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NMR STUDIES OF BRIDGED RING SYSTEMS. IX.*[1]

ANOMALY IN MAGNETIC SHIELDING OF BRIDGE-METHYLENE PROTONS IN NORBORNENE AND BENZONORBORNENE EVIDENCED BY PROTON SPIN-DECOUPLING AND DEUTERATION METHODS

K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji and H. Tanida
Shionogi Research Laboratory, Shionogi & Co., Ltd.
Fukushima-ku, Osaka, Japan

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MUCH interest has been shown in NMR spectra of bicyclo[2.2.1]heptane derivatives, as the chemistry of this system has conspicuously developed in recent years.*[2] Musher pointed out some unusual features of spectra of norbornyl alcohol derivatives (4). Unusual deshielding of the C-7 bridge-methylene protons of norbornadiene (VII) and benzonorbornadiene (XIII) has been reported in our previous paper (3), wherein we tentatively assigned the C-7 proton signals of norbornene (II) and benzonorbornene (VIII) by examination of molecular models and by consideration of anisotropic shielding effects exerted by an introduced double bond (3, 5, 6) or benzene ring (7) such that the signal of the proton syn to the π-bond appears at a higher field than does that of the anti proton. Our assignments have seemed correct because it was

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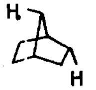
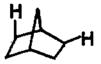
*[1] For Part VIII, see Y. Hamashima, K. Tori and A. Takamizawa, Chem. Pharm Bull. (Tokyo) **13**, 1052 (1965).

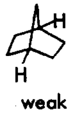
*[2] For reviews, see Refs. (1-3).

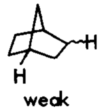
revealed, thereafter, that the C-7 *syn* proton in several C-7 *anti* substituted norbornenes (1, 8) and benzonorbornenes (9) resonates at a higher field than does the *anti* proton in their corresponding *syn* substituted epimers (1, 8, 9) (some examples are shown in TABLE I).[*3]

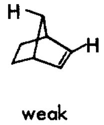
On the other hand, a number of examples of the long-range spin-couplings through more than three single bonds have recently been disclosed (10) with a theoretical explanation (11). In the bicyclo[2.2.1]heptane system, this coupling is known to be found between the pairs of protons related according to the "W-letter rule", as pictured below (1-4, 10, 12).











Our recent measurements[*4,*5] of the 100 Mc spectra of VIII as well as II showed that the two C-7 proton signals appear as a doublet of triplets (J=8.5 and 1.5 c.p.s.) at a higher field and as a doublet of quintets (J=8.5 and 2.0 c.p.s.) at a lower field, as shown in Fig. 1a. Therefore, in view of the long-range spin-couplings noted above, our previous assignment of the C-7 *syn*- and *anti*-proton signals (3) becomes reversed. The proton spin-decoupling experiments on VIII shown in Figs. 1b, 1c and 1d supported this possibility. In the bridgehead-proton spin-decoupled pattern (Fig. 1b), the higher field part of an A_2X_2-type signal due to *endo* protons at C-2 and C-3 is evidently

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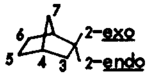
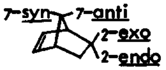
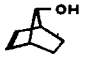
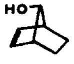
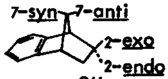
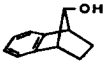
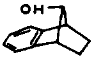
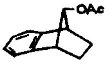
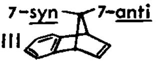
[*3] Non-critical use of the assignments of the C-7 proton signals of II have also appeared in D. R. Arnold, D. J. Trecker and E. B. Whipple, *J. Amer. Chem. Soc.* **87**, 2596 (1965).

[*4] The NMR spectra were taken with a Varian A-60 and (or) a Varian HA-100 spectrometer by using 5% (w/v) solutions in carbon tetrachloride containing tetramethylsilane as an internal reference. Calibration of the spectrometers was checked by the usual side-band method. Accuracies of the measurements are within 0.02τ for chemical shifts and 0.3 c.p.s. for coupling constants. Proton spin-decoupling experiments at 100 Mc were made by using a Hewlett-Packard HP-200ABR audio oscillator in the frequency sweep and TMS-locked mode operation.

TABLE I

NMR Spectral Data on Some Bicyclo[2.2.1]heptane Derivatives in Carbon Tetrachloride[a]

Compound	Proton Chemical Shifts (τ)					
	Bridge-methylene C-7 protons		Bridgehead C-1, C-4 protons	Bridge-ethylene C-2, C-3 protons		Olefinic protons
	syn	anti		exo	endo	
I 	8.79m		7.80m	8.51^{b}	8.82^{b}	-
II 	8.68d-qi	8.93d-t	7.17sp	8.43m^{b}	9.06m^{b}	4.07t
III 	6.48m	-	7.52sx			4.03t
IV 	-	6.34m	7.30sx			3.93t-d
V 	5.77t-t	-	7.27sx			4.02t
VI 	-	5.63t-t	7.12sx			4.08t-d
VII 	8.05t		6.47sp	-	-	3.34t
VIII 	8.27d-qi	8.52d-t	6.70qi	8.15m^{c}	8.86m^{c}	-
IX 	6.26t-m	-	6.97q			-
X 	-	6.03t-m	6.92q			-
XI 	5.53t-t	-	6.72q			-
XII 	-	5.27t	6.67q			-
XIII 	7.79d-t-t	7.72d-t	6.18qi	-	-	3.28t-d

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[a] Peak multiplicities are represented by s (singlet), d (doublet), t (triplet), q (quartet), qi (quintet), sx (sextet), sp (septet) and m (multiplet). For example, d-t represents a doublet of triplets. [b] Determined by proton spin-decoupling. [c] Determined by using deuterated derivatives.

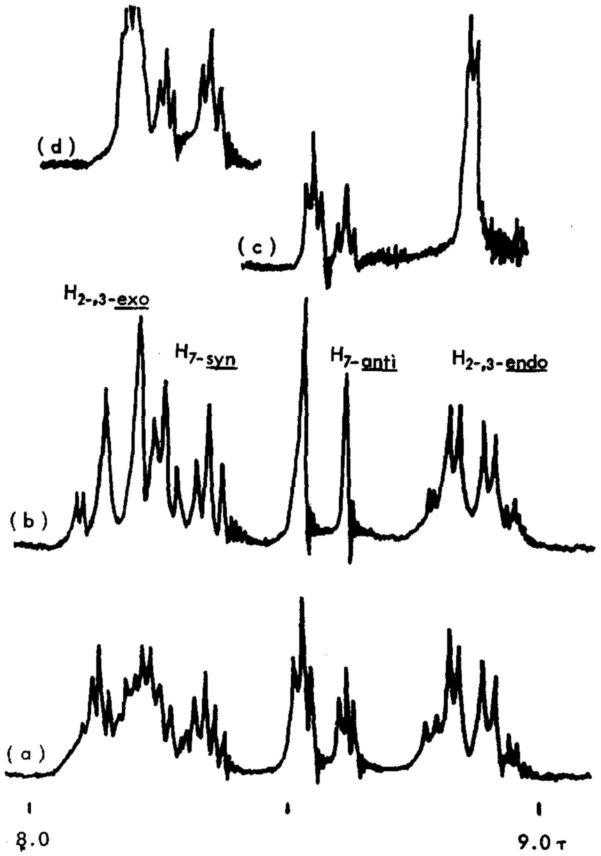

Fig. 1. NMR spectra of benzonorbornene (VIII) in carbon tetrachloride at 100 Mc. (a) Normal spectrum; (b) bridgehead-protons spin-decoupled pattern; (c) C-2 and C-3 exo protons spin-decoupled pattern; (d) C-2 and C-3 endo protons spin-decoupled pattern (shown only the high-field parts).

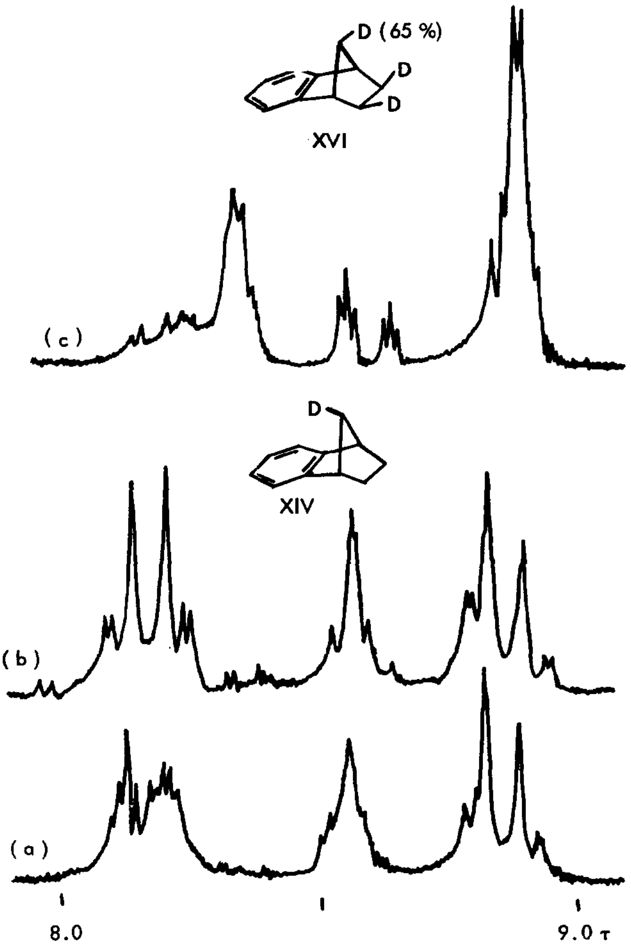

Fig. 2. NMR spectra of the deuterated benzonorbornenes (XIV and XVI) in carbon tetrachloride at 100 Mc. (a) Normal spectrum of XIV; (b) bridgehead-protons spin-decoupled pattern; (c) normal spectrum of XVI (shown only high-field parts).

coupled to the lower field doublet due to one C-7 proton, which should be syn to the benzene ring. The assignments of signals of the exo and endo protons at C-2 and C-3 is believed correct because the bridgehead proton is known to be more strongly coupled to the exo proton than to its endo counterpart (13). This fact is also seen in Figs. 1c and 1d.*5

Conclusive evidence for the assignments was obtained by the spectra of some deuterated derivatives of VIII, which we synthesized through the steps shown in Chart.*6 The structure of the compound XVI whose spectrum is shown in Fig. 2c is reliable from the reaction mechanisms.*6 Therefore, the compound XIV proved to have C-7 syn deuterium from its spectrum. In the spectrum of 7-syn-deuterobenzonorbornene (XIV) shown in Fig. 2a, the doublet of quintets signal at 8.27 τ in VIII disappears, whereas a broad signal split by deuterium appears at 8.52 τ. Thus the assignments of the C-7 proton signals were confirmed. In addition, the assignments of the C-2 and C-3 proton signals were confirmed by the spectra of the compounds XIX and XX.*5 In a similar manner, the previous assignments (3) of the C-7 proton signals in II and XIII were revealed to be reversed.*5 The chemical shift data on some norbornane derivatives are summarized in TABLE I.*5

The present reassignments of the C-7 proton signals in II, VIII and XIII do not alter the conclusion described in previous papers (3, 14) in a qualitative sense.*7 Moreover, the following two striking but important conclusions were derived from the present results.

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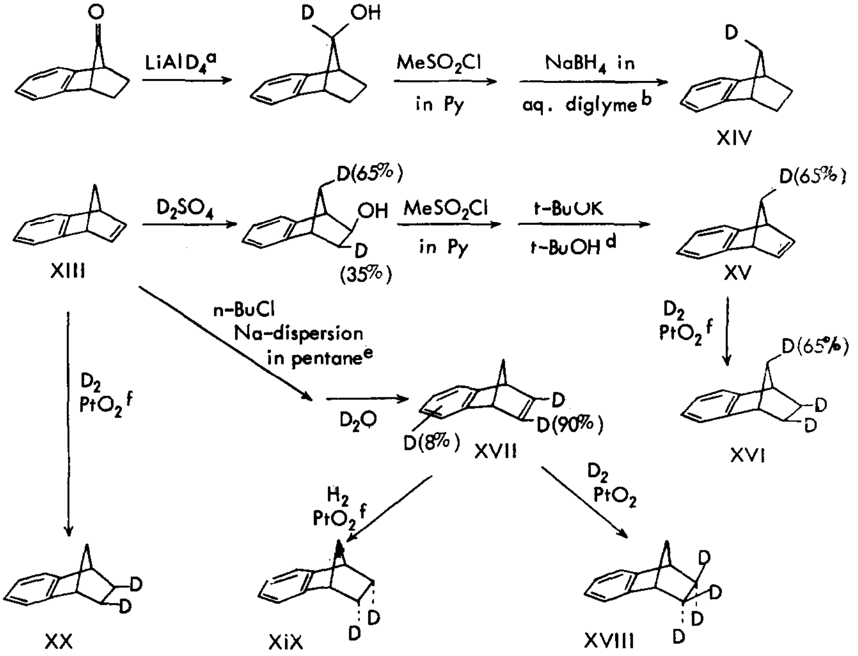
*5 The detailed spectral data on all the examined compounds in several solvents and more elaborate discussions will appear in our full paper.

*6 Detailed procedures of the syntheses of these deuterated derivatives of VIII and XIII will be described in our full paper. Contents of deuterium in the compounds shown in Chart were determined by their NMR spectra.

*7 Some minor revisions of the data described in a previous paper (14) and the discussion will be published elsewhere.

(1) NMR signals of geminal protons on a carbon in a rigid ring-system are generally assigned by comparing the chemical shift of the proton on the carbon bearing a polar substituent of known configuration with that in its epimer. No exception has been reported so far. This is true for the C-2 and C-3 protons of II and VIII(1-3, 15) as well as



Chart

[a] The reduction yields *anti*- and *syn*-alcohol in a ratio of 7 : 3, both of which were purely isolable by elution chromatography on Florisil. [b] *Regarding the mechanism of this* reaction, see H. C. Brown and H. M. Bell, *J. Org. Chem.* **27**, 1928 (1962); H. C. Brown and H. M. Bell, *J. Amer. Chem. Soc.* **85**, 2324 (1963). [c] Ionic addition from the *exo*-side, followed by the Wagner-Meerwein rearrangement. [d] *cis*-E_2-Elimination in the norbornane system was reported; see N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers and P. M. Subramaman, *J. Amer. Chem. Soc.* **85**, 3199 (1963). [e] An application of the method reported for the synthesis of 5,6-dideuteronorbornene by J. E. Franz, C. Osuch and M. W. Dietrich, *J. Org. Chem.* **29**, 2927 (1964). [f] Catalytic reduction from the *exo*-side in the bicyclo[2.2.1]heptene system is reported in Ref. in footnote *3.

TABLE II

Additional Shift Values due to Introduction of a Double Bond or a Benzene Ring in Carbon Tetrachloride

	Additional shift values (p.p.m.)[a]				
Compounds to be compared	Bridge-methylene C-7 protons		Bridge-ethylene C-2, C-3 protons		Olefinic protons
	syn	anti	exo	endo	
I - II	-0.11	+0.14	-0.08	+0.24	-
Calcd. value[b]	$+0.06_7$	-0.08_4	-0.04_2	$+0.22_1$	-
II - VII	-0.88	-0.63	-	-	-0.70
VIII - XIII	-0.80	-0.48	-	-	-
Calcd. value[b]	$+0.09_7$	-0.08_7	-	-	-0.00_9
I - VIII	-0.52	-0.27	-0.36	+0.04	-
Calcd. value[c]	-0.09	-0.32	-0.21	+0.09	-
VII - XIII	-1.14	-0.96	-	-	-0.79
Calcd. value[c]	-0.11	-0.32	-	-	-0.10

[a] Plus sign represents an upfield shift. [b] Calculated by Nakagawa and coworkers' method (3, 5, 6), using CENCO-Petersen models. [c] Calculated by Johnson-Bovey's method (7), using CENCO-Petersen models.

those of bicyclo[2.2.2]octane derivatives (6), but the C-7 protons of II and VIII constitute an exceptional case (see TABLE I).

(2) As shown in TABLE II, the C-7 protons in II and VIII are very curiously shielded by the double bond or the benzene ring. Additional shift values of these proton signals due to introduction of π-bonds are quite different from the values calculated from Nakagawa and coworkers' equation (3, 5, 6) for a double bond or from Johnson-Bovey's method (7) for a benzene ring by using CENCO-Petersen models. These calculation methods are well applicable to the C-2 and C-3 protons of II and VIII (see TABLE II) and also to protons in the bicyclo[2.2.2]octane system (3, 6). As described earlier (3), the C-7 and olefinic protons of VII and XIII are also unusually deshielded (see TABLE II).

Although the reason why these unusual magnetic shieldings are caused in the C-7 bridge-methylene protons in the bicyclo[2.2.1]heptene system is not immediately apparent, much caution should be exercised when assigning such geminal proton signals.

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