

A probe for substituent hyperconjugative power: MCD (magnetic circular dichroism) of the benzene L_b band

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Abstract - A simple MO analysis based on the perimeter model shows that the magnetic circular dichroism (MCD) of a substituted benzene provides information on the net π -electron donor or acceptor effect of the substituent. The high sensitivity of the MCD measurement to weak substituent effects makes it particularly suitable for investigations of hyperconjugation. Experimental results for several dozen formally saturated substituents are reported. The observed trends are rationalized in terms of current bonding theory.

INTRODUCTION

The interplay between a substituent and an aromatic ring system has been the subject of much attention, and studies of both the use of substituents for probing the properties of a cyclic π -electron structure and the inverse use of an aromatic system as a probe of the properties of a substituent have a venerable history. Presently, we shall deal with the use of one of the spectroscopic characteristics of the benzene chromophore to obtain information about a saturated substituent attached to it.

The spectroscopic property is the integrated intensity of the magnetic circular dichroism (MCD) of the lowest singlet-singlet transition of the benzene ring, located near 270 nm (transition from the ground to the 1L_b state). This is a signed quantity, known as the B term of the L_b transition, and obtained customarily in units of $D^2\beta_e/\text{cm}^{-1}$ (β_e is the Bohr magneton) from the measured magnetically induced ellipticity per unit magnetic field, $[\theta]_M$ (deg L m⁻¹ mol⁻¹ G⁻¹), measured as a function of wavenumber $\tilde{\nu}$ (cm⁻¹) by integration (ref. 1):

$$B = -33.53^{-1} \int d\tilde{\nu}[\theta]_M / \tilde{\nu} \quad (1)$$

It should be noted that a negative MCD peak corresponds to a positive B term and a positive MCD peak to a negative B term. We shall use the symbol $B(L_b)$ to refer to the B term of the L_b band of a perturbed benzene.

The substituent property about which information is obtained could be called its net π effect, and corresponds to the sum of the π -electron-donating and π -electron-accepting interactions of the substituent with the benzene ring. We shall see below that benzene itself has only a very small $B(L_b)$ term, induced by vibronic interactions: $0.3 \times 10^{-5} D^2\beta_e/\text{cm}^{-1}$. Substituents such as vinyl, expected on theoretical grounds to have comparable capacity as a π donor and as a π acceptor, and therefore to have no net π

effect, indeed do not change this value significantly. On the other hand, the $B(L_D)$ terms of phenyl rings attached to π donors such as the $-\text{NH}_2$ group and to π acceptors such as the $-\text{NO}_2$ group are much larger and much smaller (usually negative), respectively, than the $0.3 \times 10^{-5} \text{ D}^2\beta_e/\text{cm}^{-1}$, above value, and are roughly correlated with substituent resonance parameters such as σ^+ and σ_R^0 (ref. 2). Elsewhere, we have described the use of the perimeter model for the analysis of the MCD spectra of aromatics (ref. 3) and mentioned briefly the existence of a very simple quantitative relation between the deviation of the $B(L_D)$ value of a substituted benzene from $0.3 \times 10^{-5} \text{ D}^2\beta_e/\text{cm}^{-1}$ and the net π -electron effect of a weakly interacting substituent (ref. 4). For strongly perturbing substituents such as $-\text{NH}_2$ and $-\text{NO}_2$, the simplicity of the quantitative relation would be lost, but the saturated substituents of interest presently pose little danger in this regard. In this case, the separation of π from σ effects also is most readily justified.

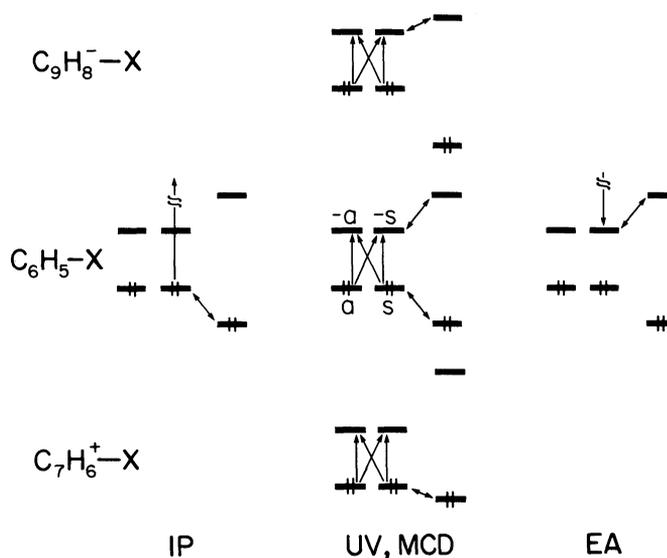


Fig. 1. Probe - substituent π interactions for C_6H_6 , C_7H_7^+ and C_9H_9^- probes in terms of MO levels. Interactions of primary importance are shown by double-headed arrows for ionization potentials (IP), electronic spectra (UV, MCD), and electron affinities (EA).

It should be noted that the present use of the benzene chromophore as a probe of the net π effect of a substituent means that strictly speaking, we shall only obtain information on the π -donor or acceptor behavior of the substituent towards the phenyl group. Much additional study would be required to produce an anywhere near full characterization of the π effect of the substituent. This could be approached in two ways. First, by the use of other annulenes in place of the benzene ring as a probe in the MCD measurements. Thus, it is clear from the arrangement of orbital energies that the vinyl substituent, which has an essentially zero net π effect when probed by benzene, will act as a good π donor when probed by the tropylium ring and as a good π acceptor when probed by the cyclononatetraenide anion (Fig. 1). The second approach would be to remove the restriction to one particular property of the probe, since the π effect of the substituent will in general also depend on the property chosen. Thus, towards a benzene ring, the vinyl substituent has no net π effect when judged by the $B(L_D)$ term of the probe, but it is a π donor when judged by the ionization potential of the probe, and it is a π acceptor when judged by the electron affinity of the probe (Fig. 1).

Because of the dependence of the substituent π effect on the structure of the probe chosen and on the probe property chosen for monitoring, it is impossible to construct a single scale of π effects (mesomeric effects, resonance effects) of substituents (ref. 5). It is argued below that a minimum of four parameters is needed to characterize the π effect of a general substituent even after it has been separated fully from any of its other effects. These parameters enter in different ways into the description of the π effect of the substituent on a particular property of a particular probe. Spectroscopic properties such as the IR intensity of certain vibrations of a phenyl ring (ref. 6) and the two-photon absorption intensity of a phenyl ring (ref. 7) are particularly valuable since, like MCD, they also permit a ready separation of the π effects from other effects. Since these various probe properties can be viewed as reflecting differently accentuated contributions from the four fundamental parameters, they are not related in a trivial fashion, but rather, complement each other in a useful way.

The common purely empirical scales of π effects, σ_R^0 , σ_R^- , σ_R^+ , and possibly others, are related to the fundamental substituent properties in even much more complicated ways than the MCD intensity used here. The reason is that they depend on the behavior of all the electrons through properties such as total electron density; this is true of some of the spectroscopic probes as well (NMR chemical shifts, IR intensities). To the contrary, properties such as UV or MCD intensities, ionization potentials and electron affinities can be reasonably approximated by restricting attention to the behavior of only one electron and are therefore more readily described in terms of simple models. The spectroscopic properties in which the initial and final state have the same number of electrons, such as UV and MCD, offer the further advantage that the orbital relaxation effects, neglected in the simple models, are relatively small and the potential headaches always associated with the use of Koopmans' theorem are then absent.

In spite of all this complexity, for many substituents the answers come out qualitatively similar no matter which probe or which probe property was used to obtain them: $-\text{NH}_2$ tends to be a donor and $-\text{NO}_2$ an acceptor no matter how the information was obtained. In this sense, the present results for a series of hyperconjugating substituents will be of general interest although they do not correlate perfectly with standard empirical parameters such as σ_R^0 . We expect them to be particularly useful for spectroscopic properties. Indeed, MCD results of this type have already been found valuable in attempts to adjust the absorption properties of a photoresist by the introduction of suitable substituents into its chromophore (ref. 8).

The text is organized as follows: first, we describe the relation of $B(L_b)$ in a perturbed benzene to its MO energies; second, we discuss the relation of these orbital energies to the fundamental π -electron properties of the substituent; third, we describe our experimental results for a series of formally saturated substituents; and fourth, we rationalize their π effects in terms of current bonding theory. A detailed comparison with previous results obtained by other investigators using other methods lies outside the scope of this contribution.

THE $B(L_b)$ TERM AND MO ENERGIES

By now, the perimeter model theory of the MCD spectra of aromatic molecules derived from a $(4N+2)$ -electron $[n]$ -atom perimeter (ref. 3; for a non-mathematical description see ref. 4 and ref. 9) has been successfully tested on well over a hundred compounds (for a recent

summary see ref. 4). It should be at its best for weakly perturbed parent annulenes; this is the case of interest here.

According to this theory, the first-order effect of a perturbation on UV absorption and MCD intensities of the L_b band of a $(4N+2)$ -electron annulene is given by three quantities. These are ΔHOMO , the splitting of the originally degenerate highest occupied MO of the annulene; ΔLUMO , the splitting of the originally degenerate lowest unoccupied MO of the annulene, and a phase angle ϕ , which for monosubstituted benzenes can only have the values 0 or π . If the energy ordering of the MO's in the perturbed annulene is $\underline{a}, \underline{s}, -\underline{s}, -\underline{a}$ or $\underline{s}, \underline{a}, -\underline{a}, -\underline{s}$ (a predominantly odd perturbation), we have $\phi = 0$, and if it is $\underline{a}, \underline{s}, -\underline{a}, -\underline{s}$ or $\underline{s}, \underline{a}, -\underline{s}, -\underline{a}$ (a predominantly even perturbation), we have $\phi = \pi$. Here, \underline{a} and \underline{s} label the MO's which are symmetric and antisymmetric, respectively, with respect to the plane of symmetry which passes through the substituted carbon atom and is perpendicular to the molecular plane. The negative signs refer to the orbital pair that arises from the degenerate LUMO of the annulene. The other orbital pair arises from the degenerate HOMO of the annulene. If either the LUMO or the HOMO pair remains degenerate after the perturbation, the value of ϕ has no effect on observable properties.

The result for $B(L_b)$ of an uncharged $(4N+2)$ -electron $[4N+2]$ -atom perimeter such as benzene is

$$\begin{aligned}
 B(L_b) = & (-\mu^-) [D(E_{1u})/2] \{ (W_4 - W_1)^{-1} (|a| - |b|)^2 [W(E_{1u}) - W(B_{2u})]^{-2} \cos^2(\phi/2) + \\
 & + (W_3 - W_1)^{-1} (|a| + |b|)^2 [W(E_{1u}) - W(B_{2u})]^{-2} \sin^2(\phi/2) + \\
 & + (W_2 - W_1)^{-1} (|a|^2 - |b|^2)^2 [W(E_{1u}) - W(B_{2u})]^{-2} [W(E_{1u}) - W(B_{1u})]^{-2} \} \\
 & + \mu^+ [D(E_{1u})/2] (|a|^2 - |b|^2)^2 [W(E_{1u}) - W(B_{2u})]^{-1} [W(E_{1u}) - W(B_{1u})]^{-1} \\
 & \{ (W_4 - W_1)^{-1} \cos^2(\phi/2) + (W_3 - W_1)^{-1} \sin^2(\phi/2) - (W_2 - W_1)^{-1} \}
 \end{aligned}$$

In this expression, $D(E_{1u})$ is the dipole strength of the transition into the E_{1u} state, $W_1 - W_4$ are the energies of the perturbed annulene states which correspond to the energies of the parent annulene states in the order of increasing energy, $W(B_{2u})$, $W(B_{1u})$, $W(E_{1u})$ and $W(E_{1u})$ (taken twice because it is degenerate), $|a| = \Delta\text{HOMO}/2$, and $|b| = \Delta\text{LUMO}/2$. The magnetic moments μ^- and μ^+ are discussed in ref. 3 and their values for various perimeters are evaluated there theoretically. For uncharged perimeters of interest here, μ^- is calculated to be an order of magnitude smaller than μ^+ . For benzene, $\mu^- = -0.3 \beta_e$ and $\mu^+ = -1.8 \beta_e$.

For the weak perturbations with which we deal presently, we can set $W_4 = W_3 = W(E_{1u})$, $W_2 = W(B_{1u})$, and $W_1 = W(B_{2u})$, and neglect terms containing the state energy differences in the inverse fourth power overall. Then,

$$\begin{aligned}
 B(L_b) = & (-\mu^-) D(L_b) [W(E_{1u}) - W(B_{2u})]^{-1} \\
 & + (-\mu^+) [D(E_{1u})/2] (|a|^2 - |b|^2)^2 [W(E_{1u}) - W(B_{2u})]^{-2} [W(B_{1u}) - W(B_{2u})]^{-1}
 \end{aligned}$$

where $D(L_b)$ is the dipole strength of the L_b band in the perturbed molecule:

$$D(L_b) = [D(E_{1u})/2] [(|a| - |b|)^2 \cos^2(\phi/2) + (|a| + |b|)^2 \sin^2(\phi/2)] [W(E_{1u}) - W(B_{2u})]^{-2}$$

In the case of benzene (ref. 10), $W(E_{1u}) = 54\,400\text{ cm}^{-1}$, $W(B_{1u}) = 48\,800\text{ cm}^{-1}$, $W(B_{2u}) = 38\,800\text{ cm}^{-1}$, and $D(E_{1u}) = 40\text{ D}^2$, so that

$$B(L_b) = 6.4 \times 10^{-5} D(L_b)(-\mu^-) + 8.23 \times 10^{-12} (|a|^2 - |b|^2)(-\mu^+)$$

where the values of $|a|$ and $|b|$ are in cm^{-1} and $B(L_b)$ is in units of $\text{D}^2\beta_e/\text{cm}^{-1}$, and

$$D(L_b) = 8.23 \times 10^{-8} [|a| - |b|]^2 \cos^2(\phi/2) + (|a| + |b|)^2 \sin^2(\phi/2)$$

in units of D^2 .

These relations can be checked independently, using Koopmans' theorem to estimate the orbital energies from experimental spectra. Although the use of this theorem involves considerable uncertainty, the results agree surprisingly well.

For instance, for toluene (ref. 11), the observed ΔHOMO is about 0.5 eV, leading to $|a| = 2000\text{ cm}^{-1}$, and the experimental upper limit for ΔLUMO is believed to be 0.1 eV. Taking $|b| = 0$, and using the theoretical values of μ^- and μ^+ (ref. 3), this leads to $D(L_b) = 0.27\text{ D}^2$ and $B(L_b) = 5.0 \times 10^{-5}\text{ D}^2\beta_e/\text{cm}^{-1}$. The μ^- contribution to $B(L_b)$ amounts to 0.5×10^{-5} and the μ^+ contribution to $4.5 \times 10^{-5}\text{ D}^2\beta_e/\text{cm}^{-1}$. This result is to be compared with the measured values of $B(L_b) = 0.18\text{ D}^2$ (of which about half is of vibronic origin) and $B_1 = 2.4 \times 10^{-5}\text{ D}^2\beta_e/\text{cm}^{-1}$ (of which about $0.3 \times 10^{-5}\text{ D}^2\beta_e/\text{cm}^{-1}$ is of vibronic origin).

The negligible nature of the μ^- contribution to $B(L_b)$ in toluene relative to the μ^+ contribution is no accident. Since $[(|a| - |b|)^2 \cos^2(\phi/2) + (|a| + |b|)^2 \sin^2(\phi/2)]$ generally is of the same order of magnitude as $(|a|^2 - |b|^2)$, one can set them equal to see what a typical ratio of the two contributions is likely to be: the answer is 3.82/35.5; i.e., the former represents about 10% of the total. Thus, to a good approximation, the $B(L_b)$ value is proportional to $|a|^2 - |b|^2$.

For the purpose of the following discussion, we therefore finally write

$$B(L_b) = 3.7 \times 10^{-12} (\Delta\text{HOMO} - \Delta\text{LUMO})(\Delta\text{HOMO} + \Delta\text{LUMO})$$

In a sense then, the MCD and absorption intensity measurements provide information on orbital energy differences in a perturbed benzenes without having to rely on Koopmans' theorem.

MO ENERGIES AND THE NET π EFFECT OF THE SUBSTITUENT

In a simple MO model, the π interaction between a probe such as the benzene ring and a substituent, such as $-\text{XY}_3$, is approximated by interactions between π -symmetry MO's of both entities, described typically by second-order perturbation theory. Examples of detailed analyses of these interactions can be found for instance in ref. 12 and ref. 13, and the reader is referred there for detail.

Briefly, four benzene orbitals and two orbitals of the $-\text{XY}_3$ substituent are considered, all antisymmetric (π) with respect to the plane of the benzene ring. The benzene orbitals are the \underline{a} , \underline{s} , $-\underline{a}$, and $-\underline{s}$ orbitals defined above. The substituent orbitals are its

π -donor orbital ϕ_D , viewed in the first approximation as a linear combination of the π -symmetry p_z orbital on atom X with suitable orbitals on atoms Y, and its acceptor orbital ϕ_A , constructed similarly as an antibonding linear combination of this p orbital on atom X with orbitals on atoms Y. The orbitals ϕ_D and ϕ_A can also be viewed as arising from suitable linear combinations of the three σ_{X-Y} and the three σ_{X-Y}^* bond orbitals, respectively. One can elaborate their description by introducing a larger basis set on atoms X and Y. This will introduce a certain amount of d character into ϕ_A and even into ϕ_D , but such refinements are not important in the present context.

The form of the six unperturbed π orbitals of interest presently, \underline{s} , \underline{a} , $-\underline{s}$, $-\underline{a}$, ϕ_D , and ϕ_A , is shown in Figure 2. The π interaction between the $2p_z$ carbon orbital on the ring atom C_1 which carries the substituent and the p_z orbital on the substituent atom X is represented by introducing the resonance integral β_{CX} between these two AO's. All

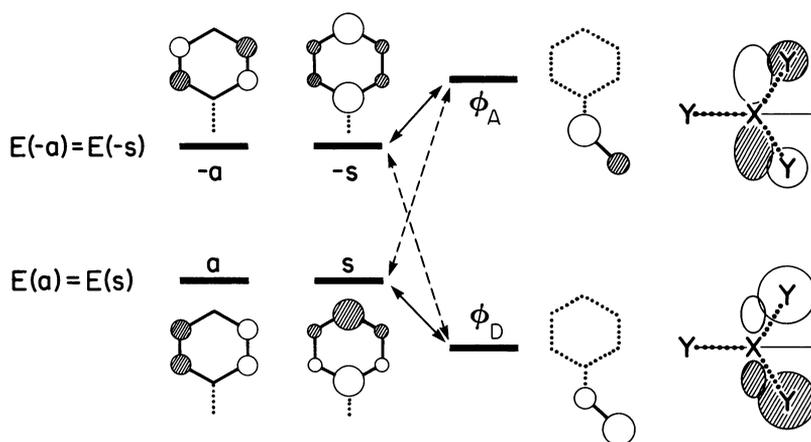


Fig. 2. Top view of the relevant π orbitals of benzene ($\underline{a}, \underline{s}, -\underline{a}, -\underline{s}$, left) and of the $-XY_3$ substituent (ϕ_D, ϕ_A) (center). Newman projection for ϕ_D, ϕ_A (right), for the case of Y more electronegative than X (schematic).

resulting changes in the orbitals \underline{a} , \underline{s} , $-\underline{a}$, and $-\underline{s}$ will be said to be due to the π effect of the $-XY_3$ substituent. In general, the substituent will also change the effective electronegativity of the $2p_z$ orbital on C_1 , but this effect of the $-XY_3$ group will not be considered a part of its π effect but rather, a part of its inductive (σ) effect. In this fashion, the term π effect is reserved for the changes wrought by merely extending the π system from benzene onto the substituent and permitting π electron flow in both directions.

The form which the π interactions take is shown in the central column of Figure 1, where only the strongest ones are indicated by double-headed arrows, and in Figure 2.

The effective resonance integral between one of the benzene orbitals and one of the substituent orbitals, ϕ_D or ϕ_A , is $c_1 c_X \beta_{CX}$, where c_1 is the coefficient of the benzene orbital on C_1 and c_X is the coefficient of the substituent orbital on X. Note that c_1 vanishes for the \underline{a} and $-\underline{a}$ MO's which have a node at C_1 . The interaction matrix is therefore block-diagonal, the \underline{a} and $-\underline{a}$ MO's are not affected, and their energies remain $E(\underline{a})$ and $E(-\underline{a})$. The remaining 4×4 matrix is further simplified in that for both

\underline{s} and $-\underline{s}$ the coefficient at C_1 is $3^{-1/2}$. Introducing the effective resonance integral for the donor orbital of the substituent, $\beta_D = 3^{-1/2} c_X(D)\beta_{CX}$, and the effective resonance integral for its acceptor orbital, $\beta_A = 3^{-1/2} c_X(A)\beta_{CX}$, the interaction matrix can be written as

$$\begin{array}{c} \phi_A \\ -\underline{s} \\ \underline{s} \\ \phi_D \end{array} \begin{pmatrix} E(A) & \beta_A & \beta_A & 0 \\ \beta_A & E(-\underline{s}) & 0 & \beta_D \\ \beta_A & 0 & E(\underline{s}) & \beta_D \\ 0 & \beta_D & \beta_D & E(D) \end{pmatrix}$$

Diagonalization of the matrix, or more simply, the use of second-order perturbation theory, produces the desired energies of the \underline{s} and $-\underline{s}$ orbitals of the perturbed benzene ring. Since the energies $E(\underline{g})$ and $E(-\underline{g})$ remained unchanged, the shifts of $E(\underline{s})$ and $E(-\underline{s})$ caused by the interaction are then directly equal to ΔHOMO and ΔLUMO , respectively (Fig. 3). This then represents a simple connection between the MCD observable $B(L_b)$ on the one hand, and the probe - substituent interaction on the other hand.

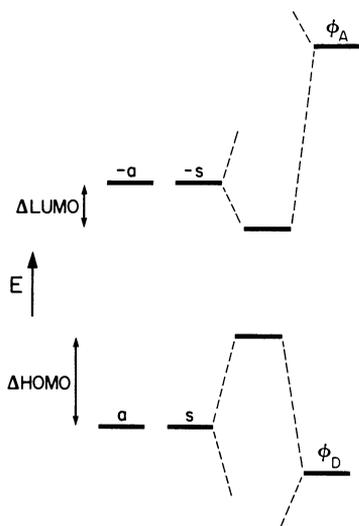


Fig. 3. Relation of ΔHOMO and ΔLUMO to the benzene - substituent interactions.

Since ϕ_D is closer in energy to \underline{s} than to $-\underline{s}$ and since the off-diagonal elements are equal, the $\phi_D - \underline{s}$ interaction is much stronger than the $\phi_D - -\underline{s}$ interaction. Similarly, the $\phi_A - -\underline{s}$ interaction is much stronger than the $\phi_A - \underline{s}$ interaction and this is indicated schematically in Figure 2. In the ground state these interactions between two occupied MO's or two empty MO's lead to no net charge transfer and therefore are not particularly accentuated in the empirical π -effect parameters based on ground state properties, such as σ_R^0 . Rather, these reflect the weaker donor-acceptor interactions between an occupied and an empty orbital, $\phi_D - \underline{s}$ and $\phi_A - \underline{s}$, which normally play only a secondary role in determining ΔHOMO and ΔLUMO . In excited states, in radical anion states, and in radical cation states, the stronger $\phi_D - \underline{s}$ and $\phi_A - -\underline{s}$ interactions lead to much more pronounced charge transfer between the substituent and the probe.

Still, as indicated above, one can expect a rough correlation between the π -donor or π -acceptor power of a substituent toward ground-state benzene and toward excited-state benzene. Inspection of the interaction matrix shows that both in the ground and in the excited states the factors which favor π donation are a high energy $E(D)$ of the donor

orbital ϕ_D and a large coefficient $C_X(D)$ of the donor orbital on atom X, hence high electronegativity of X relative to Y in $-XY_3$, while the factors which favor π withdrawal are a low energy $E(A)$ of the acceptor orbital ϕ_A and a large coefficient of the acceptor orbital on atom, X, hence high electronegativity of Y relative to X in $-XY_3$.

In a sense, then, $\Delta HOMO$ is a measure of the donor strength of a substituent and $\Delta LUMO$ a measure of its acceptor strength, although these quantities originate primarily in interactions which are not responsible for charge transfer in the ground state but rather, have more to do with its polarization. We shall take $\Delta HOMO - \Delta LUMO$ as a measure of the net effect of the substituent, whose sign indicates whether it is a better π donor or a better π acceptor.

Note that $\Delta HOMO$ and $\Delta LUMO$ by themselves are not measures of π -donor and π -acceptor effects of the substituent, since they are affected by its inductive effect. An example of a purely inductive "substituent", which does not enlarge the conjugated π system at all, is aza nitrogen, which greatly increases the effective electronegativity at C_1 . To first order in perturbation theory, it will not affect the energies of \underline{a} and $-\underline{a}$, which have a node at C_1 , but will stabilize both \underline{s} and $-\underline{s}$, thus producing non-vanishing values for $\Delta HOMO$ and $\Delta LUMO$, although it has no π effect at all.

To first order in perturbation theory, however, such a purely inductive perturbation will produce equal values of $\Delta HOMO$ and $\Delta LUMO$, since the coefficients of \underline{s} and $-\underline{s}$ at C_1 have the same absolute value. An experimental estimate is possible using the Koopman's theorem approximation. One finds $\Delta HOMO = 0.7-0.8$ eV and $\Delta LUMO = 0.57$ eV, values almost equal within experimental error (ref. 14). For the much weaker inductive perturbations of interest here, the first-order approximation is therefore surely adequate. The inductive effects will cancel to a good approximation and this is the basis for taking the quantity $\Delta HOMO - \Delta LUMO$ as a measure of the net π effect of the substituent.

Now, there is a complication in that the $B(L_b)$ term is proportional to $(\Delta HOMO - \Delta LUMO)(\Delta HOMO + \Delta LUMO)$ rather than to $\Delta HOMO - \Delta LUMO$ alone. Its sign is clear, but its magnitude will depend not only on the net π effect, but also on the sum $\Delta HOMO + \Delta LUMO$, which in turn depends also on the inductive effect of the substituent. Thus, it will have to be kept in mind that the sensitivity of the $B(L_b)$ term to the net π effect of the substituent will be large when $\Delta HOMO + \Delta LUMO$ is large, for instance, in the presence of a very large inductive effect. In general, however, the per cent change in $\Delta HOMO + \Delta LUMO$ for a series of weakly interacting substituents will be much smaller than the per cent change in $\Delta HOMO - \Delta LUMO$, so that the variation in the magnitude of the $B(L_b)$ value can still be taken as primarily reflecting changes in the latter and thus in the net π effect.

It is unfortunate that the orbital ordering, and thus the phase angle ϕ , are not known with certainty for many cases of interest here, since otherwise, the dipole strengths $D(L_b)$ could be used to considerable advantage (cf. the theory of spectroscopic moments, ref. 10). For $\phi = 0$, we have

$$D(L_b) = 2.06 \times 10^{-8} (\Delta HOMO - \Delta LUMO)^2$$

and for $\phi = \pi$, we have

$$D(L_b) = 2.06 \times 10^{-8} (\Delta HOMO + \Delta LUMO)^2$$

in units of D^2 , where $\Delta HOMO$ and $\Delta LUMO$ are in cm^{-1} . The former corresponds to a predominantly odd, the latter to a predominantly even (e.g., purely inductive, ref. 10) perturbation of the benzene ring. As long as the ordering is not known, it is difficult to utilize this additional source of information, which could otherwise permit a separate determination of $\Delta HOMO - \Delta LUMO$ and $\Delta HOMO + \Delta LUMO$, i.e., of $\Delta HOMO$ and $\Delta LUMO$, without reliance on Koopmans' theorem.

An additional complication is the somewhat larger contribution which vibronically induced intensity makes in absorption relative to MCD. This needs to be assumed constant ($0.09 D^2$ in benzene) and subtracted from the observed $D(L_b)$, or it could be measured separately using the techniques of polarized spectroscopy as in ref. 15 (where however an unrealistic assumption was made in the analysis of the polarized spectra; cf. the discussion in ref. 16). Moreover, larger problems are encountered with band overlap in the experimental determination of $D(L_b)$ than in the measurement of $B(L_b)$. We are now exploring the possibilities offered by the combination of the $D(L_b)$ and $B(L_b)$ values but for the present purposes shall rely on $B(L_b)$ alone.

B (L_b) VALUES FOR HYPERCONJUGATING SUBSTITUENTS

We have measured $B(L_b)$ and $D(L_b)$ values for a series of substituted benzenes in cyclohexane solvent. The experimental details will be reported elsewhere; here we only note that the samples were all known compounds and that a standard commercial dichrograph equipped with a commercial electromagnet were used, similarly as in our other recent work (ref. 17). The results are shown in Figures 4-9 and are subject to an experimental uncertainty of about 10%.

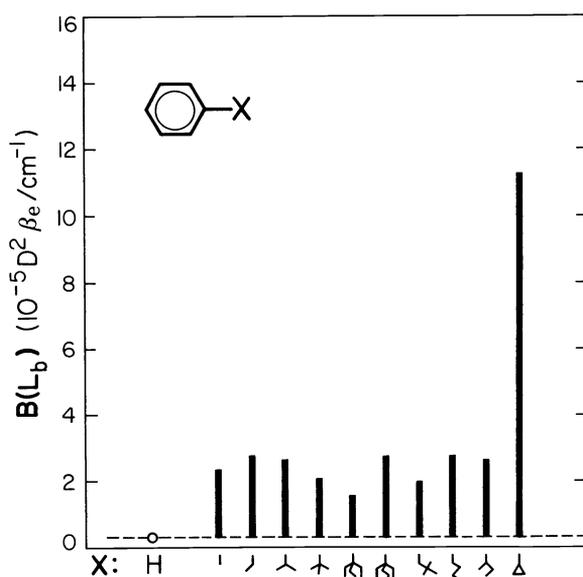


Fig. 4. $B(L_b)$ values in cyclohexane for benzene and its alkyl derivatives. From the left, Me, Et, i-Pr, t-Bu, CEt_3 , 1-bicyclo[2.2.2]octyl, neo- C_5H_{11} , n-Bu, i-Bu, cyclopropyl.

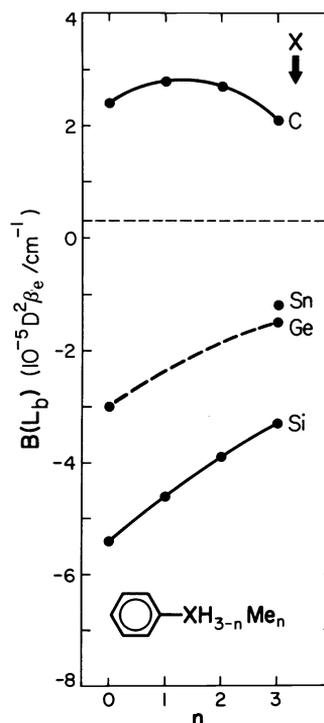
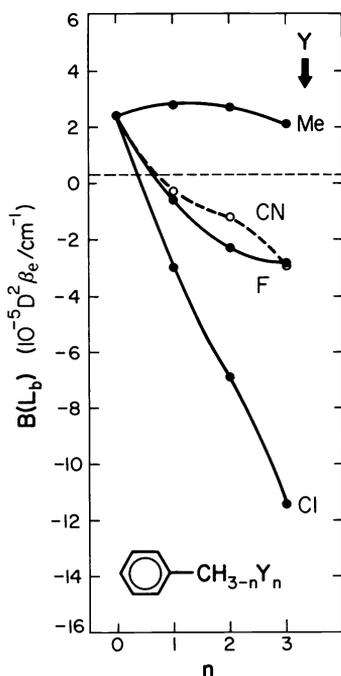
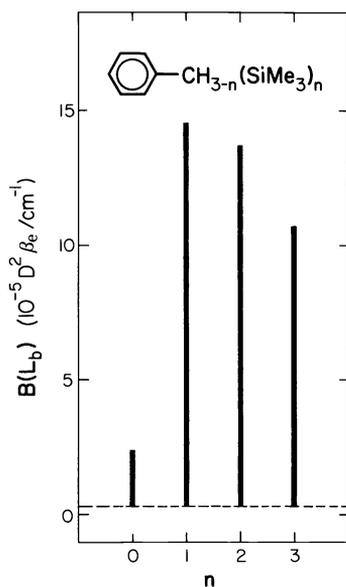
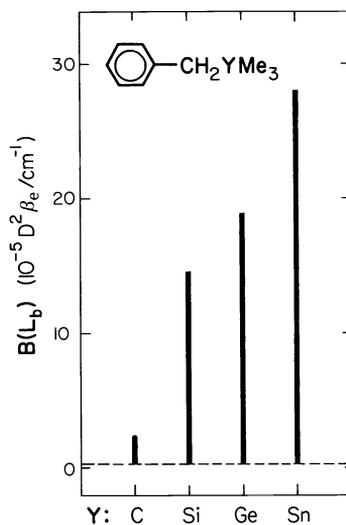
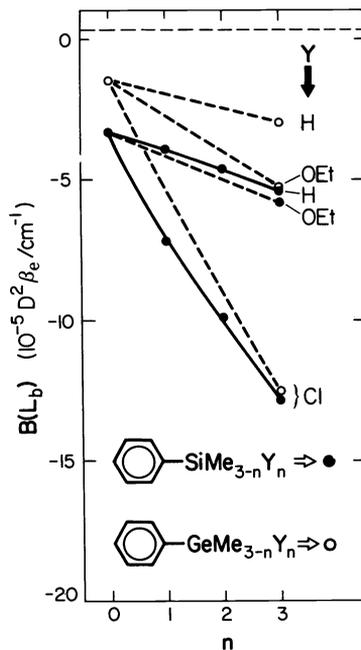


Fig. 5. $B(L_b)$ values in cyclohexane.

Fig. 6. $B(L_b)$ values in cyclohexane.Fig. 8. $B(L_b)$ values in cyclohexane.Fig. 7. $B(L_b)$ values in cyclohexane.Fig. 9. $B(L_b)$ values in cyclohexane.

NET π EFFECT AND SUBSTITUENT STRUCTURE

In the following, we shall comment briefly on the results obtained for the various hyperconjugating substituents. A detailed comparison with prior results obtained with other methods will be presented elsewhere. However, in order to set the background, we list a few $B(L_b)$ values for substituents well recognized to have an ordinary (as opposed to a hyperconjugative) π effect. In units of $10^{-5} D^2 \beta_e / \text{cm}^{-1}$, they are -18.9 for $-\text{C}\equiv\text{N}$, -37.5 for $-\text{CHO}$, -46.0 for $-\text{NO}_2$, +18.3 for $-\text{OH}$, +29.9 for $-\text{OCH}_3$, and +49.0 for $-\text{NH}_2$ (ref. 2b).

Alkyls and cyclopropyl

The nine alkyl substituents for which measurements have been made all have comparably weak positive $B(L_b)$ terms and thus are weak net π donors (Figure 4). The slight variations along the series lie barely outside the experimental error; the only apparent trend is a slight decrease of the $B(L_b)$ value with increased bulkiness of the substituent. This small effect might be possibly related to changes in the valence angles at the alpha carbon but it is also possible that it is due to small changes in the geometry of the phenyl substituent (ref. 18) rather than to real variations in the net π effect of the substituent.

The standard explanation of the weak π donation from an alkyl group to the benzene ring (ref. 13) also fits the present observations. The substituent donor orbital ϕ_D is closer in energy to the benzene HOMO's, ψ and $\bar{\psi}$, than the substituent acceptor orbital ϕ_A is to the benzene LUMO's, $-\bar{\psi}$ and $-\psi$. Neither ϕ_D nor ϕ_A is particularly polarized within the alkyl group since carbon and hydrogen have comparable electronegativities. Thus, the coefficients $c_X(D)$ and $c_X(A)$ are comparable and β_D and β_A are as well. The energy gaps above then determine the net outcome, making the alkyl group a weak donor.

There seems to be little if any difference between the hyperconjugative ability of the C-H and the C-C bonds, and the small differences between the various alkyls may well be dominated by other factors as already noted above. The one substituent that stands out in Fig. 4 is cyclopropyl, whose $B(L_b)$ term is about five times more strongly positive than that of the acyclic alkyl substituents. This substituent tends to be lined up so that the C-C bond opposite to the phenyl is perpendicular to the aromatic ring, so that one of the relatively high-energy Walsh orbitals is then ideally oriented for interaction with the ψ orbital of the benzene chromophore. One can expect that the exo-2-bicyclobutyl and particularly, 2-[1.1.1]propellyl substituents will be even stronger net π donors.

Silyl, germyl and stannyl

The already well known tendency of the silyl substituents to act as acceptors of π -electron density is confirmed by the results shown in Figure 5. The striking difference between the alkyl groups on the one hand and the silyl, germyl and stannyl groups on the other can be understood readily in terms of the substantial electronegativity difference between the X and Y atoms in the $-XY_3$ substituents in the cases X = Si, Ge, or Sn and Y = H or C, as contrasted with the lack of such a difference when X = C and Y = H or C. As noted above, when X is less electronegative than Y, the ϕ_D orbital within the $-XY_3$ substituent will be polarized towards Y and the ϕ_A orbital towards X, so that in the interaction matrix β_D will be small in absolute value and β_A large in absolute value. If all else were the same, this would cut back the π -donor ability of the substituent and enhance its π -acceptor ability. To second order in perturbation theory, the effects on $\Delta HOMO$ and $\Delta LUMO$ will go with β_D^2 and β_A^2 , so that even relatively small electronegativity differences between X and Y will be felt quite strongly. In addition, it appears likely that the energy of the substituent acceptor orbital ϕ_A is lower for X = Si, Ge, or Sn than it is for X = C, due to a somewhat stronger interaction with d orbitals in the basis set in the former case.

Both factors cooperate to make the silyl, germyl, and stannyl groups act as π -electron acceptors. The differences between these three groups of substituents need to be discussed with some caution since the stannyl substituent exerts a relatively strong

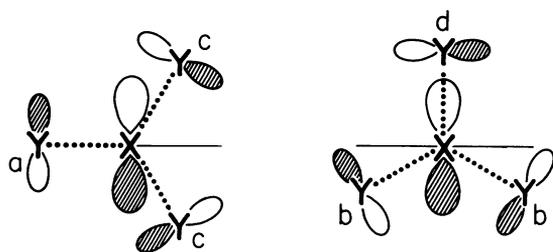


Fig. 10. Interaction of π -type p orbitals on Y with ϕ_A and ϕ_D (represented schematically by a p orbital on X).

inductive effect which will enhance the sensitivity of $B(L_D)$ to the net π effect, as discussed above. For this reason, it could well be that the π -withdrawing ability of $-\text{SnR}_3$ is substantially smaller than that of $-\text{GeR}_3$ although the $B(L_D)$ values are similar. The fact that both $B(L_D)$ values are noticeably less negative than that for $-\text{SiR}_3$, making stannyl and germyl less effective net π acceptors, can be rationalized by noting that β_{CX} is surely reduced considerably for the longer bonds made by $X = \text{Ge}$ and Si relative to $X = \text{C}$, so that β_D and β_A are both reduced.

The trend observed in the $B(L_D)$ value as the hydrogens in $-\text{SiR}_3$ are gradually replaced by methyl groups is understood readily as due to the weak π -donor effect of the methyl group. The degree to which the donor orbitals of a methyl group ($Y = \text{Me}$) attached to the benzylic silicon above ($X = \text{Si}$) can interact with the π -symmetry 3p orbital on the silicon depends on the conformation adopted by the substituent (Fig. 10).

In Fig. 10, we show only the relevant p orbital on the carbon atom of the methyl groups located in position Y. Its interaction with the ϕ_D and ϕ_A orbitals of the $-\text{XY}_3$ group (only the p orbital on X is shown) is strongest in orientation a, weaker in orientation b, and decreases further for orientation c, until there finally is no interaction for orientation d. Both the donor and the acceptor orbitals of each methyl group will interact with ϕ_D and ϕ_A ; not surprisingly the π -donor effect of the methyl group predominates. Since the C-Si bond is relatively long, there probably is essentially free rotation at room temperature, and the effects of the methyl groups on silicon are additive.

Methyl with electronegative substituents, $-\text{CH}_{3-n}\text{Y}_n$

Fig. 6 displays the effect of the successive replacement of hydrogen atoms of a methyl group by the electronegative substituents, F, Cl, and CN, and contrasts the resulting $B(L_D)$ values with the absence of any significant effect when they are replaced by methyl groups.

Since X in the $-\text{XY}_3$ substituent is now less negative than Y, the net π -accepting character of these substituents is no surprise and has in part the same origin as that of the silyl, germyl and stannyl groups, namely the different magnitudes of β_D and β_A . An additional factor again is the relatively low energy (ref. 19) of ϕ_A , particularly when $Y = \text{Cl}$, which is undoubtedly responsible for the very strong π -acceptor effect of the $-\text{CH}_{3-n}\text{Cl}_n$ groups. The stronger C-CN and C-F bonds have a larger σ - σ^* splitting and offer this opportunity to only a smaller degree.

The fact that the cases $Y = \text{CN}$ and $Y = \text{F}$ are so similar may be surprising at first. However, both F and CN are quite electronegative; and additional fact to consider is the presence of orbitals of π symmetry on both groups. On benzene, all halogens are net π

donors, while CN is a net π acceptor. It is then likely that F acts as a π donor towards the benzylic carbon, while CN acts as a π acceptor in the sense of Fig. 10. This will reduce the net π -acceptor power of fluorinated methyl groups and enhance that of cyanated methyl groups. The accuracy of the data does not warrant a discussion of the conformational effects expected according to Figure 10. It is interesting to note that already a single CN, F, or Cl substitution is sufficient to convert the methyl group from a net π donor to a net π acceptor.

Methyl with electropositive substituents, $-\text{CH}_{3-n}(\text{YMe}_3)_n$

The arguments used to rationalize the π -acceptor behavior of $-\text{XY}_3$ groups in which Y is electronegative relative to X can be reversed when Y is electropositive relative to X. Now, $|\beta_D| > |\beta_A|$, the interaction of the ring orbitals with ϕ_D is enhanced, that with ϕ_A is suppressed, and a tendency toward a net π -donor effect for the $-\text{XY}_3$ group is to be expected.

Results for trimethylsilylated, trimethylgermylated and trimethylstannylated methyl groups are shown in Fig. 7 and show that a single such replacement suffices to produce quite strong net π donors. Since the C-C bond is relatively short, steric interactions favor the conformation with the C-Si, C-Ge, or C-Sn bond lined up optimally for hyperconjugative interaction as in case d in Fig. 10. Then, the π -acceptor orbital at the Si, Ge, or Sn atom shown in Fig. 10 is oriented improperly for interaction with the π system and it does not reduce the π -donor effect. The opposite situation would be expected in the conformation in which the C-Si bond lies in the plane of the benzene ring, so that it does not contribute to the donor orbital ϕ_D , while the acceptor orbital on the Si atom is aligned perfectly for reducing the π -donor ability of the ϕ_D orbital of the CH_2 group.

These considerations are illustrated further by the results shown in Fig. 8. It is seen that only the first replacement of a hydrogen by a trimethylsilyl group enhances the net π -donor effect. The second Me_3Si group makes little difference, the third reduces the π -donor effect noticeably. If the trimethylsilyl group itself had no π -acceptor effect, one would expect the second replacement to enhance the π -donor effect and the third one to make no further change in the first approximation. Taking the conformation of the CH_2SiMe_3 compound to be the one labeled d in Fig. 10, as already discussed, and that of the $\text{CH}(\text{SiMe}_3)_2$ compound to have the Si atoms in positions labeled c, taking the resonance integrals proportional to the cosine of the twist angle, adopting the second-order perturbation approximation, and ignoring the weak hyperconjugative donation from the C-H bonds, one would expect the effects to increase in the ratio 0 : 1 : 1.5 : 1.5 instead of the roughly 0 : 1.5 : 1.5 : 1 ratio actually observed.

When the π -acceptor nature of the Me_3Si group is recognized, the apparent discrepancy disappears. Now, the Si π -acceptor orbital is lined up incorrectly in the $-\text{CH}_2\text{SiMe}_3$ compound (d in Fig. 10) for reducing the π -donor activity of the substituent, and the two π -acceptor Si orbitals are aligned at 60° in the $-\text{CH}(\text{SiMe}_3)_2$ compound. In the $-\text{C}(\text{SiMe}_3)_3$ case, one such orbital is aligned perfectly and two lie at 60° . At the same level of approximation that was used above, the efficiency with which this type of withdrawal of π -electron density from atom X to atom Y occurs thus changes in the ratio 0 : 0 : 1 : 2. Superimposing the two opposed trends produces qualitatively the behavior observed in Fig. 8.

Silyl and germyl with electronegative substituents, $-\text{SiMe}_{3-n}\text{Y}_n$ and $-\text{GeMe}_{3-n}\text{Y}_n$

As the methyl groups in SiMe_3 or GeMe_3 are replaced by substituents which are even more electronegative relative to Si and Ge, an increase in the π -acceptor power is to be expected, and is indeed observed. Fig. 9 shows the steady increase of the π -acceptor power as the methyl groups are replaced by chlorines. Comparison with Fig. 6 shows that $-\text{CCl}_3$, $-\text{SiCl}_3$, and $-\text{GeCl}_3$ have comparable $B(L_b)$ terms. The higher electronegativity of C compared to Si or Ge is presumably compensated by the larger magnitude of the C-C resonance integral β_{CC} relative to C-Si or C-Ge. Relatively low energy of the acceptor orbital ϕ_A in the Si-Cl and Ge-Cl bonds undoubtedly contributes to this strong effect.

The contributions of the individual chlorine atoms are approximately additive (Fig. 9) suggesting that the rotation about the long C-Si and C-Ge bonds is probably not hindered much. The replacement of the methyl groups in $-\text{GeMe}_3$ and $-\text{SiMe}_3$ by hydrogen atoms also increases the π -acceptor power, but only weakly. Since the electronegativities of H and C are very close, this trend is believed to be due to the loss of hyperconjugative π donation from the donor orbital of the methyl groups (Fig. 10) as they are replaced by hydrogen atoms.

A much stronger effect of this type is most likely responsible for the striking weakness of the $-\text{Si}(\text{OEt})_3$ and $-\text{Ge}(\text{OEt})_3$ groups as π acceptors (Fig. 9). There is essentially no difference between $B(L_b)$ of $-\text{SiH}_3$ and $-\text{Si}(\text{OEt})_3$ in spite of the vastly different electronegativity of hydrogen and oxygen. These groups should have an acceptor orbital ϕ_A strongly polarized towards the Si or Ge atom, but this orbital is apparently largely deactivated as an acceptor by the π -density donating effects of the oxygen lone pairs, in the sense of Fig. 10.

SUMMARY

The measurement of the $B(L_b)$ terms in the MCD spectra of substituted benzenes provides an experimentally readily accessible substituent characteristic for those substituents that do not themselves absorb strongly in the spectral region of the benzene L_b band.

We have briefly described the theoretical reasons which lead us to believe that this quantity is an approximate measure of the net π effect of the substituent, defined for the present purposes by the double orbital energy difference $\Delta\text{HOMO} - \Delta\text{LUMO}$. Those substituents that are net π donors have positive $B(L_b)$, those that are net π acceptors have negative $B(L_b)$. According to this analysis, the inductive (σ) effect of the substituent has little effect on the observed $B(L_b)$ value. Indeed, the $-\text{F}$ substituent has a positive $B(L_b)$ and the $-\text{C}(\text{CN})_3$ substituent an only weakly negative $B(L_b)$ in spite of being strong inductive acceptors, and the $-\text{SnMe}_3$ substituent has a negative $B(L_b)$ although it is a strong inductive donor.

In the above definition of the net π effect of the substituent, interactions which in the ground state are of the occupied-occupied and unoccupied-unoccupied types are given an equal opportunity to come to the fore as the ground-state occupied-unoccupied interactions. The latter are measured with selective sensitivity in studies of ground-state properties. In this sense, $B(L_b)$ is a typical excited-state substituent parameter, related to spectroscopic moments (ref. 10) and to Murrell's I_π substituent constants (Ref. 20).

We have pointed out that the description of the interactions measured by various probes such as phenyl, and various probe properties, either ground or excited-state, requires a minimum of four π -effect parameters for each substituent of the type considered here. The measurement of $B(L_b)$ values of substituted benzenes thus not only provides a useful parameter for the correlation of excited state properties, but also represents a step towards establishing such as a set of π -effect parameters, from which responses could be predicted for all probes and all probe properties which respond to the π effect of a substituent.

The $B(L_b)$ values for several dozen hyperconjugative substituents of the type $-XY_3$ are reported and discussed in terms of the electronic structure of the substituent. The critical quantities which determine the net π effect of the substituent are the electro-negativity difference between X and Y, the energies of the σ_{XY} and σ_{XY}^* orbitals, the net π effect of the Y atom or group, and in the case of $-XYZ_2$ substituents, the conformation with respect to rotation around the C-X bond.

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