A Simple Molecular Orbital Perturbation Treatment of the Switching of Bond Order Patterns within Molecular Systems

By **Martin Godfrey,** Department of Chemistry, The University, Southampton SO9 5NH

A simple molecular orbital perturbation method for determining the effects of disturbances in molecular systems is applied to predict the conditions required for small perturbations of the energy to produce major changes in individual bond orders. The results are used to explain several important physical and chemical observations concerning quantitative linear correlations which are puzzling when considered in terms of commonly used theoretical models. Their implications for simple resonance theory are also discussed. It is concluded that effects of mutual conjugation are not the principal source of differences between the various empirical scales of substituent effects on properties of benzene and its derivatives.

WE have recently described a novel theoretical model for predicting and interpreting quantitative linear correlations in organic chemistry.[1-3] The model incorporated a simple molecular orbital perturbation treatment of intra- and inter-molecular interactions, which allows the possibility that there are circumstances in which a *small* perturbation of the *energy* of a molecular system (*i.e.* a system of one or more molecules or molecular species) can produce *major* changes in *individual bond orders*. Here we first consider this aspect of the treatment of interactions within molecular systems in more detail in order to establish the theoretical conditions which favour the switching of a system from one pattern of bond orders to another. Then we discuss cases in which this phenomenon, which for brevity we shall call 'structure-switching', appears to exist and consider the general implications of its existence for the theory of structure–property relationships in organic chemistry.

THEORY AND RESULTS

The version of MO perturbation theory used in the present work is described in its application to the determination of the bond orders in planar butadiene. The butadiene molecule is first formally divided into a π-electron system and a molecular skeleton, and then the π-electron system is formally further divided into two sub-systems each of which is localised in the immediate neighbourhood of a pair of carbon atoms. In the absence of interactions between these two sub-systems, each sub-system would be equivalent to the π-electron system of an ethylene molecule (see Figure 1). The interactions between the neighbouring π-electron sub-systems have been expressed using MO perturbation theory by Salem.[4] The interactions are of two kinds, one of which involves the overlapping of the filled (bonding) MOs with the vacant (anti-bonding) MOs, and the other of which involves the overlapping of pairs of filled molecular orbitals. The first kind of interaction, which is commonly called the charge-transfer interaction, is stabilising, and the second kind of interaction, which here will be called the 'overlap–repulsion' interaction, is destabilising. Salem's expressions for the interactions are rather unwieldy for use in qualitative analyses and we have replaced them with the simpler expressions $\sum_{ij} c_i c_j \beta_{ij}$ for the charge-transfer stabilisation, and $\sum_{ij} c_i c_j \gamma_{ij}$ for the overlap–repulsion destabilisation. In these expressions, which are not suitable for use in quantitative analyses of interorbital interactions, the c_i and c_j represent the LCAO coefficients of the AOs involved in the overlapping of a given pair of sub-system MOs, and the β_{ij} and γ_{ij} are parameters for the overlap between
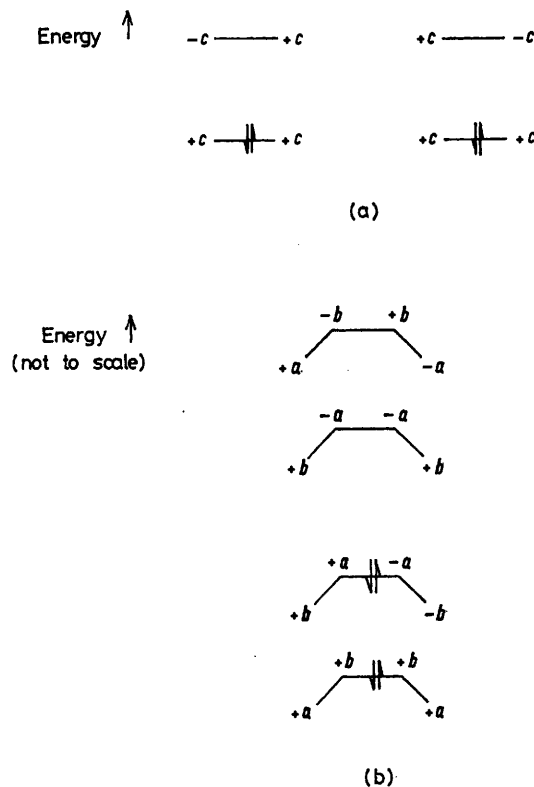

(a)

(b)

FIGURE 1   MOs of the ethylenic sub-systems in planar butadiene (*s-cis* or *s-trans*) (a) without intersystem overlap, and (b) with intersystem overlap. *a*, *b*, and *c* are LCAO coefficients in the MOs; $b > c/2^{\frac{1}{2}} > a$

orbitals i and j with values which depend on the natures of the overlapping AOs, their relative orientation, their physical separation, and their relative energies. In this simple treatment the interaction energies are the sums of changes in orbital energies and hence changes in orbital energies due to the interactions between sub-systems can be regarded as either stabilising or destabilising the whole molecular system.

[1] M. Godfrey, *J.C.S. Perkin II*, 1975, 1016.

[2] M. Godfrey, *J.C.S. Perkin II*, 1977, 769.

[3] M. Godfrey, 'Correlation Analysis in Chemistry : Recent Advances,' eds. N. B. Chapman and J. Shorter, Plenum, New York, 1978, ch. 3.

[4] L. Salem, *J. Amer. Chem. Soc.*, 1968, **90**, 543.

The magnitude and direction of the energy of interaction between two ethylenic π-systems can be determined experimentally to a good approximation * by measuring the shifts in the two π-ionisation bands in the photoelectron spectrum of butadiene relative to the position of the single π-ionisation band in the photoelectron spectrum of ethylene. The observed shifts [5,6] † are +0.96 and −1.45 eV which indicates that the net interaction is *destabilising*. Hence the two ethylenic π-systems should tend to move as far apart as resistance to stretching of the molecular skeleton will permit, *i.e.* the bond-order pattern should tend towards that described by the Lewis structure. The observed splitting of the π-ionisation bands is interpreted in terms of unavoidable overlap between the sub-systems due to the constraining influence of the molecular skeleton. The charge-transfer interactions automatically introduce anti-bonding character into the sub-systems, in addition to producing some bonding character *between* the sub-systems. As a consequence the *more* stable of the butadiene π-bonding orbitals is associated with a build up of electronic charge on the central carbon atoms at the expense of the terminal carbon atoms, and the *less* stable π-bonding orbital is conversely associated with a build up of electronic charge on the terminal carbon atoms at the expense of the central carbon atoms (see Figure 1).

In principle, the *overlap-repulsion* between the sub-systems could be reduced by polarising their π-bonds in such a way that there would be a *net* build up of electronic charge on the terminal carbon atoms.‡ This process would again introduce anti-bonding character into the sub-systems. The results of *ab initio* MO calculations on butadiene [6] suggest that this polarisation process does not in fact occur, and that consequently the essentially diene electronic structure is not lost. However in theory it would occur if it could be stabilized by more than a critical amount through the introduction of suitable chemical species into the environment of one or both of the sub-systems. Thus the introduction of suitable chemical species, as substituents or as weakly complexing agents, is predicted to permit a structure-switch from a perturbed diene to a perturbed monoene (Figure 2).

Having described our version of MO perturbation theory in its application to the determination of the bond orders in planar butadiene and its derivatives, we now consider the application of the theory to the determination of the electronic structures of other hydrocarbons.

We mentioned earlier that the π-electron binding energy of butadiene is less than that in two isolated ethylene molecules. If benzene had a cyclic triene structure we would expect that its π-electron binding energy would exceed that of three isolated ethylene molecules by *three times* the amount. However the photoelectron spectrum of benzene [7] indicates that the total destabilisation due to the interactions between the ethylenic systems is *no greater than*

in the butadiene case. We rationalise this finding in terms of our theory as follows. *Overlap-repulsion* between the ends of an *s-cis*-butadiene sub-system and the ends of an ethylene sub-system involves the *more* stable bonding MO of the butadiene system and can therefore be *reduced* by increasing charge-transfer within the butadiene system. *Charge-transfer* between the butadiene and ethylene sub-systems involves the *less* stable bonding MO and the less unstable anti-bonding MO of the butadiene system: it can therefore be *increased* by increasing charge-transfer *within* the butadiene system. Hence by increasing charge-transfer *within* the butadiene system the net interaction *between* the butadiene and ethylene systems can be in principle be made stabilising. As mentioned above, charge-transfer within the butadiene system can be increased only through increasing the overlap between its two ethylenic sub-systems: this process must be net *destabilising* because
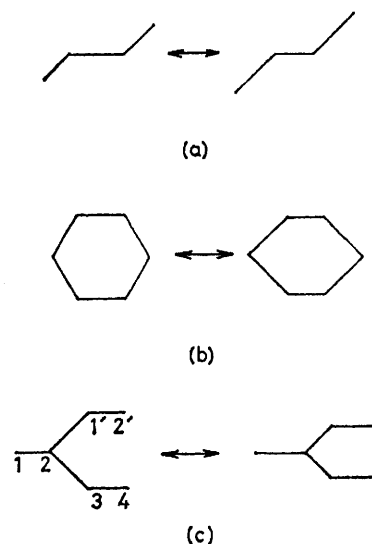

(a)

(b)

(c)

FIGURE 2 Diene to monoene and analogous structure switches in (a) butadiene, (b) benzene, and (c) 2-vinylbutadiene. The bond lengths are not drawn to scale

of the associated increase in overlap repulsion. The photoelectron spectrum of benzene is explained if this net *destabilisation* is compensated for by a net *stabilising* interaction between the butadiene and ethylene systems. Our interpretation of the photoelectron spectrum of benzene requires there to be a tendency for the overlap between all three ethylenic sub-systems to increase. It is consistent with the regular hexagonal ring structure of the benzene molecule in so far as there should be a barrier to the switching of the ring to either of the possible cyclic triene structures.

In a cyclic arrangement of *two* interacting ethylenic systems, as in cyclobutadiene, changes due to increasing *one* of the end-to-end intersystem overlaps are predicted to make the *other* end-to-end inter system overlap even more unfavourable than it would otherwise have been (Figure 3). Hence there should be no tendency for the cyclic diene to

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* The effects on the π-systems of differences between the σ-systems of butadiene and ethylene are not expected to be important since both butadiene and ethylene are non-polar molecules.[3]

† A case is argued in ref. 5 that a different assignment of the photoelectron bands from the one we use is possible. However we accept the assignment indicated by the results of *ab initio* MO calculations.

‡ *Charge-transfer* stabilisation in butadiene is not assisted by polarising the π-bonds in the ethylenic sub-systems (H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, 1955, **A68**, 601).

[5] C. R. Brundle and M. B. Robin, *J. Amer. Chem. Soc.*, 1970, **92**, 5550.

[6] R. J. Buenker and J. L. Whitten, *J. Chem. Phys.*, 1968, **49**, 5381.

[7] A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc.* (*B*), 1968, 22; M. Godfrey, *ibid.*, 1971, 1537.

switch spontaneously to a *square* ring-structure. It can be shown in similar fashion that *in general* monocyclic arrangements of an *even* number of interacting ethylenic systems are predicted to have polyene structures rather than equal
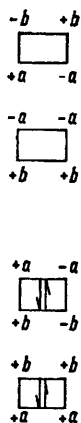

FIGURE 3   MOs of ethylenic sub-systems in cyclobutadiene with intersystem overlap. *a*, *b* as in Figure 1

carbon–carbon bond order structures. The converse structure preference found with benzene is predicted to be a possibility with other monocyclic arrangements of an *odd* number of interacting ethylenic systems although the *likelihood* is predicted to fall as the size of the ring increases.

On reversing the signs of the parameters β and γ for just one of the intersystem overlaps the prediction concerning the favourability of polyene structures in any particular cycle is reversed. The reversal of the parameter signs has the significance of converting normal Hückel MOs into Möbius MOs.[8]

The regular hexagonal benzene structure *could* be regarded as a formal union of two *allyl* sub-systems. The intersystem NO interactions for benzene would then be qualitatively similar to those between the two ethylenic sub-systems in acyclic butadiene except for an additional interaction involving the non-bonding molecular orbitals of the
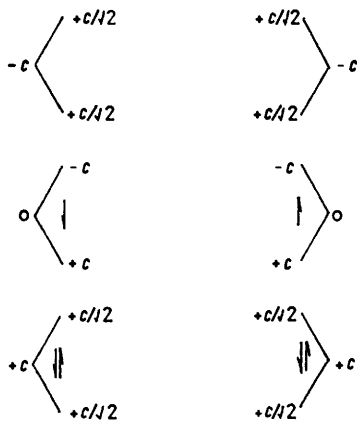

FIGURE 4   MOs of the allylic sub-systems in benzene without intersystem overlap. *Cf.* Figure 1(a)

allyl sub-systems (see Figure 4). We shall call this and all other sub-systems which contain a pair of MOs that are

[8] E. Heilbronner, *Tetrahedron Letters*, 1964, 1923.

qualitatively similar to the π molecular orbitals of ethylene ' quasi-ethylenic '. In the same way as the butadiene system could in principle switch to a monoene structure by the introduction of a suitable chemical species into the environment of one or both of the ethylene sub-systems (see above), the benzene system could switch to a quinonoid structure (Figure 2). Since the structure switch does not in itself create a net dipole in the molecule we shall label the quinonoid structure ' apolar ' to clearly distinguish it from a polar quinonoid *resonance* structure. A necessary requirement for a chemical species to be capable of inducing an apolar quinonoid structure is that it should have a low-energy *vacant* orbital which is capable of overlapping the bonding orbital of an allyl system but should not have corresponding high-energy *filled* orbitals.[3] Such a species will be labelled ' electrophilic ' in the remainder of this paper. A chemical species with a high-energy *filled* orbital which is capable of overlapping the bonding orbital of an allyl system but with no corresponding low-energy *vacant* orbitals will be labelled ' electrophobic '. In theory the apolar quinonoid structure in a monosubstituted benzene may be lost by introducing a suitable electrophobic substituent into the *para*-position or a suitable electrophilic substituent into the *meta*-position. The apolar quinonoid structure should be particularly favoured in *para*-disubstituted compounds in which *both* substituents are electrophilic. However it should not be generally favoured in *meta*-disubstituted compounds in which one substituent is electrophobic because internal charge-transfer stabilisation of the ring structure ought to be substantially reduced by the lifting of the degeneracy between the *non-bonding* orbitals of the two allylic systems. This reduction in the internal charge-transfer stabilisation would be minimised if neither substituent was attached to a carbon atom which carries a node in the non-bonding orbital, but then the advantage of polarising the bonding orbitals would be lost.

Another analogue of the diene to monoene switch is the ·branched triene to monoallyl switch in 2-vinylbutadiene which is illustrated in Figure 2. This switch is favoured by *electrophilic* substituents at positions 4 and 2′ and by *electrophobic* substituents at positions 3 and 1′.

So far we have considered only interactions within molecular π-systems. Disturbances should also affect molecular σ-*systems* both directly and *via* interactions between π- and σ-systems. The qualitative results of the MO perturbation treatment of structure-switching depend on the topologies of the interacting orbitals rather than on their symmetries. The methylene system has a pair of MOs that are topologically equivalent to the MOs of the ethylene π-system, *i.e.* the methylene system is quasi-ethylenic. Thus we can speak of ethane as a ' π-topologue ' of butadiene. The strong repulsion between the bonding orbitals of the two ethylenic systems in butadiene then suggests a strong repulsion between corresponding bonding orbitals of the two methylene systems in ethane and so on. The molecular systems involved in pericyclic reactions can be regarded as π-topologues of Hückel or Möbius unsaturated cyclic hydrocarbons. Then, for example, the cycloaddition of two polyenes is predicted to be possible only if the molecular system can switch to an intermediate fully delocalised electronic structure. The important π-topologues of some unsaturated hydrocarbons are shown in Figure 5.

To summarise, we have argued that for a hydrocarbon of any type there should be more than one qualitative pattern

of bond orders which is a reasonable candidate for the true qualitative description of the ground electronic state of each molecule, and that which of the candidates is favoured should depend on the nature of the hydrocarbon and on its chemical environment. In particular we have argued that the preferred qualitative pattern of bond orders may be changed by changing the topology of a hydrocarbon molecular system or by perturbing its chemical environment.

Structure-switching and Quantitative Linear Correlations.— In the context of the theoretical model mentioned in the Introduction,[1-3] quantitative linear correlations should exist only if there is just one particular mechanism for the transmission of chemically induced perturbations from the

$$CH_3 — CH = CH_2 \qquad\qquad CH_3 — CH_3$$

(a)

$$CH_2 = C\begin{smallmatrix}CH=CH_2\\\\CH_3\end{smallmatrix} \qquad\qquad CH_2\begin{smallmatrix}CH=CH_2\\\\CH=CH_2\end{smallmatrix}$$

$$CH_2 = C\begin{smallmatrix}CH_3\\\\CH_3\end{smallmatrix} \qquad CH_2\begin{smallmatrix}CH=CH_2\\\\CH_3\end{smallmatrix} \qquad CH_2\begin{smallmatrix}CH_3\\\\CH_3\end{smallmatrix}$$

(b)

FIGURE 5 π-Topologues of (a) butadiene and of (b) 2-vinylbutadiene

site of disturbance to the site of detection in each molecular system involved in the correlation. This mechanism involves the types of interaction considered in the previous section. It gives rise to equation (1) which relates the effects on some particular property, δP, to two parameters (**F**, a coulombic interaction parameter, and **S**, a non-coulombic interaction parameter) each of which has values that are characteristic of the nature of the perturbing group.

$$\delta P = f\mathbf{F} + s\mathbf{S} = f(\mathbf{F} + s/f\mathbf{S}) \tag{1}$$

The straight-line correlation described by equation (2) is predicted to be applicable if but only if: (i) there are at least *two* ethylenic or quasi-ethylenic sub-systems that lie between the site of disturbance and the site of detection in each molecular system involved in the correlation, and (ii) the values of s/f in equation (1) depend only on the nature of the electronic structures of the first two ethylenic or quasi-ethylenic sub-systems (relative to the site of disturbance), a condition which requires that no change anywhere in either of the basic molecular systems involved in the correlation can be accompanied by a significant change in the value of the non-coulombic parameter that is characteristic of the interaction between the second ethylenic or quasi-ethylenic sub-system and the rest of the molecular system. Equation (2) should hold not only for two different properties of the

[9] W. J. Hehre, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 1496.

same molecular system, but also for the same property of two different molecular systems.

$$\delta P_1/\delta P_2 = f_1/f_2 \tag{2}$$

Equation (1) can be valid only when the electronic structure of the molecular system concerned changes in a continuous manner during a continuous change in electronic energy. Structure-switching involving the first two ethylenic or quasi-ethylenic sub-systems should be accompanied by a change in the apparent zero-point of the δP scale and by changes in the values of f and of s. The former change comes about because the switch to the apolar quinonoid structure affects the electron population distribution in the second ethylenic or quasi-ethylenic sub-system in the same way as the introduction of a purely repulsive coulombic perturbing group. Equation (2) can be valid only when the structure-switching occurs at the same value of the quantity (**F** + s/f **S**) in each molecular system involved in the correlation.

The characteristic values of the perturbing group parameters **F** and **S** for substituent groups are conveniently obtained from the results of *ab initio* MO calculations of electron population distributions in benzene derivatives in which the benzene ring is constrained to a regular hexagonal structure.[9] We have previously shown [1] that with parameters evaluated in this way substituent effects on the pK_a value for anilinium ion in water at 25° (which are considered to define the σ^- scale of substituent effects) fit equation (1) very well for all common substituent groups, with the value of s/f depending only on the position of the substituent relative to that of the aquated ammonio-group. Furthermore we have argued [1] that these values of s/f indicate a reaction process in which there is no significant change in the non-coulombic parameter between the aquated ammonio-group and the phenylene group. We conclude that all anilinium ions have essentially the same ring structure and structure-switching involving the ring does not occur during the dissociation process.

The analysis in terms of equation (1) of substituent effects on the equilibrium between benzoic acid and benzoate ion in water at 25° is of particular interest to organic chemists since these effects define the Hammett scale σ. The effects on the *environmental* contributions to the free energy of reaction show a straight-line correlation with the σ^- scale.[3] However the effects of strongly electrophilic *para*-substituents on the corresponding *internal* contributions show marked deviations from the corresponding correlation line.[3] Since other substituents, including strongly electrophilic *meta*-substituents, *do* give rise to a straight-line correlation, no significant change in the non-coulombic parameter between the aquated carboxy-group and the phenylene group is indicated. However ring structure-switching in going from the unsubstituted acids to the acids with strongly electrophilic *para*-substituents remains a possible cause of the deviations. The results of an analysis by equation (1) of the ¹³C n.m.r. substituent chemical shifts (s.c.s.) at the *para*-positions of monosubstituted benzenes [2] also show the strongly electrophilic nitro and cyano groups to be ill behaved. These groups can be simultaneously brought into line in the s.c.s. *and* σ_p correlations by making particular adjustments to the values of the coulombic substituent parameter **F**. We conclude that if the apolar quinonoid structure occurs in *p*-nitro- and *p*-cyano-benzoic acids, it also occurs in nitrobenzene and benzonitrile.
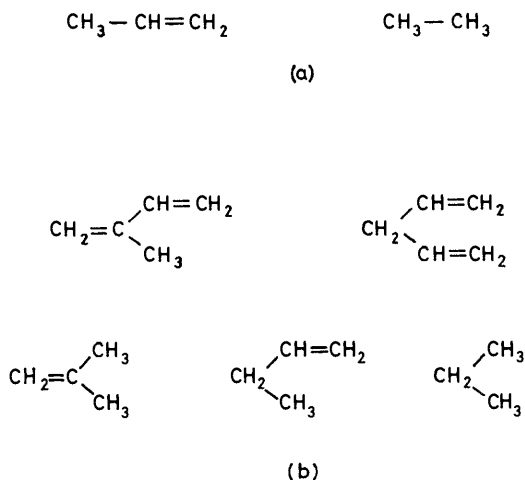
Striking support for the structure-switching hypothesis comes from the results of i.r. frequency measurements of substituted nitrobenzenes [10] and benzonitriles.[11] The observed effects of all *meta*-substituents (including the combined effects of two *meta*-substituents in one compound) and of certain electrophobic *para*-substituents on the frequencies of the 2 230.5 cm^{-1} band of benzonitrile and the 1 530.5 cm^{-1} band of nitrobenzene (measured in chloroform solution) would correlate well with the Hammett σ scale if the bands of the parent compounds were displaced to higher frequencies by *ca.* 2.5 and 5 cm^{-1} respectively. Furthermore the band displacements are not required to accommodate *meta*-substituents in compounds which already have an electrophobic *para*-substituent. No corresponding displacement effect is discernible in the case of the O–H stretching frequency for benzoic acid. These otherwise puzzling observations make sense if it is assumed that benzonitrile and nitrobenzene each has an apolar quinonoid ring structure which is retained when electrophilic groups such as the carboxy-group are introduced into the *para*-position but which switches to the regular hexagonal ring structure when electrophobic groups such as the amino-group are introduced into the *para*-position and/or when any common group is introduced into the *meta*-position.

Further support for the idea of different types of ring structure in nitrobenzene and *p*-dinitrobenzene on one hand, and *m*-dinitrobenzene and *sym*-trinitrobenzene on the other hand, comes from electronic spectral measurements. The results of calculations of electronic spectra by an MO perturbation method [12] suggest that the strongest absorption in the near u.v. region should occur at approximately the same frequency in each compound. In fact there is a large (*ca.* 4 000 cm^{-1}) increase in the frequency of maximum absorption in going from the first pair of compounds to the second.

If structure-switching is really induced by introducing electrophilic substituents into benzene, it ought to occur during the course of $S_{N}1$ reactions involving phenyl substituted carbonium ion intermediates and also in electrophilic aromatic substitution reactions involving σ-complex intermediates which are π-topologues of phenyl substituted carbonium ions. Indeed it might well occur at the *transition states* in these and other reactions. It is *possible* that the *structure* of the transition state is determined mainly by the ability of the detector group to participate in *non-coulombic* interactions with its neighbouring group while the *energy* of the transition state is determined mainly by the *coulombic* interactions between the two groups. Then on changing the nature of the perturbing group the reaction rate would vary much more markedly than the transition state structure, and equation (1) would reasonably be obeyed quite well for substituent effects on the internal enthalpy of activation (and hence on the logarithm of the rate constant).

The empirical scale of *para*-substituent effects for these reactions, the σ_p^+ scale,[13] obeys equation (1) when allowance is made for the assumption that the switch in ring structure is already present at the initial state of the reactions involving certain compounds as detailed above. The value of *s/f* is somewhat larger than that corresponding to the σ_p scale which suggests that there is a significant non-coulombic interaction between the phenylene group and the reaction site in the transition state, in accord with the idea that a structure-switch usually occurs at the transition state. It should be noted that for corresponding reactions of benzene derivatives in which the reactive group has a non-coulombic parameter for interaction with the phenylene group which does *not* vary significantly in value with changes in the molecular system that occur during the rate-determining step, the σ_p scale should be more appropriate. Thus, for example, the σ scale is more appropriate than the σ$^+$ scale for effects of substituents on the logarithmic rate of semicarbazone formation from benzaldehyde.[14]

If benzonitrile and nitrobenzene do indeed have apolar quinonoid ring structures they ought to be exceptionally susceptible to attack at the *para*-position by electrophiles in reactions in which the effects of coulombic interactions between the reactants are small relative to the effects of non-coulombic interactions, *e.g.* where the electrophile is neither positively charged nor strongly dipolar. This phenomenon has been observed experimentally in free radical substitutions.[15]

Substituent effects on certain *nucleophilic* aromatic substitution reactions of benzene derivatives correlate well with the σ$^-$ scale.[16] For the corresponding reactions occurring at the 3- or 4-positions in biphenyl derivatives the effects of strongly electrophilic substituents in the 4′-position correlate better with a scale which is a particular linear combination of the σ$^-$ and σ scales.[17] This is the expected result if the strongly electrophilic substituents can induce the apolar quinonoid ring structure in the *nearer* phenylene group in the biphenyl derivatives, and not in the *reacting* phenylene group in either the benzene or the biphenyl derivatives.

The Hammond–Leffler principle [18] concerning the relationship between transition state structure and chemical reactivity is expected to be valid only when *both* the structure *and* the energy of the transition state are determined mainly by the *same* type of interaction whether it be coulombic or non-coulombic. It should be noted that the theoretical conditions for the validity of the Hammond–Leffler principle and for the existence of linear correlations involving kinetic data are mutually exclusive. This is in accord with experimental observations collected by Johnson.[18] It should be noted also that the *slopes* of energy–reaction coordinate profiles for the bond-making and the bond-breaking processes in a chemical reaction (*e.g.* Dewar's BEP profiles [19]) ought to be discontinuous at the point of the structure-switch.

There is a good piece of evidence for structure-switching in a molecular system in which the first two quasi-ethylenic sub-systems relative to the perturbing group belong to the

[10] O. Exner, S. Kovac, and E. Solcaniova, *Coll. Czech. Chem. Comm.*, 1972, **37**, 2156.

[11] O. Exner and K. Bocek, *Coll. Czech. Chem. Comm.*, 1973, **38**, 50.

[12] J. N. Murrell, 'The Theory of the Electronic Spectra of Organic Molecules,' Methuen, London, 1963, ch. 10; M. Godfrey and J. N. Murrell, *Proc. Roy. Soc.*, 1964, **A278**, 71.

[13] L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35.

[14] W. P. Jencks, *Progr. Phys. Org. Chem.*, 1964, **2**, 63.

[15] W. A. Pryor, W. H. Davis, and J. H. Gleaton, *J. Org. Chem.*, 1975, **40**, 2099.

[16] C. Dell'Erba, G. Guanti, and G. Garbarino, *Tetrahedron*, 1971, **27**, 1807.

[17] G. Guanti, M. Novi, G. Garbarino, and C. Dell'Erba, *J.C.S. Perkin II*, 1977, 137.

[18] C. D. Johnson, *Chem. Rev.*, 1975, **75**, 755.

[19] M. J. S. Dewar and R. C. Dougherty, 'The PMO Theory of Organic Chemistry,' Plenum, New York, 1975, ch. 5.

ethano ($-CH_2-CH_2-$) group. The anomalous behaviour [20] of certain alkyl groups in plots of $\sigma^*_{CH_2X}$ versus σ_X^* (where σ^* is the Taft constant for substituent effects on properties of saturated hydrocarbons and their derivatives and X represents any substituent) is reasonably interpreted in terms of structure-switching in a branched-triene π-topologue. The structures are shown in Figure 6. The left-
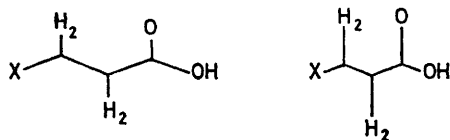

FIGURE 6   Branched triene to monoallyl structure switch in substituted propionic acids

hand structure is assumed to be the usual one and the right-hand structure the unusual one.

To summarise, several otherwise puzzling observations in the field of quantitative linear correlations involving a variety of molecular properties can reasonably be interpreted in terms of structure-switching when considered in the context of a theoretical model for quantitative linear correlations which is itself based on an MO perturbation treatment of interactions within molecular systems.

The Resonance Concept and Structure-switching.—In terms of the MO perturbation theory considered in this paper, the resonance concept is inadequate in that it does not allow for the existence of destabilising non-coulombic interactions among bonds, anti-bonds, and non-bonding centres that are not formally associated with the same atom. We have argued elsewhere [3] that because of this defect, resonance theory does not satisfactorily treat the coupling of non-coulombic and coulombic interactions within molecular systems. Consequently resonance-based theories for quantitative linear correlations incorrectly predict the circumstances in which straight-line correlations occur (they suggest that such correlations ought to be much less common than seems to be the case) and also incorrectly suggest that there is a special *kind* of interaction which is peculiar to unsaturated molecules. In the present work we have argued

that the same defect in the resonance concept also results in the failure of resonance theory to predict structure-switching within molecular systems.

According to our analysis based on MO perturbation theory, any particular cyclisation or decyclisation process which does not involve free-radical structures can occur only when structure-switching is possible, and, furthermore, structure-switching ought to be possible only under certain topological conditions. Thus structure-switching but not resonance is a viable theoretical concept for interpreting the Woodward–Hoffmann rules for stereoselectivity in pericyclic reactions.[21]

The differences among the substituent scales involved in quantitative linear correlations for benzene derivatives (σ, σ^-, and σ^+) are commonly attributed to the effects of polar resonance structures in disubstituted molecules in which one substituent has transferred an electron to the other substituent (mutual conjugation effects).[22] The fact that only the σ^- scale can be quantitatively expressed in its entirety in terms of theoretical substituent parameters whose values were obtained from data on monosubstituted benzenes in itself makes the resonance theory explanation unlikely. Furthermore, such resonance effects often fail to manifest themselves where they are clearly predicted; for example, in the equilibria between benzenediazonium salts in the presence of hydroxide ions and benzene *syn*-diazotates.[23] In the previous section we argued that the differences among the substituent scales can be more satisfactorily attributed to the effects of structure-switching. The ability of the structure-switching concept to provide a basis for explaining several different kinds of observation which were previously puzzling emphasises its superiority over the resonance concept. It should be appreciated that we are not suggesting that the ring structure in a *para*-disubstituted benzene with one electropholic substituent and one electrophobic substituent *is not quinonoid*. We are merely saying that quinonoid structures can be generated in these molecules by a *continuous* change in each bond order during a continuous energy perturbation, and that therefore no *special kind of effect* need be invoked. The apolar quinonoid ring structure can, in contrast, be generated from the regular hexagonal structure only if a discontinuous change in each bond order occurs during a continuous energy perturbation.

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