2.1.0]PENTANES: A COMPARATIVE STUDY

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**Abstract**—The detailed, computer analyzed NMR spectra of the isomeric 2,3-diphenylbicyclo[2.1.0]pentanes (1–3) are presented. It is noted that in the absence of special substituent effects, the *endo* protons on both the three- and four- membered rings are shielded relative to the *exo* hydrogens although comparison of chemical shifts for 1–3 with those of bicyclo[2.1.0]pentane itself reveals general deshielding of all protons by phenyl substituents. Restrictions imposed on the free rotation of the phenyl groups in the *cis, syn* isomer **2** are suggested to be responsible for the reversal in chemical shift order observed in this isomer. Vicinal coupling constants in both the three- and four-membered rings are consistently greater for protons in a *cis* rather than *trans* arrangement. Significant long range coupling ( $^4J > 1$  Hz) in isomers 1–3 is observed even for protons which are not in a "W" arrangement, indicating that caution should be used in assigning stereochemistry solely on the basis of the presence (or absence) of long range coupling. The availability of multiple paths and the special properties of the cyclopropane ring may account for the long range "non-W" coupling observed.

### INTRODUCTION

THE use of computer programs (such as LAOCN3<sup>1a</sup> and NMRIT<sup>1b</sup>) to analyze non-first order NMR spectra as complex as those involving seven interacting nuclei allows the determination of chemical shifts and coupling constants with an ease and level of accuracy not previously possible. Such an analysis of a series of closely related structures of known geometry would provide valuable detailed information on structural effects (e.g. geometric requirements for long range coupling, shielding by carbocyclic rings, etc.) on spectra. Bicyclo[2.1.0]pentane and derivatives are ideally suited for such an NMR study because:

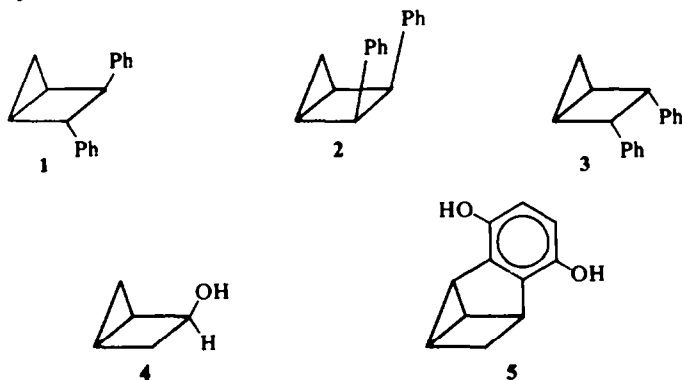
- (a) all of the coupling constants between magnetically nonequivalent nuclei may be determined for mono- as well as polysubstituted derivatives,
- (b) some NMR data are already available on a variety of substituted derivatives,
- (c) the exact geometry of the parent compound has been defined by microwave studies.<sup>2</sup>

We present here a comparative study of the NMR parameters (obtained by computer analyses and simulation) of a series of bicyclo[2.1.0]pentanes, 1–3, together with data for related structures from the literature.

The NMR spectrum of bicyclo[2.1.0]pentane was first reported by Chesick,<sup>3a</sup> although the correct interpretation thereof resulted from studies by Roth and Martin on the 2,3-dideutero derivatives.<sup>3b</sup> More recently, Wiberg has reported a complete analysis and computer simulation of the NMR spectrum of *endo*-2-hydroxybicyclo[2.1.0]pentane (**4**).<sup>4</sup> A similarly complete analysis of the non-aromatic portion of the NMR spectrum of the benzonorbornadiene photoproduct, **5**, which incorporates a bicyclo[2.1.0]pentane system as part of the carbon skeleton, has also been reported.<sup>5a</sup>

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Despite these studies and despite considerable interest in the chemistry of bicyclo[2.1.0]pentane and its derivatives,<sup>5b</sup> the available NMR data on these systems remain widely scattered in the literature.<sup>3-10</sup>



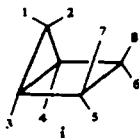
Recently we reported a simple synthesis of the 2,3-diphenylbicyclo[2.1.0]pentanes 1-3 by photocyclization of 1,5-diphenyl-1,4-pentadiene.<sup>11</sup> NMR studies, double resonance and computer simulation of the entire six-spin systems using LAOCN3,<sup>2a</sup> were an integral part of the proof of structure for these bicyclo[2.1.0]pentanes. We report herein the results of our NMR analyses as well as a comparison of NMR parameters obtained for 1-3 with those of bicyclo[2.1.0]pentane and its derivatives.

## RESULTS

The 60- or 100-MHz spectra of isomeric 2,3-diphenylbicyclo[2.1.0]pentanes 1-3 are shown in Figs 1, 2a and 3a, respectively. *Trans* isomer 1, lacking a plane of symmetry might be expected to show six separated multiplets in the aliphatic region while the *cis*, *syn*- and *cis*, *anti*-isomers, 2 and 3, with  $C_s$  symmetry should show a maximum of four multiplets each. In fact, one spectrum showed a two-proton high field multiplet and four one-proton multiplets at lower field (Fig. 1) while the other two spectra (Figs. 2a and 3a) exhibited three two-proton multiplets; in the second spectrum partial separation of the high field multiplet was observed.

The five multiplet 100 MHz spectrum in Fig. 1, assigned to *trans*-isomer 1, showed a two-proton multiplet for the cyclopropyl methylene protons  $H_1$  and  $H_2^*$  at ca.  $0.85\delta$ , an apparent triplet of doublets at  $1.84\delta$  and an apparent quartet with additional splitting at  $2.06\delta$  (1H each) assigned to the bridgehead protons  $H_3$  and  $H_4$ , a broadened doublet at  $2.84\delta$  and a broadened triplet at  $3.55\delta$  (1H each) corresponding to benzylic protons  $H_6$  and  $H_7$ . Decoupling experiments provided identification of most large coupling constants. Thus,

\* The protons of the bicyclo[2.1.0]pentane system are numbered as in (i). The carbon skeleton is numbered in the normal fashion.



- (a) irradiation at 1.84  $\delta$  (one bridgehead proton) hardly affected the 3.55  $\delta$  triplet, sharpened the 2.84  $\delta$  doublet and simplified somewhat the high field multiplet,  
 (b) irradiation of the bridgehead proton at 2.06  $\delta$  converted the 3.55  $\delta$  triplet into a doublet ( $J = 4.3$  Hz), sharpened the 2.84  $\delta$  doublet ( $J = 4.3$  Hz) and partially simplified the low field region of the 0.85  $\delta$  multiplet in a manner very similar to that observed on irradiation at 1.84  $\delta$ , and  
 (c) irradiation of the benzylic proton at 3.55  $\delta$  collapsed the 2.84  $\delta$  doublet to a singlet, changed the 2.06  $\delta$  quartet into a triplet of approximate spacing 5 Hz, but did not appreciably simplify the 0.85 and 1.84  $\delta$  multiplets.

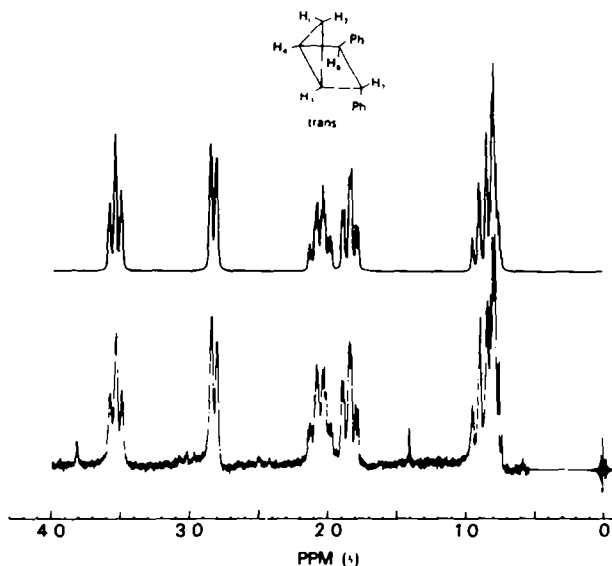


FIG. 1. Experimental (lower trace) and simulated (upper trace) 100 MHz NMR spectra of *trans*-2,3-diphenylbicyclo[2.1.0]pentane (1).

On the basis of these observations, the tentative assignments of the 3.55  $\delta$  resonance to proton H<sub>6</sub>, 2.84  $\delta$  to H<sub>7</sub>, 2.06  $\delta$  to H<sub>4</sub>, 1.84  $\delta$  to H<sub>3</sub>, and 0.85  $\delta$  to H<sub>1</sub>, H<sub>2</sub> could be made, this since *cis* cyclopropyl and cyclobutyl coupling constants are known to be considerably larger than *trans* coupling constants.<sup>12</sup> Further, approximate values of  $J_{4,6} \cong J_{6,7} = 4.3$ ,  $J_{3,4} \cong J_{1,4} = 5$  and  $J_{3,7} < 1$  Hz may be assigned. Wiberg has reported<sup>4</sup> a *trans* coupling constant corresponding to  $J_{6,7}$  of 3.52 Hz for *endo*-bicyclo[2.1.0]pentane-2-ol (4) (the corresponding *cis* coupling for protons at carbons 2,3 was determined to be 9.04 Hz). The assignment of the 3.55  $\delta$  triplet to *exo*-proton H<sub>6</sub> and the 2.84  $\delta$  doublet to *endo*-proton H<sub>7</sub> is consistent with the known shielding ability of the cyclopropane ring.<sup>3b, 12, 13</sup>

Additional decoupling experiments for **1** showed that

- (a) irradiation of H<sub>7</sub> (2.84  $\delta$ ) simplified the H<sub>6</sub> triplet (3.55  $\delta$ ) to a doublet ( $J = 4.3$  Hz), sharpened the H<sub>4</sub> quartet (2.06  $\delta$ ) giving doublets ( $J = 1.7$  Hz) on the quartet wings, sharpened the H<sub>3</sub> triplet of doublets (1.84  $\delta$ ; doublet spacing 1.6 Hz), and hardly affected high field protons H<sub>1</sub>, H<sub>2</sub> (0.85  $\delta$ ), and

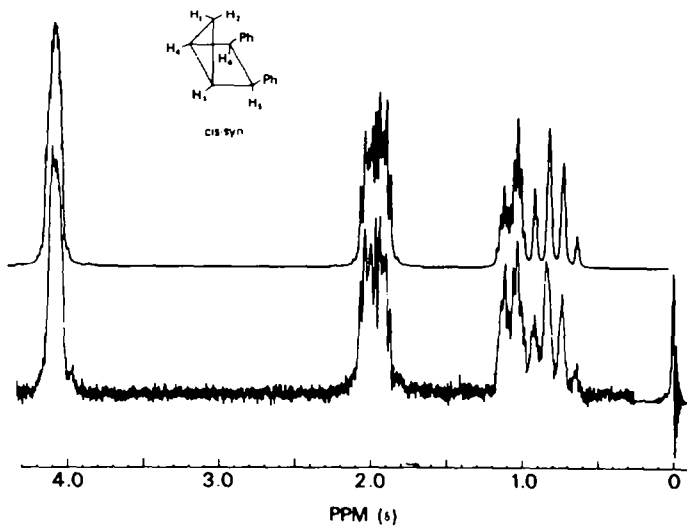


FIG. 2a. Experimental (lower trace) and simulated (upper trace) 60 MHz NMR spectra of *cis,syn*-2,3-diphenylbicyclo[2.1.0]pentane (**2**).

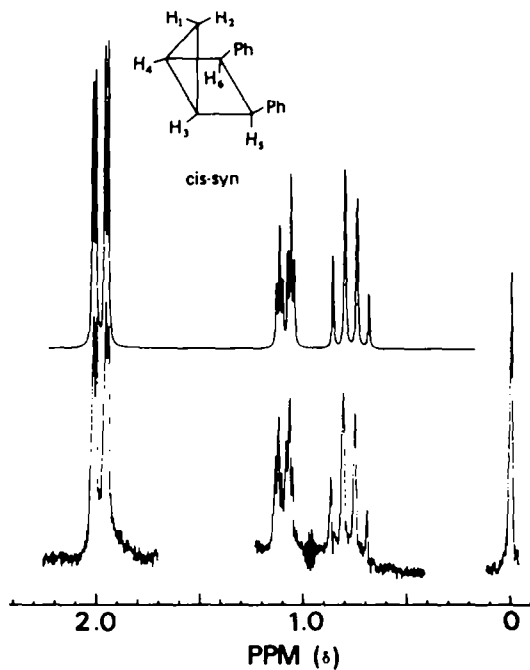


FIG. 2b. Experimental (lower trace) and simulated (upper trace) 100 MHz benzylic proton decoupled NMR spectra of *cis,syn*-2,3-diphenylbicyclo[2.1.0]pentane (**2**).

- (b) irradiation of H<sub>1</sub>, H<sub>2</sub> (0.85  $\delta$ ) led to a sharpening of H<sub>6</sub> and H<sub>7</sub> (3.55 and 2.84  $\delta$ ), converted the H<sub>4</sub> quartet (2.06  $\delta$ ) to a triplet and changed the H<sub>3</sub> triplet (1.84  $\delta$ ) to a doublet ( $J = 4.8$  Hz).

In addition to the previous assignments, the small couplings of 1.7 and 1.6 Hz may be respectively assigned to  $J_{2,4}$  and  $J_{2,3}$ , the larger couplings of 4.3 and 4.8 Hz to  $J_{4,6}$  and  $J_{3,4}$ , respectively, and  $J_{3,7} \approx 1$  Hz may be assigned. The remaining coupling constants were assigned initially using the values of Wiberg<sup>4</sup> and then further refined by means of LAOCN3.<sup>1a</sup> The calculated spectrum based on the calculated line positions and intensities using an assumed line width of 0.7 Hz is shown in Fig. 1. The chemical shifts and coupling constants are recorded in Tables 1 and 2, respectively, along with the values reported by Wiberg for 4.

TABLE 1. CHEMICAL SHIFTS\* FOR *trans*-2,3-DIPHENYLBICYCLO[2.1.0]PENTANE (1), *cis,syn*-2,3-DIPHENYLBICYCLO[2.1.0]PENTANE (2), *cis,anti*-2,3-DIPHENYLBICYCLO[2.1.0]PENTANE (3), AND *endo*-BICYCLO[2.1.0]PENTANE-2-OL (4)<sup>4</sup>

Proton	Compound 1	Compound 2	Compound 3	Compound 4
H <sub>1</sub>	0.87 } 2H	0.79 1H	1.08 } 2H	0.60 } 2H
H <sub>2</sub>	0.79 } 2H	1.07 1H	1.02 } 2H	0.84 } 2H
H <sub>3</sub>	1.84 1H	1.97 } 2H	2.00 } 2H	1.39 1H
H <sub>4</sub>	2.06 1H	1.97 } 2H	2.00 } 2H	1.82 1H
H <sub>5</sub>	—	4.09 } 2H	—	2.30 1H
H <sub>6</sub>	3.55 1H	4.09 } 2H	—	4.26 1H
H <sub>7</sub>	2.84 1H	— 1H	3.28 } 2H	1.19 1H
H <sub>8</sub>	—	—	3.28 } 2H	—
H <sub>arom</sub>	7.05 10H	6.64 10H	6.95 10H	—

\* Chemical shifts are given in ppm downfield from internal TMS.

The three multiplet 60 MHz spectrum shown in Fig. 2a shows an incompletely separated two-proton cyclopropyl methylene multiplet with peak centers at 0.79  $\delta$  (center of apparent quartet) and 1.07  $\delta$  (center of apparent doublet with additional splitting), a complex two-proton multiplet at 1.97  $\delta$  attributed to the bridgehead protons and a broad singlet for the benzylic protons at 4.09  $\delta$  (2H). The three multiplet 60 MHz spectrum in Fig. 3a has a two-proton multiplet at *ca.* 1.06  $\delta$  (cyclopropyl methylene protons), a complex multiplet at 2.00  $\delta$  (2H; bridgehead protons) and a singlet attributable to the benzylic protons at 3.28  $\delta$  (2H). The spectrum in Fig. 2a may be assigned to the *cis,syn*-isomer 2 while that in Fig. 3a may be assigned to the *cis,anti*-isomer 3. This assignment is based on the shielding of the benzylic protons in the spectrum in Fig. 3a relative to those in the spectrum in Fig. 2a (3.28  $\delta$  vs. 4.09  $\delta$ ) as well as on the sharpness of the benzylic proton signal in the spectrum in Fig. 3a compared to that in Fig. 2a (width at half height *ca.* 3 Hz in the former, 6 Hz in the latter) indicating that coupling constants to the *exo* benzylic protons are larger than those of the *endo* benzylic protons. These initial assignments are fully substantiated by more detailed spectral analysis (*vide infra*).

In the analysis of the spectrum shown in Fig. 2a and assigned to *cis,syn* isomer 2,

- (a) irradiation of the 4.09  $\delta$  benzylic proton singlet reduced the spectrum to an approximately first order four spin system as shown in Fig. 2b. At 100 MHz the

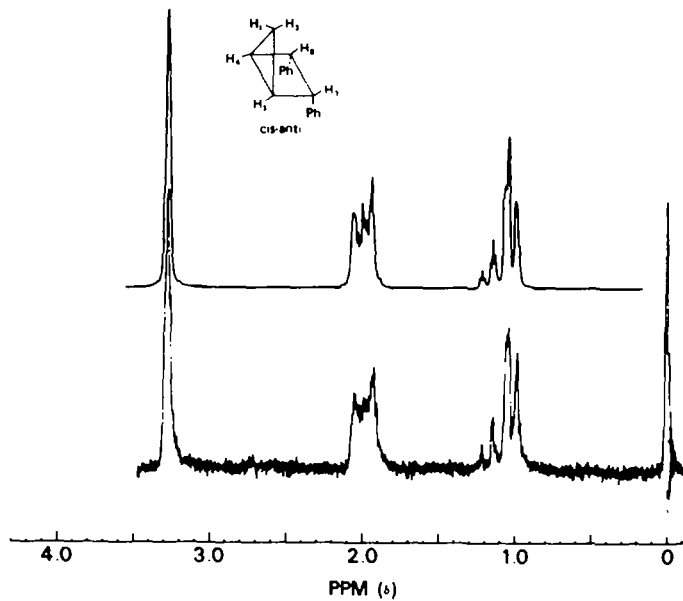


FIG. 3a. Experimental (lower trace) and simulated (upper trace) 60 MHz NMR spectra of *cis.anti*-2,3-diphenylbicyclo[2.1.0]pentane(3).

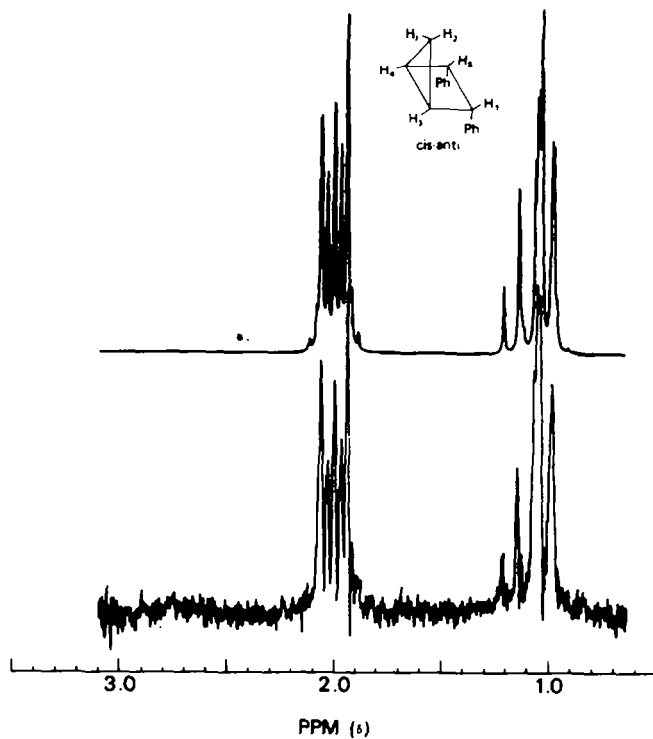


FIG. 3b. Experimental (lower trace) and simulated (upper trace) 60 MHz benzylic proton decoupled NMR spectra of *cis.anti*-2,3-diphenylbicyclo[2.1.0]pentane (3).

following estimated coupling constants could be extracted from this benzylic proton decoupled spectrum:

1. from the 1.97  $\delta$  ( $H_3$ ,  $H_4$  bridgehead protons) doublet of doublets,  $J_{1,3} = J_{1,4} = 5.5$ ,  $J_{2,3} = J_{2,4} = 1.4$  Hz,
2. from the doublet of triplets at 1.07  $\delta$  ( $H_2$  *endo* cyclopropyl methylene proton),  $J_{2,3} = J_{2,4} = 1.4$ ,  $J_{1,2} = 5.3$  Hz, and
3. from the quartet at 0.79  $\delta$  (*exo* cyclopropyl methylene proton  $H_1$ ),  $J_{1,2} = J_{1,3} = J_{1,4} = ca. 5$  Hz.

(b) irradiation of  $H_3$ ,  $H_4$  (1.97  $\delta$ ) led to a considerable sharpening of  $H_5$ ,  $H_6$  (4.09  $\delta$ ), a sharpening of  $H_2$  (1.07  $\delta$ ) with estimated  $J_{1,2} = 5.3$ , and a collapse of the  $H_1$  quartet (0.79  $\delta$ ) to a doublet with  $J_{1,2} = 5.3$ .

(c) irradiation of the high field protons  $H_1$ ,  $H_2$  (0.79 and 1.07  $\delta$ ) simplified the other multiplets somewhat but not sufficiently to permit the determination of additional coupling constants.

TABLE 2. COUPLING CONSTANTS\* FOR *trans*-2,3-DIPHENYLBICYCLO[2.1.0]PENTANE (1), *cis,syn*-2,3-DIPHENYLBICYCLO[2.1.0]PENTANE (2), *cis,anti*-2,3-DIPHENYLBICYCLO[2.1.0]PENTANE (3), AND *endo*-BICYCLO[2.1.0]PENTANE-2-OL (4)<sup>†</sup>

Parameter	Compound 1	Compound 2	Compound 3	Compound 4
$J_{1,2}$	-4.44	-5.38	-4.22	-4.64
$J_{1,3}$	5.68	5.76	5.92	5.52
$J_{1,4}$	5.61	5.76	5.92	6.11
$J_{1,5}$	—	0.73	—	1.87
$J_{1,6}$	0.87	0.73	—	0.47
$J_{1,7}$	0.81	—	1.00	0.48
$J_{1,8}$	—	—	1.00	—
$J_{2,3}$	1.38	1.46	1.26	1.49
$J_{2,4}$	1.39	1.46	1.26	1.46
$J_{2,5}$	—	1.18	—	0.01
$J_{2,6}$	1.06	1.18	—	0.47
$J_{2,7}$	0.16	—	0.27	0.00
$J_{2,8}$	—	—	0.27	—
$J_{3,4}$	4.81	indeterminant	indeterminant	4.47
$J_{3,5}$	—	4.12	—	3.98
$J_{3,6}$	0.30	0.40	—	0.49
$J_{3,7}$	0.60	—	0.01	0.48
$J_{3,8}$	—	—	1.52	—
$J_{4,5}$	—	0.40	—	0.10
$J_{4,6}$	4.57	4.12	—	4.22
$J_{4,7}$	1.19	—	1.52	1.00
$J_{4,8}$	—	—	0.01	—
$J_{5,6}$	—	indeterminant	—	9.04
$J_{5,7}$	—	—	—	-11.54
$J_{5,8}$	—	—	—	—
$J_{6,7}$	4.14	—	—	3.52
$J_{6,8}$	—	—	—	—
$J_{7,8}$	—	—	indeterminant	—

\* Values in Hertz. We have no direct experimental evidence for the sign of the coupling constants. The uncertainty in couplings involving protons 1-4 is  $\pm 0.1$  Hz while that for all other couplings is  $\pm 0.2$  Hz.

The remaining coupling constants were assigned using the values from *trans* isomer 1 as a model. The 100 MHz benzylic proton decoupled spectrum was computer simulated first (Fig. 2b; assumed line width 0.7 Hz). The refined coupling constants and chemical shifts so obtained were then used for the simulation of the 60 MHz six spin spectrum shown in Fig. 2a (assumed line width 0.5 Hz). The chemical shifts and coupling constants for isomer 2 are given in Tables 1 and 2, respectively.

In the analysis of the spectrum shown in Fig. 3a and assigned to the *cis*, *anti* isomer 3,

- (a) irradiation of the 3.28  $\delta$  benzylic singlet gave the second order spectrum shown in Fig. 3b,
- (b) irradiation at 2.00  $\delta$  ( $H_3$ ,  $H_4$ ) sharpened the benzylic proton singlet ( $H_7$ ,  $H_8$ ) and converted the 1.0  $\delta$  multiplet ( $H_1$ ,  $H_2$ ) to an AB multiplet with an intense, apparently single central peak and two wings from which  $J_{1,2} = 4$  Hz could be determined, and
- (c) irradiation of the high field multiplet ( $H_1$ ,  $H_2$ ) collapsed the multiplet at 2.00  $\delta$  ( $H_3$ ,  $H_4$ ) to a broad singlet while scarcely affecting the low field singlet ( $H_7$ ,  $H_8$ ).

The 60 MHz benzylic proton decoupled spectrum was computer simulated first (Fig. 3b; assumed line width 0.5 Hz) using coupling constants obtained from the NMR analysis of isomers 1 and 2. The refined coupling constants and chemical shifts obtained from this four spin simulation were then used for the simulation at 60 MHz of the complete spectrum shown in Fig. 3a (assumed line width 0.5 Hz). The chemical shifts and coupling constants are summarized in Table 1 and 2, respectively.

#### DISCUSSION OF RESULTS

*Chemical shifts.* Numerous reports of the NMR spectra of bicyclo[2.1.0]pentanes, as well as related bicyclo[n.1.0]alkanes, indicate that in the absence of "special" effects by substituents, the *endo*-cyclopropyl hydrogens experience shielding (relative to the *exo* hydrogens) by the cyclobutane (resp. cycloalkane) ring.<sup>3b,4,14</sup> Similarly, a marked shielding by the cyclopropane ring on *endo*-cyclobutyl protons has also been demonstrated in these systems<sup>3b,4,9d</sup> as it is well established for other systems containing the three membered ring.<sup>15</sup> The pertinent data for 1-3 and other bicyclo[2.1.0]pentanes are summarized in Table 3. Generally, these data reveal the expected shielding of *endo* protons in the bicyclo[2.1.0]pentane system. However, also revealed in this summary is a downfield shift (deshielding) for  $H_2$  in the *cis-syn* isomer 2 "unexpected" on the basis of shielding by the four-membered ring. Similar deshielding by *endo* substituents is also revealed in data by Wiberg and Barth,<sup>4</sup> Allred and Smith<sup>9d</sup> and Lay, MacKenzie and Telford<sup>10h</sup> (included in Table 3). As previously mentioned, the *substituent* is held responsible for this deshielding. A further comparison of chemical shifts for 1-3 with those of bicyclo[2.1.0]pentane itself in fact (Table 4) shows a general deshielding of *all* protons by phenyl substituents. The ( $\delta_1 - \delta_2$ ) for 2 (and perhaps for other compounds cited) is thus revealed as a combination of greater deshielding for *endo* proton ( $H_2$ ) and lesser deshielding (effective shielding) for the *exo* proton ( $H_1$ ), in accord with the early hypothesis by Winstein.<sup>16</sup>



TABLE 3. CHEMICAL SHIFT DIFFERENCES FOR *exo* AND *endo* HYDROGENS IN SOME BICYCLO[2.1.0]PENTANES


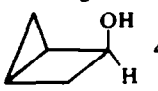
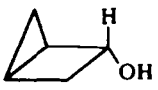
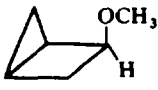
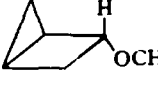

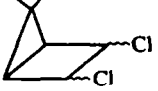
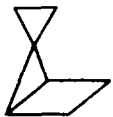
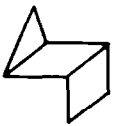
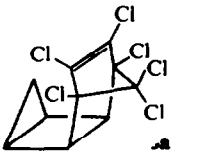
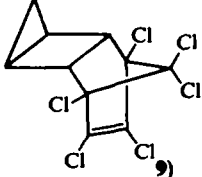
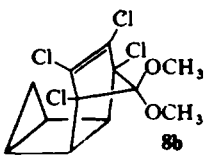
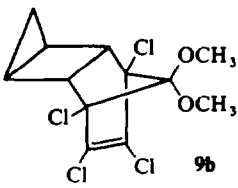
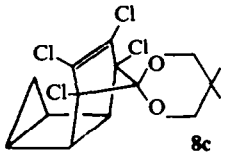
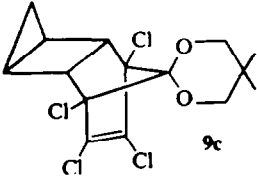

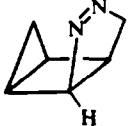
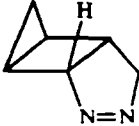
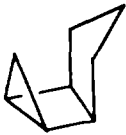

Compound	$\delta_1 - \delta_2$	$\delta_{5(6)} - \delta_{7(8)}$	Reference
	+0.17	+0.76	3a
1	+0.08	+0.71	This work
2	-0.28	} +1.19	This work
3	+0.06		This work
 4	-0.24	+1.11	} +0.53 4
	+0.15	undetermined	
	-0.25	undetermined	} ca. +0.5 9d
	+0.30	undetermined	
	—	<i>exo vs. endo</i> benzylic proton: +0.02	6a
	—	<i>cis,syn vs. cis,anti</i> (6 and 7, respectively): +0.59	9c
	—	ca. 0.6	6c
	+0.42	—	10i
	-1.41	} +0.50	10h
 9)	+0.11		

TABLE 3. (CONTINUED)

Compound	$\delta_1 - \delta_2$	$\delta_{5(6)} - \delta_{7(8)}$	Reference
	-1.35	—	10a
	+0.08	—	
} +0.52			
	-1.41	—	10a
	+0.11	—	10a
} +0.49			
	-0.15	—	10a
	+0.49	—	9e
	—	$\left( \begin{array}{c} \text{H} \\ \text{>C-N=N-} \end{array} \right)$	9e
} +0.42			
	+0.7	—	6b, 10f
	+0.45	—	6b, 10f
} +0.53			

Molecular models of 1–3 reveal that only in the *trans*-isomer (1) can the phenyl groups undergo free rotation and assume the most favourable confirmation without hindrance. In isomers 2 and 3 only conformations with phenyl groups having an essentially "parallel" arrangement are available. Such conformations result in a nearly "edge-on" orientation of the benzene rings with respect to the plane of the three-membered ring resulting in the long range deshielding of H<sub>2</sub> in isomer 2 (*cf.* Fig. 4).

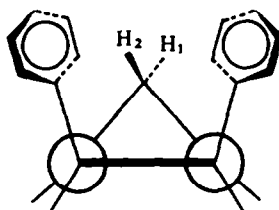


FIG. 4. Conformation of phenyl groups in *cis-syn*-isomer (2).

**Coupling constants.** Cyclopropane geminal coupling ( $^2J_{1,2}$ ) for compounds 1–3 are revealed negative (as expected) by our analysis (data for these as well as other bicyclo[2.1.0]pentanes are contained in Table 5) and have absolute values well within the range usually associated with a three-membered ring.<sup>12</sup> Noteworthy is the significantly smaller (more negative) values for this coupling in the *cis, syn*-isomer 2. This observation is in accord with arguments presented elsewhere by Bothner-By<sup>17</sup> and presumably reflects a decrease in the geminal bond angle (H<sub>1</sub>—C—H<sub>2</sub>) which might be a consequence of steric interaction with the *cis*-phenyl groups in 2 as implied in Fig. 4.

Vicinal coupling constants in planar small rings have been accepted as a criterion for stereochemistry<sup>12</sup> and were utilized in the analysis of the NMR spectra of 1–3 (as indicated above) as well as other derivatives of bicyclo[2.1.0]pentane.<sup>3b,4,8f,9c,d,10h</sup> Our values are in agreement with these expectations (*cis* > *trans*). Furthermore, cyclobutane vicinal couplings ( $^3J$  involving protons 3–8) generally follow the Karplus relationship.

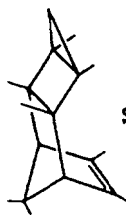
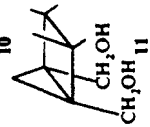
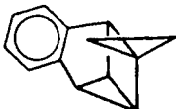
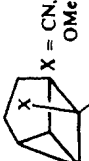
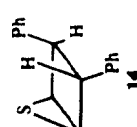







Long range couplings in bicyclo[2.1.0]pentanes were first noted by Roth<sup>3b</sup> and attributed to  $^4J_{1,5(6)}$ . In fact, the apparent geometric dependence of such coupling

TABLE 4. CHEMICAL SHIFTS AND CHEMICAL SHIFT DIFFERENCES: BICYCLO[2.1.0]PENTANE VS 1, 2 AND 3\*

	BC[2.1.0]P	1	2	3
$\delta_1$	0.65	0.87(+0.22)	0.79(+0.14)	1.08(+0.43)
$\delta_2$	0.48	0.79(+0.31)	1.07(+0.59)	1.02(+0.33)
$\delta_3$	1.50	1.84(+0.34)	1.97(+0.47)	2.00(+0.47)
$\delta_4$	1.50	2.06(+0.44)	1.97(+0.47)	2.00(+0.50)
$\delta_5$	2.11	—	4.09(+1.98)	—
$\delta_6$	2.11	3.55(+1.44)	4.09(+1.98)	—
$\delta_7$	1.35	2.84(+1.49)	—	3.28(+1.93)
$\delta_8$	1.35	—	—	3.28(+1.93)

\* Shifts from bicyclo[2.1.0]pentane (BC[2.1.0]P) in parentheses

TABLE 5. COUPLING CONSTANTS FOR BICYCLO 2.1.0]PENTANES

Cmpd.	B[2.1.0]P	4	1	2	3	10	11	6(7)	5	12	13	8	9	14	Geometry
$^2J_{1,2}$ $^2J_{3,7(4,8)}$		-4.64 -11.57	-4.44	-5.38	-4.22	~4.0	AA'BB'	~4.5	-8.6			~7	~5		
$^3J_{1,3}$ $^3J_{1,4}$		5.52 6.11	5.68	5.76	5.92	~6.0			5.4	~5.0		~7	~5.5		
$^3J_{2,3}$ $^3J_{2,4}$		1.49 1.46	1.38	1.46	1.26	~1.0						~1.5	~1.5		
$^3J_{3,4}$ $^3J_{3,5}$	ind.	4.47 3.98	4.81	ind.	ind.	ind.		ind.	4.8	~5.0		ind.	ind.	~4.0	
$^3J_{3,6}$	ind.	4.22	4.57	4.12	ind.	ind.	AA'BB'	ind.	2.9	~2.5	~3.7-3.8	~5-J <sub>3,6</sub>		5.8-J <sub>4,6</sub>	
$^3J_{3,6}$	ind.	9.04		ind.	ind.	ind.	AA'BB'	ind.	7.2		~8.0-8.3	ind.	ind.		
$^3J_{3,7}$ $^3J_{4,9}$ $^3J_{6,7}$		0.48 — 3.52	0.60	—	0.01	3.0	(~0.8)	(~0.8)	0.0				~2.5-J <sub>3,8</sub>	~1.9	
$^4J_{1,7}$ $^4J_{1,8}$		0.48 —	0.81	—	1.00	—	0.0(?)	—	0.0						
$^4J_{1,5}$ $^4J_{1,6}$		1.87 0.47	—	0.73	—	—	~1.5	—	0.0	~2.5					
$^4J_{2,7}$ $^4J_{2,8}$		0.00 —	0.16	—	0.27	—	0.0(?)	—							
$^4J_{2,5}$ $^4J_{2,6}$		0.01 0.47	—	1.18	—	—	0.0(?)	—							
$^4J_{3,6}$ $^4J_{4,5}$		0.49 0.10	0.30	0.40	—	—	—	—	2.4	~0.0		~5-J <sub>3,5</sub>			
$^4J_{3,8}$ $^4J_{4,7}$		— 1.00	—	—	1.52	—	—	—	2.7	—			~2.5-J <sub>3,7</sub>		
References	3a	4	this work		10y	8d	9c	5a	10d	10a,b	10a,b	10a	10a	1a	

has made it a valuable tool for assignment of configuration in bicyclo[2.1.0]pentanes as well as other rigid cyclic systems.<sup>19</sup> In general, protons separated by four bonds having the required "transoid", "zigzag" or "W" relationship to one another are considered as appreciably coupled, the magnitude of this coupling being 1–2 Hz. (In bicyclo[2.1.0]pentane, identification of long range coupling substantiated assignments made on the basis of chemical shift). The presence or absence of coupling between *exo*-H<sub>1</sub> and the cyclobutyl protons has often (*cf.* ref. 10*h* and examples mentioned therein) been cited as evidence respectively for or against the presence of *exo* hydrogens and thus long range coupling has been paramount in determining stereochemistry. An interesting aspect of our analysis of the NMR spectra of isomers 1–3 is the finding that long range coupling of significant magnitude is possible in bicyclo[2.1.0]pentanes even for protons which are not in a "W" arrangement.<sup>20</sup> Thus we find four-bond coupling constants of 0.81 to 1.18 Hz for H<sub>1,7(8)</sub> and H<sub>2,5(6)</sub> which appear in a "half-W" (*exo-endo*) arrangement (see entries for 1–3 in Table 5; values of 0.47–0.48 Hz for <sup>4</sup>J<sub>1,7</sub> and <sup>4</sup>J<sub>2,6</sub> in compound 4 are reported by Wiberg).<sup>\*</sup> These values may be compared with our values of 0.73 to 0.87 Hz for protons H<sub>1,5(6)</sub> in a "W" (*exo,exo*) disposition in 1 and 2 (a value of <sup>4</sup>J<sub>1,5(6)</sub> = *ca.* 1.2 Hz is indicated for bicyclo[2.1.0]pentane itself while values ranging from 0.47 to *ca.* 2.5 Hz have been reported for derivatives; see Table 5 for details). A particularly interesting example of substituent effects on long range coupling are the four bond (*exo,exo*) coupling constants for H<sub>1,5</sub> and H<sub>1,6</sub> in Wiberg's compound 4 (H<sub>5</sub> geminal to OH group) of

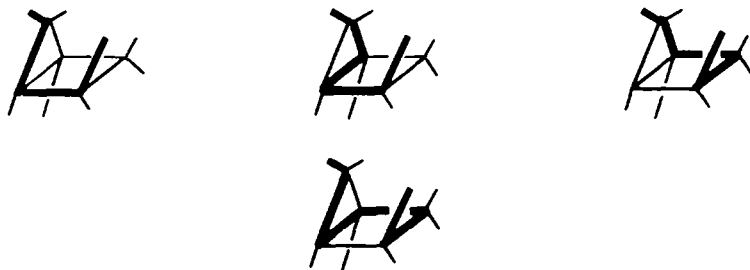


FIG. 5. Multiple pathways available for H<sub>1,7(8)</sub> coupling.

1.87 and 0.47 Hz, respectively. Other examples of non-W couplings are the <sup>4</sup>J<sub>3,6</sub>, <sup>4</sup>J<sub>4,5</sub>, <sup>4</sup>J<sub>3,8</sub> and <sup>4</sup>J<sub>4,7</sub> values indicated for a number of bicyclo[2.1.0]pentane derivatives in Table 5. It should be noted that other zig-zag arrangements with multiple paths involving <sup>3</sup>J and even <sup>6</sup>J coupling (Fig. 5) may contribute to the overall magnitude of long range coupling.<sup>10*g*</sup> By virtue of its symmetry, the cyclopropane ring is ideally suited to provide multiple coupling pathways.<sup>21</sup> A portion of the effectiveness of the three-membered ring in transmitting long range coupling may also be attributable to the "unsaturated" character of the ring.<sup>22</sup>

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<sup>\*</sup> Interestingly, even the couplings <sup>4</sup>J<sub>2,7(8)</sub> for protons in a "U" (*endo-endo*) arrangement are non-vanishing for compounds 1 and 3.

## REFERENCES

- <sup>1</sup> <sup>a</sup> A. A. Bothner-By and S. M. Castellano, *Computer Programming for Chemistry*, Vol. 1, Chapter 3. D. F. DeTar, Ed., W. A. Benjamin, Inc., New York, New York (1968):
- <sup>b</sup> J. D. Swafen and C. A. Reilly, *J. Chem. Phys.* **37**, 21 (1962)
- <sup>2</sup> R. D. Suenram and M. D. Harmony, *Ibid.* **56**, 3837 (1972)
- <sup>3</sup> <sup>a</sup> J. P. Chesick, *J. Am. Chem. Soc.* **84**, 3250 (1962):
- <sup>b</sup> W. R. Roth and M. Martin, *Ann. Chem.* **702**, 1 (1967); P. G. Gassman and K. T. Mansfield, ref. 8a.
- <sup>4</sup> K. B. Wiberg and D. E. Barth, *J. Am. Chem. Soc.* **91**, 5124 (1969)
- <sup>5</sup> <sup>a</sup> M. G. Waite, G. A. Sim, C. R. Olander, R. J. Warnet and D. M. S. Wheeler, *Ibid.* **91**, 7763 (1969):
- <sup>b</sup> P. G. Gassman, *Acc. Chem. Res.* **4**, 128 (1971)
- <sup>6</sup> <sup>a</sup> G. S. Hammond and H. Kristinsson, *J. Am. Chem. Soc.* **89**, 5970 (1967):
- <sup>b</sup> S. Moon and C. R. Ganz, *Tetrahedron Letters* 6275 (1968);
- <sup>c</sup> W. R. Roth and K. Enderer, *Ann. Chem.* **730**, 82 (1969):
- <sup>d</sup> A. P. Krapcho and R. Donn, *J. Org. Chem.* **30**, 641 (1965)
- <sup>7</sup> J. I. Brauman, L. E. Ellis and E. E. van Tamelen, *J. Am. Chem. Soc.* **88**, 846 (1966)
- <sup>8</sup> <sup>a</sup> P. G. Gassman and K. T. Mansfield, *J. Org. Chem.* **32**, 915 (1967):
- <sup>b</sup> M. J. Jorgenson, *J. Am. Chem. Soc.* **91**, 6432 (1969):
- <sup>c</sup> T. H. Kinstle, R. L. Welch and R. W. Exley, *Ibid.* **89**, 3660 (1967):
- <sup>d</sup> H. Prinzbach and H.-D. Martin, *Chimia.* **23**, 37 (1969).
- <sup>e</sup> B. R. Brook and B. V. Brophy, *Tetrahedron Letters* 4187 (1969):
- <sup>f</sup> M. Franck-Neumann, *Angew. Chem.* **81**, 189 (1969)
- <sup>9</sup> <sup>a</sup> J. R. Chapman, *Tetrahedron Letters* 113 (1966):
- <sup>b</sup> G. Maier and M. Strasser, *Ibid.* 6453 (1966):
- <sup>c</sup> M. Franck-Neumann, *Ibid.* 2979 (1968):
- <sup>d</sup> E. L. Allred and R. L. Smith, *J. Am. Chem. Soc.* **91**, 6766 (1969);
- <sup>e</sup> E. L. Allred and J. C. Hinshaw, *Ibid.* **90**, 6885 (1968)
- <sup>f</sup> S. A. Plank and J. C. Floyd, *Tetrahedron Letters* 4811 (1971) and references therein.
- <sup>10</sup> <sup>a</sup> H. Tanida and Y. Hata, *J. Org. Chem.* **30**, 977 (1965):
- <sup>b</sup> H. Tanida, J. Tsuji and T. Irie, *J. Am. Chem. Soc.* **88**, 864 (1966):
- <sup>c</sup> J. R. Edman, *Ibid.* **88**, 3454 (1966):
- <sup>d</sup> B. Trost, *J. Org. Chem.* **34**, 3644 (1969):
- <sup>e</sup> J. Meinwald and G. W. Gruber, *J. Am. Chem. Soc.* **93**, 3802 (1971):
- <sup>f</sup> P. G. Gassman and G. D. Richmond, *Ibid.* **92**, 2090 (1970):
- <sup>g</sup> J. E. Baldwin and R. K. Pinschmidt, Jr., *Ibid.* **92**, 5247 (1970):
- <sup>h</sup> W. P. Lay, K. MacKenzie and J. R. Telford, *J. Chem. Soc. (C)* 3199 (1971):
- <sup>i</sup> J. E. Baldwin and R. K. Pinschmidt, *J. Chem. Soc. (D)*, 820 (1972):
- <sup>j</sup> H. Tanida, S. Teratake, Y. Hata and M. Watanabe, *Tetrahedron Letters* 5345 (1969):
- <sup>k</sup> A. J. Schipperijn and J. Lucas, *Ibid.* 231 (1972):
- <sup>l</sup> I. G. Burstain, Ph.D. Thesis, U.C.L.A. (1967)
- <sup>11</sup> E. Block and H. W. Orf, *J. Am. Chem. Soc.*, in press
- <sup>12</sup> F. A. Bovey, *Nuclear Magnetic Resonance*, Academic Press, New York, N.Y. (1969)
- <sup>13</sup> D. J. Patel, M. E. H. Howden and J. D. Roberts, *J. Am. Chem. Soc.* **85**, 3218 (1963)
- <sup>14</sup> J. G. Traynham, J. S. Dehn and E. E. Green, *J. Org. Chem.* **33**, 2587 (1968)
- <sup>15</sup> R. S. Boikess and S. Winstein, *J. Am. Chem. Soc.* **85**, 343 (1963); C. D. Poulter, R. S. Boikess, J. J. Brauman and S. Winstein, *Ibid.* **94**, 2291 (1972)
- <sup>16</sup> S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourne, *Ibid.* **87**, 5247 (1965)
- <sup>17</sup> A. A. Bothner-By, *Adv. Magnetic Res.* **1**, 195 (1965)
- <sup>18</sup> E. Block and E. J. Corey, *J. Org. Chem.* **34**, 896 (1969)
- <sup>19</sup> S. Sternhell, *Quart. Rev.* **23**, 236 (1969)
- <sup>20</sup> G. Swaels and M. Anteunis, *Bull. Soc. Chim. Belges* **78**, 471 (1969); M. Anteunis and N. Schamp, *Ibid.* **79**, 437 (1970)
- <sup>21</sup> K. Tori and M. Ohtsuro, *Chem. Comm.* 886 (1966); W. A. Thomas, *Ann. Rev. Nucl. Magn. Resonance Spectroscopy* **1**, 78 (1968); M. Barfield and B. Chakbarti, *Chem. Rev.* **69**, 757 (1969)
- <sup>22</sup> J. I. Musher, *Mol. Phys.* **6**, 93 (1963)