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π-Electron Correlation in Alternant Hydrocarbons: Bondorder-Bondlength Relation, Force Constants and the Spectroscopic, Vibrational and Thermochemical β-Values

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The applicability of empirical relations between bondorders and bondlengths is shown to be subject to some restrictions which are of considerable importance in the calculation of force constants from MO-theories. The consequent application of a suggested correction leads to a new $\beta(r)$-relation from which correct predictions of both UV-spectra and vibrational force constants may be obtained. Force constant calculations from thermochemical parameters are shown to be unreliable; a discussion of the thermochemical evaluation of β suggests a number a possible causes of the limitations of its applicability.

Es wird gezeigt, daß der theoretische Beweis für die Existenz einer Beziehung zwischen P und r in konjugierten Kohlenwasserstoffen nicht ohne weiteres als Begründung für empirische $P(r)$-Funktionen verwendet werden soll. Aus der Verfeinerung der Theorie folgt eine neue empirische Beziehung zwischen β und r, die in Gegensatz zu älteren Funktionen solcher Art bei Berechnungen, nicht nur von UV-Spektren, sondern auch von Kraftkonstanten erfolgreich ist. Dahingegen können die bisher vorgeschlagenen thermochemischen β-Werte nicht zur Berechnung der Kraftkonstanten verwendet werden. Eine Diskussion des thermochemischen Rechenverfahrens ergibt einige mögliche Ursachen der beschränkten Anwendbarkeit der auf diesem Wege gefundenen β-Werte.

Une revision critique de la preuve de l'existence d'une relation entre P et r dans les hydrocarbures conjugués conduit à la conclusion que cette preuve est valable seulement pour une courbe théorique qui peut différer assez fortement d'une courbe empirique. En introduisant les corrections nécessaires nous arrivons à une nouvelle relation entre β et r, qui peut être appliquée avec succès dans les calculations des spectres UV aussi bien que des constantes de force. Par contre une évaluation correcte des constantes de force est impossible si l'on emploie les valeurs thermochimiques de β proposées jusqu'à présent; il apparait que ce résultat négatif doit probablement être attribué à quelques simplifications qui font part de la méthode thermochimique.

1. Introduction

Several empirical relations have been proposed between the π-bondorders P in aromatic molecules and the equilibrium bondlengths r. Of these relations the one given by Coulson and Golebiewski [1]

$$r = 1.517 - 0.18\,P\,\text{Å} \tag{1}$$

is most widely used[1]. It is based on the experimental bondlengths of benzene, ethylene and graphite, which are known with good accuracy, and on the SCF-bondorders of these molecules, which are determined from symmetry considerations only.

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[1] An alternative relation, based on thermochemical data, is discussed in Sect. 5.

On the other hand Longuet-Higgins and Salem [2] proved the existence of a $P(r)$-relation, depending on the correctness of a few reasonable assumptions. In the following analysis we intend to show that the identification of (1) with the relation predicted in [2] is in principle not allowed; particularly the application of the derivative of empirical $P(r)$-functions in the calculation of force constants may introduce serious errors.

2. The Existence of *P*(*r*) and the SCF-Approximation

The Hückel type argument for the existence of a $P(r)$-relation [2] is easily transposed into its SCF-counterpart. We maintain two assumptions introduced by Longuet-Higgins and Salem: the σ-electron energy is built up from independent contributions from the individual bonds i:

$$E_\sigma = \sum_i f_i\,, \tag{2}$$

and f'_i, β'_i (and, in the present analysis, γ'_i) are taken to be unique functions of r_i for all i.

If we use Pople's expression [3] for E_π the total energy of the molecule may be written as

$$E = \sum_i \left(f_i + 2p_i\beta_i - \frac{1}{2} p_i^2 \gamma_i \right) + \frac{1}{4} \sum_p \gamma_{pp} - \sum_p \sum_q{}'' \frac{1}{4} p_{pq}^2 \gamma_{pq}\,. \tag{3}$$

The symbol $\sum\sum''$ indicates that terms with $p=q$ and those with $p=q\pm1$ are not included in the summation. The present analysis is made slightly more complicated than its Hückel counterpart by the occurrence of long-distance terms in the energy expressions. In order to maintain the analogy with [2] we split E into two parts, the "SCF local energy" E^{sl} and a correction term E^{Δ}:

$$E = E^{sl} + E^{\Delta}\,, \tag{4}$$

where E^{sl} is defined as

$$E^{sl} = \sum_i \left(f_i + 2p_i\beta_i - \frac{1}{2} p_i^2 \gamma_i \right). \tag{5}$$

It follows from (3), (4) and (5) that in the SCF-approximation

$$E^{\Delta} = \frac{1}{4} \sum_p \gamma_{pp} - \frac{1}{4} \sum_p \sum_q{}'' p_{pq}^2 \gamma_{pq}\,. \tag{6}$$

We now define a parameter r^s, with the dimension of a length, by the condition that

$$\frac{\delta E^{sl}}{\delta r_i} \equiv f'_i + 2P_i\beta'_i - \frac{1}{2} P_i^2 \gamma'_i = 0 \quad \text{for} \quad r_i = r_i^s\,, \tag{7}$$

where the symbol P denotes an equilibrium bondorder. It follows from (7) that r^s is a unique function of P. On the other hand the actual equilibrium bondlength,

r^e, is defined by the condition

$$\frac{\delta E}{\delta r_i} = 0 \quad \text{for} \quad r_i = r_i^e . \tag{8}$$

Because of (4) and (7)

$$\frac{\delta E}{\delta r_i} = \frac{\delta E^{\Delta}}{\delta r_i} \quad \text{for} \quad r_i = r_i^s . \tag{9}$$

We may approximate r_i^e by applying the Newton method to (8) and (9):

$$r_i^e - r_i^s \approx - \frac{\delta E^{\Delta}/\delta r_i}{\delta^2 E/\delta r_i^2} \quad (r_i = r_i^s) . \tag{10}$$

The denominator in (10) is a force constant, for which experimental data are available. The numerator may be evaluated, E^{Δ} being given by (6). We recall that according to Fischer-Hjalmars' interpretation of the ZDO-approximation [4] γ_{pp} should be regarded as a function of the r_i. From detailed calculations of the numerator in (10), given in [5], it follows that the derivatives of the two terms in (6) are both very small, and of opposite signs, so that the SCF-approximation suggests that $r_i^e \approx r_i^s$. It follows then from (7) that the experimental bondlength r^e may be regarded as a function of P.

3. π-Electron Configurational Interaction

One conceivable objection against the preceeding argument might be directed against the assumption that f_i', β_i' and γ_i' are each given by one function of r_i, valid for all bonds in conjugated systems. A confirmation or a refutation of this assumption can only be obtained from a further development of all-electron calculation methods; for the time being we can only justify its application in empirical methods by means of the resulting interpretation of molecular properties.

In the present section we undermine the conclusion that r^e is a function of P, using a different starting point: it will appear that the inclusion of the π-electron correlation in E_π seriously affects the value of $r_i^e - r_i^s$. Using the formalism of the CI-method we may write the π-electron wave functions as

$$\Psi = \sum_{k=0}^{N} g_k \psi_k , \tag{11}$$

where the ψ's are configurational wave functions, based on the SCF-MO's, and the coefficients g_k are chosen so as to minimalise E_π, which is given by

$$E_\pi = \sum_k \sum_l g_k^* g_l H_{kl} , \tag{12}$$

where

$$H_{kl} = \int \psi_k^* \boldsymbol{H}_{\text{op}} \psi_l \, d\tau , \tag{13}$$

$\boldsymbol{H}_{\text{op}}$ being the Hamiltonian operator for the molecule. H_{kl} is a linear function of the β_i's and the γ's. Writing out H_{kl} and collecting terms in the several parameters we may replace (12) by

$$E_\pi = \sum_i (2\tilde{p}_i \beta_i - \vartheta_i \gamma_i) + \sum_p \vartheta_p \gamma_{pp} - \sum_p \sum_q{}'' \vartheta_{pq} \gamma_{pq} , \tag{14}$$

where the coefficients $\tilde{p}$ and ϑ are functions of the LCAO-MO coefficients and of the g_k. Contrary to the result of the SCF-approximation there is no simple relation between the coefficients of a β_i and the corresponding γ_i: generally

$$\vartheta_i \neq \frac{1}{2} \tilde{p}_i^2 .$$

In (14) $\tilde{p}_i = \tilde{p}_{pq}$ is the CI-bondorder, defined as

$$\tilde{p}_{pq} = \sum_{kl} g_k^* g_l p_{pq}^{kl} \tag{14a}$$

where p_{pq}^{kl} is the coefficient of $\chi_p^*(1)\,\chi_q(1)$ in $\int \psi_k^* \psi_l \, d\tau_2 \ldots d\tau_n$. It is readily seen that both for $k = l$ and for $k \neq l$ p_{pq}^{kl} is the coefficient of β_{pq} in H_{kl}, so that the coefficient of β_i must indeed be $2\tilde{p}_i$. If it is kept in mind that E_π is minimalised with respect to the g_k it may be verified that

$$\frac{\delta E_\pi}{\delta r_i} = \sum_k \sum_l g_k^* g_l \frac{\delta H_{kl}}{\delta r_i}, \tag{15}$$

or, in view of (12), (14) and the linearity of H_{kl} in the parameters:

$$\frac{\delta E_\pi}{\delta r_i} = 2\tilde{p}_i \beta_i' - \vartheta_i \gamma_i' + \sum_p \vartheta_p \frac{\delta \gamma_{pp}}{\delta r_i} - \sum_p \sum_q{}'' \vartheta_{pq} \frac{\delta \gamma_{pq}}{\delta r_i} . \tag{16}$$

We may now again follow the argument which resulted in (10), using, however, (14) instead of the SCF-expression for E_π. It follows from (4), (5) and (6) that the numerator in (10) is now given by

$$\frac{\delta E^{\Delta}}{\delta r_i} = 2(\tilde{p}_i - p_i)\, \beta_i' + \left(\frac{1}{2} p_i^2 - \vartheta_i\right) \gamma_i' + \sum_p \left(\vartheta_{pp} - \frac{1}{4}\right) \frac{\delta \gamma_{pp}}{\delta r_i} - \sum_p \sum_q{}'' \vartheta_{pq} \frac{\delta \gamma_{pq}}{\delta r_i} . \tag{17}$$

We use (10) and (17) to evaluate $r_i^e - r_i^s$ for ethylene and benzene. It should be considered that, contrary to the symmetry-determined SCF-bondorders for the molecules, $\tilde{p}_i$ depends on the choice of β- and γ-values. For the problem of the present section we arrive at practically the same solution whether we apply Pariser's parameters [6], derived from the benzene spectrum with neglect of all CI, or a new set of parameter values (cf. Sect. 4.2 and Ref. [5]), which reproduces the electronic excitation energies of benzene if extensive CI is included. We found [5] that $r_i^s = 1.393$ Å for benzene ($r^e = 1.397$ Å) and 1.323 Å for ethylene ($r^e = 1.336$ Å).

Now we have shown that only r^s may be regarded as a function of P. A calculation of r^s from r^e and (10) for other molecules than ethylene and benzene is not very useful for the calibration of a $P(r)$-curve, either because the uncertainty in the experimental r^e-value is at least as large as $r^e - r^s$, or because, in the case of graphite, a CI-calculation is somewhat beyond our possibilities. So we are constrained by the available information to approximate r^s as a linear function of P, determined by the values for ethylene and benzene:

$$r^s = 1.533 - 0.21\, P \text{ Å} . \tag{18}$$

4. Applications

4.1. *The Calculation of Bondlengths*

From the existence of $r^s(P)$ and from (10) it follows that in a P-r^e-diagram we should expect to find the points representing actual measurements scattered around a theoretical curve. Further a calculation of r^e should proceed through several stages: an SCF-calculation, followed by the evaluation of r^s from (18), and a CI-calculation which gives the necessary data for the application of (17) and (10). It appears, however, that the application of (18) and the ensuing complications instead of (1) gives the least spectacular improvement for the problem where $P(r)$ relations are most frequently used: the calculation of bondlengths in the ground state of a conjugated system. It is easily seen why this should be the case. If $\delta E^{\Delta}/\delta r_i$, defined by (17), is large, this will almost certainly be due to the first term in the right hand member. A comparison of $\tilde{p}_i$ and p_i in this term may be based on (14a). The SCF-value p_{pq} is obtained by putting in (11) and (14a) $g_k = 1$ if $k=0$, $g_k = 0$ if $k \neq 0$. If now p_{pq}^{00} is large (> 0.7, say), this will almost certainly be due to the occurrence of positive and zero terms only in the well-known expansion

$$p_{pq}^{00} = 2 \sum_j c_{p,j}^* c_{q,j} \tag{19}$$

where $c_{p,j}$ is a coefficient in the SCF-LCAO MO expansion. Because of the Pople-Brickstock alternation rules [7] this implies that for all $k \neq 0$ $p_{pq}^{kk} \leqq p_{pq}$. Moreover in the CI-expansion (14a) $g_o < 1$, so that $\tilde{p}_i < p_i$ for large p_i. Similarly it is reasonable to expect a tendency according to which $\tilde{p}_i \approx p_i$ if $0.5 < p_i < 0.7$, and $\tilde{p}_i > p_i$ if $p_i < 0.5$. Because β'_i is positive we may conclude from (10) and (17) that $r^e > r^s$ for strong double bonds, and $r^e < r^s$ for weak double bonds. Then it follows from a comparison of (1) and (18) that the Coulson-Golebiewski relation (1) should be a quite generally useful formula for r^e.

On the other hand it seems that for calculations of bondlengths in excited states (10) and (18) provide a more promising starting point than (1). Because the usual one-configurational wave functions for excited states, based on ground state SCF-MO's, are less reliable than ground state SCF-functions, and because even in the SCF-approximation of the energy of the excited state the coefficient of γ_i is not equal to $-\frac{1}{2}p_i^2$, we should be prepared to meet rather large values of $|r^e - r^s|$ in the calculation of bondlengths in excited states. We performed the calculation for the ${}^1B_{2u}$ and ${}^3B_{1u}$ states of benzene, where $P_i = \frac{1}{2}$ for all i. For both excitations $\Delta r^s = 0.035$ Å according to (18). $r^e - r^s$ amounts to 0.004 Å for the ground state and the ${}^1B_{2u}$-state, and to 0.003 Å for the ${}^3B_{1u}$-state. It follows that the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ and ${}^3B_{1u} \leftarrow {}^1A_{1g}$ excitations are accompanied by an increase of the equilibrium bondlength of 0.035 and 0.034 Å, respectively. The corresponding experimental values, derived from the relative intensities of the members of the main progression of the absorption bands, are 0.037 [8] and 0.036 Å [9]. Eq. (1) predicts a lengthening by only 0.030 Å for both excitations.

It is dubious whether the same method may be used to calculate the C–C distance in the first excited singlet state of ethylene. Though there is considerable difference of opinion about the equilibrium geometry of this state [10] it seems to be certain that it is far from planar. This implies that the vital assumption that E'_σ is given by one function of r_i for all C–C-bonds is probably incorrect for this state. Therefore the bondlength which may be calculated from (10) and (18), $r^e = 1.49$ Å, should not be regarded as reliable.

4.2. The Evaluation of Force Constants from Spectroscopic Parameters

SCF-expressions for the force constants Λ_1 and Λ_2 of the a_{1g} and b_{2u} C–C streching vibrations of benzene are derived in [11]:

$$\Lambda_1 = -2P'\left(\beta' - \frac{1}{3}\gamma'\right), \tag{20}$$

$$\Lambda_2 = \Lambda_1 \left(1 + \frac{\Lambda_1}{P'^2 \left\{2\beta + \frac{1}{3}(\gamma_{12} - \gamma_{14})\right\}}\right). \tag{21}$$

From analyses of IR and Raman spectra Λ_1 is found to be $48.0 \pm 0.5\,\mathrm{eV/Å^2}$; values for Λ_2 are reported in the range 24–27 $\mathrm{eV/Å^2}$ [12–14], based on the Mair-Hornig interpretation of the benzene spectrum [15], or as 32.2 $\mathrm{eV/Å^2}$ [12] if the Ingold assignment [16] is used. The preference for the Mair-Hornig assignment which appears from a majority of these investigations is supported by Nieman's recent analysis of the benzene phosphorescence spectrum [17].

Hückel and SCF calculations of Λ_2, however, tend to support the Ingold assignment if (21) is combined with the β- (and γ)-values evaluated from UV-spectra; on the other hand a calculation of β from (21) and a Λ_2-value of about 26 $\mathrm{eV/Å^2}$ leads to widely diverging "vibrational" and "spectroscopic" β's [2, 11]. If we wish to obtain a more attractive result by accounting for the π-electron correlation we must firstly replace (20) and (21) by more complete expressions, based on a CI-analysis. Secondly we must find β- and γ-values which reproduce the experimental benzene UV-spectrum after a CI-calculation.

It is shown in [5] that (20) is a very nearly correct expression for Λ_1 even if CI with all excited configurations is taken into account. More generally it may be argued that in calculations of force constants CI gives a minor correction of of the π-electron energy, whereas the main effect is due to the σ-electrons. Therefore we may assume that the results obtained from (20) and (21) are very close to those which could be derived from the corresponding CI-formulae.

The required parameter values, which give correct values for the singlet-singlet excitations in benzene after CI including all configurations which are at most triply excited with respect to the ground configuration, are [5]:

$$\beta = -2.65, \quad \gamma_{11} = 10.5, \quad \gamma_{12} = 6.9, \quad \gamma_{13} = 5.55, \quad \gamma_{14} = 5.0\,\mathrm{eV}^{2}. \tag{22}$$

In order to find the correct value of P' to be substituted into (20) and (21) we recall that Λ_1 and Λ_2 are primarily obtained as $f'' + \frac{1}{6}E''_\pi$, where the latter derivative is

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[2] These results correspond closely with those found by Karwowski from a similar analysis [18, 19]; however, the present author does not agree with Karwowski's opinion that such parameters give a bad fit for the lowest triplet state. The necessary extension of Karwowski's argument, contained in [5], will be presented in a later paper.

taken with respect to the appropriate symmetry coordinate [2, 11]. A second expression for f'' is then found by differentiating (7), and the value of P' is obtained by the differentiation of an empirical function, e. g. (1). However, we have shown that a function $P(r^e)$ does not exist, so that there is an element of lawlessness in using its derivative. P' can only be obtained from (18); its value is $-1/0.21$ Å^{-1}.

It follows now from (21) that $\Lambda_2 = 26.2$ eV/Å^2, in excellent agreement with the values based on the Mair-Hornig assignment. Using for γ' the Pariser-Parr value -2.0 eV/Å we find from (20) that $\beta' = 4.35$ eV/Å, and the data on β and β' suffice for the calibration of an exponential $\beta - r$ function:

$$\beta = -2.12 \exp\left(\frac{1.533 - r}{0.61}\right) \text{eV}. \tag{23}$$

The new relations (18) and (23) were successfully applied in the interpretations of both force constants and UV-spectra of small π-electron systems [5]. Details of the latter and of the calibration procedure will be given in a future paper. The results of some force constant calculations are as follows. From the SCF-formulae [11] for Λ_3 and $2\Lambda_4$ in benzene, corresponding to the e_{2g} and e_{1u} vibrations, we found that $\Lambda_3 = 44.0$ eV/Å^2 (exp. 47.2 [13] or 41.5 [14]) and $2\Lambda_4 - \Lambda_1 = 0$ (0 [13] or 0.1 eV/Å^2 [14]). The force constant for the symmetric C–C stretching mode in the $^1B_{2u}$ electronic state of benzene is calculated to be 42 eV/Å^2; from the structure of the 4.7 eV absorption band McKenzie cs [8] derived the value 41.3 eV/Å^2. For the C–C stretching vibration in ethylene $\Lambda = -2P'(\beta' - \frac{1}{2}\gamma')$; from this equation and (18) and (23) we find that $\Lambda = 55.4$ eV/Å^2, in excellent agreement with one of the values proposed by Crawford cs [20], 55.2 or 68.6 eV/Å^2.

5. Calculations of Force Constants from Thermochemical Parameters

Alternative estimates of Λ's for benzene may be based on the parameters proposed by Dewar and de Llano [21] or by Lo and Whitehead [22]. The basic data in their evaluations of the parameters include bondlengths and force constants (as was the case for (18) and (23)), and heats of atomisation where we used UV excitation energies. In both calculations $\gamma(r)$ was assumed to be given by the Ohno formula $\gamma = 1/(r^2 + a^2)^{\frac{1}{2}}$ [23] with $\gamma_{11} = 11.13$ eV. Dewar and de Llano used a linear $P - r$ relation with $P' = -1/0.174$, whereas the non-linear $P(r)$-relation of Lo and Whitehead was derived from the thermochemical data which also furnished the values of $\beta(r)$ and $f(r)$. Though only $P(r)$ and $\gamma(r)$ in [21], and $f'(r)$, $\beta'(r)$ and $\gamma'(r)$ in [22], are given analytically, we can obtain some information about the values of the non-symmetrical benzene force constants determined by the parameters under discussion.

According to Dewar and de Llano the stretching force constant κ of a C–C-bond is a function of the bondlength only; for single, double and triple bonds κ is given by

$$\kappa = -31.76\, r^{-2} + 131.91\, r^{-4} - 71.90\, r^{-6}, \tag{24}$$

which is the correct version of Eq. (14) of [21]; r is expressed in Å, κ in 10^5 dyne/cm.

For a benzene bond κ is calculated to be 8.72×10^5 dyne/cm which differs considerably from the value obtained from the vibrational spectrum: 7.03×10^5 [13] or 6.73×10^5 [14]. Because $\kappa = 1/6\ (\Lambda_1 + \Lambda_2 + 2\Lambda_3 + 4\Lambda_4)$ [13] we find from the Λ's calculated in Sect. 4 that $\kappa = 6.85 \times 10^5$ dyne/cm. It follows then that the correct value for Λ_1 obtained in [21] is an incidental succes, because at least one of the remaining force constants must be seriously wrong.

In the Lo-Whitehead scheme $P'(1.397\ \text{Å})$ can be evaluated from (20) and the β' and γ' given in [22]; on substitution of $P' = -1/0.190$ for benzene, $\beta = -1.83$ eV and $\gamma_{12} - \gamma_{14} = 3.0$ eV into (21) we find that $\Lambda_2 = 17.0\ \text{eV/Å}^2$, about 8 eV/Å^2 below the experimental value.

It appears that parametrisations which give an often very good prediction of groundstate energies need not be of any use in the calculation of either vibrational or electronic excitation energies. Particularly the difference between the benzene β-values used in the calculations of heats of atomisation (-1.75 eV [21], -1.83 eV [22]) and of excitation energies (-2.65 eV) is so large that at least an indication of some of the possible causes seems to be in place. We note that Dewar's explanation [24], which ascribes the difference between the "ground state β" and the "excitation β" to the neglect of differential overlap, cannot be maintained in view of more recent investigations of the ZDO approximation [4, 5, 28].

The schemes of Dewar and de Llano and of Lo and Whitehead are both based on a Pople-type one-determinantal description of the π-electron system. The Dewar-de Llano analysis is partly based on the properties ascribed to a hypothetical pure sp^2-single bond, introduced by Dewar and Schmeising [25], which has been the subject of some criticism because of the neglect of hyperconjugation [26]. Because the uncertainty on this point may introduce some confusion which is not relevant to the present discussion we concentrate on the analysis given by Lo and Whitehead. We remark, however, that the two calculations are closely related, both by the use of the same γ's and CH bond energy (which will be discussed below) and by the calculated parameter values.

According to Lo and Whitehead β is given by

$$\beta(r) = \frac{3}{2}\left[-E_{\mathrm{b}}^{\mathrm{C=C}}(r)_{\mathrm{eth}} + E_{\mathrm{b}}^{\mathrm{C=C}}(r)_{\mathrm{benz}} - \frac{1}{4}\gamma_{11} + \frac{5}{18}\gamma_{12} - \frac{1}{36}\gamma_{14}\right] \tag{25}$$

where $E_{\mathrm{b}}^{\mathrm{C=C}}(r)_{\mathrm{benz}}$ is the energy of one benzene C=C bond for a bondlength r. E_b is given by a Morse function, defined by E_e, the energy for the equilibrium length, and the experimental force constant. In cases where all N_{CC} C–C bonds are equivalent E_e can be calculated from the heat of atomisation ΔH_a and

$$N_{\mathrm{CC}}\, E_e + N_{\mathrm{CH}} \cdot E_{\mathrm{CH}} = \Delta H_a \tag{26}$$

by the substitution of a suitable value for E_{CH}. The following factors may be of importance for an explanation of the difference between the thermochemical and the spectroscopic β-values:

1. Configurational interaction. In the $E_{\pi b}$-equations from which (25) is derived this correction may be accounted for by adding a constant term of 0.22 eV to $E_{\pi b}$ (eth.) and of 0.09 eV to $E_{\pi b}$ (benz.). It should be noted that the explicit con-

sideration of π-electron correlation tends to make $1/P'$ much more negative, so that the A_2-value from (21) and the Lo-Whitehead parameters will be even less than 17 eV/Å^2.

2. The choice of γ-values. Ohno's γ_{11}, used in [21] and [22], is based on the Pariser-Parr argument [27], according to which in a first approximation $\gamma_{11} = I - A$. The approximative character of this expression is brought out if we recall that Pariser and Parr regard $\gamma_{11} - \gamma_{12}$ as the energy difference between a covalent and an orthopolar VB-structure, whereas $I - A$ is evaluated from data on non-interacting C-atoms.

If a C^+- and a C^--ion occupy neighbouring positions in a molecule we should expect that both the interaction between the ions and the polarisation of the σ-bond will affect the energy of the polar state, so that the approximation of γ_{11} by $I - A$ may be rather rough. It seems to be preferable to use γ-values obtained from purely molecular data.

If CI is explicitly taken into account the γ-values in (22) should be used. On substitution of these data and of the correlation energy into (25) we find that for benzene $\beta = -1.87$ instead of -1.83 eV.

An alternative consistent procedure can be based on the neglect of CI for the ground state; then Pariser's γ-values [6] should be used, and β is found to be -2.22 eV, in reasonable agreement with the spectroscopic value -2.39 eV.

3. In the PPP-method several large energy terms, such as the zeropoint vibrational energy and the Coulomb penetration integrals, are not considered explicitly. Now these terms are not of interest if we calculate the energy differences between two vibrational or electronic states of one molecule, but they should be taken into account if the absolute energies of different molecules are compared. We have to admit, of course, that such a detailed analysis is at present impossible because of the scarcity of data about $\sum_i h\nu_i$ for large molecules and about values for penetration integrals that can be used in empirical calculations (cf. the comparison between the theoretical and the empirical values of $(p:pp)$ in [27]). From the fact that the Lo- Whitehead formalism gives very good predictions of the heats of atomisation of many molecules we may conclude that the formally neglected energy terms can be perfectly accounted for by a suitable choice of the parameters E_{CH}, f and β; it is impossible to say, however, how strongly specifically β is affected by the simplifications.

4. A comparison of the calculations of Lo and Whitehead with some investigations on paraffins suggests that some more simplifications may have influenced the calculated parameters. In Tatevkii's succesful analysis of the paraffins, quoted in [26], the basic parameters are not E_{CC} and E_{CH}, but sums of energies of C–C-bonds, distinguished according to the number of neighbouring C-atoms, and of an appropriate part of the adjacent C–H bonds. This implies that we have considerable freedom in the choice of E_{CH}; as a matter of fact, in Tatevskii's scheme the energies of the three types of C–H-bonds, C being primary, secondary or tertiary, may be freely chosen. The importance of this fact for the calibration of β appears from (25) and (26); a lowering of E_{CH} by 1 Kcal/mol makes β 0.20 eV more negative.

Further in most successful methods for calculations on paraffins E_{CC} is regarded as a function of the number of neighbouring C–C-bonds, either directly or through the introduction of bond-bond interaction terms; this circumstance causes some uncertainty in a calibration based on the assumption of one $E_{CC}(r)$-function for ethylene and benzene.

It follows from these considerations that the parametrisation proposed by Lo and Whitehead is by no means necessarily unique. Though leading to a consistently good prediction of heats of atomisation the parameters may be so seriously contaminated by the implicit energy terms mentioned sub 3 that they should not be used in the calculation of any other molecular property.

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