*Long-range Proton Spin-Spin Interactions in Ketones. II.**
The Substitution Effect

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A previous communication¹⁾ has reported that multiplet structures have been observed in the spectra of the methyl group adjacent to the carbonyl group in ethyl methyl ketone and isopropyl methyl ketone. A similar multiplet structure was observed also in the $^{13}CH_3$ satellites of acetone by Holmes and Kivelson.²⁾ The aim of the present article is to get more extensive data to aid in understanding the mechanism of the long-range proton spin-spin interactions through the carbonyl groups in these ketones. In this paper we should like to present our experimental results and to discuss the substitution effect on such a long-range coupling in some substituted acetones. Some studies related to this problem have been

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* Presented at the Symposium on Molecular Structure of the Chemical Society of Japan, Sendai, October, 1963. This is part II in the series (see Ref. 1 and Ref. 14 for parts I and III).

1) K. Takahashi, This Bulletin, 35, 1046 (1962).

2) J. R. Holmes and D. Kivelson, *J. Am. Chem. Soc.*, 83, 2959 (1961).

TABLE I. PMR DATA FOR THE SUBSTITUTED ACETONE IN A 5 MOL. % CARBON TETRACHLORIDE SOLUTION, AT 60 Mc. p. s.

No.	Compound	Coupling c. p. s.	Chemical shift, p. p. m.*1		
			CH_3CO	CH_2XCO	CHX_2CO
1	CH_3COCH_3	0.57±0.03*2	2.09	—	—
2	$CH_3COCH_2CH_3$	0.48±0.05*2	2.05_5	2.38	—
3	$CH_3COCH(CH_3)_2$	0.45±0.05*2	2.06	—	2.40
4	$CH_3COC(CH_3)_3$		2.05	—	—
5	$CH_3COCH_2CH_2COCH_3$	~0.2	2.12_5	2.59	—
6	$CH_3COCH_2COCH_3$	0.45±0.05	2.16_5	3.46	—
7	$CH_3COCH_2COOC_2H_5$	0.42±0.03	2.20	3.29_5	—
8	$CH_3COCH_2SC_6H_5$	0.42±0.03	2.18_5	3.51_5	—
9	CH_3COCH_2Br	0.37±0.03	2.34	3.76	—
10	$CH_3COCHBr_2$	0.40±0.03	2.54_5	—	5.69_5
11	$CH_2BrCOCH_2Br$		—	4.09_5	—
12	CH_3COCH_2Cl	0.22±0.05	2.28	3.93_5	—
13	$CH_3COCHCl_2$	0.30±0.03	2.42_5	—	5.68_5
14	$CH_3COCH(OH)CH_3$	<0.2	2.15	—	4.12
15	$CH_3COCH{=}C(CH_3)_2$	*3	2.07	—	—
16	$CH_3COCH{=}CH_2$	<0.2	2.20_5	—	—
17	$CH_3COCH{=}CHC_6H_5$	<0.2	2.27_5	—	—

*1 Referred to TMS.
*2 The value in the pure liquid.
*3 Not clear because of overlapping.

reported recently by Sasaki,3) Wittstruck4) and van Meurs.5) In 2, 3-dihalopropenes, the solvent-dependence of the long-range coupling constants and rotational isomerism have been reported by Whipple.6)

Experimental

The wiggle beat method7) for measuring these small couplings was used in addition to the steady-state method used in the previous report.1) The compounds examined were commercially-available products except for dibromoacetone, chloroacetone and phenylmercapto-2-propanone. Dibromoacetone was measured in the mixture with monobromoacetone and other small amounts of by-products which had been prepared by the bromination of acetone. Measurements were carried out with 5 mol.% solutions in carbon tetrachloride, which had been degassed and which contained small amounts of tetramethylsilane (TMS) as an internal reference. Spectra were obtained at a temperature of 22.8±0.5°C, and at a frequency of 60 Mc.p.s. on a Varian 4300B spectrometer. The sweep rate of the magnetic field for chemical shift measurements was calibrated by measuring the displacement between the two peaks for a benzene-cyclohexane mixture (1 : 1 by volume). The value for this displacement in the present work is taken to be 5.746 p.p.m.8)

Results and Discussion

The results of the measured coupling constants are shown in Table I, along with the values previously reported in measurements for the pure liquid state. In this table <0.2 shows no evidence of coupling; ~0.2 does show some evidence of coupling, but it is too small to resolve. For convenience, the chemical shifts are also given in the same table in p. p. m. with reference to TMS. In the case where the signal is split by the indirect spin-spin interaction, the chemical shift given in Table I is that for the center of the multiplet structure. The magnitude of the long-range coupling in question, as shown in Table I, seems to decrease as the electronegativity of the substituent, such as methyl, bromine or chlorine, increases; that is, the more the electronegativity of the substituent, the less the coupling constant seems to become. In the case of acetoin (No. 14 in Table I), the hydroxy-substituted compound of ethyl

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3) Y. Sasaki, paper presented at the 1st Symposium on High-resolution NMR of the Chemical Society of Japan, Tokyo, November, 1961; Y. Sasaki, Y. Kondo and G. Miyajima, paper presented at the 3rd Symposium on NMR of the Chemical Society of Japan, Osaka, November, 1963.

4) T. A. Wittstruck, private communication; T. A. Wittstruck, S. K. Malhotra, H. T. Ringold and A. D. Cross, *J. Am. Chem., Soc.*, **85**, 3038 (1963).

5) N. van Meurs, *Spectrochim. Acta*, **19**, 1695 (1963).

6) E. B. Whipple, *J. Chem. Phys.*, **35**, 1039 (1961).

7) J. J. Turner, *Mol. Phys.*, **3**, 417 (1960).

8) The author wishes to express his thanks to Dr. M. Matsuoka (the Institute for Solid State Physics, the University of Tokyo) for measuring this displacement by the usual side-band technique; it is 232.50±0.25 c.p.s. at 40.462 Mc.p.s. and 24.0±0.1°C.

methyl ketone, there is no evidence of the coupling in question via the carbonyl group. This shows quite a decrease in the coupling as compared with that of ethyl methyl ketone. On the other hand, the sulfur compound of No. 8 holds a coupling of about 0.4 c. p. s. Consequently, it can be assumed that the introduction of an electronegative substituent, such as a halogen or hydroxyl group, causes the decrease in the coupling constant under consideration.

However, a further examination of the compounds listed under No. 16 in Table I shows no clear evidence of coupling. In these ketones, the first atom in the substituent is carbon, so that it may, from the consideration described just before, be expected to have a coupling of about 0.4 c. p. s. Similar is the case of 2, 5-hexanedione, No. 5 in Table I. Moreover, in the cases of the disubstituted acetones, isopropyl methyl ketone shows some decrease in coupling constant as compared with ethyl methyl ketone, but dichloro- and dibromoacetone show some increase as compared with chloro- and bromoacetone respectively.

For the sake of a plausible explanation of these results, first of all, it will be supposed that the internal rotation about the carbon-carbon bond in $CO-CHX_2$ may be more hindered than that in $CO-CH_2X$. The consideration of this kind of rotational hindrance brings the discussion to a consideration of the angular dependence of the long-range couplings in these ketones. Karplus[9] presented an approximate formula of the long-range coupling in some unsaturated hydrocarbons as follows:

$$A_{HH'}(\pi) = 2.1 \times 10^{-15}\sum(a_H \cdot a_{H'}/\Delta\pi)$$

where $\Delta\pi$ is the average singlet-triplet excitation energy in eV., and a_H is the hyperfine constant for a π-electron radical fragment in c. p. s. in ESR spectra. Holmes and Kivelson[2] have also shown an expression similar to the coupling observed in acetone, assuming the $CH_3-\dot{C}-\dot{O}$ triplet. The hyperfine constant a_H in radicals of the $CH_3-\dot{C}$ type has been found, both experimentally[10] and theoretically[11], to be positive and of the form:

$$a_H = A_0 + A_1\cos^2\varphi$$

where φ is the dihedral angle between the $H-C-\dot{C}$ plane and the axis of the unpaired π-electron. The ESR data show us that A_0 is negligible as compared with A_1, so that it may be assumed to be $a_H \propto \cos^2\varphi$. This comes to $a_H = 0$ at $\varphi = 90°$. The absence of the coupling in the compounds of Nos. 16 and 17 prompts us to regard this assumption as reasonable. In these ketones, Nos. 16 and 17, if the conjugation between C=O and C=C bonds is supposed, φ will be nearly 90° and a_H will be approximately zero in ageement with the experimental results.

To predict the long-range coupling in ketones, depending upon the dihedral angle assumed above, it is necessary to average $a_H(\varphi)$ for all possible conformations, weighted with respect to the potential barrier hindering internal rotation. If such a barrier is significantly greater than ***RT***, it is sufficient only to sum up the couplings for the conformation of some considerable rotational isomers. In each ketone, the NMR spectrum of the methylene or the methyl protons shows no differently-oriented conformations, only a single peak as a mean in the measurement at room temperature.

Now we will consider two extreme cases; the one is free rotation, and the other is a fixed conformation about the CO–CH bond as an axis. In each case, the factor ($\cos^2\varphi$) of the long-range coupling in question, depending on the dihedral angle stated above, is shown in Table II. In the case of the protons in CH_2 or CH_3, we took the average between the factors of two or three protons respectively. If we want to include some substituted acetones, the combination of two proton groups must be considered, as is shown in Table III. If any other constants remain approximately constant, the factor depending on the dihedral angle must play a significant role in the coupling. The variation of this factor appears rather large in the cases concerned with a smaller number of protons, such as the methine-methine system. The magnitude of the coupling observed in acetone is about 0.5 c. p. s., and if the methyl group in acetone is assumed to rotate freely around the CO–CH axis, the factor must be taken to be 1/4. Therefore, under these conditions, a coupling of about 2 c. p. s. may be observed in some cases. Further studies of some other ketones, such as cyclic ketones with limited conformations, would be of interest.

TABLE II. $\cos^2\varphi$

No. of protons	3	2	1
Free rotation	1/2	1/2	1/2
Fixed conformation ($\varphi=0\sim2\pi$)	1/2	1/4∼3/4	0∼1

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[9] M. Karplus, *J. Chem. Phys.*, 33, 1842 (1962).

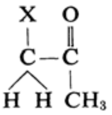
[10] C. Heller and H. M. McConnell, ibid., 32, 1535 (1960); D. Pooley and D. H. Whiffen, *Mol. Phys.*, 4, 81 (1961).

[11] A. D. McLachlan, ibid., 1, 233 (1958); W. Derbyshire, ibid., 5, 225 (1962).

TABLE III. $\cos^2\varphi$

No. of protons	Combination of rotation				Range of variation
	Free-Free	Free-Fix	Fix-Free	Fix-Fix	
3-3	1/4	1/4	1/4	1/4	1/4
3-2	1/4	1/8～3/8	1/4	1/8～3/8	1/8～3/8
3-1	1/4	0～1/2	1/4	0～1/2	0～1/2
2-2	1/4	1/8～3/8	1/8～3/8	1/16～9/16	1/16～9/16
2-1	1/4	0～1/2	1/8～3/8	0～3/4	0～3/4
1-1	1/4	0～1/2	0～1/2	0～1	0～1

In chloroacetone, Mizushima[12] and Bellamy[13] suggested two rotational isomers, I and II, on the basis of their infrared and dipole moment studies. The carbonyl-stretching frequencies of this compound were observed at 1752 and 1726 cm^{-1} in a carbon tetrachloride solution,[13] corresponding to the two rotational isomers, the cis-form (I) and the trans-form (II) with respect to the Cl-atom and the CO group respectively. The former is more polar than the latter, so that a very marked change in the relative intensities of these bands was observed on passing from the solution in carbon tetrachloride to that in acetonitrile.[13] Similar is the case with dichloroacetone, as is shown in III, IV and V. In theses cases, the hyprefine constants,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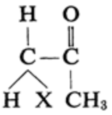
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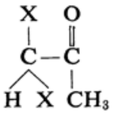
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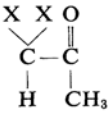
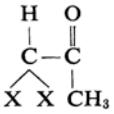

IV


V

which are considered to depend upon the dihedral angle, φ, in question, are as follows:

$$\bar{a}\,(\mathrm{Cl}) \doteqdot P_{\mathrm{I}}a(30^\circ) + P_{\mathrm{II}}[a(30^\circ)+a(90^\circ)]/2$$

$$\doteqdot (1+P_{\mathrm{I}})\ a(30^\circ)/2$$

$$\bar{a}'(\mathrm{Cl}_2) \doteqdot P_{\mathrm{III}}a'(30^\circ) + (P_{\mathrm{IV}}+P_{\mathrm{V}})a'(90^\circ)$$

$$\doteqdot a'(30^\circ)$$

where P_i is the population of the i isomer (i.e., $P_{\mathrm{I}}+P_{\mathrm{II}}=1$ for chloroacetone and $P_{\mathrm{III}} \doteqdot 1$ for dichloroacetone; P_{IV} and P_{V} are supposed to be negligible in view of the band intensities of the carbonyl-stretching frequencies). From the consideration of electronegativity described before, it is rather difficult to explain the decrease in the coupling in chloroacetone as compared with dichloroacetone. However, it is possible to explain the experimental results if we consider the contribution of some rotational isomers. Even in the case of $a(30^\circ) > a'(30^\circ)$, $\bar{a}(\mathrm{Cl})$ depends upon the population of P_{I} in a very limited sense; therefore, $\bar{a}(\mathrm{Cl}) < \bar{a}'(\mathrm{Cl}_2)$ is possible under some conditions.

Now we do not know enough to come to a final conclusion, but it must be noted about the long-range coupling in some substituted acetones, CH_3COCH_2X or CH_3COCHX_2, that (1) the more electronegative X is, the less the constant becomes, and that (2) this coupling is dependent upon the dihedral angle between the C–H bond and the π-orbital of carbon atom in the carbonyl group. From this standpoint, it is of interest of investigate the solvent or temperature effects of these coupling constants. Only a few compounds have been examined briefly in pure liquid and in a carbon tetrachloride solution.[14] The coupling constants in chloroacetone and bromoacetone seem to decrease upon dilution with carbon tetrachloride. This supports the assumptions of the dependence of the coupling constant on the dihedral angle and of the presence of the rotational isomers in these haloketones. These points are now under investigation.

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[12] S. Mizushima, T. Shimanouchi, T. Miyazawa, I. Ichishima, K. Kuratani, I. Nakagawa and N. Shido, *J. Chem. Phys.*, **21**, 815 (1953).

[13] L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, **1957**, 4394.

[14] K. Takahashi, This Bulletin, **37**, 291 (1964).