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MECHANISTIC SIGNIFICANCE OF THE MAGNITUDE OF CROSS-INTERACTION CONSTANTS

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The relationship between the magnitude of the cross-interaction constant, $|\rho_{ij}|$, and the force constant of activation, $\Delta F_{ij}^{\ddagger}$, has been derived and their equivalence has been shown, where $\Delta F_{ij}^{\ddagger}$ = (force constant in the transition state, $\Delta F_{ij}^{\ddagger}$ – force constant in the ground state, F_{ij}^{0}). When bond formation is involved in the activation process, $\Delta F_{ij}^{\ddagger}$ becomes equal to $F_{ij}^{\ddagger}$ and $|\rho_{ij}|$ is inversely related to the distance, $r_{ij}^{\ddagger}$, between reaction centres R_i and R_j. However, for bond-breaking processes, interpretation of $|\rho_{ij}|$ becomes complicated, since $\Delta F_{ij}^{\ddagger} = F_{ij}^{\ddagger} - F_{ij}^{0}$ may be negative or positive depending on the relative size of $F_{ij}^{\ddagger}$ and F_{ij}^{0}. Some examples of re-examination are given for various cases of $|\rho_{ij}|$ in the bond-breaking processes.

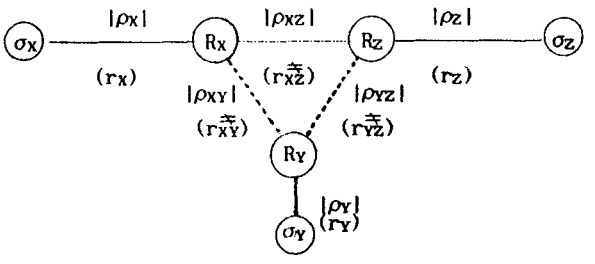
INTRODUCTION

For several years we have been involved with developing the use of cross-interaction constants, ρ_{ij} in equation (1), as a mechanistic tool for organic reactions in solution:[1]

$$\log(k_{ij}/k_{HH}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \qquad (1)$$

As a typical example, we have attempted to correlate the magnitude $|\rho_{ij}|$ with the transition-state (TS) structure, especially of S_N2 reactions (Scheme 1).[2]

In contrast to the simple Hammett coefficient ρ_i (or ρ_j), which is of limited use within a particular family of closely related reactions,[2,3] we found that the magnitude of ρ_{ij} provides a quantitative measure of bond length r_{ij} between reaction centres R_i and R_j (i, j = X, Y or Z in Scheme 1) when both substituents i and j (denoted σ_i and σ_j in Scheme 1) interact with their respective reaction centres simultaneously in the TS.[1,2]



Scheme 1

On the other hand, theoretical analysis has shown[4] that the positive stretching force constants $F_{ij}^{\ddagger}$ of the symmetric vibrational modes in the TS are correlated with the bond length $r_{ij}^{\ddagger}$ by an equation similar to the empirical expression known as Badger's rule:[5]

$$r_{ij}^{\ddagger} = \alpha - \beta \log F_{ij}^{\ddagger} \qquad (2)$$

where α and β are constant for a related series of bonds.

If we assume a sufficiently small change in the distance, δr_i, due to a variation of substituent, $\delta\sigma_i$, a linear correlation between the two may be assumed to exist.[6] It has indeed been shown based on the analysis of experimenatal data[7] that the distance between the reaction centres in the TS varies ($\delta r_i^{\ddagger}$ or $\delta r_j^{\ddagger}$) linearly with the substituent constant in a reactant, $\delta\sigma_i$ or $\delta\sigma_j$:

$$\delta r_i^{\ddagger} = a\delta\sigma_i \text{ and } \delta r_j^{\ddagger} = b\delta\sigma_j \qquad (3a)$$

$$\delta r_{ij}^{\ddagger} = \delta r_i^{\ddagger} + \delta r_j^{\ddagger} = a\delta\sigma_i + b\delta\sigma_j \qquad (3b)$$

where $\delta r_i^{\ddagger}$ and $\delta r_j^{\ddagger}$ represent the portions of $\delta r_{ij}^{\ddagger}$ due to changes in σ_i and σ_j, respectively. In particular for identity exchange reactions, equation (4) with XN = LZ, where X, Y and Z are the substituents in nucleophile (N), substrate (R) and leaving group (L) respectively, the constants a and b are found to be negative, and the small distance changes, δr_i, are linearly correlated with $\delta\sigma_i$:[7]

$$XN + YRLZ = XNRY + LZ \qquad (4)$$

Hence a more electron-donating substituent, e.g. X = Z = *p*-MeO for which $\sigma_X = \sigma_Z < 0$, leads to a greater distance between the two identical groups in

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the TS, $\delta r^{\ddagger}_{XZ} \approx 2\delta r^{\ddagger}_{XY} \approx 2\delta r^{\ddagger}_{YZ} > 0$, since $a < 0$ and $\sigma_X = \sigma_Z < 0$. Conversely, a more electron-withdrawing substituent, e.g. X = Z = *p*-NO_2, leads to a decrease in the distance, $\delta r^{\ddagger}_{XZ} \approx 2\delta r^{\ddagger}_{XY} \approx 2\delta r^{\ddagger}_{YZ} < 0$.

It is by no means clear, however, how the magnitude of cross-interaction constant, $|\rho_{i,j}|$, is correlated with the distance between the reaction centres in the TS, $r^{\ddagger}_{ij}$. A clear understanding of the correlation between the two should provide a sound basis for the application of $|\rho_{ij}|$ as a quantitative measure of the TS structure. In this work, we show that $|\rho_{ij}|$ is related to the difference in the force constant between the initial and transition states, $\Delta F^{\ddagger}_{ij}$, which may be termed a 'force constant of activation,' and the mechanistic interpretation of $|\rho_{ij}|$ should therefore be re-examined in accordance with this postulate.

SIGNIFICANCE OF THE MAGNITUDE OF CROSS-INTERACTION CONSTANTS

Let us consider a system consisting of two interacting fragments i and j with substituents σ_i and σ_j and reaction centres R_i and R_j at a distance r_{ij} (Scheme 2). One can define the potential energy of activation, $\Delta U^{\ddagger}$, as the potential energy difference between ground state (GS) and transition state (TS).[8] The potential energy of the GS, U^0, is expanded in a Taylor series around a reference point $\sigma_i = \sigma_j = 0$ (U^0_0) which is not necessarily at the minimum point of the potential energy surface. Neglecting cubic and higher terms (for sufficiently small displacement, higher terms are negligible in general[9]),

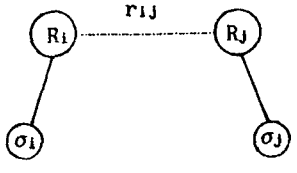
$$\delta U^0 = U^0 - U^0_0 = U^{0\prime}_i\sigma_i + U^{0\prime}_j\sigma_j + \tfrac{1}{2}U^{0\prime\prime}_{ii}\sigma_i^2 + \tfrac{1}{2}U^{0\prime\prime}_{jj}\sigma_j^2 + U^{0\prime\prime}_{ij}\sigma_i\sigma_j \quad (5)$$

Likewise for the potential energy of the TS,

$$\delta U^{\ddagger} = U^{\ddagger} - U^{\ddagger}_0 = U^{\ddagger\prime}_i\sigma_i + U^{\ddagger\prime}_j\sigma_j + \tfrac{1}{2}U^{\ddagger\prime\prime}_{ii}\sigma_i^2 + \tfrac{1}{2}U^{\ddagger\prime\prime}_{jj}\sigma_j^2 + U^{\ddagger\prime\prime}_{ij}\sigma_i\sigma_j \quad (6)$$

The difference of the two gives the variation in the potential energy of activation ($\delta\Delta U^{\ddagger}$) due to substituents σ_i and σ_j from the potential energy of activation at the reference point, $\Delta U^{\ddagger}_0$. Hence δ and Δ represent the variation of a quantity due to changes in substituent, $\delta\sigma_i$ or $\delta\sigma_j$, and in state from GS to TS, respectively.

$$\delta\Delta U^{\ddagger} = \delta(U^{\ddagger} - U^0) = \Delta U^{\ddagger\prime}_i\sigma_i + \Delta U^{\ddagger\prime}_j\sigma_j + \tfrac{1}{2}\Delta U^{\ddagger\prime\prime}_{ii}\sigma_i^2 + \tfrac{1}{2}\Delta U^{\ddagger\prime\prime}_{jj}\sigma_j^2 + \Delta U^{\ddagger\prime\prime}_{ij}\sigma_i\sigma_j \quad (7)$$



Scheme 2

Obviously,

$$\Delta U^{\ddagger\prime}_i = \left(\frac{\partial\Delta U^{\ddagger}}{\partial\sigma_i}\right)_0, \qquad \Delta U^{\ddagger\prime\prime}_{ij} = \left(\frac{\partial^2\Delta U^{\ddagger}}{\partial\sigma_i\partial\sigma_j}\right)_{00}, \text{ etc.} \quad (8)$$

On the other hand, a Taylor expansion of $\log(k_{ij}/k_{HH})$ up to second order is given by[1]

$$\log\left(\frac{k_{ij}}{k_{HH}}\right) = -\frac{\delta\Delta G^{\ddagger}}{2\cdot 3RT} = \rho_i\sigma_i + \rho_j\sigma_j + \tfrac{1}{2}\rho_{ii}\sigma_i^2 + \tfrac{1}{2}\rho_{jj}\sigma_j^2 + \rho_{ij}\sigma_i\sigma_j \quad (9a)$$

$$= -\frac{1}{2\cdot 3RT}\{\Delta U^{\ddagger\prime}_i\sigma_i + \Delta U^{\ddagger\prime}_j\sigma_j + \tfrac{1}{2}\Delta U^{\ddagger\prime\prime}_{ii}\sigma_i^2 + \tfrac{1}{2}\Delta U^{\ddagger\prime\prime}_{jj}\sigma_j^2 + \Delta U^{\ddagger\prime\prime}_{ij}\sigma_i\sigma_j\} + \Delta\Theta(T) \quad (9b)$$

where k_{ij} is the rate constant for a reaction with dual substituents σ_i and σ_j in the reactants, $\rho_i = (\partial \log k_{ij}/\partial\sigma_i)_0$, $\rho_{ij} = (\partial^2 \log k_{ij}/\partial\sigma_i\partial\sigma_j)_{00}$, etc., and $\Delta\Theta(T)$ is a term which includes corrections for zero-point energies and other temperature-dependent factors including entropy terms.[8,10] For sufficiently small displacements from the reference point, $\delta r_i = a\sigma_i$ and $\delta r_j = b\sigma_j$ with $\delta r_i + \delta r_j = \delta r_{ij}$, where a and b are constants[6,7] [equations (3)], so that equations (8) become

$$\Delta U^{\ddagger\prime}_i = \frac{1}{a}\left(\frac{\partial\Delta U^{\ddagger}}{\partial r_i}\right)_0 = \frac{1}{a}\Delta f^{\ddagger}_i$$

$$\Delta U^{\ddagger\prime\prime}_{ij} = \frac{1}{ab}\left(\frac{\partial^2\Delta U^{\ddagger}}{\partial r_i\partial r_j}\right)_{00} = \frac{1}{ab}\Delta F^{\ddagger}_{ij} \quad (10)$$

where $\Delta f^{\ddagger}_i$ and $\Delta F^{\ddagger}_{ij}$ may be deemed the force and force constant of activation, respectively.

Thus, at a constant temperature, neglecting pure second-order terms,[11]

$$\log\left(\frac{k_{ij}}{k_{HH}}\right) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \quad (11a)$$

$$= -\frac{1}{2\cdot 3RT}\left(\frac{1}{a}\Delta f^{\ddagger}_i\sigma_i + \frac{1}{b}\Delta f^{\ddagger}_j\sigma_j + \frac{1}{ab}\Delta F^{\ddagger}_{ij}\sigma_i\sigma_j\right) + \Delta\Theta(T) \quad (11b)$$

where $\Delta\Theta(T)$ can be a constant or negligible for substituent variations at constant temperature.[12] This means that we can ignore the temperature-dependent term, $\Delta\Theta(T)$. It is widely known and generally accepted that the Gibbs free energy changes, $\Delta G^{\ddagger}$ or ΔG^0, brought about by *meta* and *para* substituents are virtually changes in $\Delta U^{\ddagger}$ or ΔU^0 since substituent does not greatly affect entropy changes, i.e. $\delta\Delta G^{\ddagger} \approx \delta\Delta U^{\ddagger}$ or $\delta\Delta G^0 \approx \delta\Delta U^0$ in solution-phase reactions.[12] Comparison of equations (11a) and (11b) indicates that the magnitudes of ρ_i and ρ_{ij} are related to the magnitudes of the force and force constant of activation, $\Delta f^{\ddagger}_i$ and

$\Delta F^{\ddagger}_{ij}$, respectively:

$$|\rho_i| = A\,|\Delta f^{\ddagger}_i| \qquad |\rho_{ij}| = B\,|\Delta F^{\ddagger}_{ij}| \tag{12}$$

where A and B are positive constants. Since the force constant F_{ij} is a change in the interaction (potential) energy between the two substituents σ_i and σ_j (through R_i and R_j) per unit distance changes, i.e. $\delta\Delta U_{ij}$ for $\delta r_1 = \delta r_2 = 1{\cdot}0$, $\Delta F^{\ddagger}_{ij}$ represents a change in the intensity of interaction from the GS to the TS, $\Delta I^{\ddagger}_{int}(i, j)$:

$$\begin{aligned}\Delta F^{\ddagger}_{ij} &= F^{\ddagger}_{ij} - F^{0}_{ij}\\ &= (\text{intensity of interaction between } \sigma_i \text{ and } \sigma_j \text{ through } R_i \text{ and } R_j \text{ in the TS}) - (\text{intensity of interaction between } \sigma_i \text{ and } \sigma_j \text{ through } R_i \text{ and } R_j \text{ in the GS})\\ &= I^{\ddagger}_{int}(i, j) - I^{0}_{int}(i, j)\\ &= \Delta I^{\ddagger}_{int}(i, j)\end{aligned} \tag{13}$$

Since force f is a product of the force constant, F, and displacement r, i.e. $\Delta f_i = F_{ij}\Delta r_j$, the use of $|\rho_i|$ ($\propto |\Delta f^{\ddagger}_i|$) as a measure of r_{ij} should be limited to the systems with a constant r_j ($\propto \sigma_j$), i.e. Δr_j = constant. Thus the $|\rho_i|$ values for different reaction series cannot be directly compared to deduce changes in r_{ij} unless $R(\sigma_j)$ is constant.[1,3] This is why the simple Hammett's coefficient has a serious limitation in its scope of application as a measure of TS structure.

The relationship betwen the two quantities, $|\rho_i|$ and $|\rho_{ij}|$ (i.e. $|\Delta f^{\ddagger}_i|$ and $|\Delta F^{\ddagger}_{ij}|$) is similar to that between rate and rate constant, k_{ij}; in general, rates for different reacting systems are legitimately compared at unit concentration of the reactants, i.e. using rate constants. This means that it is more appropriate to use $|\rho_{ij}|$ rather than $|\rho_i|$ for comparing the intensities of interaction between two reaction centres for different reacting systems. Since the change in the intensity of interaction, $\Delta I_{int}(i, j)$, is intimately related to the distance r_{ij}, the magnitude of ρ_{ij} provides a more general measure of the TS structure. In other words, the magnitude of ρ_{ij} can be a direct measure of the TS structure, whereas $|\rho_i|$ gives only a relative measure requiring the constancy of the other reaction centre, $R_j(\sigma_j)$.[13]

APPLICATION

Let us examine the significance of $|\rho_{ij}|$ in a typical S_N2 reaction, Scheme 1, where X, Y and Z fragments represent nucleophile, substrate and leaving group (LG), respectively.

For a rate-limiting bond-formation process, there will be no significant bond cleavage in the TS, $F^{\ddagger}_{YZ} = F^{0}_{YZ}$ and $\Delta F^{\ddagger}_{YZ} = 0$; according to equation (12) this will lead to a vanishing ρ_{YZ} value, $\rho_{YZ} = 0$.[1] Likewise, for a rate-limiting bond-breaking process, $F^{\ddagger}_{XY} = F^{0}_{XY}$ and $\Delta F^{\ddagger}_{XY} = 0$ so that $\rho_{XY} = 0$[1] [equation (12)].

Another special case is a reaction type in which the two substituents, σ_i and σ_j, can interact through multiple channels; if there are two interaction channels available, two force constant changes will result and give two separate ρ_{ij} values leading to a greater $|\rho_{ij}|$ when added together;[1] e.g.

$$|\rho_{ij}|(1) = B\,|\Delta F^{\ddagger}_{ij}|(1)$$
$$|\rho_{ij}|(2) = B'\,|\Delta F^{\ddagger}_{ij}|(2)$$

[equation (12)], and hence

$$|\rho_{ij}|(\text{total}) = |\rho_{ij}|(1) + |\rho_{ij}|(2)$$

The resulting ρ_{ij}, $|\rho_{ij}|$ (total), will be greater than that for any of the single-component channel:

$$|\rho_{ij}|(\text{total}) > |\rho_{ij}|(1) \text{ or } |\rho_{ij}|(2)$$

For i, j = X, Y or X, Z, $F^{0}_{ij} = 0$, since in the GS the nucleophile can be considered to be at an infinite distance:

$$\Delta F^{\ddagger}_{ij} = F^{\ddagger}_{ij} - F^{0}_{ij} = F^{\ddagger}_{ij} = I^{\ddagger}_{int}(i, j)$$

Since

$$r_{ij} = \alpha + \beta \log\left(\frac{1}{F_{ij}}\right)$$

[equation (2)], it follows that

$$r^{\ddagger}_{ij} = \alpha + \beta \log\left(\frac{1}{F^{\ddagger}_{ij}}\right) = \alpha' + \beta' \log\left(\frac{1}{|\rho_{ij}|}\right) \tag{14}$$

The distance $r^{\ddagger}_{ij}$ between R_i and R_j in the TS is a logarithmic inverse function of $|\rho_{ij}|$, provided that the distances r_i and r_j between R_i and σ_i and between R_j and σ_j, respectively, are kept constant during the activation process.[1] Hence the greater is $|\rho_{ij}|$, the shorter is the distance between the two reacting centres, R_i and R_j. Therefore, straightforward application of equation (14) is possible for the cases of i, j = X, Y or X, Z, with the inverse relationship between $r^{\ddagger}_{ij}$ and $|\rho_{ij}|$.[1,2] It has been shown that the degree of bond formation is greater (i.e. $r^{\ddagger}_{XY}$ is shorter) when $|\rho_{XY}|$ is greater[2] and the tighter the TS (the shorter is $r^{\ddagger}_{XZ}$) the greater is $|\rho_{XZ}|$.[14] Such a simple relationship between $r^{\ddagger}_{ij}$ and ρ_{ij} does not exist, however, for i, j = Y, Z or for processes involving bond cleavage in the TS, and re-examination of the significance of the magnitude $|\rho_{YZ}|$ is necessary. In the bond-breaking process, $F^{\ddagger}_{ij} < F^{0}_{ij}$, i.e. the force constant (or intensity of interaction) decreases from GS to TS, since the distance between the two reacting centres increases in the TS:

$$\Delta F^{\ddagger}_{ij} = F^{\ddagger}_{ij} - F^{0}_{ij} < 0$$
$$\Delta I^{\ddagger}_{int}(i, j) = I^{\ddagger}_{int}(i, j) - I^{0}_{int}(i, j) < 0$$

The difference, however, will become greater, i.e. the magnitude of $\Delta F^{\ddagger}_{ij}$ or $\Delta I^{\ddagger}_{int}(i, j)$ increases, with the

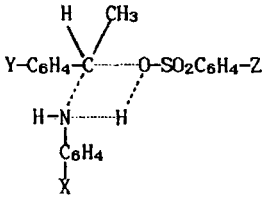
degrees of bond cleavage, so that

$$|\rho_{YZ}| \propto |\Delta I^{\ddagger}_{int}(Y, Z)|$$
$$\propto |\Delta r^{\ddagger}_{YZ}| = r^{\ddagger}_{YZ} - r^{0}_{YZ}, \text{ with } r^{\ddagger}_{YZ} > r^{0}_{YZ}$$
$$\propto r^{\ddagger}_{YZ}, \text{ since } r^{0}_{YZ} = \text{constant.}$$

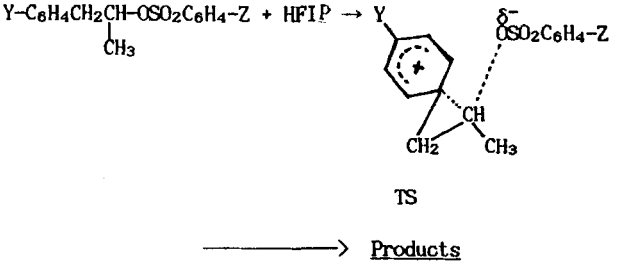
An example is the ρ_{YZ} value for an S_N1 reaction, for which a large ρ_{YZ} is obtained. For the solvolyses of α-*tert*-butylbenzyl (Y) arenesulphonates (Z), ρ_{YZ} was 0·4–0·5 [the ρ_{YZ} values were estimated for the solvolyses of α-*tert*-butylbenzyl (Y) arensulphonates (Z) in 80% aqueous acetone and 80% aqueous ethanol using Y = *p*-*tert*-butyl, *m*-CH_3, *m*-Cl, *m*-CN, *p*-CF_3, *m*-NO_2, *p*-CN and *p*-SO_2Me and Z = *p*-CH_3 and *m*-NO_2, taken from Ref. 15]. There can be exceptional cases where $F^{\ddagger}_{ij}$ is abnormally large or small so that $|\rho_{YZ}|$ is abnormally small or large, or in some cases $F^{\ddagger}_{ij}$ can be greater than F^{0}_{ij} and hence $\Delta F^{\ddagger}_{ij} > 0$ for i, j = Y, Z:

(i) multiple interaction paths exist in the TS by hydrogen-bond bridge formation;
(ii) bond contraction takes place in the TS;
(iii) resonance shunt occurs.

Examples are as follows. (i) In the reactions of 1- and 2-phenethyl benzenesulphonates with anilines, a four-centre TS is possible by a hydrogen-bond bridge providing dual interaction routes:



Thus $\Delta F^{\ddagger}_{YZ} = F^{\ddagger}_{YZ} - F^{0}_{YZ}$ = small and hence $|\rho_{YZ}|$ is small ($\rho^{H}_{YZ} = 0{\cdot}11$ and $0{\cdot}07$ respectively),[16] since $F^{\ddagger}_{YZ}$ is enhanced, i.e. $F^{\ddagger}_{YZ} \approx F^{0}_{YZ}$. (ii) In the solvolysis of 1-phenyl-2-propyl arenesulphonates in hexafluoroisopropanol (HFIP), aryl participation results in a TS in which one C—C bond is bypassed between σ_Y and σ_Z, and $F^{\ddagger}_{YZ}$ can be substantially greater than F^{0}_{YZ}, hence a large $|\rho_{YZ}|$ (= 0·41) is obtained:[17]



Rough estimates of bond length changes (based on values in Ref. 18) during the activation process, i.e. reduction of one C—C bond and stretching a C—O bond, give a *ca* 1·0 Å decrease in the distance between the two substituents through reaction centres:

$\Delta d^{\ddagger}_{(C-C)} \approx -1{\cdot}53$ Å (reduction of one C—C bond)

$\Delta r^{\ddagger}_{(C-O)} \approx 1{\cdot}91 - 1{\cdot}42 \approx 0{\cdot}50$ (stretching of C—O bond, assuming *ca* 35% stretching at the TS)[19]

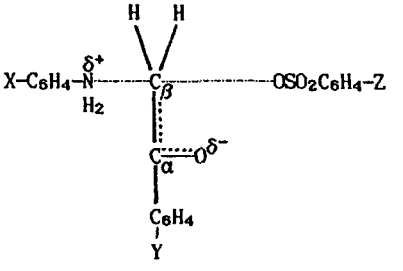
Total $\Delta d^{\ddagger} = -1{\cdot}53 + 0{\cdot}50 \approx -1{\cdot}0$ Å

Hence

$$\Delta F^{\ddagger}_{YZ} \gg 0$$

(iii) In the reactions of phenacyl arenesulphonates with anilines, the charge transfer from the nucleophile leaks to the carbonyl oxygen so that interaction between σ_Y and σ_Z is reduced, leading to an enhanced $|\delta F^{\ddagger}_{YZ}|$ and hence a greater value of $|\rho_{YZ}|$ (= 0·62) is obtained,[13b] since $F^{\ddagger}_{YZ}$ is abnormally low:

$$\Delta F^{\ddagger}_{YZ} = \Delta F^{\ddagger}_{YZ} - \Delta F^{0}_{YZ} \ll 0$$



The interaction between substituents Y and Z is considerably reduced since the electron density change on C-β is strongly coupled to the carbonyl oxygen rather than to Y.

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