

EVIDENCE FOR "THROUGH-SPACE" LONG-RANGE PROTON-PROTON COUPLING IN ACETONE

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According to the theory of long-range proton spin coupling by pi electrons, $|J_{\text{HH}}|$ in acetone should decrease with increasing polarity of the carbonyl group. Experimentally the opposite has been found. To explain the observed trend a "through-space" mechanism is proposed. J_{HH} is now interpreted as the result of a negative coupling by the pi electrons and a positive "through-space" contribution. On this hypothesis a better fit numerically can also be obtained.

Introduction

In the proton NMR spectrum of acetone in natural isotopic abundance one finds two small satellites due to the 2.2 per cent of the molecules containing one $^{13}\text{CH}_3$ group. These satellites are split into 1:3:3:1 quadruplets¹⁻⁴. The splitting is caused by a long-range spin-spin coupling of the $^{13}\text{CH}_3$ protons to the non-equivalent $^{12}\text{CH}_3$ protons four sigma bonds away. The spacing in the quadruplets is equal to the coupling constant J_{HH} and is highly dependent on the concentration and the nature of the solvent. Measurements of this kind have been published in a previous publication⁴. The magnitude of J_{HH} is somehow related with the degree of ionic character in the C=O bond. However, the calculation given by *Holmes and Kivelson*² based on pi electron coupling predicts variations in J_{HH} contrary to those observed.

Discussion

A theory of long-range coupling by pi electrons is given by *Karplus*⁵. He related J_{HH} to the hyperfine constants of radical fragments known from e.s.r.-measurements. *Holmes and Kivelson*² extended the theory to acetone, i.e. proton-proton interaction through sigma bonds geminal to an unsaturated bond (*isopropylidenic* coupling). The two groups of methyl

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¹ *H. Dreeskamp and E. Sackmann*, Z. Physik. Chem. 27, 136 (1961).

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

³ *N. van Meurs*, Spectrochim. Acta, 19, 1695 (1963).

⁴ *W. H. de Jeu, H. Angad Gaur and J. Smidt*, Rec. Trav. Chim. 84, 1621 (1965).

⁵ *M. Karplus*, J. Chem. Phys. 33, 1842 (1960).

hydrogen nuclei couple to the same pi electron in the double bond. The result is a negative coupling constant (parallel proton spins). Since in acetone (*along pi* coupling) and in 2-butene (*across pi* coupling) the same e.s.r. hyperfine constant plays a part, the two coupling constants are related by

$$J_{\text{HH}}(\pi, \text{acetone}) = -\eta^2 \frac{\Delta\pi_{\text{C=C}}}{\Delta\pi_{\text{C=O}}} J_{\text{HH}}(\pi, \text{2-butene}) \quad (1)$$

$(1-\eta^2)$ indicates the ionic character of the C=O bond, $\Delta\pi_{\text{C=C}}$ and $\Delta\pi_{\text{C=O}}$ are the excitation energies to the triplet states $\text{CH}_3-\text{C}^{\cdot}-\text{C}^{\cdot}-\text{CH}_3$ of 2-butene and $(\text{CH}_3)_2\text{C}^{\cdot}-\text{O}^{\cdot}$ of acetone.

For two reasons the theory described by equation (1) is not sufficient. First, $|J_{\text{HH}}|$ of acetone increases by up to 30 per cent in solvents capable of forming hydrogen bonds with the carbonyl group⁴. Since hydrogen bonding gives an increase in ionic character of the C=O bond, the experimental evidence is exactly opposite to that expected from equation (1). Secondly, the J_{HH} predicted by (1) for pure acetone is about twice the experimental value of 0.52 Hz. If one estimates $\Delta\pi_{\text{C=C}} = 6.0$ eV and $\Delta\pi_{\text{C=O}} = 6.3$ eV², a percentage ionic character of 46 for the C=O bond⁶ ($\eta^2 = 0.54$), and takes the value of +2.0 Hz calculated by Karplus⁵ for $J_{\text{HH}}(\pi, \text{2-butene})$, then the result is: $J_{\text{HH}}(\pi, \text{acetone}) = -1.0$ Hz⁷.

As a possible explanation for the aforementioned two discrepancies we assume that, apart from the *along pi* coupling discussed by Holmes and Kivelson², there is another contribution to J_{HH} of about 0.5 Hz and opposite in sign. This could be the result of a "through-space" mechanism. It is possible to construct a four electron model for this case (Fig. 1b) in a formal analogy to the one used by Gutowsky *et al.*⁸ to describe the geminal H-H coupling (Fig. 1a). In this model

$$J_{\text{HH}}(\text{direct}) = \lambda [2K(\text{C}_2, \text{H}_1) - K(\text{H}_1, \text{H}_2) - K(\text{C}_1, \text{C}_2)] \quad (2)$$

where

$$K(\text{A}, \text{B}) = \int \text{A}(1)\text{B}(2) \text{HB}(1)\text{A}(2) d\tau \quad (3)$$

represents the exchange, and λ is a positive quantity depending on $K(\text{C}_1, \text{H}_1)$. Relation (2) given here for the "through-space" or direct contribution to

⁶ C. A. Coulson, "Valence" 2nd edn. Oxford Univ. Press, 1961, p. 195.

⁷ Karplus' calculated value of +2.0 Hz for 2-butene is somewhat higher than the experimental results for substituted 2-butenes of 1.2 Hz to 1.8 Hz (ref. 12). This can be attributed partly to the substituents. Other deviations may be caused by an imperfect pairing of the two CH_3-C fragments. In acetone the same deviations will not come into play. So one should in equation (1) use the calculated value for $J_{\text{HH}}(\pi, \text{2-butene})$ of +2.0 Hz and not an experimental value.

⁸ H. S. Gutowsky, M. Karplus and D. M. Grant, J. Chem. Phys. 31, 1278 (1959).

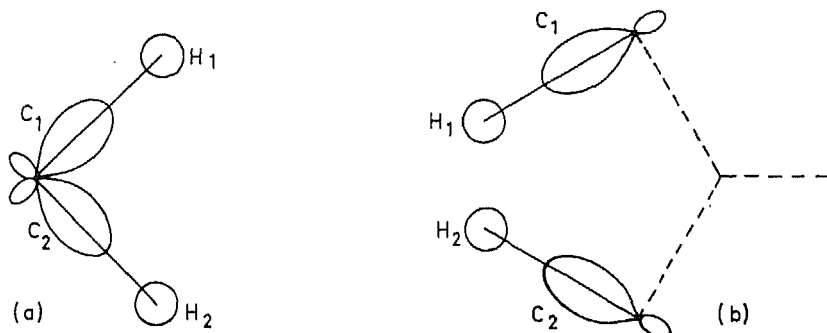


Fig. 1. Geminal coupling (a) and "through-space" coupling (b) in a four-electron four-orbital model.

J_{HH} is similar to the expression derived by Barfield⁹ to deal with coupling across four bonds. The sign of $J_{HH}(\text{direct})$ depends on the numerical values of the exchange integrals¹⁰. In case (b) $K(H_1, H_2)$, which is negative, can be expected to be the most important one. So a positive contribution to the coupling will result according to (2).

Assuming a "through-space" coupling of about +0.5 Hz for pure acetone, it is also possible to understand the variations observed for J_{HH} in various solvents⁴. $J_{HH}(\text{direct})$ will be very sensitive to variations in the CCC-angle of acetone. As a result of hydrogen bonding the hybridization at the carbonyl C-atom will change. From the variations observed for $J^{13}C_{CH}$ of the methyl groups⁴ and for the chemical shift of ^{13}C -resonance in the carbonyl group¹¹, it follows that the hybridization goes from sp^2 in the direction of sp . So the CCC-angle increases. This makes a maximum variation of $J_{HH}(\text{direct})$ from +0.5 Hz to 0 Hz possible. From the variations of $\delta(^{13}C\text{-res.})$ in the carbonyl group¹¹, one can estimate a maximum increase in ionic character of the C=O bond by hydrogen bonding from 46 per cent to about 60 per cent. According to equation (1) $J_{HH}(\pi)$ then increases from -1.0 Hz to about -0.7 Hz. In this way the experimental coupling constant $J_{HH}(\pi) + J_{HH}(\text{direct})$ will vary from about -0.5 Hz to -0.7 Hz. This is in almost exact agreement with the experimental results. The absolute value of J_{HH} was found to vary from 0.52 Hz in pure acetone to 0.66 Hz in formic acid solution⁴.

As has been pointed out already by Holmes and Kivelson², it is unlikely that there is an important sigma contribution to J_{HH} of acetone. In general, examples of resolvable long-range coupling through sigma bonded systems involve compounds in which there are fixed or highly favoured conformations

⁹ M. Barfield, *ibid.* 41, 3825 (1964).

¹⁰ S. Alexander, *ibid.* 34, 106 (1961).

¹¹ G. E. Maciel and J. J. Natterstad, *ibid.* 42, 2752 (1965).

about the carbon-carbon bonds through which the protons interact¹². This is not probable in acetone. Although according to *Barfield*⁹ a positive coupling is possible for $J_{HH}(\sigma)$ across four bonds, there is also theoretical evidence that this kind of coupling is negative^{13, 14}.

"Through-space" coupling has already been very useful in explaining both fluorine-fluorine¹⁵ and proton-fluorine¹⁶ coupling constants. One case of probable "through-space" proton-proton coupling has also been reported¹⁷. To confirm the hypothesis of a "through-space" contribution to long-range proton-proton coupling, more data are required. Measurements of coupling between geminal methyl groups will be especially useful.

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¹² *S. Sternhell*, *Rev. Pure Appl. Chem.* **14**, 15 (1964).

¹³ *C. N. Banwell* and *N. Sheppard*, *Disc. Faraday Soc.* **34**, 115 (1962).

¹⁴ *S. Koide* and *E. Duval*, *J. Chem. Phys.* **41**, 315 (1964).

¹⁵ (a) *S. Ng* and *C. H. Sederholm*, *ibid.* **40**, 2090 (1964);

(b) *N. Boden*, *J. Feeney* and *L. H. Sutcliffe*, *J. Chem. Soc.* **1965**, 3482;

(c) *K. L. Servis* and *J. D. Roberts*, *J. Am. Chem. Soc.* **87**, 1339 (1965).

¹⁶ (a) *A. D. Cross*, *ibid.* **86**, 4011 (1964);

(b) *P. C. Myhre*, *J. W. Edmonds* and *J. D. Kruger*, *ibid.* **88**, 2459 (1966).

¹⁷ *F. A. L. Anet*, *A. J. R. Bourn*, *P. Carter* and *S. Winstein*, *ibid.* **87**, 5249 (1965).