The Nuclear Magnetic Resonance Spectra of Olefinic Protons and the Substituent Effects. V.[*1] Spin-spin Coupling in *trans*-1, 2-Disubstituted Ethylenes[*2]

Jun NIWA

Chemical Laboratory, Department of General Education, Nagoya University, Chikusa-ku, Nagoya

(Received February 10, 1967)

The present author has measured the spin-spin coupling constant, J_{trans}, for a variety of *trans*-1, 2-disubstituted ethylenes, $R_iCH=CHR_j$, in a CCl_4 solution and has tried to determine how the magnitude of J_{trans} depends on the electronegativity of the substituent, as has been proposed by Cavanaugh *et al.*[1)]

[*1] Part IV: J. Niwa, This Bulletin, **40**, 1512 (1967).

[*2] Presented in part at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

1) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961); P. Laszlo and P. R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2709 (1963); W. Gordy and J. O. Thomas, *J. Chem. Phys.*, **24**, 439 (1956).

TABLE 1. COUPLING CONSTANTS OF OLEFINIC PROTONS IN *trans*-1, 2-DISUBSTITED ETHYLENES, $R_iCH{=}CHR_j$, IN cps, AND VALUES OF SUBSTITUENT ELECTRONEGATIVITIES

	Substituent				
	R_i	R_j	J_{trans}		$\sum E(R)$1,3)
1	H	Li	23.9a)		2.1+1.0
2	H	Al	21.4a)		2.1+1.5
3	H	Hg	21.0a)		2.1+1.9
4	H	Sn	20.3a)		2.1+1.9
5	H	Pb	19.6a)		2.1+1.9
6	H	Sb	19.5a)		2.1+2.0
7	H	As	19.1a)		2.1+2.1
8	H	H	19.0a)		2.1+2.1
9	H	CN	18.2a)		2.1+2.49
10	H	COR	18.0a)		2.1+2.5
11	H	C_6H_5	18.0b)	18.0c)	2.1+2.75
12	CH_2OOCCH_3	CH_2OOCCH_3	18.0b)		2.12+2.12
13	CN	C_6H_5	17.1b)	17.5c)	2.49+2.75
14	H	pyridyl	17.5a)		2.1+2.5
15	H	C_2H_5	—	17.4d)	2.1+2.5
16	H	CO_2CH_3	17.2a)	17.2c)	2.1+2.55
17	H	CH_3	—	16.8e)	2.1+2.5
18	$CO_2C_2H_5$	2-furyl	16.8b)		2.55+2.50
19	H	sulphone	16.6a)		2.1+3.0
20	CN	CH_3	16.0b)	16.5c)	2.49+2.5
21	*p*-$C_6H_5OCH_3$	CH_3	16.4b)		2.74+2.5
22	CO_2CH_3	$COCH_3$	—	16.2c)	2.55+2.70
23	H	NR	16.1a)		2.1+3.0
24	C_6H_5	$CO_2C_2H_5$	15.9b)		2.75+2.55
25	C_6H_5	CO_2H	15.8b)	15.8c)	2.75+2.60
26	CHO	2-furyl	15.7b)		2.69+2.50
27	CO_2CH_3	CH_3	15.5b)	15.7c)	2.55+2.5
28	$COCH_3$	CH_3	—	15.7c)	2.70+2.5
29	CHO	CH_3	—	15.6c)	2.69+2.5
30	CO_2CH_3	C_6H_5	—	15.6c)	2.55+2.75
31	CHO	C_6H_5	15.9b)	15.6c)	2.69+2.75
32	C_6H_5	C_6H_5	15.6b)		2.75+2.75
33	C_6H_5	CH_3	15.6b)		2.75+2.5
34	$CO_2C_2H_5$	C_2H_5	15.6b)		2.55+2.5
35	$CO_2C_2H_5$	$CO_2C_2H_5$	15.5b)		2.55+2.55
36	$COCH_3$	C_6H_5	16.3b)	15.5c)	2.70+2.75
37	COCl	C_6H_5	—	15.5c)	(*2.57*+2.75)
38	C_6H_5	$SCH_2C_6H_5$	15.5b)		2.75+2.75
39	COCl	CH_3	—	15.5c)	(*2.57*+2.5)
40	Br	H	15.2a)		2.96+2.1
41	NO_2	H	15.0a)		3.70+2.1
42	Cl	H	14.6a)		3.25+2.1
43	C_6H_5	SC_6H_5	14.4b)		2.75+2.82
44	NO_2	2, 3-$C_6H_3(OCH_3)$	14.4b)		3.70+2.5
45	Br	C_6H_5	—	14.3c)	2.96+2.75
46	OR(alkyl)	H	14.2a)		3.5+2.1
47	Cl	C_6H_5	—	14.0c)	3.25+2.75
48	OOCR	H	13.9a)		3.5+2.1
49	OR(aryl)	H	13.7a)		3.5+2.1
50	Br	CH_3	—	13.7c)	2.96+2.5
51	Br	CO_2CH_3	—	13.5c)	2.96+2.55
52	NO_2	C_6H_5	13.3b)	13.5c)	3.70+2.75
53	Cl	CO_2CH_3	—	13.3c)	3.25+2.55

Table 1. (Continued)

	Substituent R_i	R_j	J_{trans}	$\sum E(R)$[1,3]
54	phosphate	H	13.2[a]	3.5+2.1
55	Cl	CH_2Cl	13.1[a]	3.25+2.26
56	NO_2	CH_3	— 12.8[c]	3.70+2.5
57	F	H	12.75[a]	3.92+2.1
58	$OOCCH_3$	C_5H_{11}	12.5[b]	3.72+2.5
59	OR	alkyl	12.0—12.6[b]	3.5+2.5
60	Cl	Cl	12.1[b]	3.25+3.25
61	Br	Br	11.8[b]	2.96+2.96
62	F	CH_3	11.1[b]	3.92+2.5
63	F	Br	11.0[b]	3.92+2.96
64	F	F	9.5[b]	3.92+3.92

a) Cited from Ref. 2.

b) Cited from Ref. 3.

c) Measured by the present author. The condition of measurement was described in Parts I and III. H. Kasiwagi and J. Niwa, This Bulletin, **36**, 405 (1963); J. Niwa and H. Kasiwagi, *ibid.*, **36**, 1414 (1963).

d) Cited from Solomon *et al.* I. Solomon and N. Bloembergen, *J. Chem. Phys.*, **25**, 261 (1956).

e) Cited from Bothner-By *et al.* A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961).

As for the correlation between the proton coupling constant, J, and the substituent electronegativity, E(R),[1,3] it was pointed out by Banwell *et al.*[2] in 1962 that the J-value in vinyl compounds, $H_2C{=}CHR$, was correlated with E(R) according to this relationship, for example:

$$J_{trans}=19(1-0.17\Delta E) \qquad (1)$$

where ΔE was the difference in electronegativity between the substituent, R, and the hydrogen atom it replaced ($\Delta E=E(\mathrm{R})-E(\mathrm{H})$) and where the range of E(R) examined was 1.0(Li) to 3.92(F). Later, Laszlo *et al.*[3] proved that the J-values for a variety of 1, 2-disubstituted ethylenes, $R_iCH{=}CHR_j$, depended on the sum of the substituent electronegativities as expressed in the form, for example, of:

$$J_{trans}=19.0(1-0.17\sum\Delta E) \qquad (2)$$

where $\sum\Delta E=(E(\mathrm{R}_i)-E(\mathrm{H}))+(E(\mathrm{R}_j)-E(\mathrm{H}))$. In this case, Laszlo *et al.* were solely concerned with 1, 2-disubstituted ethylenes and the variation in the substituent was not yet sufficiently extensive, for the E(R) range examined was restricted to from 2.1(H) to 3.92(F). It is possible, however, to regard vinyl compounds as belonging to *trans*-1, 2-disubstituted ethylenes bearing hydrogen as an invariable substituent, R_i, trans to R_j. Therefore, it may be worth inquiring whether a common correlation exists between J_{trans} and $E(\mathrm{R}_i)+E(\mathrm{R}_j)$ in the series of both vinyl compounds and *trans*-1, 2-disubstituted ethylenes over the extended E(R) range of from 1.0(Li) to 3.92(F). In the present paper, 14 new data on the 1,2-disubstituted ethylenes are supplied. Table 1 compiles the J_{trans}-values for 64 compounds belonging to the 1, 2-disubstituted ethylenes, including 21 compounds measured by the present author. The E(R) values employed are also given in the table, where the E(R) value for COCl is calculated by using Eq. (3) for cinnamoyl chloride. As is shown in Fig. 1, the collected data fairly well fit by the relationship:

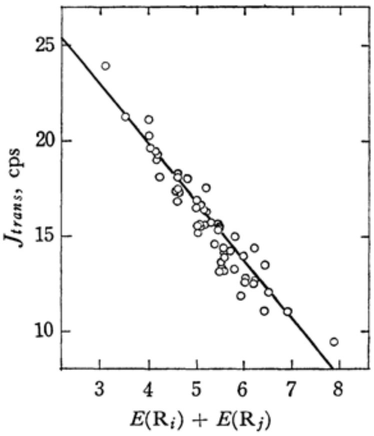

Fig. 1. Correlation between J_{trans} and $\sum E$(R). The data are from Table 1.

$$J_{trans}=19(1-0.17\sum\Delta E) \qquad (3)$$

which shows the same result as that obtained by Banwell *et al.* and by Laszlo *et al.* The values of the standard deviation and the correlation coefficient were 0.88 and 0.95, respectively. The present paper thus substantiates, with much more extensive data, the relationship found by Schaefer, Banwell, Laszlo, and their co-workers.

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2) C. N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, **34**, 115 (1962); T. Schaefer, *Can. J. Chem.*, **40**, 1 (1962).

3) P. Laszlo and P. R. Schleyer, *Bull. Soc. Chim. France*, **1964**, 87.