On the Analysis of Substituent Effects. Part 3.[1] The Geometry of the Ring in Substituted Benzenes

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In Part 1 it was proposed that in any substituted benzene molecule the ring exists in one of two discrete states, neither of which possesses regular hexagonal geometry at zero substituent field. Here further physical and chemical evidence for the existence of such ring states is presented and discussed within the context of a polarisation and charge-transfer analysis of electronic effects. A quantitative expression for the ring bond angles in terms of electronic characteristics of the substituents is given.

The two states are labelled H (for higher) and L (for lower) according to their relative abilities to transmit substituent electronic effects. The difference is explained in terms of the balance between charge transfer and overlap repulsion within the ring. Deviations from the quantitative expression in certain *para*-disubstituted benzenes are interpreted in terms of two kinds of enhanced intra-ring charge-transfer effect, one of which has no analogue in resonance theory.

This series of papers is concerned with Hammett-like correlations involving standard substituent constants based on a ground-state physical property, namely, the ^{13}C substituent chemical shifts at the β site in ring-substituted styrenes (σ_{ST}, sigma styrene), and their interpretation in terms of a polarisation and charge-transfer analysis of substituent electronic effects. In Part 1[2] we reported that the plot of the σ^+ scale of *meta*- and *para*-substituent constants against σ_{ST} (reproduced in Figure 1) was bilinear, with the slope changing magnitude abruptly at a critical point, and with no trace of deviation for any *para* π-donor. This remarkable result makes the usual interpretation of the σ^+ scale untenable. We attributed the bilinearity to a flip between two (perturbed) discrete electronic structures of the benzene ring at a critical extent of polarisation.† We cited as supporting evidence for the existence of two discrete ring states, the observation that a plot of *ortho* ring angles against an experimental measure of σ-electron polarising power (the σ_I scale) gives two discrete parallel lines, one for π-donors and one for π-acceptors. In Part 2[1] we specified the considerable consequences which the flipping of the ring structure would have for the overall pattern of rate–equilibrium and rate–rate relationships for chemical reactions, and we cited reports of several otherwise puzzling experimental observations which are in accord with various features of the predicted pattern.

In this paper we report, and comment on, further evidence for the existence of two accessible ring states. The new evidence consists of plots of experimental substituent effects on physical and chemical properties of series of disubstituted benzenes against a measure of substituent polarising power, and analyses of the geometrical parameters of the ring as determined by X-ray crystallography. Our measure of the substituent polarising power is the blended σ_{ST} scale, $\sigma_{ST}(\lambda) = \sigma_{ST} - \lambda(\sigma_{ST} - \sigma_I)$. The values of σ_{ST} and of σ_I for some common substituents are listed in Part 1.[2]

$\sigma_{ST}(\lambda)$

Figure 1. Plots of (*A*) σ^+ against σ_{ST} (0.0) and (*B*) gas-phase acidities of phenols[3] against $\sigma_{ST}(0.3)$. In this and subsequent figures: (*i*) the symbols ∇ and $\bigcirc$ refer to substituents which are π-donors and π-acceptors respectively, and the symbol ● represents the point for no substituent; (*ii*) both *meta*- and *para*-substituents are included; (*iii*) the lines have no statistical significance: they are for guidance in the detection of qualitative patterns.

group attached to a benzene ring becomes more strongly π-electron attracting, whereas the gas-phase acidity of phenol involves a process in which a functional group attached to a benzene ring becomes more strongly π-electron repelling. Both plots show bilinearity with the slope changing by a factor of three: this implies that the benzene ring is three times better at transmitting substituent effects to *meta* and *para* side chains in some molecules than in others, and is consistent

Results and Discussion

The Plots.—Figure 1 shows the plot of the σ^+ scale against $\sigma_{ST}(\lambda)$ together with a plot of substituent effects on the gas-phase acidity of phenol.[3] The σ^+ scale is associated, among other things, with chemical processes in which a functional
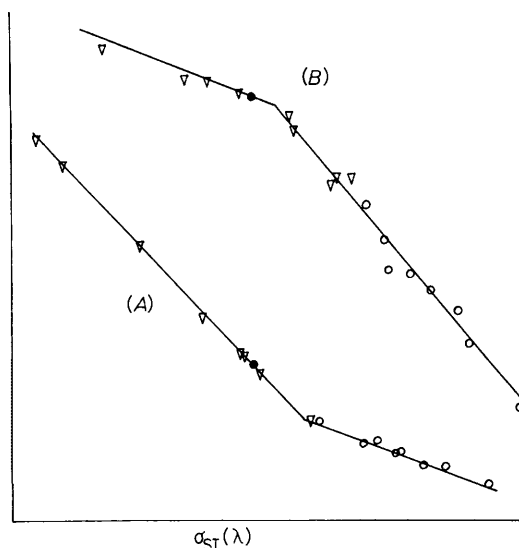
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† The existence of discrete ring states does not imply that in any particular substituted benzene there is an electronically excited state that lies just above the ground state. It merely means that substituted benzene molecules can be grouped into classes with qualitatively different ring structures.
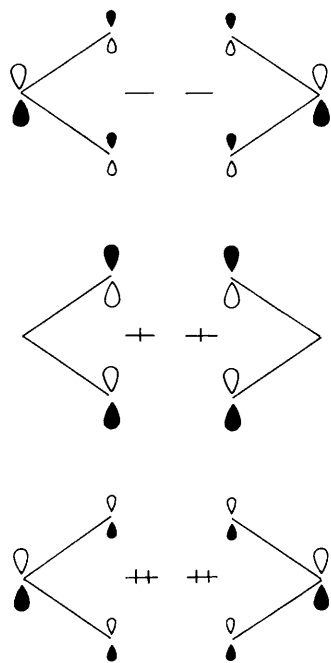
Figure 2. Localised π-orbitals of the benzene ring. Charge transfer involves interactions between overlapping occupied and unoccupied or half-occupied pairs of localised orbitals. Overlap repulsion involves interactions between overlapping pairs of occupied localised orbitals.

σ_{ST} (λ)

Figure 3. Plots of (A) C=N stretching frequencies in benzonitriles[a] against $\sigma_{ST}(0.1)$, (B) O–H stretching frequencies in benzoic acids[b] against $\sigma_{ST}(0.2)$, and (C) pK_a values of benzoic acids in DMF[c] against $\sigma_{ST}(0.3)$. See footnotes to Figure 1. [a] O. Exner and K. Bocek, *Collect. Czech. Chem. Commun.*, 1973, **38**, 50. [b] O. Exner and E. Svatek, *ibid.*, 1971, **36**, 534. [c] M. Ludwig, V. Baron, K. Kalfus, O. Pytela, and M. Vecera, *ibid.*, 1986, **51**, 2135.

with our proposal of two ring states. For convenience we shall label these ring states H (for higher) and L (for lower) according to their relative abilities to transmit substituent effects. The two plots differ in that on going from the π-repelling to the π-attracting end of the spectrum of substituent polarising power, the slope decreases in the first case and increases in the second case. The observed pattern of bilinearity would be rationalised if, in disubstituted benzenes, the H state was only adopted when one of the substituents was a strong π-attractor. When both substituents were strong π-attractors the L state would be adopted.

Among common substituents, strong π-attractors (with respect to polarising power), such as m- and p-CO₂Me (CF₃, CN, and NO₂) are also π-acceptors (with respect to charge-transfer power): π-repellers and weak π-attractors, such as m- and p-NH₂ (OMe, Me, and F) are also π-donors. Our rationalisation of the plots in Figure 1 makes it reasonable to identify the parallel lines for π-acceptors and π-donors in the above-mentioned plot of ring bond angle against σ_I for monosubstituted benzenes, with the H state and the L state, respectively.

The existence of the two ring states can be explained in terms of charge transfer (which is always energetically favourable) and overlap repulsion (which is always energetically unfavourable) interactions between sets of π-orbitals which are formally localised on two three-carbon fragments of the benzene ring as shown in Figure 2. Where the effects of the charge-transfer interactions predominate, overlap between these localised orbitals is maximised and the ring goes into the H state, but where the effects of overlap repulsion are the greater, overlap between the orbitals is minimised and the ring goes into the L state. Substituents which are π-repellers tend to increase overlap repulsion in the ring, thus favouring the L state. On the other hand, substituents which are π-attractors tend to reduce overlap repulsion, thus favouring the H state. When two π-attractors are present each tends to polarise the ring in a
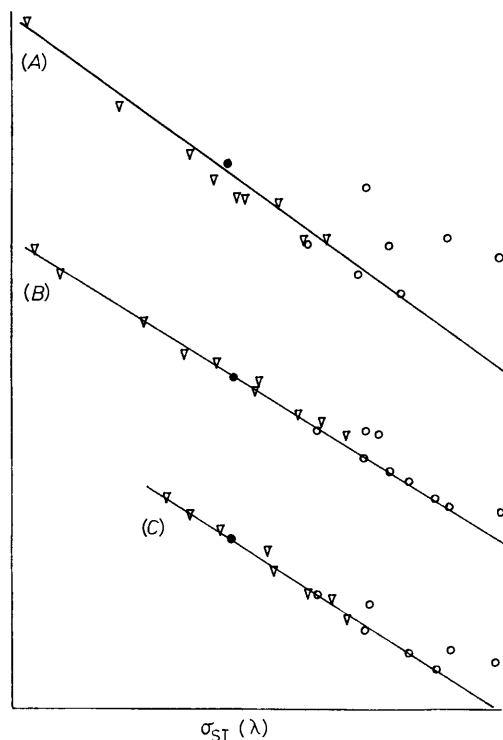
direction which reduces the π-accepting strength of the other, thus reducing the energetically favourable charge transfer between the substituents and the ring. This intersubstituent effect is less pronounced when the ring is in the L state and, therefore, the L state may be adopted with certain combinations of π-attractors.

If the bilinearity in Figure 1 is correctly associated with a flip between L and H ring states in the molecules involved in the chemical processes, then the σ_{ST} scale must be associated with a set of molecules in which the ring does not flip. Since the vinyl group in styrenes can act as both a good π-acceptor and a good π-donor it is reasonable to suppose that the ring is in the H state in all substituted styrenes.

This interpretation of bilinear plots leaves the problem of why benzoic acid dissociation in water gives a linear rather than a bilinear plot (Figure 2 of Part 1).[2] A clue to the solution is contained in plots, shown in Figure 3 of the present paper, of substituent effects on properties of disubstituted benzenes in which at least one substituent is a π-acceptor. In each case, the points for molecules in which both substituents are π-acceptors in the *para* disposition deviate significantly from a single straight line. The extent of the deviation follows, at least qualitatively, the charge–transfer power (the T^0 value in Table 2 of Part 1) of the variable substituent, and the substituent effect is always diminished.

Charge transfer involving the middle pair of localised π-orbitals of the ring is particularly favoured when these orbitals are degenerate or near-degenerate. Hence, when each localised orbital of the pair is perturbed by a substituent which is similar in electronic characteristics to the other, this enhanced intra-ring charge transfer will be favoured. This
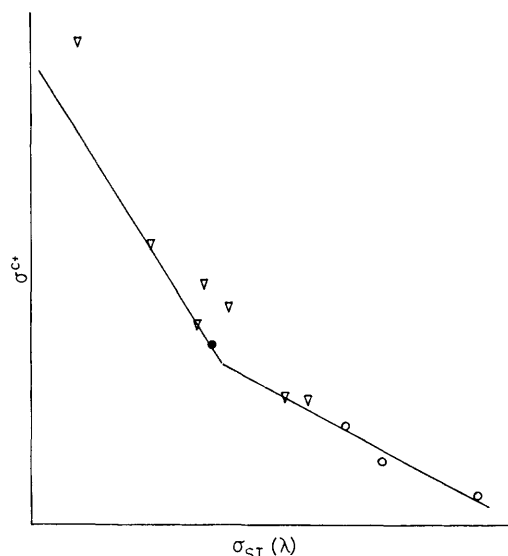
Figure 4. A plot of the σ^{C+} scale[5] against $\sigma_{ST}(0.0)$. See footnotes to Figure 1.

factor will tend to favour the adoption of the H state by the ring. We suggest that the ring adopts the H state in all the molecules involved in Figure 3. Intra-ring charge transfers involving the upper and the lower localised π-orbitals compete with, and hence diminish, charge transfer between the ring and the substituents, especially when the substituents are *para* to each other.* Thus, we can explain the observed deviations from linearity.

One of the pair of intra-ring charge transfers involving the upper and the lower localised π-orbitals can interact with the direct charge transfer between a π-donor substituent and a π-acceptor substituent, and enhance both charge-transfer effects on the ground state of the disubstituted benzene. This interaction is particularly large when the two substituents are *para* to each other.* The plot, shown in Figure 4, of the σ^{C+} scale[4] of substituent effects exhibits marked deviations from bilinearity in which the effects of π-donors *para* to the cationic substituents are enhanced.

The enhancement of intra-ring charge transfer in *para*-disubstituted benzenes with certain π-donor/π-acceptor pairs is analogous to the involvement of quinonoid structures in resonance theory. However, the enhancement of intra-ring charge transfer in *para*-disubstituted benzenes with certain π-acceptor/π-acceptor pairs has no analogous effect in resonance theory. The former phenomenon is responsible for much of the difference between the σ^{C+} and the σ^{+} scales of substituent effects, but does not contribute to the difference between the σ^{+} and the σ scales. The latter phenomenon contributes to the difference between the σ and the σ_{ST} scales.

The Geometry of the Benzene Ring.—The implications of our proposals concerning the transmission of substituent electronic effects in disubstituted benzenes for the geometry of the benzene ring will now be set out.

(*i*) The geometry of the ring should be different in the unperturbed H and L states. In each unperturbed state the geometry is determined by the magnitudes of the charge transfer and the polarisation which result from the interactions of the

two sets of localised π-orbitals. These interactions are larger in the H state than in the L state.

Let us label the *ipso*(α) and the *ortho*(β) ring bond angles at zero substituent field ($\sigma_I = 0$), α_L^0, β_L^0, α_H^0, and β_H^0, according to the ring state. At other values of σ_I the values of α and β are given by equations (1) and (2). We find that bond angles obtained by Domenicano and Murray-Rust[5] from analyses of *X*-ray crystallographic and other physical data on mono- and *para*-di-substituted benzenes fit these equations quite well when $\alpha_H^0 = 117.2°$, $\alpha_L^0 = 118.4°$, $\beta_L^0 = 120.8°$, $\beta_H^0 = 121.4°$, and $\rho_\alpha = 10$.

$$\alpha = (\alpha_L^0 \text{ or } \alpha_H^0) + \rho_\alpha \sigma_I \qquad (1)$$

$$\beta = (\beta_L^0 \text{ or } \beta_H^0) - (\rho_\alpha \sigma_I)/2 \qquad (2)$$

(*ii*) Where charge transfer to a substituent is assisted by the polarising effect of a second substituent the *ipso–ortho* bond should lengthen (due to the loss of electronic charge from the bonding localised orbital) and the α angle should consequently decrease, especially where the ring is in the H state. There is evidence[6] that π-repellers reduce the angle in benzoic acids by up to 2° compared with π-attractors. This might possibly be a consequence of a direct charge-transfer effect, but there is no indication of such effects on the OH stretching frequency in benzoic acids (see Figure 3).

(*iii*) Enhanced intra-ring charge transfers should shorten the *ortho–meta* bonds (the consequence of maximising overlap between the localised orbitals), lengthen the *ipso–ortho* bonds (due to the loss of electronic charge from the bonding localised orbital and the gain of electronic charge by the antibonding localised orbital), and consequently reduce the α bond angles. There is evidence for such effects in benzene molecules containing identical π-acceptors in the *para* disposition, in a report[7] that α in *p*-dinitrobenzene is 1.4° less than α in nitrobenzene. The angle (124.8°) in the latter is close to the angle (124.4°) predicted by equations (1) and (2). Charge transfer to each nitro group in the *p*-dinitrobenzene is hindered by the polarising effect of the other nitro group, and consequently in the absence of the enhanced intra-ring charge transfer in the disubstituted molecule, we would have expected α to be greater in *p*-dinitrobenzene than in nitrobenzene.

(*iv*) The geometry of the ring in the unsubstituted benzene molecule corresponds to that of a perturbed H or L state with an effective σ_I value of 0.28 or 0.16 respectively.

Conclusions

The evidence reported here strengthens the case for the existence of two discrete ring states in substituted benzenes, neither of which possesses regular hexagonal equilibrium geometry at zero substituent field ($\sigma_I = 0$). However, a lack of extensive, accurate, published experimental data on ring geometries prevents a really thorough test of our predictions. If our analysis of the origins of substituent effects on ring geometries is validated by such a test, then the parameters we have used in applying equations (1) and (2) would have to be recalculated after the exclusion of molecules in which enhanced intra-ring charge-transfer effects were significant.

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