123. *An Empirical Determination of the Hückel Parameter* β *and of the* C–C *and* C–H *Bond Energies in Aromatic Hydrocarbons.*

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The atomic orbital interaction integral, β, is calculated from appropriate Morse functions and the Hückel theory of π-molecular orbitals, consistent results being obtained from data for benzene and ethylene. A third value, lying between these, has been derived from the heats of combustion of some aromatic hydrocarbons, and estimates of the σ-bond energies of the C–C and C–H bonds in such compounds have been made.

1. CALCULATION OF β(*r*)

The energy of the *i*th π-electron molecular orbital as calculated using the simple Hückel theory is of the form

$$\varepsilon_i = \alpha - x_i\beta \tag{1}$$

where x_i is the " Hückel number " of the *i*th molecular orbital and has a negative value for the levels contributing to the ground state, α is the energy of a $2p_\pi$ atomic orbital χ, *i.e.*, $\alpha = \int\chi^*\mathbf{H}\chi\,d\tau$ (in which $\mathbf{H}$ is the non-explicit Hamiltonian operator), and β is the matrix element, $\int\chi_s^*\mathbf{H}\chi_t\,d\tau$, expressing the interaction between the two atomic orbitals χ_s and χ_t, at this level of approximation, *i.e.*, when overlap is neglected. β is a function of the distance r between the atoms s and t, but in the simple Hückel approximation it is considered negligible unless s and t are neighbours, in which case all β's are taken as equal (within the compound under discussion), although it is frequently proposed to derive bond orders and hence to infer differing bond lengths.

The total π-electron energy of the ground state of a molecule containing a system of n neighbouring $2p_\pi$ atomic orbitals is obtained by summing eqn. (1) over the $\frac{1}{2}n$ doubly occupied levels:

$$2\sum_{i=1}^{\frac{1}{2}n}\varepsilon_i = n\alpha - 2\beta\sum_{i=1}^{\frac{1}{2}n}x_i,$$

from which it may be inferred that the total binding energy of the π-component of the bonds is given by

$$\varepsilon_\pi = -2\beta\sum_{i=1}^{\frac{1}{2}n}x_i \tag{2}$$

For a system in which the π-molecular orbitals are spread over m equivalent bonds, the total energy of the π-component of each of these is $E_\pi = \varepsilon_\pi/m$. In ethylene, $m = 1$ and $\Sigma x_i = -1$, while for benzene these are 6 and -4, respectively. Hence

$$E_\pi(\text{ethylene}) = 2\beta \tag{3}$$

and

$$E_\pi(\text{benzene}) = \tfrac{4}{3}\beta \tag{4}$$

The terms on the left of eqns. (3) and (4) are, however, not directly measurable, since a π-bond is known only in association with a σ-bond. Nevertheless, from the energies of a " $\sigma + \pi$ "-bond and of a σ-bond of the same length, we can calculate the energy of the corresponding pure π-bond if we neglect interaction of σ- and π-electrons. Thus,

$$E_\pi(r) = E_{\sigma+\pi}(r) - E_\sigma(r) \tag{5}$$

In general, $E_{\sigma+\pi}$ and E_σ are known only at particular, unequal values of r, *viz.*, the equilibrium distance r_e. To calculate them at other bond-lengths we require to take into account the energies of compression or expansion of the bonds. This may be done conveniently by use of the Morse function,

$$E(r) = E(r_e)\{e^{-2a(r-r_e)} - 2e^{-a(r-r_e)}\}$$

The quantity a is characteristic of the particular bond, and can be calculated from the stretching force constant.

However, the further difficulty arises that there is ample evidence[1-3] that $E_\sigma(r)$ depends on the hybridisation of the atoms involved, and that C–C in ethylene should be compared not with that in ethane but with that in a hypothetical C–C σ-bond between sp^2-hybridised atoms. The length of such a bond is not unequivocally established, and, in the nature of things, its stretching force constant and energy cannot be directly known. We have taken[2] $r_e = 1{\cdot}48$, with $E_\sigma(r_e)$ and a as in ethane. Otherwise our data are those selected by Coulson and Dixon and are as follows:

C–C bond	r_e (Å)	$E(r_e)$ (kg.-cal./mol.)	a (Å^{-1})	C–C bond	r_e (Å)	$E(r_e)$ (kg.-cal./mol.)	a (Å^{-1})
Ethylene ...	1·33	151	2·189	Ethane ...	1·54	84	2·028
Benzene ...	1·39	124	2·093	sp^2–sp^2 ...	1·48		

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[1] Coulson and Dixon, *Tetrahedron*, 1962, **17**, 215.

[2] Dewar and Schmeising, *Tetrahedron*, 1959, **5**, 166; 1960, **11**, 96.

[3] Coulson, Victor Henri Memorial Volume, " Contribution a l'Étude de la Structure Moléculaire," Desoer, Liège, 1948; Lide, *Tetrahedron*, 1962, **17**, 125; Bastiansen and Traetteberg, *ibid.*, p. 147, etc.

From eqns. (3)—(5) we then have

$$\beta(\text{ethylene})(r) \doteq \{E(\text{ethylene})(r) - E_\sigma(r)\}/2 \qquad (6)$$

$$\beta(\text{benzene})(r) = 3\{E(\text{benzene})(r) - E_\sigma(r)\}/4 \qquad (7)$$

and within the limits of our approximations these should be equal, *i.e.*, $\beta(r)$ is obtained from two independent sets of data; the results are:

r (Å)	1·33	1·36	1·39	1·42	1·45	1·48	1·51	1·54
β(ethylene)(r) (kg.-cal./mol.)	38·81	36·38	34·04	31·79	29·64	27·59	25·64	23·80
β(benzene)(r) (kg.-cal./mol.)	36·30	34·39	32·53	30·71	28·95	27·26	25·63	24·08
β(benzene) (r)/β(benzene) (1·39) ...	1·116	1·057	1·000	0·944	0·890	0·838	0·788	0·740

The bottom line gives a ratio which is frequently used in attempting to improve the simple Hückel approximation by allowing for the dependence of β on r and assuming that the β of the simple Hückel method (β_0 of the next section) is the same for all aromatic compounds.

The difference between the two values of β(1·39), 1·39 being the benzene C–C bond-length, is only 1·5 kg.-cal./mol., *i.e.*, 2·2%. Greater reliance should be placed on the benzene curve since r_e is nearer the middle of the range of values for r used; this results in a more favourable application of the Morse function.

The " least-squares " quadratic expression

$$\beta(r) = 31{\cdot}83r^2 - 149{\cdot}52r + 178{\cdot}85$$

fits the calculated curve almost exactly.

2. β AND BOND ENERGIES FROM HEATS OF COMBUSTION

For molecules containing only σ-bonds, heat of combustion is a simple additive property of the individual bond energies. For molecules containing, in addition, π-molecular orbitals it is necessary to include a further term even if σ–π-interaction is neglected. This term is the total π-electron energy calculated usually by the simple Hückel approximation and given in eqn. (2).

If we consider the heat of combustion as determined in two steps, first atomisation and secondly the conversion of the atomic fragments into the products of combustion, we have, neglecting energy terms due to changes in hybridisation,

$$\mathrm{C}_x\mathrm{H}_y + (x + \tfrac{1}{4}y)\mathrm{O}_2 \longrightarrow x\mathrm{C} + y\mathrm{H} + (2x + \tfrac{1}{2}y)\mathrm{O} + n_{\mathrm{CC}}E_{\mathrm{CC}} + n_{\mathrm{CH}}E_{\mathrm{CH}} + (x + \tfrac{1}{4}y)E_{\mathrm{OO}} + \varepsilon_\pi \qquad (8)$$

$$x\mathrm{C} + y\mathrm{H} + (2x + \tfrac{1}{2}y)\mathrm{O} \longrightarrow x\mathrm{CO}_2 + \tfrac{1}{2}y\mathrm{H}_2\mathrm{O} - xQ_{\mathrm{CO}_2} - \tfrac{1}{2}yQ_{\mathrm{H}_2\mathrm{O}} \qquad (9)$$

where n_{CC} = number of C–C bonds and n_{CH} = number of C–H bonds in the hydrocarbon $\mathrm{C}_x\mathrm{H}_y$, E_{CC} = energy of the C_{sp^2}–C_{sp^2} bond ($=E_\sigma$ of the previous section), E_{CH} = energy of the C_{sp^2}–H bond, E_{OO} = dissociation energy of the oxygen molecule, Q_{CO_2} is heat of atomisation of CO_2, and $Q_{\mathrm{H}_2\mathrm{O}}$ that of $\mathrm{H}_2\mathrm{O}$.

Adding expressions (8) and (9) we have

$$\mathrm{C}_x\mathrm{H}_y + (x + \tfrac{1}{4}y)\mathrm{O}_2 \longrightarrow x\mathrm{CO}_2 + \tfrac{1}{2}y\mathrm{H}_2\mathrm{O} + C \qquad (10)$$

where

$$C = n_{\mathrm{CC}}E_{\mathrm{CC}} + n_{\mathrm{CH}}E_{\mathrm{CH}} + (x + \tfrac{1}{4}y)E_{\mathrm{OO}} + \varepsilon_\pi - xQ_{\mathrm{CO}_2} - \tfrac{1}{2}yQ_{\mathrm{H}_2\mathrm{O}} \qquad (11)$$

C being the heat of combustion of $\mathrm{C}_x\mathrm{H}_y$. The available experimental quantities on the right of eqn. (11) are $Q_{\mathrm{H}_2\mathrm{O}}$, Q_{CO_2}, and E_{OO} for which we have taken the following values:[4] $Q_{\mathrm{CO}_2} = 2 \times 192 = 384$ kg.-cal./mole., $Q_{\mathrm{H}_2\mathrm{O}} = 2 \times 110{\cdot}6 = 221{\cdot}2$ kg.-cal./mol., and $E_{\mathrm{OO}} = 119{\cdot}1$ kg.-cal./mol. Using the known heats of combustion of the three aromatic

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[4] Cottrell, " The Strengths of Chemical Bonds," Butterworths, London, 1958.

hydrocarbons benzene, naphthalene, and anthracene (789·1, 1249·7, and 1712·1 kg.-cal./mol.), we obtain three equations in the unknowns E_{CC}, E_{CH}, and β_0, where β_0 represents a standard β supposedly applicable to all these compounds. Then,

$$C(\text{benzene}) = 789{\cdot}1 = 6 \times 384 + 3 \times 221{\cdot}2 - 6E_{\mathrm{CC}} - 6E_{\mathrm{CH}} - (6 + 1{\cdot}5)E_{\mathrm{OO}} - 8{\cdot}000\beta_0$$

or

$$1285{\cdot}27 = 8\beta_0 + 6E_{\mathrm{CC}} + 6E_{\mathrm{CH}},$$

and

$$2045{\cdot}9 = 13{\cdot}683\beta_0 + 11E_{\mathrm{CC}} + 8E_{\mathrm{CH}},$$

$$2904{\cdot}75 = 19{\cdot}314\beta_0 + 16E_{\mathrm{CC}} + 10E_{\mathrm{CH}}$$

Hence, $\beta_0 = 32{\cdot}96$ kg.-cal./mol., $E_{\mathrm{CC}} = 77{\cdot}58$ kg.-cal./mol., and $E_{\mathrm{CH}} = 92{\cdot}68$ kg.-cal./mol.

This β_0 value compares very favourably with β(1·39) (= 32·53 kg.-cal./mol.) determined in the previous section. This is particularly interesting since (a) β_0 may vary somewhat from compound to compound, and (b) β(*r*) varies with interatomic distance, *r*, even within the same molecule. It seems however to encourage confidence in the β(*r*) values of the previous section.

E_{CC}, which we have noted as the E_σ of the first part of this paper has a numerically smaller value than the 84 kg.-cal./mol. which we supposed to be applicable to the pure sp^2–sp^2 σ-bond. However, we know that all the C–C bonds in the reference compounds are substantially shorter than 1·48 Å; in fact the average of the thirty-three bonds [5] is 1·401 Å, with a spread from 1·361 Å to 1·436 Å. Application of the Morse equation for the sp^2–sp^2 σ-bond to this average gives $E_\sigma(1{\cdot}40) = 81{\cdot}4$ kg.-cal./mol., which is in reasonable agreement with our value of 77·58 kg.-cal./mol. when the approximations are borne in mind.

Substituting the values for β_0, E_{CC}, E_{CH}, $Q_{\mathrm{CO_2}}$, $Q_{\mathrm{H_2O}}$, and E_{OO} in eqn. (11), the general equation for the heat of combustion of a hydrocarbon becomes (within the limits of our approximation)

$$C = 264{\cdot}9x - 80{\cdot}8y - 77{\cdot}58n_{\mathrm{CC}} - 92{\cdot}68n_{\mathrm{CH}} + 65{\cdot}92\sum_{i=1}^{\frac{1}{2}n} x_i \qquad (12)$$

the (negative) Hückel numbers being summed over all the (doubly) occupied levels, *i.e.*, the occupation number (2) has been included in the term 65·92.

Using eqn. (12), we calculate the following heats of combustion (in kg.-cal./mol.; observed values in parentheses): phenanthrene 1708·4 (1705·0); triphenylene 2163·6 (2164·4); 1,2-benzanthracene 2169·3 (2169·8); chrysene 2166·4 (2165·0). It is interesting to note that the quite small differences between the heats of combustion of the last three compounds are so accurately mirrored by the Hückel energies.

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[5] Stoicheff, *Canad. J. Phys.*, 1954, **32**, 339; Cruickshank, *Acta Cryst.*, 1956, **9**, 915; 1958, **11**, 507.