Tetrahedron Letters No. 3, pp 299 - 302, 1974. Pergamon Press. Printed in Great Britain.

LONG RANGE INTERPROTON COUPLING IN NORBORNENES
THE ^4J SICKLE PATHWAY

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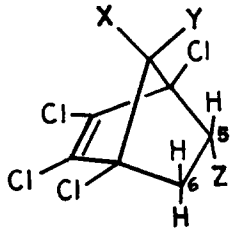
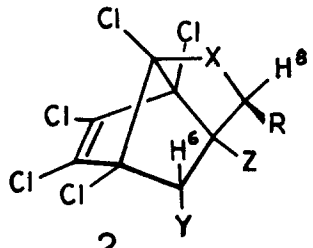
(Received in USA 11 October 1973; received in UK for publication 10 December 1973)

The recognition of distinct and significant interproton coupling across four saturated bonds along the W pathway [1-4] greatly facilitated stereochemical structure assignments and generated considerable theoretical activity. [5-6] The rigid norbornane and norbornene skeletons provide several W arrangements for protons and were especially thoroughly investigated. We now wish to report that these frameworks also provide examples for distinct, directly measurable $^4J_{HH}$ interactions along a non-W pathway as well.

The two main classes of substituted norbornenes which consistently revealed in our investigation the steroisomeric, non-W $^4J_{HH}$ coupling, are illustrated by 1 and 2 and their pertinent coupling parameters are abstracted in Table I and II.



1



2

It is apparent the both structure types provide, in addition to the well known W arrangement, three additional $^4J_{HH}$ pathways. Two of these can be referred to as the sickle (⌐) and one as the fork (∪) arrangement. Whereas the latter and one of the former showed no coupling directly detectable

by splitting or line broadening, one sickle pathway consistently revealed significant $^4J_{HH}$ coupling, whose magnitude often overlapped with the range assigned to the W structure in norbornanes and norbornenes (1-4 Hz).[6]

While a more thorough analysis of the stereochemical, especially angular, requirements for coupling interaction along the sickle pathway is deferred to the full paper, qualitative correlations are apparent from an inspection of molecular models. Thus, in the more revealing of the two classes, in compounds of 2, an extension of the H-C bond representing the "handle" of the sickle points toward and comes close to a hydrogen atom four bonds away in the strongly coupled pairs (H^6 and H^8), whereas it misses considerably the equivalent proton in the alternate, non-coupled sickle arrangement (Y and R). The model thus suggests that, as in the case of the W coupling, a direct interaction between the bonds of the coupled nuclei might be operational, except that in the sickle arrangement the rear lobe of one of the hydrogen-bearing sp^3 carbons and the s orbital of the other hydrogen appear to be involved.

The data presented above indicate that the presence of significant $^4J_{HH}$ coupling alone cannot serve unequivocally to assign the W arrangement to protons separated by two C-C sigma bonds in the norbornane-norbornene skeleton. Determination of the sign of coupling may be necessary, since in contrast to the positive value of the W coupling, the sign of the sickle coupling may well be negative.[7]

TABLE I

$|^4J_{HH}|$ Parameters (Hz) of 1*

	X	Y	Z	H_5-X	H_5-Y	H_{6ex}-X	H_{6ex}-Y	H_{6en}-X	H_{6en}-Y
				⌐⌙	⌙⌐	⌐⌙	⌙⌐	⌇	⌐⌙
a	H	Cl	Cl	0.37	-	0.32	-	2.12	-
b	Cl	H	Cl	-	~0	-	~0	-	~0
c**	H	Cl	F	0.30	-	~0	-	2.32	-
d†	Cl	H	F	-	~0	-	~0	-	~0

* All new compounds gave correct elemental and spectral analyses

** $|^4J_{F-X}| = 2.60$ Hz

† $|^4J_{F-Y}| = 1.66$ Hz

TABLE II

$|^4J_{HH}|$ Parameters (Hz) of 2*

	X	R	Y	Z	Y-R	Y-H^8	H^6-R	H^6-H^8
					⌐⌙	⌇	⌙⌐	⌐⌙
a	O	H	H	H	~0	2.14	~0	1.22
b	O	H	H	Cl	~0	2.72	~0	1.08
c	O	H	H	CH_3	~0	2.67	~0	0.85
d	O	H	H	C_6H_5	~0	2.40	~0	1.40
e	O	H	CH_3	H	~0	-	~0	0.93
f	S	H	H	H	~0	1.55	~0	1.10
g	S	H	H	CH_3	~0	2.02	~0	1.10

* All new compounds gave correct elemental and spectral analyses

* Much of the work described herein was carried out at Hooker Chemical Corporation.

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