The Correlation of the Crystal and Molecular Structure with the Nuclear Magnetic Resonance Spectrum of a Bicyclo[1.1.1]pentane Derivative[1]

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Received January 20, 1968

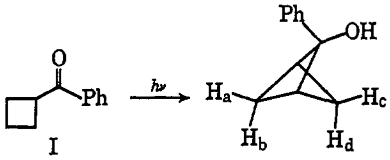
Abstract: The urethan derivative III derived from 2-hydroxy-2-phenylbicyclo[1.1.1]pentane was prepared by the irradiation of cyclobutyl phenyl ketone and subsequent reaction with *p*-bromophenyl isocyanate. Structure III crystallized in space group $P2_1$ with lattice parameters $a = 11.476$ Å, $b = 13.013$ Å, $c = 5.209$ Å, $\beta = 96.74°$. The structure was determined by the heavy atom method and refined by least squares to an R value of 0.067. The bond lengths in the bicyclo[1.1.1]pentane portion of III were found to be on the average 1.54 Å and the angles are 87° at the bridgeheads and 75° about the other two carbons. The dihedral angles of the cyclobutane rings are 60°. An explanation based on the short "nonbonded" contact between the two bridgehead carbon atoms is advanced to rationalize the abnormally large four-bond coupling (J = 18 Hz) observed.

Concurrent with the ever increasing applications of nmr spectroscopy to a broad range of chemical and physical problems there have appeared many reports of long-range spin–spin coupling of nuclei.[2–7] These long-range interactions are most apparent in bridged bicyclic compounds and seem to depend primarily upon the spatial arrangements of the interacting protons, although other factors such as electronegativity and steric effects of substituents are of some importance. The reports show the four-bond couplings to be at a maximum for a near-planar zigzag arrangement of the protons and to diminish when one or both of the coupling protons are rotated appreciably from the planar conformation.[6] One interpretation of the accumulated data suggests that the transmission of spin-state knowledge between the coupling nuclei occurs through orbital overlap across space.[8] Wiberg and his collaborators have indicated that the Fermi contact potential, which is generally assumed to give the principal contribution to normal spin–spin coupling, is not the most important contributor to four-σ-bond couplings.[9] It has been suggested by Meinwald and Lewis that the long-range interaction may be due to a direct overlap between the small posterior lobes associated with the C–H bonds of the interacting protons.[10] Alternatively, the stereochemical requirements might be indicative of a need to maintain a highly favorable set of bond angles along the chain of bonds connecting the coupling nuclei, to permit transmission of the spin-state knowledge through the intervening bonding electrons. The evidence accumulated so far does not point overwhelmingly in favor of either possible mechanism. Indeed both modes of coupling may be in operation, though to differing extents.

Although definite geometrical arrangements appear to be required for long-range coupling to take place in rigid bicyclics, little is known about the precise geometry of these compounds and therefore a more quantitative treatment of coupling constants has not been possible. Of the bicyclic small-ring systems known, bicyclo[1.1.1]pentane is of particular interest since the bridgehead long-range coupling is the largest thus far reported (J = 18 Hz).[11,12] In order to obtain a more quantitative correlation of coupling constant with geometry and to determine the detailed stereochemical structure of a representative bicyclo[1.1.1]pentane, an X-ray single-crystal structure analysis of a derivative of 2-hydroxy-2-phenylbicyclo[1.1.1]pentane (II) was undertaken.

Results and Discussion

We recently reported that the irradiation of cyclobutyl phenyl ketone (I) afforded a respectable yield of 2-hydroxy-2-phenylbicyclo[1.1.1]pentane (II).[13] The structure of the photoproduct was deduced on the basis of its analytical and spectral data. Thus, its infrared spectrum (in CCl_4) displayed hydroxyl bands at 2.87 and 3.02 μ and a carbon–oxygen stretching band at 8.25 μ; its ultraviolet spectrum exhibited an absorption spectrum characteristic of an isolated benzene ring (λ_{max} 258 mμ (ϵ 220)). Final confirmation of the structure of II was available from its unique nmr spectrum (Fig-



I

II

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(1) This investigation was supported in part by the National Cancer Institute (Grant CA-10104) and the National Science Foundation (Grant GP-6511).

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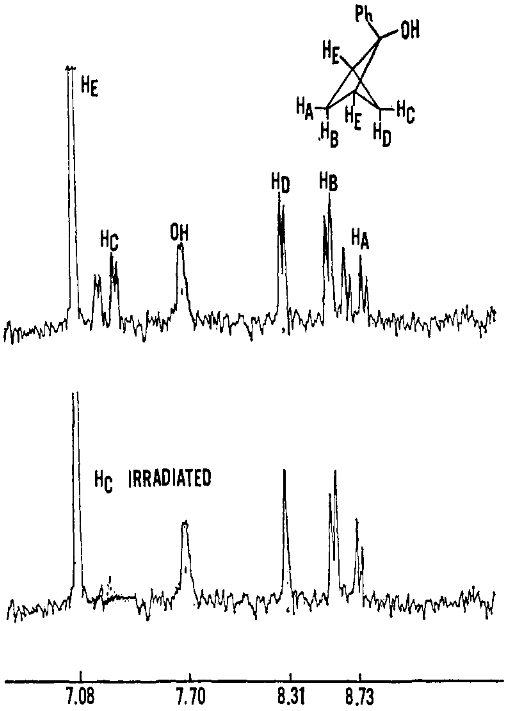


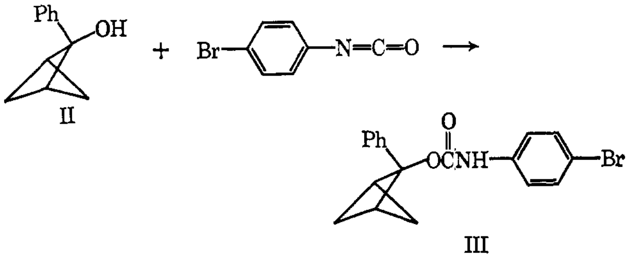
Figure 1. 100-Mc nmr spectra of II in deuteriochloroform.

ure 1). The 100-MHz nmr spectrum of II showed the aromatic hydrogens as a singlet at τ 2.73, the two bridgehead hydrogens as a singlet at τ 7.08, the hydroxyl proton as a singlet at τ 7.70, H_c as a doublet of doublets (J = 10.0, 3.0 Hz) at τ 7.24, H_d as a doublet (J = 3.0 Hz) at τ 8.31, H_b as a doublet (J = 3.0 Hz) at τ 8.58, and H_a as a doublet of doublets (J = 10.0, 3.0 Hz) at τ 8.73. The decoupled spectrum of II (Figure 1) bears out the above assignments. When H_c was saturated with an external field,[13] the H_d doublet collapsed to a singlet, H_b was unaffected, and H_a collapsed to a doublet (J = 3.0 Hz).

The bridgehead–bridgehead long-range coupling in II was determined by examination of the ^{13}C satellites of the low-field peak. The ^{13}C–H coupling constant was 164 Hz for the bridgehead hydrogens, is identical in value with that observed for the parent compound, and is essentially that observed with cyclopropane (161 Hz).[11] The H-H long-range coupling constant (J = 18 Hz) is also the same as the bridgehead hydrogens of bicyclo[1.1.1]pentane.[12] The large-bridgehead long-range coupling was further confirmed by the preparation of 2-hydroxy-2-phenylbicyclo[1.1.1]pentane-1-*d* *via* the irradiation of cyclobutyl phenyl ketone-1-*d*. The nmr spectrum of the monodeuterated compound showed a coupling constant of 2.70 ± 0.1 Hz between the deuterium and the bridgehead hydrogen. Hydrogen–hydrogen coupling should be 6.55 times as great as deuterium–hydrogen coupling,[14] and thus the value obtained is in excellent agreement with the 18-Hz H-H coupling. It can be deduced from the nmr spectrum of II that $J_{AB} = J_{CD} = -3.0$ Hz, this coupling constant being expected to be negative.[15]

Compared to the results generally obtained for $|J_{gem}|$[16] this value is quite small, but, as the geminal coupling constant for methylene groups depends on the H-C-H angle,[8] this value is not surprising in light of the rigidity and strain in the system.

Attempts to obtain an X-ray crystal analysis of II were unsuccessful because of its high volatility and, instead, II was converted to its urethan derivative III by reaction with *p*-bromophenyl isocyanate.



The crystals of urethan III (mp 156–158°, recrystallized five times from benzene) belong to the monoclinic system with a = 11.476 Å, b = 13.013 Å, c = 5.209 Å, and β = 96.74°. The phases of the structure factor amplitudes were obtained by the heavy-atom method and the molecular structure was shown to be consistent with III. Refinement proceeded to a crystallographic R factor of 0.067, and the calculated distances and angles are shown in the accompanying figures. Figure 2 shows the over-all configuration of III as viewed down the crystal's c axis. The bond distances and angles for the phenyl rings and the urethan portion of the molecule, as shown in Figure 2, are in general agreement with their expected values.[17] In Figures 3 and 4, the details of the structure of the bicyclo[1.1.1]pentane moiety are shown. The average carbon–carbon bond length in this system, 1.54 Å, is in excellent agreement with those found by electron diffraction of cyclobutane[18] (1.548 ± 0.003 Å), microwave spectroscopy of bromocyclobutane[19] (1.544 ± 0.003 Å), and X-ray diffraction[20] of cubane (1.551 ± 0.003 Å). The bridgehead angles about C_1 and C_3 (average 87°) are also very similar in magnitude to those found in cyclobutane[18] (88°). The angles about the methylene carbons are considerably smaller than the latter angle, having a mean value of 75°. This is reasonable in light of the constrictions placed on the system. In Figure 4 the nonbonding distances between the ring carbons are shown by the dashed lines. The methylene carbons form an equilatoral triangle with sides of 2.12 Å, which is similar in length to the nonbonded contacts in cyclobutane structures. However, the C_1–C_3 distance (1.89 Å) is significantly shorter than these other nonbonded contacts and, to the authors' knowledge, is the shortest carbon–carbon nonbonded contact known. Atoms C_1H and C_3H are collinear, within the limits of their errors, to the line from C_1 to C_3. This line is perpendicular to the plane passing through the methylene carbons.

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(16) For cyclobutanone, by example, $J_{gem\text{-}\alpha}$ = |16–17| Hz and $J_{gem\text{-}\beta}$ = |12| Hz: B. Braillon, J. Salaun, J. Gore, and J. M. Conia, *Bull. Soc. Chim. France*, 1981 (1964).

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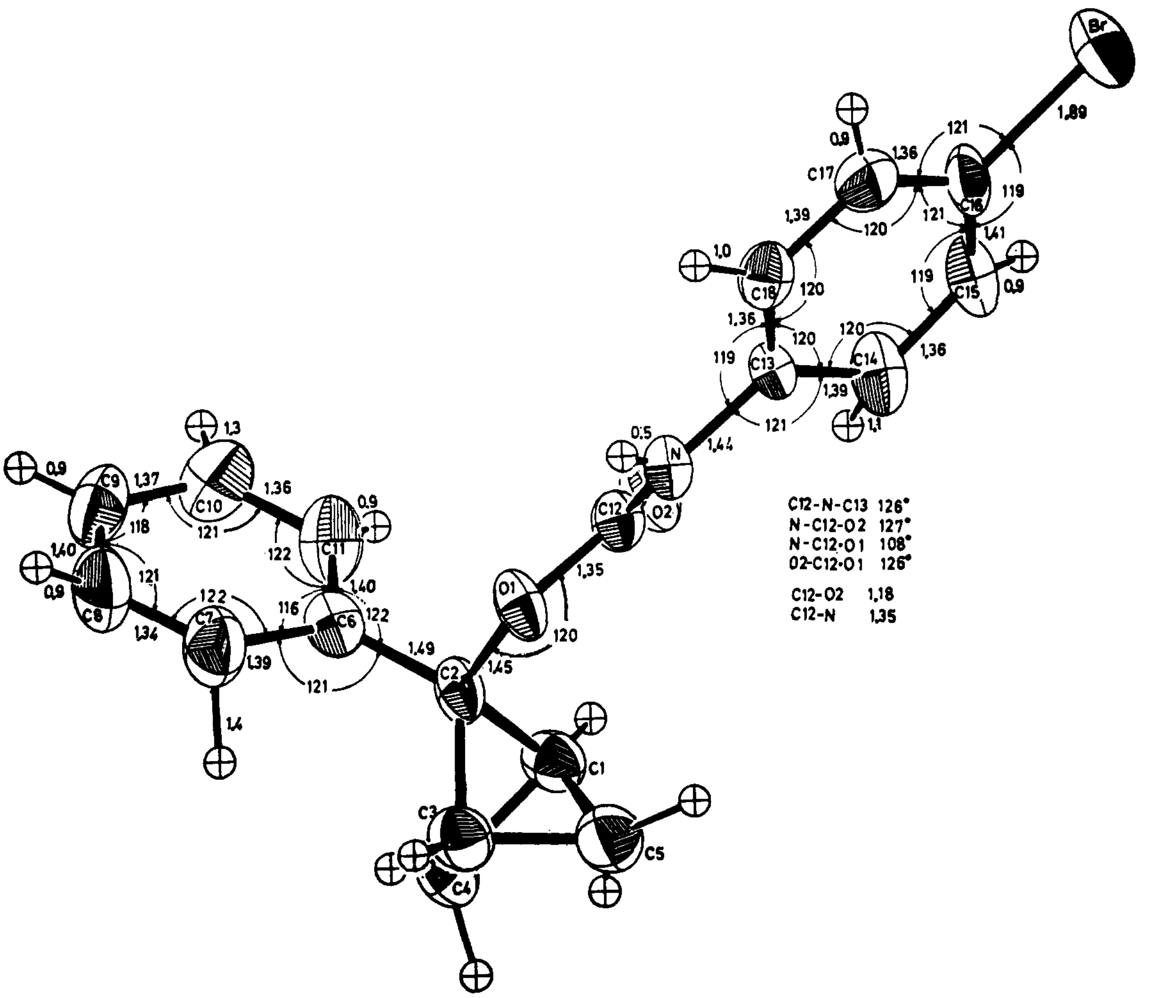

Figure 2. Stereographic view of compound III as observed down the *c* axis of the crystal. The thermal ellipsoids drawn in this and the following figures enclose a probability density of 0.5 for the nonhydrogen atoms.

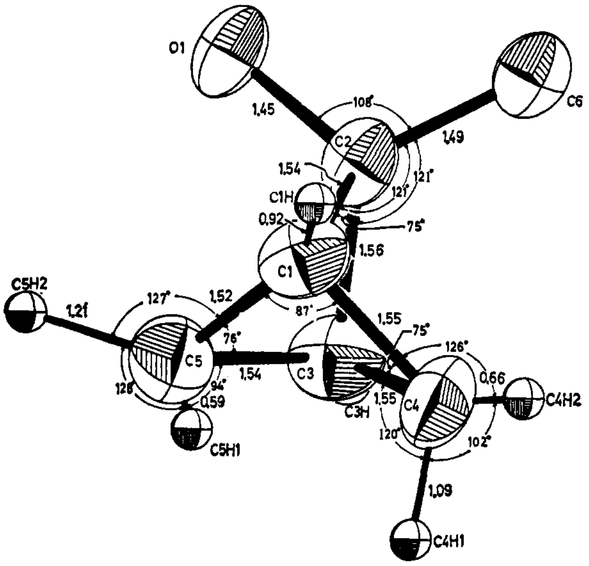

Figure 3. A general view of the bicyclo[1.1.1]pentane portion of the molecule.

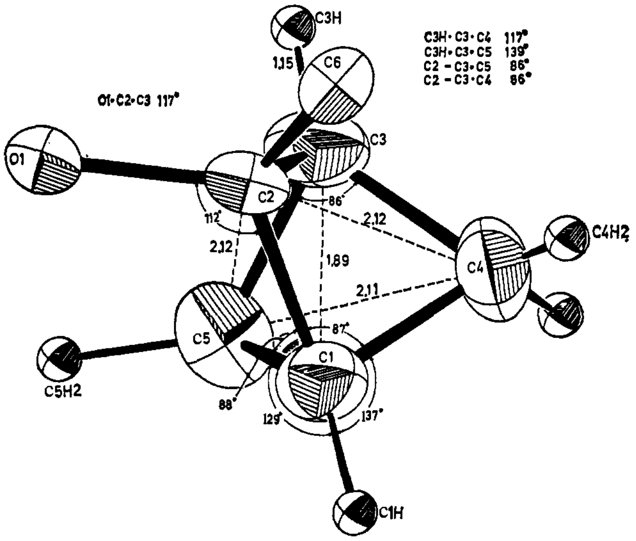

Figure 4. Another general view of the bicyclo[1.1.1]pentane system.

The puckering of the cyclobutane ring is usually described in terms of a dihedral angle, *i.e.*, the angle between the normals of the two planes intersecting at the diagonal of the ring. The values usually found for cyclobutane derivatives range from 20°[21] to 37°.[22] The three dihedral angles in this structure (average 60 ± 1°) are well above the latter values. It is also of interest

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Table I. Final Least-Squares Parameters for Nonhydrogen Atoms[a,b]

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	94 (9)	1591 (8)	5505 (19)	75 (8)	52 (6)	352 (41)	−12 (12)	146 (30)	26 (26)
C(2)	84 (7)	2731 (7)	4690 (16)	44 (6)	56 (7)	272 (30)	−18 (9)	97 (21)	−17 (21)
C(3)	785 (9)	2165 (7)	2714 (18)	70 (7)	46 (6)	310 (34)	−16 (10)	102 (26)	−14 (23)
C(4)	−197 (9)	1341 (9)	2584 (19)	61 (7)	62 (7)	346 (37)	−31 (12)	−41 (27)	−22 (27)
C(5)	1374 (9)	1557 (9)	5045 (21)	70 (8)	56 (7)	420 (42)	−6 (13)	2 (30)	57 (29)
C(6)	−1033 (8)	3271 (8)	3812 (15)	57 (7)	54 (6)	212 (27)	−14 (11)	42 (23)	−57 (22)
C(7)	−2028 (10)	3134 (11)	5069 (23)	68 (9)	81 (9)	504 (49)	7 (15)	127 (34)	67 (36)
C(8)	−3042 (10)	3612 (11)	4289 (26)	60 (9)	93 (10)	598 (58)	−4 (15)	137 (36)	−13 (39)
C(9)	−3159 (9)	4248 (11)	2107 (22)	55 (8)	83 (9)	449 (45)	35 (14)	−30 (29)	−65 (34)
C(10)	−2184 (11)	4413 (11)	894 (23)	92 (11)	81 (9)	438 (46)	41 (16)	57 (35)	31 (35)
C(11)	−1156 (9)	3120 (11)	1661 (17)	69 (9)	97 (9)	250 (32)	0 (14)	111 (27)	11 (29)
C(12)	1595 (7)	3994 (7)	5926 (16)	47 (6)	46 (5)	253 (29)	−4 (10)	54 (21)	1 (22)
C(13)	3127 (7)	5111 (7)	8247 (19)	37 (6)	41 (5)	423 (39)	−16 (9)	53 (25)	4 (23)
C(14)	3966 (8)	5055 (10)	6535 (17)	51 (7)	87 (9)	229 (30)	−19 (21)	25 (23)	−42 (26)
C(15)	4823 (8)	5775 (10)	6597 (18)	44 (7)	82 (8)	316 (35)	−29 (12)	36 (25)	18 (29)
C(16)	4919 (7)	6520 (9)	8579 (19)	29 (6)	64 (7)	421 (41)	−15 (10)	−10 (24)	47 (28)
C(17)	5878 (9)	1552 (8)	−316 (20)	65 (8)	48 (6)	404 (41)	14 (11)	39 (29)	47 (26)
C(18)	6798 (8)	848 (8)	−117 (16)	50 (6)	57 (6)	234 (29)	12 (10)	5 (23)	28 (22)
Br	6136 (1)	7500[c]	8692 (3)	59 (1)	78 (1)	822 (7)	−52 (2)	11 (4)	21 (5)
O(1)	752 (5)	3369 (6)	6616 (10)	47 (4)	63 (4)	238 (20)	−35 (7)	69 (16)	−39 (16)
O(2)	1771 (5)	4183 (6)	3795 (10)	59 (5)	68 (5)	190 (18)	−42 (8)	47 (15)	30 (16)
N	2167 (6)	4389 (6)	8105 (13)	38 (5)	51 (5)	280 (26)	−5 (8)	35 (18)	−2 (19)

[a] The values given in the parentheses are the estimated standard deviation × 10^4. [b] The temperature factor is in the form, temp = exp·$-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})$. [c] y coordinate arbitrarily chosen at 0.7500.

to note that the various ring torsional angles are 43 ± 2° on the average, which is also greater than those found in cyclobutane. There are no unusually short intermolecular contacts found in the structure and it therefore appears that the molecules are packed into the lattice by van der Waals forces.

Analysis of the nmr spectrum of II demonstrates the intervention of an exceedingly large (J = 18 Hz) long-range coupling over four σ bonds. The possible coupling mechanism may now be evaluated in light of the X-ray data. The rationalization offered by Meinwald and Lewis[10] involving "fairly extensive overlap between the small lobes of the orbitals directed 180° away from the directions of the C–H bonds" continues to account for the data observed. The collinear geometry of the bridgehead bonds and the extremely short cross-ring distance (1.89 Å) of the bicyclo[1.1.1]pentane system readily rationalize the large coupling observed. This back-lobe interaction has also been advanced to explain the enhanced solvolytic activity of 1-chlorobicyclo[1.1.1]pentane (compared with 1-chloronorbornane).[23] In conclusion, it appears that the magnitude of long-range coupling over four σ bonds is dependent on both the distance between and the spatial arrangements of the interacting protons. The rigid bicyclo[1.1.1]pentane framework is unique in both of these respects.

Experimental Section

2-Hydroxy-2-phenylbicyclo[1.1.1]pentane (II). A solution of 10.0 g of cyclobutyl phenyl ketone (I) in 1 l. of benzene was irradiated at room temperature in a nitrogen atmosphere with a Hanovia 450-W mercury arc lamp using a Pyrex filter to eliminate wavelengths below 280 mμ. The progress of the reaction was followed by vapor phase chromatography with a 5 ft × 0.25 in. aluminum column packed with 5% DEGS on Chromosorb W at a flow rate of 60 cc/min and at a temperature of 120°; after 144 hr the reaction was 80% complete. The solvent was removed on a rotary evaporator, and the remaining liquid was distilled. The fraction boiling at 74–78° (5.0 mm) was collected. The colorless oil slowly solidified upon standing for several days. Recrystallization from pentane gave a white solid, mp 64–65°, yield 1.5 g.

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.29; H, 7.46.

2-Hydroxy-2-phenylbicyclo[1.1.1]pentane (II) (50 mg) and p-bromophenyl isocyanate (60 mg) were dissolved in 2 ml of benzene, and the solution was refluxed for 24 hr. Evaporation of the solvent left a pale yellow solid which was recrystallized from benzene, mp 156–158°. The structure of this material is assigned as the urethan derivative III of II on the basis of a X-ray single-crystal structure analysis.

Compound III crystallized from benzene as colorless monoclinic plates elongated along [0.0.1]. The crystal data obtained for these are

$a = 11.476 \pm 0.002$ Å $d_m = 1.53 \pm 0.01$ g/cm³ (by flotation)
$b = 13.013 \pm 0.002$ Å
$c = 5.209 \pm 0.001$ Å $d_c = 1.540$ g/cm³ (for $Z = 2$)

$\beta = 96.74 \pm 0.02°$ space group $P2_1$

The cell dimensions and the intensity data were measured on a GE XRD-6 spectrogoniometer and goniostat using a scintillation counter and Cu Kα radiation. The intensities were collected by the stationary-counter–stationary-crystal method using balanced Ni–Co filters. A crystal fragment (approximate size 0.45 mm along c and 0.2 × 0.1 mm in girth) was mounted about the c axis. In the range of the intensity measurements (0 to 140° in 2θ) 1418 reflections of the 1534 examined had peak counts significantly greater than their respective background counts. Lorentz and polarization factors were applied to these data as well as a correction for the α_1–α_2 splitting. The data were also adjusted for the anisotropy of transmission about the φ axis as a way of correcting for absorption (μ = 41 cm^{-1}). This factor was determined by measuring the intensity of the 0.0.3 reflection at χ = 90° as a function of the angle φ. The structure factors were put on an absolute scale by use of Wilson statistics.

The position of the bromine atom was readily derived from a three-dimensional Patterson synthesis. Subsequent electron density maps, calculated first with the phases of the structure factors based on the bromine position, enabled the positions of all the nonhydrogen atoms to be found. The positional and thermal parameters of these atoms were refined by least squares using a block diagonal approximation to the normal least-squares equations. A three-dimensional difference electron density synthesis calculated after anisotropic temperature factors was introduced and R (usual discrepancy index) was 0.09 and showed positive regions where hydrogens were expected. These positions were then refined in the final cycles of least squares with arbitrary temperature factors of 3.0 Å². The weighting scheme utilized in the latter stages of re-

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(23) K. B. Wiberg and V. Z. Williams, Jr., *J. Am. Chem. Soc.*, **89**, 3374 (1967).

Table II. Positional Parameters and esd's for Hydrogens ($\times 10^3$)[a]

Atom	x/a	y/b	z/c
C(1)H	−24 (11)	147 (11)	701 (23)
C(3)H	102 (10)	248 (14)	78 (21)
C(4)H(1)	2 (11)	53 (11)	233 (24)
C(4)H(2)	−72 (12)	138 (11)	191 (23)
C(5)H(1)	129 (11)	115 (12)	453 (24)
C(5)H(2)	221 (11)	182 (11)	654 (24)
C(7)H	−192 (11)	224 (10)	680 (22)
C(8)H	−355 (11)	379 (11)	538 (24)
C(9)H	615 (12)	456 (11)	189 (24)
C(10)H	−242 (11)	483 (11)	−143 (24)
C(11)H	−85 (12)	401 (12)	20 (25)
C(14)H	358 (11)	466 (11)	465 (25)
C(15)H	519 (12)	592 (11)	531 (26)
C(17)H	592 (11)	211 (10)	−136 (22)
C(18)H	735 (11)	94 (11)	−139 (24)
NH	180 (12)	449 (11)	862 (24)

[a] The isotropic temperature factors were arbitrarily assigned a value of 3.0 Å^2.

finement was $w^{-1} = ((|F_o| - 2.5)/20)^2 + 1$, such that $\langle w\Delta^2\rangle$ was relatively constant over the whole range of the $|F_o|$'s. The unobserved data were given zero weight. The final R value was 0.067 for the observed data, and the goodness of fit ($\Sigma w\Delta^2/(m - n)$), 1.03.[24]

In all the above calculations the atomic form factors utilized where those of Cromer and Waber,[25] except those for hydrogen.[26] The bromine atom was corrected for the real part of the anomalous scattering curve. Tables I and II show the final least-squares parameters for the various atoms. The numbering scheme is shown in the accompanying figures. The estimated standard deviations were calculated from the inverse of the full equation blocks for each atom (*i.e.*, 9×9 blocks for x, y, z and the β_{ij}'s). The esd's for the bond lengths and angles between the nonhydrogen atoms are on the average 0.015 Å and 0.4°, respectively. The hydrogen atoms were found to have standard deviations about ten times greater than the other atoms, which precludes any detailed discussion of them.

Acknowledgment. We are very appreciative to the University Computing Center for the generous gift of computing time, and to Mrs. Phyllis Sackman for her technical assistance. We are also indebted to Mr. David Eastman for the ^{13}C–H nmr measurements.

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[24] A list of the observed and calculated structure factors will be included in the Ph.D. thesis of E. Alexander, State University of New York at Buffalo, Buffalo, N. Y.

[25] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 18, 104 (1965).

[26] "International Tables for X-ray Crystallography," Vol. III, Kynock Press, Birmingham, 1962.

On the Question of 7-*syn*- and 7-*anti*-Proton Absorptions in the Nuclear Magnetic Resonance Spectra of Norbornenes

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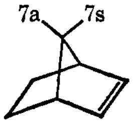
Contribution from the Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey 07036. *Received December 22, 1967*

Abstract: The analysis of the nmr spectrum of *exo,exo*-5,6-dideuterionorbornene by means of spin decoupling clearly demonstrates that the 7-*syn* proton absorbs at lower fields than the 7-*anti* proton. A geometric argument is invoked as a rationale for the observed phenomenon.

Shielding and deshielding effects have been employed as a basis for structural assignments of various tricyclic[2] and bicyclic compounds and in particular for various norbornenyl derivatives.[3] In their first paper[3] Tori, *et al.*, incorrectly assigned the 7-*syn* (7s) proton to a higher field than the 7-*anti* (7a) proton in the nmr spectra of norbornene (I) and benzonorbornene (II).



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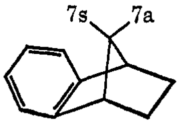
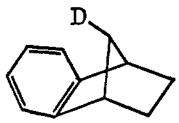
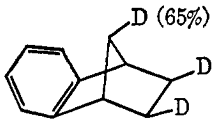


II

However, in their second paper,[4] Tori and coworkers reversed their initial assignment of the 7-*syn* and 7-*anti* proton absorptions by spin-decoupling compounds III and IV; the 7s proton was assigned to a lower field than that of the 7a proton. Tori did not spin-decouple



III



IV

an analogously deuterated norbornene (I); however, on the basis of his results with III and IV he revised his previous chemical shift assignments[3] of the 7s and 7a protons in compound I.

The well-known shielding of protons above the plane of the double bond phenomenon[5] would predict that the 7s proton *should* resonate at a higher field than the 7a proton, contrary to Tori's observed results. Indeed, this is exactly what is observed for 7-substituted norbornenes (V and VI).[6] In addition, it has been

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