Tetrahedron. Vol. 32, pp. 537 to 542. Pergamon Press 1976. Printed in Great Britain

REASONS FOR THE NONEQUIVALENCE OF THE *EXO-EXO* AND *ENDO-ENDO* VICINAL NMR COUPLING CONSTANTS IN NORBORNANES

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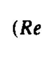
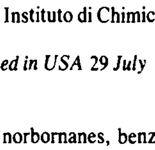
(*Received in USA* 29 *July* 1975; *Received in UK for publication* 16 *October* 1975)

Abstract—In a series of norbornanes, benzonorbornenes, and norbornenes, the vicinal cis couplings $^3J_{exo,exo}$ and $^3J_{endo,endo}$ are determined. A trend is recognized in which $J_{exo,exo}$ steadily decreases in this series while $J_{endo,endo}$ remains relatively constant; in norbornenes $J_{exo,exo}$ and $J_{endo,endo}$ are about the same. These observations are understood by means of theoretical calculations performed for representative compounds of the series. This study indicates that interactions of the C_7-methylene bridge with the bonds of the C_2–C_3 ethylene bridge are responsible for the nonequivalence of $J_{exo,exo}$ and $J_{endo,endo}$ in norbornanes, and that in norbornenes interaction of the olefin functionality with bonds of the ethylene bridge is responsible for bridging $J_{exo,exo}$ back fortuitously close to $J_{endo,endo}$.

Nonequivalence of the *exo–exo* (*ca.* 12 Hz) and *endo–endo* (*ca.* 9 Hz) vicinal H–H coupling constants has been clearly demonstrated[1] in norbornanes **1**. This observation has been perplexing in view of experimental results for substituted norbornenes **2a**, which exhibit[2] almost identical *exo–exo* and *endo–endo* coupling constants. In both cases the dihedral angles between the C–H bonds containing the coupled protons are close to 0° so that equal values would be expected from theoretical considerations.[3] Opening out of the H–C–C angles[1] would be expected[4] to decrease the vicinal coupling, but there is no structural data which suggests that the H_{exo}–C–C angle in **2a** is greater than the corresponding internal angle in **1**.



1



2a

In the present study the *exo–exo* and *endo–endo* coupling constants are determined for a series of norbornanes, benzonorbornenes, and norbornenes. Theoretical techniques are then used to investigate the two types of coupling in norbornane and norbornene, and it is clearly shown that the *exo–exo* coupling in both compounds is *enhanced* by interaction with the electrons of the CH_2 (C_7) bridge, but in norbornene the *exo–exo* coupling is *reduced* by about the same amount owing to interactions of the rear-lobes of the C–H bonds with the electrons of the double bond. The implications of these findings are profound: *structural groups which are several bonds removed from the coupling sites, but which are in proximity to both of the bonds containing the coupled nuclei, can provide important, alternative mechanisms for transmission of the coupling.*

RESULTS

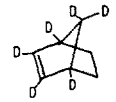
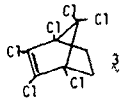
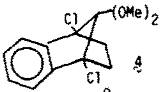
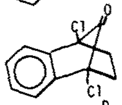
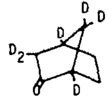
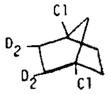
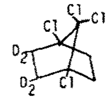
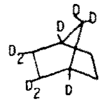
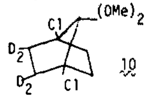
In an effort to establish the generality of the features of the vicinal *exo–exo* and *endo–endo* couplings discussed here, accurate data from nine compounds were collected and appear in Table 1. The NMR spectra of **2–5**, **9** were performed and analyzed in the present study; those of **6–8**, **10** have been previously reported.[1,5] Compounds **2**, **3**, **6–10** were synthesized by us, while compounds **4** and **5** were generously supplied by Dr. James W. Wilt.

The NMR analyses of **2–5**, **7–10** involved the routine solutions of AA'BB' patterns. The NMR analysis of **6** was more complex,[5] but the ethylene bridge of **6** is virtually symmetrical[5] and in this paper will be treated as such.

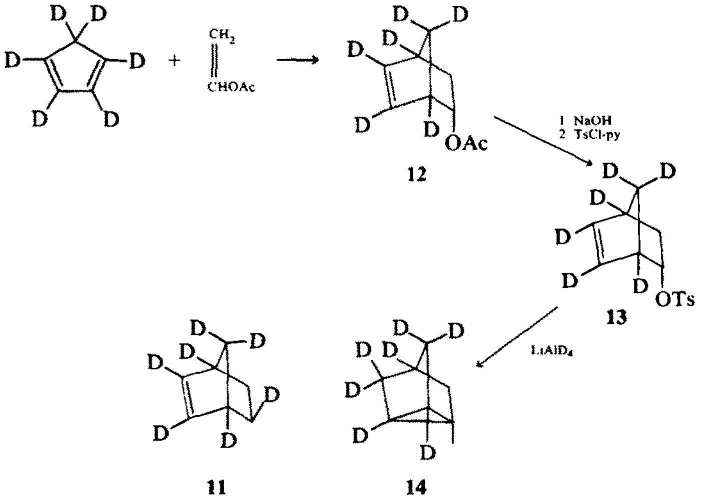
Since an AA'BB' pattern is bilaterally symmetrical, one cannot distinguish from the NMR pattern itself between $J_{AA'}$ and $J_{BB'}$. Experiments done by our group have further established that spin-tickling studies cannot furnish this information. Therefore, there was initially some doubt in our minds if in **2** the *exo–exo* coupling were in fact greater than the *endo–endo* coupling (compare 9·30 with 9·02 Hz). To resolve this uncertainty, the heptadeuterio derivative **11** was synthesized (Scheme 1). A by-product of the last step was deuterated nortricyclene **14**. Analysis of the AA'B pattern of **11** verified the respective *J* values. That $^3J_{exo,exo} > {}^3J_{endo,endo}$ in norbornenes has also been observed in 1,2,3,4,7,7-hexadeuterionorbornen-5-yl carboxylate (9·4, 9·0 Hz).[2]

The syntheses of **2**, **3**, **9** are described in the Experimental. As an example of NMR analysis involved

Table 1. NMR parameters for various norbornenes, benzonorbornenes and norbornanes[a,b]

Compound	Ref.	$J_{exo,exo}$	$J_{endo,endo}$	$J_{exo,endo}$	δ_{exo}	δ_{endo}
 2	c	9.30	9.02	3.87	1.57	0.97
 3	c	9.52	9.10	3.70	2.50	2.06
 4	c	10.76	9.80	4.56	2.44	1.52
 5	c	11.35	11.35	4.90	2.48	1.96
 6	d	12.05	9.12	4.64	1.76	1.42
 7	e	13.20	9.15	4.74	1.79	1.54
 8	e	12.50	9.97	4.47	2.00	1.43
 9	c	12.22	9.05	4.62	1.43	1.13
 10	e	12.71	9.82	4.46	2.17	1.54

[a] J values in Hz, with probable errors less than 0.05 Hz. [b] Chemical shifts in ppm downfield from tetramethylsilane. [c] This work. [d] Ref 5. [e] Ref 1.



Scheme 1.

in this study, Fig. 1 shows observed and simulated NMR patterns for 9.

Inspection of Table 1 makes it clear that throughout a wide variety of parent and substituted compounds, $J_{endo,endo}$ remains at 9–10 Hz, and $J_{exo,exo}$ is 9–10 Hz for norbornenes and 12–13 Hz for norbornanes. An intermediate value of

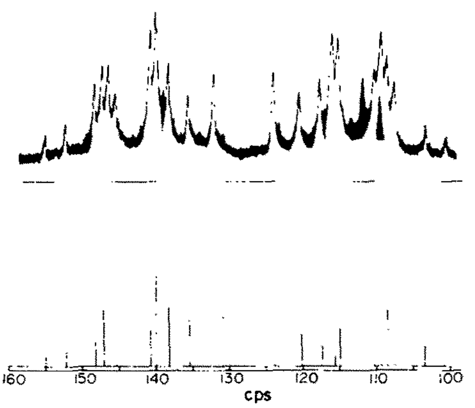


Fig. 1. *Top:* 100 MHz proton NMR spectrum of **9**. The shaded areas represent contributions to the NMR spectrum from isotopic (^{1}H) impurities. *Bottom:* Calculated (LAOCOON III) 100 MHz proton NMR spectrum of **9**.

$J_{exo,exo}$ is seen for the benzonorbornenes **4**, **5**; and an anomalously high $J_{endo,endo}$ appears for **5**, which has an sp^2-hybridized C-7 carbon atom.

THEORETICAL RESULTS AND DISCUSSION

Calculated results in this section are based on the coupling constant formulation of finite perturbation theory (FPT) in the intermediate neglect of differential overlap (INDO)[6,7] approximation of self-consistent-field (SCF) molecular orbital (MO) theory. This method has been quite useful for calculating molecular properties such as geometries, dipole moments, and hyperfine and nuclear spin–spin coupling constants. In the usual applications of the method[6] it is difficult to sort out the individual electronic factors which lead to the calculated coupling constants. For this reason, it is useful to adopt a procedure which has been quite useful in studies of long-range H–H[8] and H–F[9] coupling constants. In the INDO procedure[10] off-diagonal elements of the Fock matrices are of the type

$$F^{\alpha}_{\mu\nu} = \tfrac{1}{2}(\beta_A{}^0 + \beta_B{}^0)S_{\mu\nu} - P^{\alpha}_{\mu\nu}\gamma_{AB}, \qquad (1)$$

where $F^{\alpha}_{\mu\nu}$ is the off-diagonal element of the Fock matrix for electrons of α-spin, $\beta_A{}^0$ and $\beta_B{}^0$ are empirical parameters for atoms A and B, $S_{\mu\nu}$ is the overlap integral between atomic orbitals μ and ν, $P^{\alpha}_{\mu\nu}$ is an element of the charge density-bond order matrix for electrons of α-spin, and γ_{AB} is approximated as a Coulomb integral involving valence shell s-type orbitals for atoms A and B. A similar expression can be written for $F^{\beta}_{\mu\nu}$.[10] These elements can be set equal to zero by choosing $S_{\mu\nu}$ and γ_{AB} to be equal to zero. From a large number of calculations, which were intended to eliminate certain elements of the Fock matrices from the calculations,[8] it was found sufficient to simply set the $S_{\mu\nu}$ for the atoms of interest equal to zero. This is reasonable since one expects $P_{\mu\nu}$ to be quite small unless μ and ν are centered on bonded atoms.

The INDO-FPT calculations for norbornane were based on an electron diffraction structure.[11] The geometry gave identical internal angles for H_{exo}–C–C and H_{endo}–C–C and, therefore, the calculated results reported here do not include complications from this variable. In the absence of suitable structural data for norbornene, one of the ethylene bridges of norbornane was replaced by the fragment –CH=CH–, for which the geometry was taken from the X-ray crystallographic data on *anti*-7-norbornenyl brosylate.[12] The INDO-FPT results for norbornane and norbornene, which are entered in Column I of Table 2, are in quite acceptable agreement with the experimental results in Table 2. Furthermore, $^3J_{exo,exo}$ in norbornane is about 2 Hz greater than in norbornene, whereas $^3J_{endo,endo}$ is just about the same in the two compounds. In norbornene the *exo–exo* coupling is only slightly larger than the *endo-endo* coupling. In all cases the calculated *exo–endo* coupling constants are too large, but this may simply be due to inaccuracies in the H–C–H angles.

In an attempt to recognize the mechanism responsible for the larger *exo–exo* coupling in norbornane, an initial guess was made that the rear lobes of the two *exo* C–H bonds of the two ethylene bridges might interact as depicted in Fig. 2(a). Entry II of Table 2 shows the results for the case in which all of these overlaps across the ring were set to zero. That $J_{exo,exo}$ is still substantially larger than $J_{endo,endo}$ implies that this interaction is not the responsible one.

Next, all of these overlaps were restored and the effect of the C-7 methylene bridge was investigated by setting all of the interactions between the C-7 carbon in norbornane (and its two hydrogens) and the C$_2$ and C$_3$ carbons (and their hydrogens) to zero. The effect (see entry III in Table 2) is dramatic: now $J_{endo,endo}$ is significantly greater than $J_{exo,exo}$. It thus appears that in the norbornane molecule, it is the interaction of the *exo* and *endo* bonds with the methylene bridge that gives rise to the nonequivalence of the *exo–exo* and *endo–endo* coupling constants.

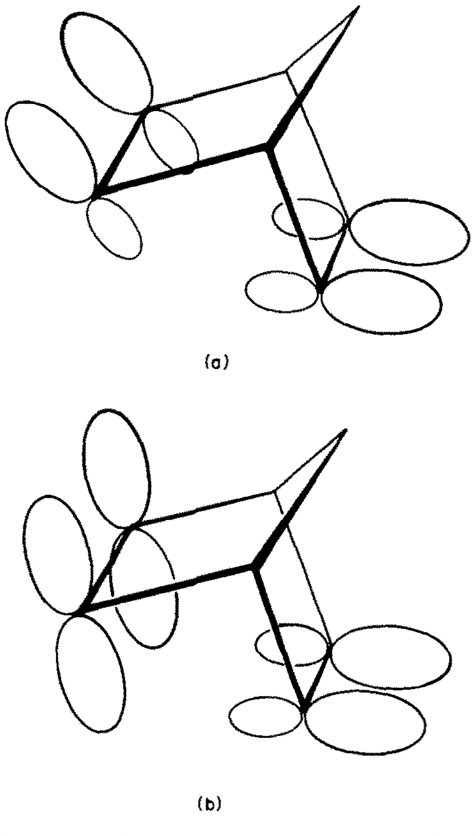


Fig. 2. (a) Schematic representation of exo-carbon hybrid orbitals on C$_2$, C$_3$, C$_5$, and C$_6$ norbornane (**1**). (b) Schematic representation of exo-carbon hybrid orbitals on C$_5$ end C$_6$, and $2p_z$ atomic orbitals on C$_2$ and C$_3$ of norbornene (**2a**).

Table 2. Experimental and calculated vicinal J values for norbornane and norbornene (of the ethylene bridge)[a]

Entry	Experimental	Calculated				
		I[d,e]	II[f]	III[g]	IV[h]	V[i]
$J_{exo,exo'}$ Norbornane	12.2[b]	11.39[d]	12.91	11.06		
$J_{endo,endo'}$ Norbornane	9.1[b]	8.82[d]	8.94	13.57		
$J_{exo,endo'}$ Norbornane	4.6[b]	5.45[d]	5.83	5.58		
$J_{exo,exo'}$ Norbornene	9.30[c]	9.62[e]			11.01	9.68
$J_{endo,endo'}$ Norbornene	9.02[c]	8.85[e]			8.03	9.96
$J_{exo,endo'}$ Norbornene	3.87[c]	5.44[e]			5.83	5.63

[a] In Hz. [b] Taken from compound 9. [c] Taken from compound 2. [d] Normal INDO-FPT calculation on norbornane. [e] Normal INDO-FPT calculation on norbornene. [f] INDO-FPT calculation on norbornane with C_2,C_3,C_5,C_6 interactions (ethylene bridge-ethylene bridge) set to zero. [g] INDO-FPT calculation on norbornane with C_2,C_3,C_7 interactions (ethylene bridge-methylene bridge) set to zero. [h] INDO-FPT calculation on norbornene with C_2p_z,C_3p_z,C_5,C_6 interactions (π-bond contribution) set to zero. [i] Normal INDO-FPT calculation on 7-ketonorbornene.

Since it appears that the C-7 methylene bridge can affect $J_{exo,exo}$ and $J_{endo,endo}$ in such a manner, it now remains to determine the reason for the equivalence of the coupling constants in norbornene. Since the main difference between the two molecules is the olefin, we surmised that the additional mechanistic feature of norbornene might be the π-interaction of the olefin with the back lobes of the *exo*-hydrogens as in Fig. 2(b). Accordingly, this interaction was set to zero by removing the overlap between the p_z orbitals of C_2 and C_3 and the orbitals of C_5 and C_6. Entry IV of Table 2 shows the results: $J_{exo,exo}$ is now substantially larger than $J_{endo,endo}$. This interaction with the π-bond, therefore, seems to be responsible for bringing the $J_{exo,exo}/J_{endo,endo}$ ratio close to unity.

Although the internal angle may still be a factor in norbornane and norbornene in determining the final observed *exo–exo* and *endo–endo* couplings, additional mechanisms via indirect coupling appear to be operating: *other groups removed from the coupling site can provide significant pathways for the transmission of the coupling.* Undoubtedly, many anomalous results in other systems may well be attributable to mechanisms of this general type.

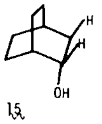
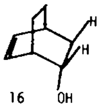
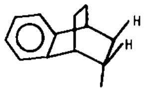
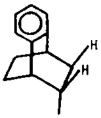
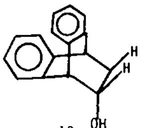
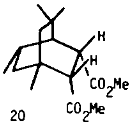
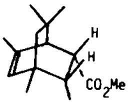
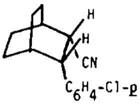
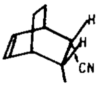
It should be realized that this additional mechanistic feature must be operating for bonds of *both* of the coupling nuclei. For example, norcamphor (**6**) has a $J_{exo,exo}$ value in the "norbornane category" because (regarding the C_5–C_6 ethylene bridge) the functionality is interacting with the bonds on only C_6.

Although a similar theoretical treatment of the benzonorbornenes would be prohibitively expensive, a qualitative assessment can be made of these compounds on the basis of the discussion above. Regarding compound **4** (Table 1), the effects of the 7,7-dimethoxy and 1,4-dichloro functionalities would seem in themselves not to affect significantly $J_{exo,exo}$ and $J_{endo,endo}$ (note these functionalities exist in the norbornane **10**, whose J values are "normal"). The interaction with the π-bond, however, would not be as significant in benzonorbornenes as in norbornenes, owing to a lower π-bond order in the former type of compound. Accordingly, one would anticipate the major difference in benzonorbornenes would be a $J_{exo,exo}$ value intermediate between those of norbornenes and of norbornanes. This is precisely what is observed.

One should be aware that the generalizations $J_{exo,exo} > J_{endo,endo}$ in norbornanes and $J_{exo,exo} \simeq J_{endo,endo}$ in norbornenes may be limited to symmetrical molecules and/or molecules without large distorting groups. Clearly, the dihedral angular dependence will continue to be the main factor affecting vicinal coupling constants, and in asymmetrically substituted norbornanes there can easily be twisting of the overall norbornane skeleton[13] that can lead to significantly different J values.[14] Further, one should be cautious in extending these generalizations to systems with greatly different functionalities with different hybridizations—compound **5** is such an example. Here the $J_{endo,endo}$ value is distinctly different from the pattern of the other compounds of the series. Aside from the distorting effect imposed by strain,[15] there exists the possibility of different coupling mechanisms. In an attempt to uncover the effect of the C-7 ketone, calculations were run on 7-ketonorbornene itself; the results appear in entry V of Table 2. The calculated $J_{endo,endo}$ has increased substantially, consistent with the observed results.

Although examples of accurately determined $^3J_{cis}$ values in rigid systems other than norbornane are not

Table 3. Vicinal J_{cis} values for various bicyclo[2.2.2]octanes

Compound	$^3J_{cis}$	Ref
 15	9.0	b
 16	8.3	b
 17	8.8	b
 18	9.2	b
 19	8.5	c
 20	11.9	d
 21	10.9	d
 22	11.0	e
 23	10.2	e

[a] In Hz. [b] K. Tori, Y. Takano, and K. Kitahonoki, Chem. Ber., 97, 2798-2815 (1964). [c] S. J. Cristol, T. W. Russell, J. R. Mohrig, and D. E. Plorde, J. Org. Chem., 31, 581-4 (1966). [d] Gurudata and J. B. Stothers, Can. J. Chem., 47, 3516-28 (1969). [e] D. B. Roll and A. C. Huitric, J. Pharm. Sci., 54, 1110-17 (1965).

common in the literature, there is sufficient data from the bicyclo[2.2.2]octyl system to make a comparative analysis (Table 3). In the alcohols **15-19**, it is seen that an olefin perturbing the backside of a *cis* vicinal pair of hydrogens (**16**) decreases the coupling; this effect is similar but smaller in magnitude for a benzo functionality (**17**). In the compound pairs **20**, **21** and **22**, **23** the same effect of the olefin is observed. Thus, the same general phenomenon appears to be operating in the bicyclo[2.2.2]octanes as in the bicyclo[2.2.1]heptanes.

EXPERIMENTAL

1,2,3,4,7,7-*Hexadeuterionorbornene* (**2**) was synthesized by the previously published procedure[16] from perdeuteriocyclopentadiene[2] and ethylene.

1,2,3,4,7,7-*Hexachloronorbornene* (**3**) was synthesized by the previously published procedure[17] from hexachlorocyclopentadiene and ethylene.

1,2-*Dichloro*-7,7-*dimethoxybenzonorbornene* (**4**) and 1,2-*dichloro*-7-*ketobenzonorbornene* (**5**) were furnished by James W. Wilt, Loyola University of Chicago.

1,3,3,4,7,7-*Hexadeuterionorcamphor* (**6**) was synthesized and analyzed as previously reported.[5]

1,2,2,3,3,4,7,7-*Octadeuterionorbornane* (**9**). The hydrogenolysis-reduction of 2[17] utilizing deuterium over PdC was carried out as described[18] to give **8**, which was deuteriodechlorinated using sodium and t-butanol-O-d_1 in THF to give **9**, using the procedure of Gassman and Marshall.[19] A pentane soln of **9** thus prepared was purified via preparative gas chromatography (20 ft × 3/8 in SE-30, 30% on 45/60 mesh Chromasorb P; injector temp. 150°, column temp. 110°, He carrier gas, 85 ml/min); under these conditions **9** had a retention time of 32 min. The deuterium content of **9** thus obtained was determined by mass spectrometry (*Found:* 35·0% d_8, 35·4% d_7, 17·9% d_6, 6·4% d_5, 3·0% d_4, 1·8% d_3, 0·8% d_2, 0·0% d_1, 0·0% d_0). The NMR spectrum of **9** appears in Fig. 1.

1,2,3,4,exo-5,7,7-*Heptadeuterionorbornene* (**11**) was synthesized according to the following sequence. A mixture of *exo* and *endo* isomers was carried through to the last step. First, perdeuteriocyclopentadiene[2] (10·35 g) and vinyl acetate (62·0 g) were heated in a steel bomb under N_2 at 195° for 10 hr.[20] The product was distilled off at 70–75° (20 mm) to give 14·0 g (62%) of deuterated acetate **12**. NMR analysis indicated 79:21 *endo*:*exo* isomers.

Compound **12** was saponified with 8% NaOHaq (100 ml) by stirring at room temp. for 22 hr. The alcohol product was isolated by extraction with two 100-ml portions of ether, drying ($MgSO_4$), and concentration under reduced pressure to give 10·2 g (99%) of white semi-solid. The crude product was tosylated according to the procedure of Tipson[21] by its reaction with 25·0 g of *p*-toluenesulfonyl chloride in 120 ml of dry pyridine at −5° for 24 hr. Workup in the usual manner gave 18·24 g (77%) of crude tosylate **13**. NMR analysis indicated 80:20 *endo*:*exo* isomers. Fractional crystallization from petroleum ether gave 11·56 g of white needles, m.p. 58·0–62·5°, NMR analysis 95:5 *endo*:*exo* isomers.

Reaction of 11·56 g of **13** with 3·3 g of lithium aluminum deuteride in a manner identical to that of Nickon for the saturated analog[22] gave, after sublimation (100°, 760 mm) 0·5 g of white semi-solid. NMR analysis indicated at 60:40 ratio of **11**:**14** (norbornene:nortricyclene). The NMR signals of **14** did not interfere with those of **11**, and the mixture was not further purified.

NMR analyses were performed on a JEOL PS-100 NMR spectrometer, with saturated samples in chloroform-*d* with 1% v/v TMS internal standard, utilizing internal lock field sweep mode. The NMR parameters were obtained by analyzing the NMR data with the LAOCOON III program.[23] As an example of this analysis, the observed and simulated spectra of **9** are shown in Fig. 1.

Acknowledgements—The authors are indebted to North Texas State University Faculty Research, to the Robert A. Welch Foundation (B-325), and to the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work. The services of the University of Arizona Computer Center are gratefully acknowledged. We are grateful to Dr. R. E. Wasylishen of the University of Winnipeg for providing coordinates for norbornane.

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