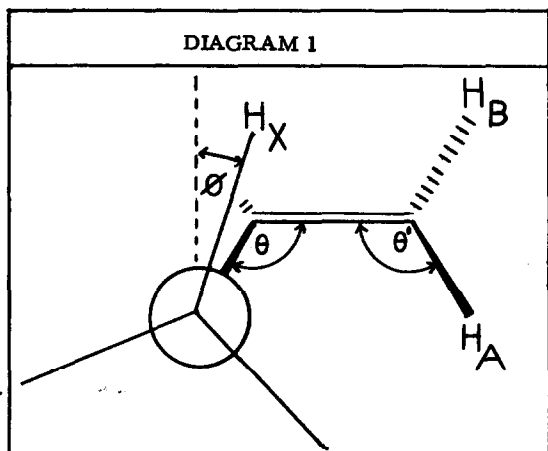


A RE-EVALUATION OF THE STERIC DEPENDENCE OF ALLYLIC COUPLING CONSTANTS

G. P. Newsoroff and S. Sternhell

Department of Organic Chemistry, University of Sydney, N.S.W. 2006, Australia

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Interproton allylic spin-spin coupling

(defined in diagram 1 as cisoid = J_{AX} and transoid = J_{BX}) has received considerable attention and the very large number of data have been thoroughly reviewed and interpreted¹⁻⁵ while the theoretical background is due to Karplus⁶, Barfield^{3,7}, Hoffman⁸ and others^{1,5}.

It is commonly observed¹⁻⁵, and theoretically justified^{2,3,9}, that in acyclic compounds J_{cisoid} has a larger (in fact negative) absolute value than the corresponding J_{transoid} , although very similar sets of values and small reversals have been observed¹⁻⁵. In view of the fact that substituents undoubtedly influence the values of allylic coupling constants and that the conformation in acyclic compounds is often uncertain (see below for examples of pairs of conformationally unequivalent isomers), these slight reversals have not been considered significant from the theoretical point of view and merely emphasise that the relation $|J_{\text{cisoid}}| > |J_{\text{transoid}}|$ is unreliable as a basis of structural assignments in acyclic systems^{5,9}.

We have previously observed¹⁰ a significantly larger $|J_{\text{transoid}}|$ than $|J_{\text{cisoid}}|$ in a structure devoid of conformational ambiguity. We have since prepared a large number of analogous compounds, conducted a literature search for further examples and obtained a number of compounds from other laboratories for accurate NMR measurements. A selection from these results is given in table 1. It can be seen that with four-membered,

TABLE I. ALLYLIC COUPLING CONSTANTS²

No.	Structure	J _{AX} or J _{BX} (Hz)		No.	Structure	J _{AX} or J _{BX} (Hz)	
		cisoid	transoid			cisoid	transoid
1		i R=H	1.72	7 ^d		1.98	2.32
		ii R=Me	1.44			1.15	
		iii R=Ph	1.35			1.13	
		iv R=Cl	1.50				
		v R=Br	1.38				
2		i R=H	1.48	8		1.66	
		ii R=Me	1.24			2.05	1.61
3 ^b				9 ^e			3.0 ± 0.1
4 ^c				10 ^f			3.28
5		i R=H	1.86	11 ^g			3.10
		ii R=Me	1.67			2.21	
		iii R=Ph	1.40			2.20	
		iv R=Cl	1.68			1.88	
		v R=Br	1.63			2.34	
6		i R=H	2.10				
		ii R=Me	1.95			2.38	

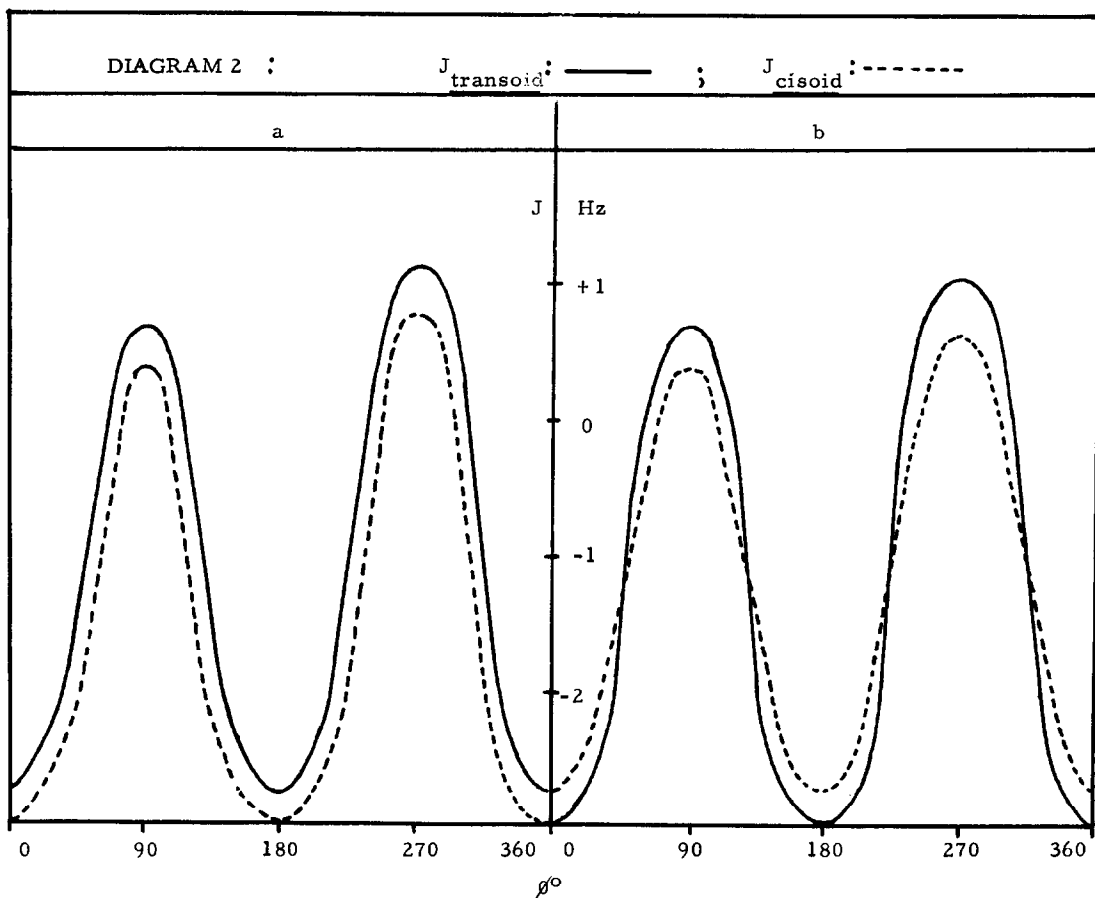
Footnotes to Table 1

a All new compounds gave correct elementary analyses and spectroscopic constants. NMR assignments were made on the basis of well established shielding effects by neighbouring groups. Unless otherwise stated, the coupling constants are significant to $\pm .02$ Hz. Where no signs are indicated the coupling constants can be assumed to be negative by analogy (c. f. references in text). All data from these laboratories were obtained with a Varian HA100 instrument for approximately 10% solutions in CDCl_3 or CCl_4 . b M. Mühlstädt, M. Hermann and A. Zschunke, Tetrahedron, 24, 1611 (1968). c G. Van Binst, J. C. Nouls, J. Stokoe, C. Danheux and R. H. Martin, Bull. Soc. Chim. Belges, 74, 506 (1965); J. C. Nouls, P. Wollast, J. C. Braekman, G. Van Binst, J. Pecher and R. H. Martin, Tetrahedron letters, 2731 (1968). d We are grateful to Prof. Takashi Tsuji for a sample of a precursor of this compound. See also T. Tsuji, I. Moritani, S. Nishida and G. Tadokoro, Bull. Chem. Soc. Japan, 40, 2344 (1967). e We are grateful to Prof. Dr. M. Mühlstädt for a sample of a precursor of this compound. See also M. Mühlstädt and H. Meinhold, J. Prakt. Chem., 37, 162 (1968). f W. Cherry, Q. N. Porter and S. Sternhell, unpublished data. g We are grateful to Prof. E. Ritchie and Dr. W. C. Taylor for this sample. See also L. N. Mander, E. Ritchie, and W. C. Taylor, Aust. J. Chem., 20, 1021 (1967) and reference 1. The value quoted here represents accurate remeasurement.

five membered, rigid six-membered and probably also with three-membered¹¹ rings with exocyclic methylene, alkylidene etc. groups $\left| J_{\text{transoid}} \right| > \left| J_{\text{cisoid}} \right|$. The apparent inconsistency with some non-rigid six-membered rings (Table 1) can be easily resolved by considering the following points: (i) In compounds (1i) and (2i) the six-membered rings are probably not planar and hence the angles θ are not approximately 30° and 150° , as with flat rings, but approximately 15° and 105° (Dreiding models). The allylic coupling constants are therefore averages for these two angles and should be similar to those in propene³ as is indeed found. (ii) The sets of isomeric pairs (1ii - 1v) and (2ii) are not expected to exist in identical average conformations, and examination of models and the established¹⁻⁵ relationship between

θ and the magnitude of allylic coupling leads to the expectation of larger $|J_{\text{allylic}}|$ for the flatter trans series than for the more puckered cis series, as is indeed found.

From the examination of the data for planar compounds (Table 1, entries 3-9 and other examples collected by us) we conclude that as the angle θ approaches 0 or 180° (i.e. for large, presumably negative, allylic coupling constants) J_{transoid} becomes consistently larger than J_{cisoid} . This, besides being of obvious empirical usefulness in the interpretation of NMR spectra¹², explains the series of uncertain values for acyclic compounds (see above) as lying close to the "cross-over" point and also the fact that the largest (absolute magnitudes) allylic coupling constants are observed for transoid cases (e.g. entries 3, 10 and 11 in Table 1). Clearly, a reinterpretation of the theoretical basis of allylic coupling is required.



For the purposes of structural determination, Barfield's curves³ (Diagram 2a) will still be found useful, although clearly a modification to a form shown in Diagram 2b must be made. As pointed out by Garbisch² there is also some uncertainty about the values of J_{cisoid} for $\theta = \text{ca. } 90^\circ$, where the scarce experimental data suggest that the calculated³ values are too far to the positive side. Further, recent calculations by Barfield⁷ indicate that the large negative maxima at $\theta = 0^\circ$ and 180° in Diagrams 2 should be deeper by approximately 0.4 Hz. Entries 3, 10 and 11 in Table 1 support this. The remaining portions of the thus modified two curves in Diagram 2b fit quite well the numerous experimental results assembled by us, which will be published elsewhere.

It cannot be overemphasised that some rare substituent effects⁵, bond orders less^{4,5} than 2, the possibility of alternative simultaneous coupling paths in small cyclic systems, steric strain and unusual magnitudes of the planar angles (θ and θ' in Diagram 1) in the allylic system will cause significant deviations^{1-5, 13} from the general relationships summarized in Diagram 2. The best example of such a discrepancy is found in cyclobutene derivatives¹⁴ where the (transoid) allylic coupling constants have much smaller (negative) values than expected from the magnitude of θ . This is most likely due to the presence of two "sigma"³ coupling paths leading to a larger positive (cancelling) contribution.

References

- 1 S. Sternhell, Rev. Pure and Appl. Chem., 14, 15 (1964).
- 2 E. W. Garbisch, J. Am. Chem. Soc., 86, 5561 (1964).
- 3 M. Barfield, J. Chem. Phys., 41, 3825 (1964).
- 4 N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry - Illustrations from the Steroid Field", Chap. 5, Holden-Day 1964.
- 5 L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Chap. 4-4, Pergamon 1968.
- 6 M. Karplus, J. Chem. Phys., 33, 1842 (1960).
- 7 M. Barfield, J. Chem. Phys., 48, 4463 (1968).

- 8 R. A. Hoffman, Arkiv för Kemi, 17, 1 (1961).
- 9 H. Rottendorf, S. Sternhell, and J. R. Wilmshurst, Austral. J. Chem., 18, 1759 (1965).
- 10 D. Brookes, S. Sternhell, B. K. Tidd, and W. B. Turner, Austral. J. Chem., 18, 373 (1965).
- 11 W. Rahman and H. G. Kuivila, J. Org. Chem., 31, 772 (1966); A. W. Herriott and W. M. Jones, Tetrahedron letters 2387 (1967); E. Ciganek, J. Am. Chem. Soc., 88, 1979 (1966); H. G. Peer and A. Schors, Rec. Trav. Chim., 86, 161 (1967).
- We are grateful to Professors H. G. Kuivila and W. M. Jones for the opportunity to examine the NMR spectra run in their laboratories, for samples and for helpful correspondence.
- 12 We have found that, with very few exceptions, the allylic coupling constants for exocyclic groups in the literature are either misinterpreted or left uninterpreted.
- 13 P. Laszlo, Doctoral Thesis, University of Paris, 1965.
- 14 E. H. Hill and J. D. Roberts, J. Am. Chem. Soc., 89, 2047 (1967); S. Farid, W. Kothe and G. Pfundt, Tetrahedron letters, 4151 (1968); P. Dowd, J. Am. Chem. Soc., 89, 715 (1967). The measurement of the allylic coupling constant in 3-methylcyclobutenone (± 0.63 Hz) was carried out in this laboratory. We are grateful to Dr. P. Dowd for the sample of this material.