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The Mechanism of Long-Range Proton-Proton Coupling

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The perturbation treatment of proton-proton coupling developed in earlier papers, has been extended to allow for electron delocalization through intervening C–C and C–H bonds.

The meta-coupling constant in benzene obtained from this perturbation treatment is in reasonable agreement with that obtained by a full MO calculation. The para coupling constant is not in good agreement suggesting that para-coupling arises from electron spin polarization in more than one intervening bond.

Das Störungsverfahren für Proton-Proton-Kopplung wurde erweitert, um die Elektronendelokalisierung infolge dazwischenliegenden C–C- und C–H-Bindungen zu berücksichtigen.

Die meta-Kopplungskonstante für Benzol, die sich auf diese Weise ergibt, stimmt befriedigend mit derjenigen überein, die bei einer vollständigen MO-Rechnung herauskommt. Bei der entsprechenden Größe für die para-Stellung ist dies dagegen nicht der Fall, was den Schluß nahe legt, daß die para-Kopplung auf mehr als eine dazwischentretende Bindung zurückgeht.

Le traitement de perturbation du couplage proton-proton développé dans des articles précédents est étendu afin de tenir compte de la délocalisation électronique à travers les liaisons C–C et C–H qui interviennent.

La constante de couplage méta dans le benzène, obtenue par cette méthode, est en accord raisonnable avec celle obtenue par un calcul complet d'orbitales moléculaires. Par contre, la constante de couplage para ne donne pas un bon accord, ce qui suggère que le couplage en para provient de la polarisation de spin électronique sur plus d'une liaison.

The Pople-Santry independent electron MO theory [1] has been very successful in providing a qualitative understanding of nuclear spin-spin coupling constants. Particular success has been obtained for the coupling between vicinal protons and for understanding the effect of substituents on C–H and Si–H-coupling constants [2]. Less success has been obtained with proton-proton geminal coupling constants due to the lack of electron correlation in the theory, although the trend for a series of geminal coupling constants is reasonably well produced.

In recent papers [1, 3] a perturbation approach to the MO theory of proton-proton coupling in hydrocarbons has been used to elucidate the routes through which the coupling of vicinal and geminal protons occur. An expression for the coupling constant was obtained from a basis of localized bonding and antibonding MO's of two C–H bonds with delocalization terms introduced as a perturbation. Vicinal and geminal coupling constants calculated from this expression agree well with those obtained from a full MO treatment.

Although this expression is in principle applicable to long range coupling, being the mathematical description of a through space coupling mechanism, the values it gives for the meta and para coupling constants of benzene are much smaller than those obtained from a full MO treatment; the latter being in good agreement

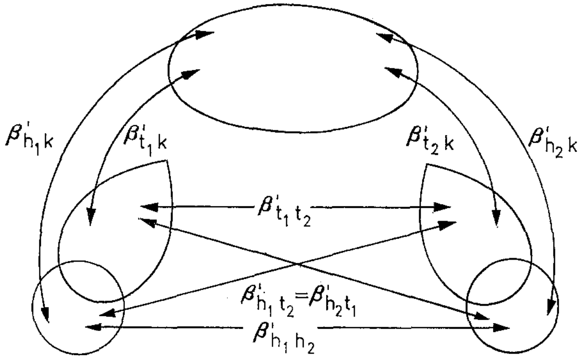

Fig. 1

with experiment. Also calculations of the meta and para coupling through the π-electrons has given values only about 10% of those observed [4, 5]. It appears, therefore, that meta and para coupling at least, arise from the delocalization of electrons through intermediate C–H and C–C σ bonds, rather than from a through space delocalization or through the π-electrons.

The purpose of this paper is to examine the mechanism of this long range coupling by extending the earlier perturbation approach to higher orders. We take as basis localized MO's formed from carbon hybrids and hydrogen 1*s* orbitals, together with another set of localized MO's (ψ_k) which may be bonding or antibonding, and which may be associated with C–C bonds or other C–H bonds (Fig. 1). Within the approximation that the coulomb integrals of the carbon hybrids (t) and the hydrogen orbitals (h) are equal,

$$\text{i.e.}\quad \langle t_1 \mid H \mid t_1\rangle = \langle h_1 \mid H \mid h_1\rangle = \alpha$$

the first term in the perturbation expression for the hydrogen-hydrogen atom-atom polarizability, which in the Pople-Santry theory is proportional to the coupling constant is [1, 3]*,

$$\pi^{(1)} = \frac{1}{16\beta^3}\left(4\beta'^2_{th} - \beta'^2_{hh} - 5\beta'^2_{tt} + 2\beta'_{hh}\beta'_{tt}\right) \tag{1}$$

β is the resonance integral for a C–H bond (β_{th}) and the β' are the resonance integrals between orbitals associated with different C–H bonds** as defined in Fig. 1.

We now consider the effect of delocalization terms between the carbon hybrids and hydrogen orbitals and the localized MO ψ_k, which we indicate as β'_{tk} and β'_{hk} as shown in Fig. 1. Two cases need to be considered: either ψ_k is a bonding orbital occupied by two electrons, or it is a vacant antibonding orbital. In the first case we assume it to have an energy $(\alpha + \beta)$ and in the second an energy $(\alpha - \beta)$. We now seek an expression for the atom-atom polarizability π, which includes these additional delocalization parameters.

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* In Ref. [3] the symbols R, S and T were used for $2\beta'_{th}$, $2\beta'_{hh}$ and $2\beta'_{tt}$ respectively. We feel that the continued retention of the factor 2 is likely to cause confusion. The symbols used in Ref. [1] have the disadvantage that they were chosen specifically for geminal and vicinal coupling and not for proton-proton coupling in general.

** If the two C–H bonds are not equivalent, then providing the two resonance integrals $\beta_{t_1h_1}$ and $\beta_{t_2h_2}$ are equal, expression (1) can be generalised by replacing β'_{th} by $\frac{1}{2}(\beta'_{t_1h_2} + \beta'_{t_2h_1})$.

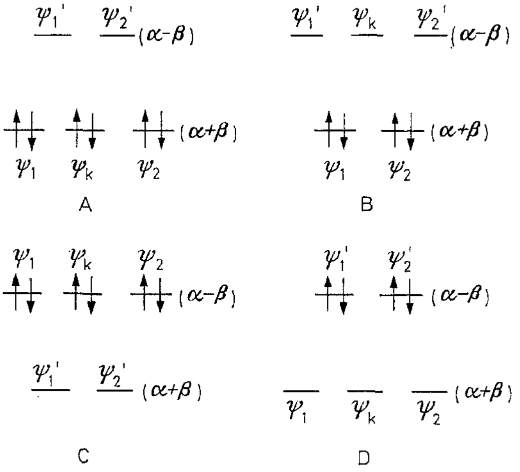

Fig. 2

It was shown in Ref. [3] that there are no contributions to π of the type KL/β^3, where K and L are members of the set β'_{tk}, β'_{hk} etc. We have found that the leading terms involving these parameters are of the form*

$$\pi^{(3)} = \sum_{PKL} C_{PKL}\, PKL/8\beta^4 \tag{2}$$

where P is a member of the set β'_{hh}, β'_{ht}, β'_{tt}. The coefficients C_{PKL} have been determined by numerical method. The eigenvalues and eigenfunctions of the Hamiltonian matrices appropriate to our basis set were obtained for selected small values (of the order of $10^{-2}\,\beta$) of the delocalization parameters to give a set of simultaneous equations relating π to the coefficients C_{PKL}. These equations were then solved for the coefficients. It can be shown that for the two cases of ψ_k being a bonding or an antibonding MO, the coefficients have the same magnitude but may either be of the same sign or of opposite sign. The reasoning is as follows.

Suppose the localized bonding C–H orbitals are labelled ψ_1 and ψ_2 and the corresponding antibonding orbitals ψ'_1, and ψ'_2, then in the zero-overlap approximation

$$\begin{aligned} \psi_1 &= \sqrt{\tfrac{1}{2}}\,(t_1 + h_1)\,, \\ \psi'_1 &= \sqrt{\tfrac{1}{2}}\,(t_1 - h_1)\,, \\ \psi_2 &= \sqrt{\tfrac{1}{2}}\,(t_2 + h_2)\,, \\ \psi'_2 &= \sqrt{\tfrac{1}{2}}\,(t_2 - h_2)\,. \end{aligned} \tag{3}$$

We then wish to compare the polarizabilities for cases A and B in Fig. 2. We use two results. Firstly the contribution to π of order $1/\beta^4$ will be the same for system A as for system C because they differ only in the sign of β. Secondly the polarizability of a system having m orbitals occupied and n vacant is equal in magnitude but opposite in sign to that of a system with n occupied and m vacant. Thus the

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* If the carbon hybrid and hydrogen coulomb integrals are not equal then it has been shown that there is a contribution to π of $\pi^{(2)} = \left(\frac{\alpha_h - \alpha_t}{4\beta^4}\right)\beta'_{ht}\,(1.5\,\beta'_{hh} - 2.5\,\beta'_{tt})$.

Table

	Coefficient in $\pi^{(3)}$	
	ψ_k bonding	ψ_k antibonding
$\beta'_{t_1k}\beta'_{t_2k}\beta'_{tt}$	+2.17	−2.17
$\beta'_{t_1k}\beta'_{t_2k}\beta'_{th}$	−0.32	−0.32
$\beta'_{t_1k}\beta'_{t_2k}\beta'_{hh}$	−0.35	+0.35
$\beta'_{h_1k}\beta'_{h_2k}\beta'_{tt}$	−0.31	+0.31
$\beta'_{h_1k}\beta'_{h_2k}\beta'_{th}$	+0.38	+0.38
$\beta'_{h_1k}\beta'_{h_2k}\beta'_{hh}$	+0.19	+0.19
$\beta'_{t_1k}\beta'_{h_2k}\beta'_{tt}$	−0.33	−0.33
$\beta'_{t_1k}\beta'_{h_2k}\beta'_{th}$	−0.62	+0.62
$\beta'_{t_1k}\beta'_{h_2k}\beta'_{hh}$	+0.16	+0.16

polarizability of system A is of opposite sign to that of D. Now from a consideration of the following matrix elements

$$\begin{aligned}
\langle\psi_k \mid H \mid \psi_1\rangle &= 2\sqrt{2}\,(\beta'_{tk} + \beta'_{kh})\\
\langle\psi_k \mid H \mid \psi'_1\rangle &= 2\sqrt{2}\,(\beta'_{kh} - \beta'_{tk})\\
\langle\psi_1 \mid H \mid \psi_2\rangle &= 1/2\,(2\beta'_{th} + \beta'_{hh} + \beta'_{tt})\\
\langle\psi'_1 \mid H \mid \psi'_2\rangle &= 1/2\,(-2\beta'_{th} + \beta'_{hh} + \beta'_{tt})
\end{aligned} \tag{4}$$

we deduce that system B would have the same polarizability as D if one changed the signs of β'_{th} and β'_{tk}. It follows that the signs of the β^{-4} contributions to the polarizability of systems A and B will be the same for terms $\beta'_{t_1k}\beta'_{t_2k}\beta'_{th}$, $\beta'_{h_1k}\beta'_{h_2k}\beta'_{th}$, for example, but opposite for $\beta'_{t_1k}\beta'_{t_2k}\beta'_{hh}$ etc.

The coefficients of these β^{-4} terms are given in the table. The coefficients of all other β^{-4} terms, such as β'^3_{tt}, β'^3_{kt}, $\beta'_{kt}\beta'_{kh}\beta'_{tk}$ were found to be small in our numerical experiments and within the error incurred in neglecting higher order terms. We have therefore taken these coefficients to be zero. Because we have neglected these and higher order terms, and because of rounding errors in our calculations we estimate that the coefficients listed in the table are only accurate to ± 0.05.

To obtain the polarizability for a given hydrocarbon we therefore add to expression (1), a β^{-4} contribution for every localized bonding and antibonding C–C and C–H orbital. β'_{th}, β'_{hh} and β'_{tt} are fixed for a given pair of C–H bonds but β'_{kt}, must be calculated for each intermediate orbital ψ_k. The following treatment of meta and para coupling constants in benzene illustrates the approach.

Resonance integrals between hybrids of different atoms were calculated from the formula

$$\beta_{\mu\nu} = -10\, S_{\mu\nu}\ (\text{eV}) \tag{5}$$

where $S_{\mu\nu}$ is the overlap integral between orbitals μ and ν. The resonance integral between two sp^n hybrids of the same carbon atom, is $(\alpha_s - \alpha_p)/(n+1)$ and we have taken $(\alpha_s - \alpha_p) = -3$ eV as this was found to give the best overall values for C–H and H–H coupling constants in earlier work [6]. We have used Slater orbitals with exponents 1.625 for carbon $2s$ and $2p$ and 1.2 for the hydrogen $1s$ orbital.

Meta Coupling

It is seen from Fig. 3 that there are three important routes through which coupling occurs: through the intermediate C–C or C–H bonds and through the non-intermediate C–C bonds adjacent to the coupled C–H bonds. Coupling through the other bonds is negligible because they all involve one β' which is very small. The results for the three routes are given below [π is in units of $(\mathrm{eV})^{-1}$].

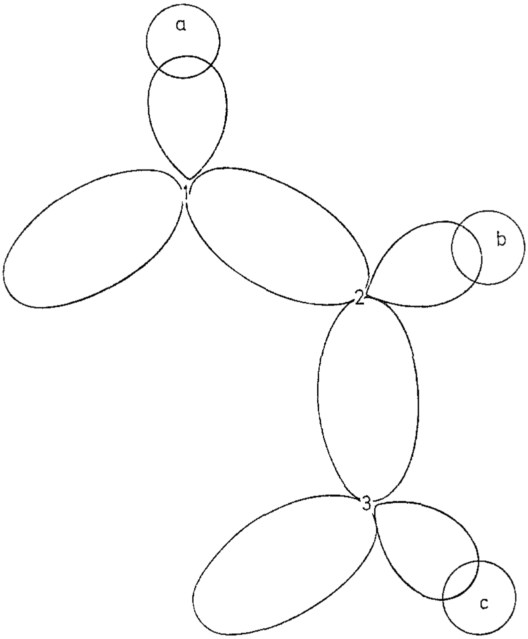

Fig. 3

1. Coupling through the 1 – 2 bond (which involves the bonding and the antibonding orbital)

$$\pi^{(3)} = 0.45 \times 10^{-4} .$$

A similar contribution arises from the coupling through the 2 – 3 bond.

2. Coupling through the 2 – b bond

$$\pi^{(3)} = -0.36 \times 10^{-4} .$$

3. Coupling through the 1 – 6 bond

$$\pi^{(3)} = 0.18 \times 10^{-4} .$$

A similar contribution arises from the coupling through the 3 – 4 bond.

The contribution from $\pi^{(1)} = 0.13 \times 10^{-4}$.
The total is $\pi^{(1)} + \pi^{(3)}_{\text{total}} = 1.01 \times 10^{-4}$.

This is in reasonable agreement with a full MO calculation using the same parameters as above and with $\alpha_h = \frac{1}{2}(\alpha_s + \alpha_p)$: $\pi = 1.53 \times 10^{-4}$.

Para Coupling

It is seen from Fig. 4 that there are three important types of route through which coupling occurs: through the intermediate C–C or C–H bonds. The results for the three routes are given below.

1. Coupling through the 1 – 2 bond

$$\pi^{(3)} = 1.47 \times 10^{-5}\,.$$

There are similar contributions from the coupling through the 3 – 4, 1 – 6, and 4 – 5 bonds.

2. Coupling through the 2 – 3 bond

$$\pi^{(3)} = -4.54 \times 10^{-5}\,.$$

A similar contribution arises from the coupling through the 5 – 6 bond.

3. Coupling through the 2 – *b* bond

$$\pi^{(3)} = -0.10 \times 10^{-5}\,.$$

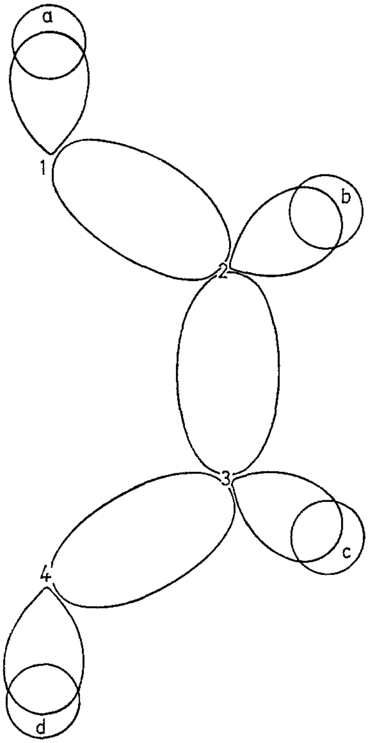

Fig. 4

Similar contributions arise from coupling through the 3 – *c*, 5 – *e* and 6 – *f* bonds.

The contribution from $\pi^{(1)} = 1.01 \times 10^{-5}$.

The total is $\pi^{(1)} + \pi^{(3)}_{\text{total}} = -2.40 \times 10^{-5}\,(\text{eV})^{-1}$.

In this case the full MO calculation gives 0.94×10^{-4} (eV)$^{-1}$ and the two are in poor agreement. There are clearly other routes, of higher order in perturbation which make important contributions to the coupling. The full MO calculation gives $J_{\text{meta}} = 2.5$ c.p.s, $J_{\text{para}} = 0.7$ c.p.s. in good agreement with the experimental values $J_{\text{meta}} = 1.37$ c.p.s., $J_{\text{para}} = 0.69$ c.p.s. [7].

Conclusions

From the perturbation analysis of long-range coupling in benzene that we have given and its comparison with the full MO calculation we draw the following conclusions.

1. The coupling constant between distant protons (further than the distance between vicinal protons) does not arise from a through space mechanism.

2. The third order perturbation formula gives a good approximation to the coupling constant between protons separated by two carbon-carbon bonds. For such protons the coupling via the intermediate C–C and C–H bonds is the most important mechanism.

3. For protons separated by more than two C–C bonds the perturbation formulae are inadequate, suggesting that the coupling must involve two or more intervening localized bond orbitals, or intervening delocalized orbitals. To assign definite routes to such coupling would require a higher order of perturbation.

4. The perturbation formulae are useful for an analysis of the spin coupling mechanism in those situations where they are valid but if one is just interested in calculating coupling constants it is usually more convenient to make the full MO calculation.

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