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NMR STUDIES OF RIGID BICYCLIC SYSTEMS. II.[1] EVIDENCE FOR THE NONEQUIVALENCE OF EXO,EXO AND ENDO,ENDO COUPLING CONSTANTS IN 7-SUBSTITUTED-1,4-DICHLORO-2,2,3,3-TETRA-DEUTERIONORBORNANES[2].

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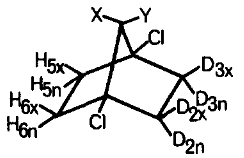
We previously reported the nmr spectrum of 1,4,7,7-tetrachloronorbornane;[4] however, detailed analysis of the spectrum was precluded by its complexity, (8 spins). As an approach to the analysis of the nmr spectrum of 1,4,7-7-tetrachloronorbornane, we have selectively deuterated the 2- and 3-positions, affording an AA'BB' system which is amenable to computer analysis. Additionaly, we have examined several other 1,4-dichloro-2,2,3,3-tetradeuterionorbornanes which bear different substituents in the 7- position with an eye toward generalizing the effect of 7-substituents on the parameters of the AA'BB' system.

Normal and deuterium-decoupled 100 MHz nmr spectra of compounds I-IV have been obtained.[5]



I: $X=Y=OCH_3$ IV: X=Y=H

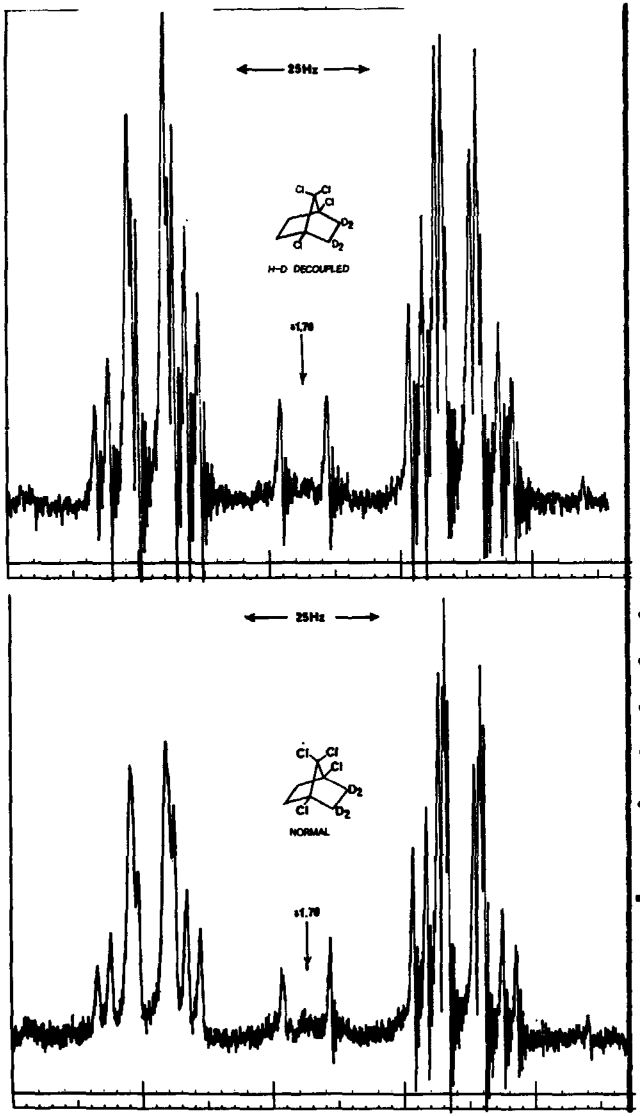
II: X=OAc, $Y=H_7$

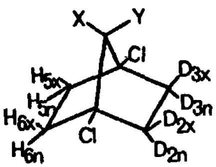
III: X=Y=Cl

The 100 MHz nmr spectrum of a pyridine solution of an additional compound, V,(X=H, Y=Cl), displays a singlet for the 5,6-exo- and 5,6-endo- protons, (accidental degeneracy).

Long range hydrogen-deuterium coupling in accord with Meinwald's "W-letter" rule [6] is evident in the spectra of compounds I-IV. Typically, the normal spectrum of III (Figure 1, Bottom) reveals a distinct broadening in the lowfield half of the centrosymmetric AA'BB' pattern which disappears upon application of deuterium decoupling (Figure 1, Top).

Analyses of the AA'BB' systems I-IV have been carried out using the LAOCOON III program kindly supplied by the authors[7]; the coupling constant and chemical shift values thus obtained are shown in Table I. Some features of Table I deserve comment. Firstly, compound II shows a small, but finite,





	I	II	III	IV
	X = OMe Y = OMe	X = OAc Y = H_{7s}	X = Cl Y = Cl	X = H Y = H
$\nu_{5n} = \nu_{6n}$	153.70±.01	154.06±.01	143.14±.03	154.26±.02
$\nu_{5x} = \nu_{6x}$	217.44±.01	214.21±.01	200.09±.03	178.98±.02
ν_{7s}	- -	536.16±.01	- -	188.90±.02
ν_{7a}	- -	- -	- -	188.90±.02
J_{5n6n}	9.82±.02	9.15±.02	9.97±.04	9.15±.04
$J_{5n5x} = J_{6x6n}$	-11.78±.02	-12.15±.01	-12.31±.04	-12.09±.03
$J_{5n6x} = J_{5x6n}$	4.46±.02	4.16±.01	4.47±.04	4.74±.03
$J_{5n7a} = J_{6n7a}$	- -	- -	- -	(0.09±.09)
$J_{5x7s} = J_{6x7s}$	- -	|0.40±.01|	- -	- -
$J_{5n7s} = J_{6n7s}$	- -	|1.16±.01|	- -	-2.19±.08
J_{5x6x}	12.71±.02	12.85±.02	12.50±.04	13.20±.04

LEFT: Figure 1. Normal (Bottom) and Deuterium-Decoupled (Top) 100 MHz NMR Spectra of Compound III.

RIGHT: Table I. Calculated Values of Coupling Constants and Chemical Shifts (Hz) for Compounds I-IV.

value for $J_{5x,7s}$; to our knowledge, this is the first observation of this non-W-letter long range coupling in a substituted norbornane. Secondly, the presence of substitutents in the 7-position seem to have a small but consistent effect on the magnitude of the AA'BB' system coupling: a _syn_-substituent (Y= Cl, OMe) appears to slightly increase J_{5x6x} and J_{5n6x} and decrease J_{5n6n}, (compare II and IV with I and III in Table I).

Importantly, in all cases we observe that $J_{5n6n} \neq J_{5x6x}$. A significant observation is that our vicinal coupling constants are uniformly _larger_ than those that have been previously reported by other investigators who have studied variously-substituted norbornanes. The brief table below affords a comparison among some typical literature values:

Vicinal J_{HH}	This Work	Ref. 8	Ref. 9	Ref. 10
5x,6x	12.5-13.2	8.9-11.4	9.5	8.9-9.7
5n,6n	9.1-10.0	5.8- 7.7	6.8	5.8-7.7
5x,6n	4.2- 4.8	2.2- 5.8	2.6-2.9	2.2-4.0

Results of calculations on 1,2,2,3,4,7,7-octadeuterionorbornane[11] suggest that the larger values which we observe are characteristic of the norbornane ring system and not the result of the cumulative ponderal and/or electronic effects of the 1, 4, and 7 substituents in I-IV.

Symmetry considerations require that the dihedral angles formed between the 5x and 6x bonds and between the 5n and 6n bonds be equal (zero), and hence, application of the Karplus equation[12] suggests that the corresponding coupling constants, J_{5x6x} and J_{5n6n}, should be equal. A particularly attractive explanation for their observed _non_equivalence in this work lies in the possibility of non-equivalence of the interatomic (through-space) distances r_{exo} and r_{endo} between the 5x,6x and 5n,6n protons, respectively.

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(5) Satisfactory elemental microanalyses have been obtained for nondeuterated analogs of all new compounds reported in this paper. Melting points (corrected) and deuterium analyses (mass spectroscopy) for I-V are shown below:

Compound	Melting Point	$\%d_o$	$\%d_1$	$\%d_2$	$\%d_3$	$\%d_4$
I	92.5 - 93.0	0.2	1.8	6.5	23.0	68.6
II	92.0 - 93.0	0.	0.	6.	24.	70.
III	213.5 -215.0	0.	0.	0.	7.3	92.7
IV	78.0 - 78.5	0.7	1.4	3.6	14.5	79.8
V	68.0 - 68.5	0.5	2.6	11.7	30.4	54.8

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