Fermi Contact Contributions to Spin–Spin Coupling between Directly Bonded Carbons and Hydrogens in Small-Ring Compounds[1a]

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Abstract: Approximate self-consistent perturbation theory was applied to the directly bonded CH spin–spin coupling constants in small-ring compounds. Saturated cyclic hydrocarbons, amines, ethers, and ketones with ring sizes from three through six were investigated. Promising agreement was obtained with experimental data.

In recent years various theoretical formulations of the indirect nuclear spin–spin coupling constant have been presented. These have been aimed largely at correlating experimental coupling data with the electronic structure of molecules.[2] Perhaps the most intriguing correlation was the apparently simple proportionality of J_{CH} and the "carbon s character" in the CH bond of simple hydrocarbons.[3] This relationship was rationalized by localized molecular orbital theory[3] and valence-bond theory,[4] both of which gave results essentially equivalent to those obtained by McConnell's formula,[5] given here in the form

$$J_{AB} = (4/3)^2 h\beta^2\gamma_A\gamma_B(\Delta E)^{-1}s_A{}^2(0)s_B{}^2(0)P_{s_As_B}{}^2 \qquad (1)$$

In this equation β is the Bohr magneton, γ_A is the magnetogyric ratio of nucleus A, ΔE is a mean electronic "excitation energy", $s_A{}^2(0)$ is the value of the valence s-orbital electron density of the nucleus A, and $P_{s_As_B}$ is the element of the first-order density matrix corresponding to the valence s orbitals on atoms A and B. It is the assumed constancy of $(\Delta E)^{-1}s_A{}^2(0)s_B{}^2(0)$, for simple hydrocarbons, that leads to interpretations based on "carbon s character" *via* the $P_{s_As_B}{}^2$ term. This assumption has been criticized on theoretical grounds.[3,6–8]

The molecular orbital approach of Pople and Santry,[9] although avoiding the average energy approximation, is more arduous to apply since it requires knowledge of the excited-state wave functions for the molecule of interest. Numerical problems also arise due to cancellation difficulties. The analogous valence-bond treatment appears to share this difficulty.[10]

A general theoretical treatment of second-order properties, recently introduced by Pople, McIver, and Ostlund,[11,12] has been applied to spin–spin coupling and avoids the above-mentioned difficulties. Briefly, it involves the computation of an unrestricted,[13] MO wave function in the presence of a contact perturbation. In the single-determinantal, INDO (intermediate neglect of differential overlap)[14] MO approximation usually employed with the approach, the perturbation due to the nuclear moment μ_B has the form given by

$$h_B = (8\pi/3)\beta\mu_B s_B{}^2(0) \qquad (2)$$

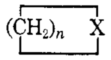
With the aid of the Hellman–Feynmann theorem, it was shown that the indirect coupling constant can be expressed as

$$J_{AB} = (4/3)^2 h\beta^2\gamma_A\gamma_B s_A{}^2(0)s_B{}^2(0) \times [(\partial/\partial h_B)\rho_{s_As_A}(h_B)]_{h_B=0} \qquad (3)$$

where $\rho_{s_As_A}(h_B)$ is the diagonal element of the spin density matrix (in the presence of the contact perturbation h_B) corresponding to the valence s orbital of atom A.

Recently this formalism has been applied to the directly bonded CH and CC coupling constants in an extensive series of molecules.[15,16] Good agreement with experimental trends was obtained for hydrocarbons, and some important patterns of substituent effects were accounted for qualitatively. With those molecules for which the experimental trends were satisfactorily reproduced, a sensitivity to substituent effects was found which is closer to the experimental results than those that would have been obtained by eq 1. All of the molecules covered in the previous work were acyclic and ostensibly unstrained, most of them having molecular geometries that could be approximated by a "standard geometrical model."[17]

The purpose of the present study was to assess the capability of eq 3 to predict the observed structural dependence of the CH coupling constants in a series of small-ring compounds that are represented by the general formula



$(CH_2)_n\,X$

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[1] (a) Supported in part by NSF Grant No. GP 8119; (b) NDEA Fellow 1968–1969.

[2] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, Chapter 12.

[3] (a) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, 31, 768, 1471 (1959); (b) J. N. Shoolery, *ibid.*, 31, 1427 (1959).

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[8] V. M. S. Gil and J. J. C. Teixeira-Dias, *Mol. Phys.*, **15**, 47 (1968).

[9] J. A. Pople and D. P. Santry, *ibid.*, **8**, 1 (1963).

[10] M. Barfield, *J. Chem. Phys.*, **48**, 4458, 4468 (1968).

[11] J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *Chem. Phys. Lett.*, 1, 465 (1967).

[12] J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960, 2965 (1968).

[13] J. A. Pople and R. K. Nesbet, *ibid.*, **22**, 571 (1954).

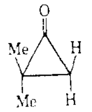
[14] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **47**, 2026 (1967).

[15] G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 1 (1970).

[16] G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *ibid.*, **92**, 11 (1970).

[17] J. A. Pople and M. S. Gordon, *ibid.*, **89**, 4253 (1967).

Table I. Directly Bonded CH Coupling Constants in Molecules of the General Type $(CH_2)_nX$

	Calculated[a,b]						Experimental[a]			
Compound	Geometry	HCH angle	$J_{CH}{}^{\alpha}$	$P_{s_Cs_H}{}^2$	$J_{CH}{}^{\beta}$	$P_{s_Cs_H}{}^2$	$J_{CH}{}^{\alpha}$	Ref	$J_{CH}{}^{\beta}$	Ref
$X = CH_2$										
C_4H_6 (I) C_a–H	*c*		190.5	0.3512			202	*v, cc*		
C_4H_6 (I) C_b–H_{endo}	*c*	115° 34′	165.1	0.2913			170	*v, cc*		
C_3H_6	*d*	114°	155.2	0.2858			161	*w*		
C_4H_6 (I) C_b–H_{exo}	*c*	115° 34′	148.1	0.2775			152	*v, cc*		
C_4H_8	*e*	110° 44′	128.3	0.2511			134.6	*w*		
C_5H_{10} (II)	*f*	111°	120.1	0.2344			128.5	*w*		
C_5H_{10} (II)	*g*	111°	121.0	0.2361			128.5	*w*		
C_5H_{10} (III)	*f*	111°	120.1	0.2344			128.5	*w*		
C_6H_{12}	*h*	109° 28′	118.1	0.2292			124	*w*		
C_5H_{10} (planar)		111°	117.1	0.2294			128.5	*w*		
$X = NH$										
C_2H_5N	*i*	116° 42′	163.4	0.3002			168.0	*x*		
C_3H_7N	*j*	111°	132.4	0.2606	131.6	0.2590	140.0	*x*	134.0	*x*
C_4H_9N (II)	*k*	111°	132.5	0.2511	122.1	0.2375	139.1	*x*	131.4	*x*
$C_5H_{11}N$	*l*	109° 28′	124.9	0.2405	119.5	0.2315	133.7	*x*	125.6	*x*
$X = O$										
C_2H_4O	*m*	116° 42′	166.1	0.3078			175.7	*y*		
C_3H_6O	*n*	110° 44′	142.8	0.2670	122.2	0.2387	148	*y*	137.3	*y*
C_4H_8O (II)	*o*	111°	140.7	0.2650	122.6	0.2386	144.6	*y*	133.2	*y*
$C_5H_{10}O$	*p*	109° 28′	133.6	0.2537	116.1	0.2256	139.4	*y*	128.0	*y*
$X = CO$										
C_3H_4O	*q*	114° 8′	152.2	0.2870						
	*r*	114° 8′	150.7	0.2857			160	*z*		
C_4H_6O	*s*	112° 27′	123.4	0.2397	124.6	0.2474	134.8	*aa*	138.7	*aa*
							131	*bb*	136	*bb*
C_5H_8O	*t*	110°	117.0	0.2284	122.3	0.2358	129.4	*aa*		*aa*
$C_6H_{10}O$	*u*	110°	115.8	0.2257	121.5	0.2312	128.0	*aa*		*aa*

[a] Values of the coupling constants given in hertz. [b] For molecules having nonequivalent hydrogens the calculated values are the appropriate averages. The Roman numerals refer to conformations discussed in the text. [c] K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50,** 1976 (1969). [d] Geometry based on data given in L. E. Sutton, Ed., "Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958, M182 and M983. [e] S. Meiboom and L. Snyder, *J. Amer. Chem. Soc.*, **89,** 1038 (1967); A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15,** 711, (1961). [f] Reference 21. [g] Reference 22. [h] Reference 17. [i] T. E. Turner, V. C. Fiora, and W. M. Kentrick, *J. Chem. Phys.*, **23,** 1966 (1955). [j] Bond lengths: C_β–C_α = 1.55, C_α–N = 1.50, CH = 1.09, NH = 1.00 Å. Bond angles: $C_\alpha NC_\alpha$ = 90.0, $NC_\alpha C_\beta$ = 87.91, $C_\alpha C_\beta C_\alpha$ = 86.42, HCH = 111.0, dihedral angle of 20.0°. [k] C–N bond length of 1.50 Å and a $C_\alpha NC_\alpha$ bond angle of 110.5°, fit to a C_2 cyclopentane. [l] Combination of molecular fragments from the standard geometrical models for cyclohexane and piperazine; see footnote *h.* [m] G. L. Cunningham, A. W. Boyd, R. J. Myers, W. A. Gwinn, and W. I. LeVan, *J. Chem. Phys.*, **19,** 676 (1951). [n] S. I. Chan, J. Zinn, and W. D. Gwinn, *ibid.*, **34,** 1319 (1961). [o] J. Y. Beach, *ibid.*, **9,** 54 (1941). A C–O bond length of 1.46 Å fit to a C_2 cyclopentane. [p] Combination of molecular fragments from the standard geometrical models for cyclohexane and 1,4-dioxane; see footnote *h.* [q] J. M. Poochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, **91,** 1896 (1969). [r] Formed by replacing two hydrogens by "standard" CH_3 groups. [s] A. Bauder, F. Tank, and H. Günthard, *Helv. Chim. Acta*, **6,** 1453 (1963); L. H. Sharpen and V. W. Laurie, *J. Chem. Phys.*, **49,** 221 (1968). [t] H. Kim and W. D. Gwinn, *ibid.*, **34,** 1319 (1961). [u] J. B. Lambert, R. E. Carhart, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **91,** 3567 (1969). [v] K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21,** 2749 (1965). [w] T. Yonezawa, I. Moreshima, M. Fujii, and K. Fukuii, *Bull. Chem. Soc. Jap.*, **38,** 1226 (1965). [x] E. Lippert and H. Prigge, *Ber. Bunsenges. Phys. Chem.*, **67,** 415 (1963). [y] P. Laszlo, *Bull. Soc. Chim. Fr.*, 558 (1966). [z] N. J. Turro and W. B. Hammand, *Tetrahedron*, **24,** 6017 (1968). [aa] Present work. [bb] C. S. Foote, *Tetrahedron Lett.*, **9,** 579 (1963). [cc] K. Wuthrich, S. Meiboom, and L. C. Snyder, *J. Chem. Phys*, **52,** 230 (1970).

where X = CH_2, NH, O, and CO, and *n* ranges from 2 to 5. Such systems have the advantage that theoretically troublesome conformational uncertainties are frequently minimized, since the ring geometries are highly constrained; furthermore, they provide critical tests of the theory for strained systems.

Experimental Section

$\alpha,\alpha,\alpha',\alpha'$-$d_4$-Cyclopentanone and -cyclohexanone were prepared by refluxing a mixture of the undeuterated ketone, anhydrous potassium carbonate, and deuterium oxide (Bio-Rad, 99.8% D_2O), in a 1:2:20 mole ratio, respectively, for 24 hr. The ketone was then separated from the aqueous layer and its deuterium content measured from its proton nmr spectrum. The ketone was recycled until the deuterium content was at least 95%.

The ^{13}C nmr results were obtained at 25.14 MHz under slow-passage conditions. The basic spectrometer system has been described previously.[18] Spinning 8-mm tubes were employed with the internal lock provided by 50% ^{13}C-enriched carbon disulfide. Proton decoupling was accomplished by using a Varian V3512-1 heteronuclear noise decoupler. The basic decoupler frequency was generated by a Hewlett-Packard 5100-A frequency synthesizer. A Varian C-1024 time averaging computer (CAT) served as the signal enhancement device.

Results

All calculations are based on eq 3. The computations were performed on a CDC 3400 computer. As in

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(18) G. E. Maciel, P. D. Ellis, and D. C. Hover, *J. Phys. Chem.*, 71, 2106 (1967).

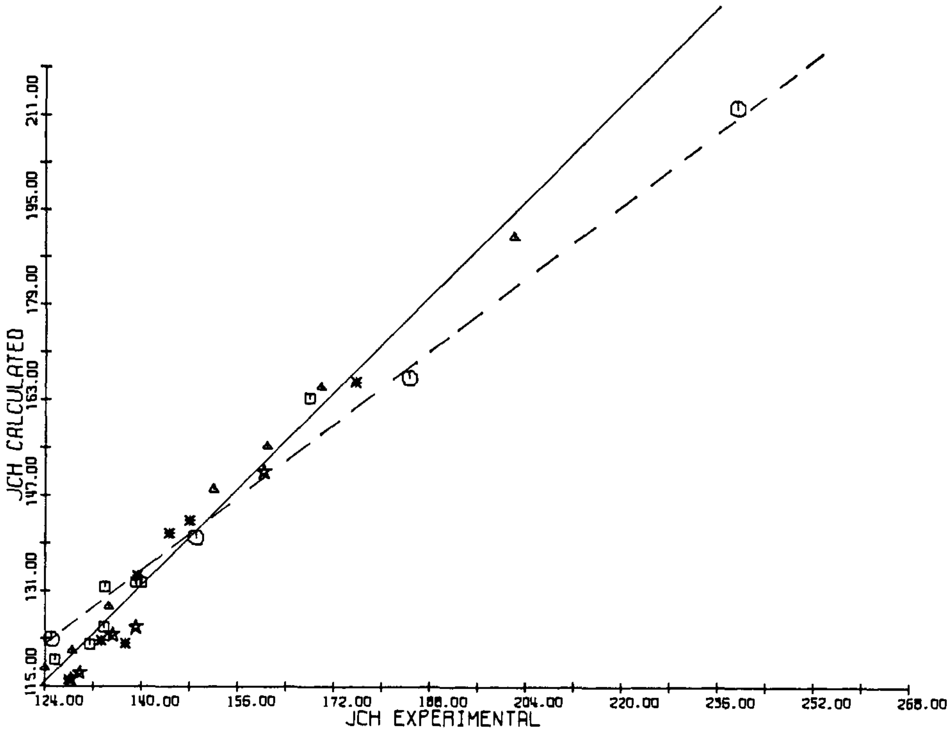

Figure 1. Plot of J_{CH}(calculated) *vs.* J_{CH}(experimental) for **1**, where △, □, *, and ☆ represent X = CH_2, NH, O, and CO, respectively. Methane and the fluoromethanes, CH_nF_{4-n}, n = 3–1, are represented by ○. The dashed line is drawn through points calculated for methane and the fluoromethanes.

previous work[12] the convergence requirement for all the calculations was such that the root-mean-square difference between two successive density matrices was less than or equal to 10^{-9}. The only parameters used in the calculations, other than those used in the INDO approximation, were the $s_A^2(0)$ values as given by Pople and coworkers.[12]

The computed coupling constants are presented in Table I. Table I contains the values of J_{CH} for the four series of small ring compounds represented by the general formula **1**, where X = CH_2, NH, O, and CO. Actual reported geometries were used whenever possible. Estimated geometries were based upon known structures of similar compounds and are summarized in the table. In addition to the computed couplings, the calculated values for $P_{s_Cs_H}{}^2$ are given in Table I. These were calculated from the perturbed INDO wave functions; however, the computed values of $P_{s_Cs_H}{}^2$ do not differ significantly from those calculated from unperturbed wave functions.[16] Also included in Table I are the available experimental coupling constants.

Discussion

Overall Trends. Some promising patterns of qualitative agreement with experimentally established trends can be observed in the calculated results presented in Table I. Beginning with the six-membered ring and progressing toward the three-membered ring, both the calculated and experimental values of J_{CH} increase in the series of related compounds represented by the general formula **1** for a given X, where X = CH_2, CO, NH, or O. In addition, for compounds **1** of fixed ring size n, both the calculated and experimental values of $J_{CH}{}^{\alpha}$ (α to the substituent) increase in the order CH_2, CO, NH, and O.

The overall relationship between calculated and experimental coupling constants is demonstrated in Figure 1. From the near-unity value of the slope of the least-squares-adjusted line in Figure 1 one can see that the calculated results from finite perturbation theory have nearly the same sensitivity to structural effects as the experimental results.

The same qualitative trends hold for the values of $P_{s_Cs_H}{}^2$. These results are summarized in Figure 2. By comparing Figures 1 and 2 one can see that eq 3 yields results that have a sensitivity to structural effects which is about the same as the results that would be obtained from application of eq 1.

In addition to the J_{CH} calculations we have computed J_{CC} for the same series of compounds. Because of the paucity of experimental J_{CC} values in small ring compounds it is difficult to assess the ability of eq 3 to predict the structural dependence of these couplings. The few comparisons we have made[19,20] indicate there may be some problems either with the geometries used or possible limitations of eq 2. These couplings will be the subject of a future publication.

Compounds 1 with X = CH_2. Examination of Table I reveals an excellent agreement between the J_{CH} values predicted by eq 3 and the available experimental data. The calculated values of the coupling constant generally are 5–8 Hz lower than the corresponding experimental values; the exception to this is the bridgehead J_{CH} in bicyclo[1.1.0]butane (I). However, it should be pointed out that, within the table, the bicyclobutane

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(19) P. D. Ellis and G. E. Maciel, unpublished results.

(20) F. J. Weigert, Ph.D. Thesis, California Institute of Technology, 1968.

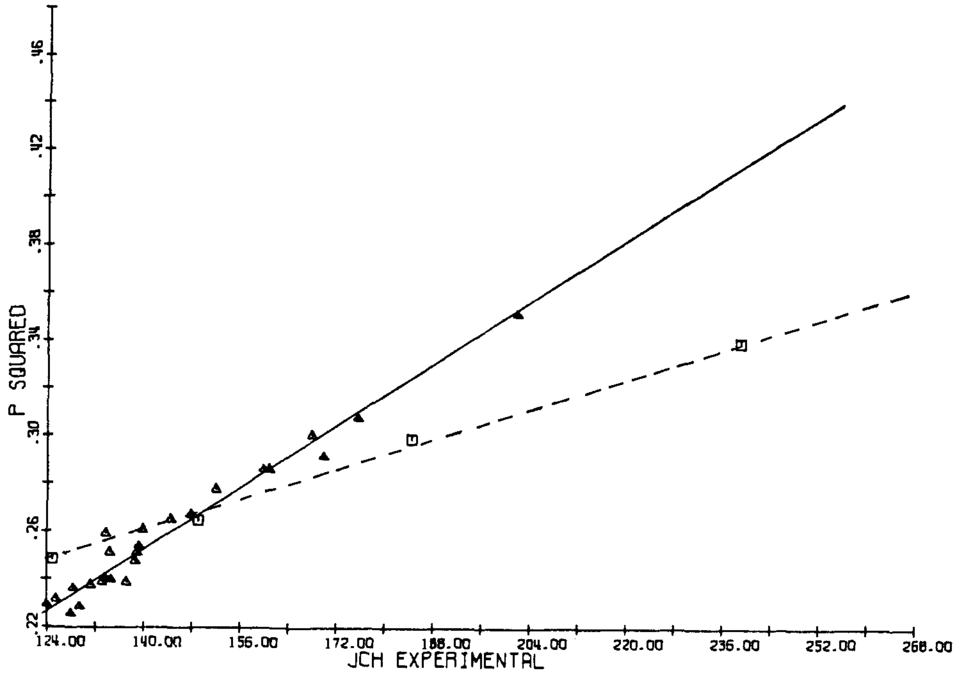
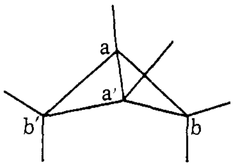


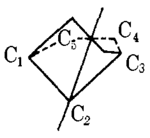
Figure 2. Plot of $P_{2s2s}{}^2$ *vs.* J_{CH}(experimental) for **1**, X = CH_2, NH, O, and CO. Methane and the fluoromethanes are represented by □. The dashed line is drawn through points calculated for methane and the fluoromethanes.

coupling does represent an upper extreme experimentally and, to that extent, is represented qualitatively by the present theory.



I

It is noteworthy that the calculated value of J_{CH} for the planar structure of cyclopentane is not in accord with the other calculated values for the hydrocarbons. In 1947 Kilpatrick, Pitzer, and Spitzer[21] studied the thermodynamic properties of cyclopentane. In order to account for its abnormally high entropy, they found it necessary to postulate a new type of vibration. This motion was described as essentially an out-of-plane ring-puckering vibration, but with the ring atoms moving in such a way as to cause the phase of the puckering to rotate around the ring. The vibration was called a pseudorotation. According to this view there are two distinct pseudorotational isomers, one with C_2 symmetry (II), and the other with C_s symmetry (III). The dashed lines in structure II represent the lines in the $C_1C_2C_3$ plane through which the C_1–C_5 and C_1–C_3 bond axes pass during the vibration. A similar description applies to structure III. When either the C_2 or C_s geometry suggested by those authors is used in the calculation of J_{CH} by eq 3, the resulting average value is more in accord with the overall correlation of the calculated and experimental values of J_{CH} for the other hydrocarbons in Table I. A possible refinement of the C_2 geometry has been proposed by Löw.[22] When this geometry was used the resulting average calculated coupling constant differed very little from that of the geometry based on thermodynamic considerations.



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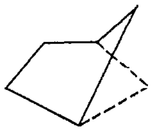

III

Compounds 1 with X = NH, O, and CO. Introducing heteroatoms into the ring does not alter the overall pattern of agreement between the calculated $J_{CH}{}^\alpha$ values and the experimental data. This is illustrated in Table I and Figure 1. The computed $J_{CH}{}^\alpha$ values differ from the corresponding experimental values by amounts ranging from −4 to −10 Hz. It is evident from Figure 1 that the values of $J_{CH}{}^\alpha$ predicted by eq 3 have essentially the same structural sensitivity as the experimental data.

It should be noted that for **1**, with X = NH and where n = 3, 4, and 5, there is little or no detailed structural information available. The geometries used in the calculations are "averages" of geometries of the analogous hydrocarbons and ethers; these geometries are noted in Table I. Although there is no experimental evidence that pyrrolidine (n = 4) exists in the C_2 (II) conformation, this conformation seems reasonable since there is thermodynamic evidence that cyclopentane exists in either the C_2 or C_s conformation, and there are microwave data which demonstrate that tetrahydrofuran exists in the C_2 conformation.[23]

The calculated values of $J_{CH}{}^\beta$ (β to the heteroatom) have larger deviations from the corresponding experimental values than the $J_{CH}{}^\alpha$ values. This may be

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(21) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Amer. Chem. Soc.*, **69**, 2483 (1947).

(22) M. Löw, *Acta Chim.* (*Budapest*), **25**, 1425 (1960).

(23) D. O. Harris, G. G. Engerholm, C. A. Tolman, A. C. Luntz, R. A. Kellar, H. Kim, and W. D. Gwinn, *J. Chem. Phys.*, **50**, 2438 (1969).

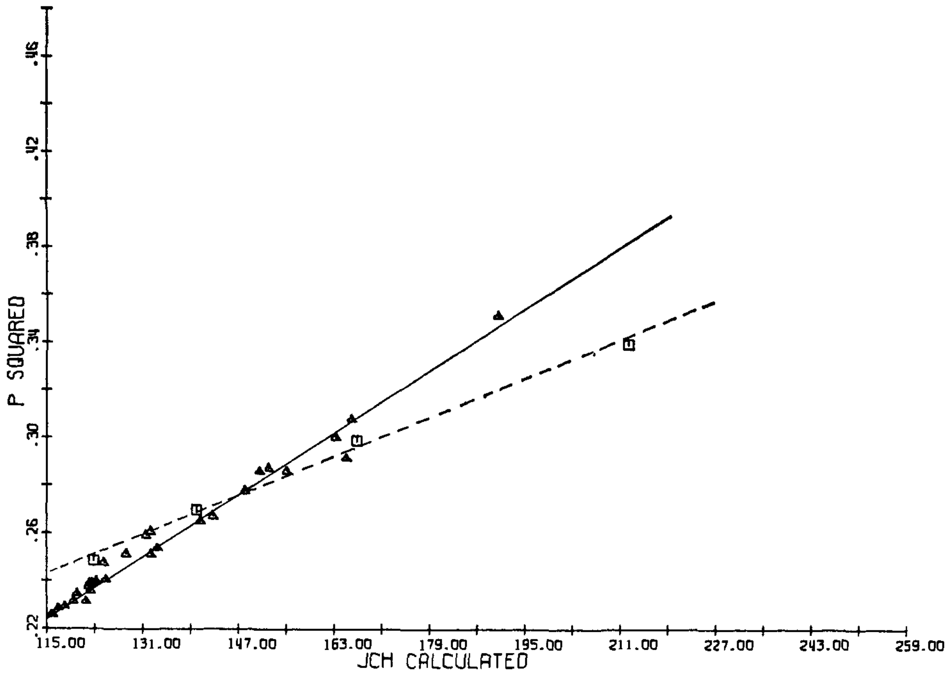

Figure 3. Plot of J_{CH}(calculated) *vs.* P_{2s2s}^2 for **1**, X = CH_2, NH, O, and CO. Methane and the fluoromethanes are represented by □. The dashed line is drawn through points calculated for methane and the fluoromethanes.

due in part to possible limitations of the present method to represent substituent effects at the β position, or possible uncertainties in the geometries used.

From Table I it can be seen that the overall qualitative agreement between the finite perturbation theory results and the experimental data are preserved when the hetero substituent is the carbonyl group. Nevertheless, the calculated values of $J_{CH}{}^{\alpha}$ for the ketones have the largest deviations from the experimental values of the coupling constant, typically −10 to −13 Hz. If one considers a carbon α to a carbonyl group as a carbon β to an oxygen atom, then one might expect that the calculated value of $J_{CH}{}^{\alpha}$ in ketones would differ from the experimental value in about the same way as $J_{CH}{}^{\beta}$ in the ethers. Examination of Table I bears out this point.

Summary and Conclusions

Application of the Pople–McIver–Ostlund finite perturbation theory in the INDO MO approximation gives spin–spin coupling constants for directly bonded carbon and hydrogen atoms that qualitatively reproduce the experimentally known trends in the cyclic systems studied here. The sensitivity of either the computed couplings or the $P_{s_Cs_H}{}^2$ values to variations of molecular structure is about the same as that which has been observed experimentally for J_{CH} in these systems. This similarity of sensitivities is analogous to the results of previous calculations in acyclic systems,[15] if one considers in that work only the effects of gross structural changes, such as carbon coordination number (*e.g.*, comparing ethane, ethylene, and acetylene or ethyl fluoride, vinyl fluoride, and fluoroacetylene). In the previous work the theoretically predicted J_{CH} sensitivity to *substituent* effects on a given, invariant, hydrocarbon framework was somewhat lower than the experimental sensitivity. Also, for *substituent* effects, the calculated structural sensitivity of J_{CH} was much closer than that of the $P_{s_Cs_H}{}^2$ values to the experimental structural J_{CH} sensitivity. Similar relationships are summarized in Figures 1, 2, and 3 for the present results. Figure 1 displays the relationship between experimental data and results obtained from applying eq 3. Figure 2 shows the corresponding relationship between experimental data and the computed P^2 parameters relevant to eq 1. In both figures, the dashed lines represent the points for methane and fluoromethanes, and typify substituent effects within a fixed, tetrahedral framework. These lines emphasize that the failures of either eq 1 or eq 3 to account for structural effects with appropriate sensitivity are more serious when the structural effects are due primarily to the attachment of substituents rather than alterations of a carbon framework. A comparison of Figures 1 and 2 shows that the descrepancies between calculated and experimental sensitivity to structural effects is greater for eq 1 than eq 3 with the fluoromethanes. The relationship between the two types of calculations is displayed directly in Figure 3. Hence, the tentative conclusions here are that the present theory is somewhat more successful in accounting for gross geometrical effects than substituent effects, and for the latter case, the direct computation of J_{CH} values is much more reliable than pursuing the $P_{s_Cs_H}{}^2$ view, which is especially unsuccessful in accounting for *substituent* effects.

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