An Interpretation of Observed Long-range Couplings

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Long-range spin-spin interactions between protons separated more than three bonds in saturated and unsaturated compounds have recently become the subject of a number of reports.[1] With respect to this problem, the importance of the straight zig-zag path (the M- or W-rule) in saturated systems has been pointed out by Rassat et al.[2] A similar case holds with some aromatics.[3]

In this note, we should like to point out the additivity of the coupling constants with respect to the paths across which the long-range couplings take place. Such an empirical rule has not yet been pointed out in the previous reports. It seems to fit especially the large long-range couplings observed. The decrease in the coupling constant with the increase in the number of the bonds between nuclei was pointed out by Aihara.[4] Therefore, when the

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1) S. Sternhell, *Rev. Pure and Appl. Chem.,* **14**, 15 (1964); many references are cited therin.
2) A. Rassat, C. W. Jefford, J. M. Lehn and B. Waegell, *Tetrahedron Letters,* **1964**, 233.

3) a) K. Takahashi, T. Kanda, F. Shoji and Y. Matsuki, This Bulletin, **38**, 508 (1965); b) M. M-Smith, S. T. Reid and S. Sternhell, *Tetrahedron Letters,* **1965**, 2393.
4) E. Aihara, *J. Chem. Phys.,* **26**, 1347 (1957).

TABLE I. SOME EXAMPLES SHOWING THE ADDITIVE CONTRIBUTION OF THE EFFECTIVE COUPLING
PATHS BETWEEN TWO PROTONS

No.	Compound	No. of bonds	No. of paths	Observed coupling constant, c.p.s.	Ref.
1	2-Endo, 3-endocamphane-2, 3-diol	4	1	1.4, 1.0	a
2	Exo-3-substituted norcamphors	4	1	3—4	b
3	Bicylo(2, 2, 1)-heptanes	4	1	1	b
4	cis-1, 3-Dihalogenocyclohexanes	4	1	1.9	c
5	Bicyclo(2, 1, 1)-hexanes	4	2	7	b
6	Tricyclo(1, 1, 1, 0)-pentane	4	3	14	d
7	1, 3-Dioxanes	5	2	0.9	e
8	Thianaphthenes	6	1	0.6	f
9	Indoles	6	1	0.4	g
10	Thienopyrroles	6	2	1.3	h
11	Thienothiophene	6	2	1.55	i

a) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961); b) J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963); c) H. M. vanDort and Th. J. Sekuur, *Tetrahedron Letters*, **1963**, 1301; d) S. Masamune, *J. Am. Chem. Soc.*, **86**, 735 (1964); e) Ref. 6; f) Ref. 3; g) Ref. 3b; h) R. J. Tuite, A. D. Josey, H. R. Snyder, *J. Am. Chem. Soc.*, **82**, 4360 (1960); i) B. Gestblom, R. A. Hoffman and S. Rodamar, *Acta Chem. Scand.*, **18**, 1222 (1964).

magnitudes of the coupling constants are first compared, the number of the bonds between nuclei must be taken into consideration. The notation of J_{ij}^{n} will be used here; n denotes the number of bonds between two nuclei, i and j, in series. The magnitude of the J^4 value between two protons is too small to be observed in usual saturated compounds, but it sometimes amounts to about 2 c. p. s. with one straight zig-zag path, as is shown by the examples of Nos. 1, 2, 3 and 4 in Table I. A theoretical approach to this problem was formulated by Barfield.[5] On the other hand, in bicyclo(2, 1, 1)hexanes (No. 5 in Table I), J^4 amounts to about 7 c. p. s., and, in this case, the number of paths connecting two protons is two; therefore, the magnitude of coupling may be expected to be approximately twice as much as is the case with only one path. No. 6

in Table I shows an abnormally large long-range coupling of 14 c. p. s.; this magnitude of coupling is considered to be about three times the magnitude of the examples with only one path. Recently, the J^5 value between protons has been observed with some 1, 3-dioxanes;[6] in this case the paths are also considered to be two. J^6 values between protons have been observed with some aromatics.[2] As can be seen from a comparison between the values of Nos. 10 and 11 and Nos. 8 and 9 in Table I, the cases with two paths show values of the coupling constants about twice as large as those in which only one path is effective. From the above-mentioned data, it may be concluded that the additive contribution of the effective coupling paths holds, to a good approximation, in the long-range couplings observed.

5) M. Barfield, ibid., **41**, 3825 (1964).

6) K. C. Ramey and J. Messick, *Tetrahedron Letters,* **1965**, 4423; J. Delmau and J. Duplan, ibid., **1966,** 559.