

# Contributions to the Nuclear Spin-Spin Coupling Constants of Directly Bonded Carbons

Jerome M. Schulman\*<sup>1a</sup> and Marshall D. Newton<sup>1b</sup>

Contribution from the Departments of Chemistry, Queens College, City University of New York, Flushing, New York 11367, and Brookhaven National Laboratory, Upton, Long Island, New York 11973. Received April 22, 1974

**Abstract:** The three contributions to spin-spin coupling constants for directly bonded carbon atoms (orbital dipole,  ${}^1J_{CC}{}^{od}$ ; spin dipole,  ${}^1J_{CC}{}^{sd}$ ; and Fermi contact,  ${}^1J_{CC}{}^{Fc}$ ) are calculated using the coupled Hartree-Fock perturbation formalism of Blizard and Santry, at the INDO level of approximation. After evaluating the parameters  $S_C^2(0)$  (s orbital density at the carbon nucleus) and  $\langle r^{-3} \rangle_C$  by a least-squares fit of calculated and experimental values for 16 single bonds in a representative set of acyclic and cyclic hydrocarbons, predictions of  ${}^1J_{CC}$  are made for a variety of other bonds. The standard deviation of the fit is 3.4 Hz. For three-membered rings a strong reduction in the contact contribution is found, relative to typical values in the other hydrocarbons. The spin-dipolar term for single bonds is generally  $\sim 1$  Hz, except for three-membered rings where values of  $-0.3$  to  $-1.0$  are found. Typical orbital-dipolar values range from  $-2$  to  $-3$  Hz, although positive values are found for fused four-membered rings. An important overall result is that noncontact terms make a large relative contribution to  ${}^1J_{CC}$  for three-membered rings. The results from perturbation theory are compared with predictions based on per cent s character in the carbon bonding hybrids and generally good agreement is found, leading to the suggestion that the negative intercept of the per cent s correlation simulates the negative noncontact contributions to  ${}^1J_{CC}$ . While hybridization trends can account for the reduced cyclopropane  ${}^1J_{CC}{}^{Fc}$  values, alternative mechanisms involving indirect coupling are briefly discussed. In this connection, calculated values of geminal coupling constants,  ${}^2J_{CC}$ , are presented for four-membered rings (typically  $-7$  to  $-10$  Hz) and are found to be consistent with available experimental data.

As is well known from the work of Ramsey,<sup>2</sup> nuclear spin-spin coupling constants of rapidly tumbling molecules result from three distinct, physically inseparable coupling mechanisms: (1) orbital-dipole interaction between the magnetic field arising from orbital motion of the electron and the nuclear magnetic dipole; (2) magnetic spin-dipolar interaction between the electronic and nuclear spins, and (3) Fermi-contact interaction between electronic and nuclear spins. In obvious notation

$$J_{AB} = J_{AB}{}^{od} + J_{AB}{}^{sd} + J_{AB}{}^{Fc} \quad (1)$$

for coupled nuclei A and B. Most theoretical attention has been given to mechanism 3 which, except for the case of fluorine among first-row atoms, has generally been assumed to be the sole contributor. This viewpoint is supported by analogy with the HD molecule, for which elaborate calculations indicate noncontact involvement to the extent of only a few per cent,<sup>3</sup> and also by semiempirical studies, principally on H, C, N, and F.<sup>4-6</sup> This simplification of the coupling constant problem is of practical importance, since the Fermi contact mechanism is far easier to treat, at least on a semiempirical level, than mechanisms 1 or 2, for which the perturbed molecular orbitals are complex valued

and the perturbing matrix elements are harder to compute. However, the calculations reported in the present paper indicate that the orbital and spin-dipolar mechanisms can make significant relative contributions to the coupling constants for directly bonded carbons,  ${}^1J_{CC}$ ,<sup>7</sup> when the bond is incorporated into a strained ring. Thus, in addition to their intrinsic importance in nmr spectroscopy, the values of  ${}^1J_{CC}{}^{od}$  and  ${}^1J_{CC}{}^{sd}$  are of interest in theoretical organic chemistry, where  ${}^1J_{CC}$  is a traditional probe of hybridization.<sup>8,9</sup>

## I. Method and Results

The method of calculation employed here was that described by Blizard and Santry.<sup>6</sup> In essence, it is a matrix version of the coupled Hartree-Fock perturbation treatment, implemented with INDO parametrizations and approximations for the unperturbed molecular orbitals and limited to one-center contributions to the matrix of the perturbing operator.<sup>10,11</sup> This semiempirical approach is rapid, and it furnishes a contact contribution proportional to the square of the s-electron density at the pertinent carbon atoms,  $S_C^2(0)$ , and orbital and spin-dipolar contributions proportional to the square of the average value of  $r^{-3}$  at each carbon,

(1) (a) Queens College; Alfred P. Sloan Fellow; (b) Brookhaven National Laboratory.

(2) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).

(3) (a) E. Ishiguro, *Phys. Rev.*, **111**, 203 (1958); (b) E. A. G. Armour, *J. Chem. Phys.*, **49**, 5445 (1968); (c) J. M. Schulman and D. N. Kaufman, *ibid.*, **53**, 477 (1970).

(4) H. H. McConnell, *J. Chem. Phys.*, **24**, 460 (1956).

(5) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(6) A. C. Blizard and D. P. Santry, *J. Chem. Phys.*, **55**, 950 (1971); *ibid.*, **58**, 4714 (1973). The reader should note that the  ${}^1J_{CC}$  values of Blizard and Santry differ somewhat from those presented here, since their least-square parameters were based on a rather diverse set of molecules, including triple bonds, while our set was restricted to single bonds.

(7) For a review of spin-spin coupling constants between directly bonded atoms, see T. W. McFarlane, *Quart. Rev., Chem. Soc.*, **23**, 187 (1969).

(8) (a) K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **38**, 1216 (1963); (b) Z. B. Maksic, M. E. Maksic, and M. Randic, *Theor. Chim. Acta*, **22**, 70 (1970).

(9) M. D. Newton, J. M. Schulman, and M. M. Manus, *J. Amer. Chem. Soc.*, **96**, 17 (1974).

(10) For the Fermi-contact term this method gives identical results, within computer round-off error, with the finite-perturbation method of J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2965 (1968).

(11) The exclusion of many-center perturbation matrix elements has not been adequately tested. In particular, part of the orbital contribution,  ${}^1J_{AB}{}^{od}$ , vanishes in this approximation.<sup>9</sup>

**Table I.** Contributions to  ${}^1J_{CC}$  (Hz) for Single Bonds

Molecule	Bond <sup>a</sup>	${}^1J_{CC}^{od}$	${}^1J_{CC}^{sd}$	${}^1J_{CC}^{Fc}$	Total ${}^1J_{CC}$	Exptl <sup>b</sup>	${}^1J_{CC}$ from hybridization <sup>c</sup>
Ethane		-2.3	1.1	36.8	35.6	34.6	40.0
Methylacetylene		-2.0	0.8	62.0	60.8	67.4	68.9
Toluene		-2.2	1.1	38.5	37.4	44.2	43.4
Neopentane		-1.8	1.2	31.7	31.1	33.7	32.2
Cyclopropane		-2.8	-0.3	16.3	13.2	(10.0) <sup>d</sup>	13.2
Cyclobutane		-0.8	1.1	30.5	30.8	29.8	28.6
Spiropentane		-2.6	-0.5	21.3	18.2	20.2	18.8
Bicyclobutane	C <sub>1</sub> C <sub>2</sub>	-3.3	-0.5	25.2	21.4	21.0	23.2
	C <sub>1</sub> C <sub>3</sub>	-2.9	-1.3	-1.4	-5.6	(16) <sup>e</sup>	-8.4
Bicyclopentane	C <sub>1</sub> C <sub>2</sub>	-0.8	1.0	40.3	40.5	36.7	37.1
	C <sub>1</sub> C <sub>4</sub>	-2.1	-0.8	6.6	3.7		6.0
	C <sub>1</sub> C <sub>5</sub>	-2.9	-0.5	19.3	15.9	16.0	15.8
Norbornane	C <sub>1</sub> C <sub>2</sub>	-1.7	1.1	34.2	33.6	33.4	32.2
	C <sub>1</sub> C <sub>7</sub>	-1.5	1.2	34.9	34.6	32.5	28.3
Nortricyclene	C <sub>1</sub> C <sub>7</sub>	-1.7	1.1	44.6	44.0	40.4	38.3
	C <sub>3</sub> C <sub>4</sub>	-1.6	1.2	34.1	33.7	29.8	30.2
Quadricyclene	C <sub>1</sub> C <sub>2</sub>	-2.5	-0.6	17.0	13.9	12.6	14.0
	C <sub>1</sub> C <sub>7</sub>	-1.9	1.1	44.9	44.1	41.5	39.5
Prismane	C <sub>1</sub> C <sub>2</sub>	-2.1	-0.8	14.2	11.3		10.4
	C <sub>1</sub> C <sub>4</sub>	1.6	1.1	50.1	52.8		39.7
Dewar benzene	C <sub>1</sub> C <sub>2</sub>	-1.7	0.5	41.1	39.9		41.5
	C <sub>1</sub> C <sub>4</sub>	2.0	1.7	23.1	26.8		10.6
Benzvalene	C <sub>1</sub> C <sub>2</sub>	-2.4	-0.5	26.1	23.2		18.5
	C <sub>1</sub> C <sub>6</sub>	-3.5	-1.2	-7.5	-12.2		-4.0
[2.2.2]Propellane	C <sub>1</sub> C <sub>2</sub>	-0.3	1.1	39.8	40.6		36.5
	C <sub>1</sub> C <sub>4</sub>	4.5	4.9	16.5	25.9		-3.5
Cubane	C <sub>1</sub> C <sub>2</sub>	0.8	0.5	29.6	30.9		24.7

<sup>a</sup> The bond referred to is the unique carbon-carbon  $\sigma$  bond unless otherwise specified. <sup>b</sup> For literature references to the experimental values see the caption to Figure 1 of ref 9. <sup>c</sup> From eq 2 in the text. <sup>d</sup> From extrapolation of  ${}^1J_{CC}$  values for derivatives of cyclopropane.<sup>14</sup> <sup>e</sup> From the 1-cyano derivative: M. Pomerantz and D. F. Hillenbrand, *J. Amer. Chem. Soc.*, **95**, 5810 (1973).

$\langle r^{-3} \rangle_C$ . Both these parameters are treated here as least-squares variables used to fit the experimental  ${}^1J_{CC}$  values of 16 carbon-carbon single bonds in various cyclic and acyclic hydrocarbons, essentially all the known values. The parameters obtained,  $S_C^2(0) = 3.54 \text{ au}^{-3}$  and  $\langle r^{-3} \rangle_C = 2.50 \text{ au}^{-3}$ , are comparable with the values cited previously<sup>6</sup> for an isolated carbon atom, 2.767 and  $1.692 \text{ au}^{-3}$ , respectively. The standard deviation of the least-squares fit is 3.4 Hz, approximately 11% of the average of the  ${}^1J_{CC}$  values used, 31.5 Hz. (If the contact term alone is employed,  $S_C^2(0) = 3.49$  and the standard deviation is 3.7 Hz.)

Table I contains the results obtained for a number of singly bonded carbons, including those used in the fit. In all cases, the equilibrium geometry was employed when known, and an INDO optimized geometry was used otherwise.<sup>12</sup> The need for equilibrium geometries arises from the sensitivity of  ${}^1J_{CC}$  to geometry (especially bond angle variation). For example, the Fermi-contact term for ethane at standard single bond lengths<sup>12b</sup> and tetrahedral angles is 32.1 Hz, whereas for the experimental geometry<sup>12a</sup> it is found to be 36.8 Hz.

Several patterns are discernible from the values of the  ${}^1J_{CC}$  contributions given in Table I. The Fermi-contact interaction for single bonds ranges from 30 to

45 Hz, except when the bonded carbons belong to a cyclopropane ring, the range then being  $-7$  to  $+25$  Hz. Cyclopropane itself, at 16 Hz, lies in the middle of this range. The spin-dipolar term for single bonds is generally *ca.*  $+1$  Hz, but when contained in a cyclopropane ring, negative values of  $-0.3$  to  $-1.0$  are found. The relatively large positive value for the central bond in [2.2.2]propellane may well be related to the unusual nature of this bond, which has been the subject of previous theoretical studies.<sup>13</sup> Values of  ${}^1J_{CC}^{od}$  typically range from  $-2$  to  $-3$  Hz; however, when the bond is contained in a cyclobutane ring the orbital contribution is slightly less negative (*e.g.*,  $-0.8$  Hz for cyclobutane and bicyclopentane) or even positive if the bond is common to more than one four-membered ring, as occurs in cubane, prismane, Dewar benzene, and [2.2.2]propellane.

The consequence of these patterns is that the orbital and spin-dipolar terms partially cancel in most cases, except for cyclopropane bonds, where they are both negative or, for bonds common to two or three four-membered rings, where they are both positive. Since the Fermi-contact term is smallest for cyclopropane bonds, the noncontact terms have their greatest relative influence in those cases. Two such examples are cyclopropane and the C<sub>1</sub>C<sub>3</sub> bond of bicyclo[2.1.0]pentane, for which  ${}^1J_{CC}$  is calculated to be 13.2 Hz (the experimental value is 10.0 Hz<sup>14</sup>) and 3.7 Hz, respectively, and the magnitudes of the noncontact terms comprise 24 to 79% of the total  ${}^1J_{CC}$  values.

Two especially interesting cases are the C<sub>1</sub>C<sub>3</sub> bond of

(12) (a) Pertinent experimental structural data are discussed in ref 9. INDO-optimized bond angles generally are in good agreement with available experimental data. See ref 9 and M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970). The INDO HCC angles are often slightly larger ( $\sim 1-3^\circ$ ) than experimental values (a misstatement in section II B of ref 9 should be revised so as to read: "the HCC angles at the double bonds were then decreased by  $3^\circ$ ,... the amount the ethylene HCC angle is exaggerated by INDO theory."). In the case of cyclopropane, the difference in INDO ( $119.5^\circ$ ) and experimental ( $117.7^\circ$ ) HCC angles leads to a difference of only 1.4 Hz in  $J_{CC}$ . (b) The  ${}^1J_{CC}$  values reported in ref 6 were based on the standard geometries of J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

(13) W. D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 779 (1972); M. D. Newton and J. M. Schulman, *ibid.*, **94**, 4391 (1972).

(14) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **94**, 6021 (1972).

bicyclobutane and the C<sub>1</sub>C<sub>6</sub> bond of benzvalene, on which we have commented previously.<sup>9,15</sup> Here, the Fermi-contact terms, as well as the two noncontact terms, are small and negative.<sup>16</sup> The sign of  ${}^1J_{CC}$  is usually positive.<sup>7,17</sup> However, negative signs for  ${}^1J_{AA}$  (like nuclei) have been found for phosphorus in some instances,<sup>7</sup> and a negative sign has been suggested for  ${}^1J_{FF}$  in F<sub>2</sub>.<sup>5</sup>

## II. Comparison with ${}^1J_{CC}$ Computed from Hybridizations

We have previously shown<sup>9</sup> that  ${}^1J_{CC}$  is linearly related to the product of INDO per cent s characters in the bonding hybrids by

$${}^1J_{CC} = 0.0621(\%s_A)(\%s_B) - 10.2 \text{ Hz} \quad (2)$$

This least-squares fit was obtained for the same 16 C–C bonds used in the present work and had a standard deviation of 2.4 Hz. In most cases, there is good agreement between the results from eq 2 shown in the last column of Table I and those obtained by the INDO coupled Hartree–Fock calculation of each term in eq 1. This is due largely to the fact that the usually dominant Fermi-contact term,  ${}^1J_{CC}^{Fc}$ , is a nearly linear function of the product %s character, although  ${}^1J_{CC}^{od} + {}^1J_{CC}^{sd}$  is not. One of the roles of the negative intercept<sup>18</sup> appears to be simulation of  ${}^1J_{CC}^{od} + {}^1J_{CC}^{sd}$  (consistent with our earlier intuition<sup>9</sup>) as the negative sign accounts for the fact that the poorest agreement between eq 1 and 2 is for those few cases where  ${}^1J_{CC}^{od} + {}^1J_{CC}^{sd}$  makes a significant positive contribution to  ${}^1J_{CC}$ , *i.e.*, single bonds common to two or three four-membered rings. The negative intercept also includes other deficiencies in the hybridization approximation. For example, the appropriate average energy varies somewhat from molecule to molecule.<sup>19</sup>

## III. Discussion

One of the most striking effects revealed by Table I is the occurrence of strongly reduced  ${}^1J_{CC}^{Fc}$  values (relative to ethane) in CC bonds common to one or more three-membered rings. A similar but smaller effect is found for the  ${}^1J_{CC}^{sd}$  terms. We have also calculated that the contact coupling between the olefinic carbon atoms in cyclopropene, 47 Hz, is lower than that of ethylene, 67 Hz, by an amount similar to that by which  ${}^1J_{CC}^{Fc}$  of ethane exceeds that of cyclopropane.

Direct calculation *via* eq 2 shows that the reduction

(15) M. D. Newton and J. M. Schulman, *J. Amer. Chem. Soc.*, **94**, 767 (1972).

(16) Since the central bonds in bicyclobutane and benzvalene are found to have very little 2s character,<sup>9</sup> one must consider the possibility that for these molecules the one-center contribution from the 2s orbital, usually the dominant matrix element of the contact operator, is surpassed in magnitude by other terms, in particular the contribution from the 2p orbital on the other atom in the bond (*i.e.*,  $\int 2p_{\sigma B} \delta(r_A) 2p_{\sigma B} d\tau$ ). From a detailed examination of the first-order density matrix,<sup>9</sup> we have ascertained that while the other terms are not negligible they would not greatly change the results from the one-center approximation. Furthermore, the small contribution of the  $2p_{\sigma B}$  term to  ${}^1J_{CC}^{Fc}$  would be *negative*.

(17) A. A. McLauchlan, *Chem. Commun.*, 105 (1965).

(18) If eq 2 is correct,  ${}^1J_{CC}$  should never fall below *ca.* –10 Hz. Of course, the particular value of the intercept in eq 2 would be expected to vary somewhat with the method of obtaining the hybridization values. A negative intercept was also noted in ref 8b and 14.

(19) This arises partly from the fact that the various contributions to  $J_{CC}$  utilize different average-energy denominators.

in  ${}^1J_{CC}^{Fc}$  for the cyclopropane rings may be adequately accounted for in terms of hybridization, in agreement with earlier suggestions.<sup>14</sup> However, it may also be possible to view the reduction in terms of contributions from indirect coupling, an effect which would be washed out by the average energy approximation implicit in eq 2; *i.e.*, one can consider that excess  $\alpha$  spin on carbon 1 induces  $\beta$  spin polarization on carbon 2 in the direct interaction, whereas by indirect coupling excess  $\alpha$  spin on 1 polarizes carbon 2  $\alpha$  *via* the induced  $\beta$  spin on carbon 3. The latter phenomenon clearly seems to be involved in geminal CC coupling constants,  ${}^2J_{CC}$ , for which typical calculated values of the contact contribution<sup>20</sup> in four-membered rings are –7 to –10 Hz: cyclobutane, –9.9 Hz; bicyclo[2.1.0]pentane, –8.2 Hz; prismane, –6.8 Hz; cubane, –9.1 Hz; and [2.2.2]propellane, –8.3 Hz.<sup>21,22</sup> Not only does the magnitude calculated for  ${}^2J_{CC}^{Fc}$  in cyclobutane agree well with experimental values for cyclobutane derivatives (9.0–9.5 Hz),<sup>14</sup> but the negative sign is consistent with previous arguments, based on analogy with geminal proton coupling constants.<sup>14,23</sup>

It is possible that the negative  ${}^1J_{CC}^{sd}$  values in cyclopropane rings, and the tendency for positive  ${}^1J_{CC}^{od}$  terms in cyclobutane rings, are due to additional geminal and vicinal interactions, respectively. However, further study would clearly be necessary to establish this point.

Although the present study gives new insight into the importance of  ${}^1J_{CC}^{od}$  and  ${}^1J_{CC}^{sd}$  and the relationships between  ${}^1J_{CC}$  computed directly by the INDO coupled Hartree–Fock method and from a linear least-squares fit to hybridization, the reader is cautioned to consider these numerical results as indicative rather than final. Based on semiempirical theories which have many inherent deficiencies, they still leave room for further improvement in many cases. The authors wish to encourage experimental work to obtain additional values of  $J_{CC}$ , particularly for strained rings, in order to test whether the approach adopted here, in conjunction with improved parametrization, will remain useful in predicting and interpreting spin–spin coupling data.

**Acknowledgment.** We gratefully thank Professor D. P. Santry for providing us with his computer program for the coupling constants and acknowledgment is also made to the CUNY Research Foundation for a grant-in-aid to J. M. S. This research was carried out in part under the auspices of the U. S. Atomic Energy Commission. Computations were performed on the Brookhaven CDC 6600.

(20) The noncontact contributions are calculated to be <0.5 Hz.

(21) The calculations for  ${}^2J_{CC}^{Fc}$  were based on the least-squares parameters quoted in section II. When sufficient experimental  ${}^2J_{CC}$  data become available, a separate least-squares fit for  ${}^2J_{CC}$  values can be made.

(22) A theoretical discussion of long range coupling between protons is given by M. Barfield and B. Charkrabarti, *Chem. Rev.*, **69**, 757 (1969).

(23) An especially interesting case is bicyclo[1.1.1]pentane, where the calculated  ${}^2J_{CC}^{Fc}$  between the nonbonded bridgehead carbon atoms is –17.6 Hz. Although a unique through-space interaction may be possible in this case due to the very short nonbonded contact (see discussion of M. D. Newton and J. M. Schulman, *J. Amer. Chem. Soc.*, **94**, 773 (1972)), the enhanced magnitude, relative to cyclobutane, might also be accounted for by noting that (1) the atoms in question are linked by three methylene groups, as opposed to two; and (2) the CCC angles at the methylene carbon atoms are especially small ( $\sim 77^\circ$ ); see ref 14 for a discussion of the possible effect of CCC bond angles on  ${}^2J_{CC}$ .