On the calculation of bond energies from atomization energies†

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It is possible (and occasionally preferable) to define bond energies of polyatomic molecules by dissociation of the molecule at a given bond into two radical fragments, *e.g.* for a tetra-atomic molecule ABCD.

However it has long been recognized that the quantity derived in this manner will bear little relation to the actual energy content of the bond in the molecular ground-state equilibrium geometry, due to internal reorganization of the radical fragments. Clearly, a rigorous method for determining the distribution of bonding energy at the equilibrium geometry of a polyatomic molecule using its wavefunction or charge density would be highly desirable. In particular, it would provide a powerful analytical tool for quantum chemistry by enabling precise, quantitative statements to be made about the nature of bonds in a given environment, as an alternative to other indirect measures such as bond lengths; bond orders; charges or higher multipoles; or (in some cases) aromaticity indices.[1,2]

$$E\,(\mathrm{B{-}C}) \equiv E(\mathrm{ABCD}) - \mathrm{E}(\mathrm{AB}^{\cdot}) - \mathrm{E}(\mathrm{CD}^{\cdot}) \qquad (1)$$

Traditionally, the energies of specific bonds in a molecule have been estimated from its atomization energy ΣD_0 (if vibrationally corrected) or ΣD_e by making assumptions about other bonds in the molecule. For example, the energy of the C–C bond in ethyne, ethene or ethane may be calculated 'precisely' if the C–H bond energy is assumed to be either constant for all three compounds, or the same as the bond energy in methane (trivially $\Sigma D_e/4$). Other approaches to calculating bond energies which should be mentioned here include Grimme's idea of parameterizing the atomization energy in terms of bond critical point (topological) properties;[3] Bader's proposal of relating the bond energy to the integral of the energy density over the interatomic surface;[4] and Krygowski *et al*'s method of parameterizing the C–C bond energies as a single exponential function of experimentally observed bond lengths.[5]

Like Grimme's approach, the method outlined here does not make any assumptions about the constancy of C–C bond energies across any series of compounds, enabling *individual* bond energies to be derived for each such bond in a molecule. Our approach is to parameterize the potential energy surface for each bond in a way which best reproduces the atomization energies across a series of related compounds, assuming only that chemically similar types of atoms interact *via* the same potential.

Molecular geometries and total energies of benzene, naphthalene, five linear polyacenes (anthracene, tetracene, pentacene, hexacene and heptacene), five angular phenacenes (phenanthrene, chrysene, picene, fulminene and [7]phenacene) and four 'composite' benzenoid hydrocarbons (triphenylene, pyrene, perylene, coronene) were obtained at B3LYP/6-311G** level of theory, and used in the subsequent fitting procedure. Comparing the best experimental bond length values for benzene, naphthalene and anthracene, derived from low-temperature crystallographic studies and corrected for librational effects,[6] we find very good agreement with structures optimized at this level of theory, around 0.006 Å mean difference. Vibrationless atomization energies ΣD_e were derived from the molecular total energies by subtracting the energies of the free ground state atoms at the same level of theory, *i.e.* C(^3P) = −37. 85599 and H(^2S) = −0.50216, in Hartree atomic units. The parameterization procedure begins by defining a set of additive bond energies with respect to an estimated vibrationless atomization energy ΣD_e^{calc}:

$$\Sigma D_e^{\text{calc}} = \sum_{n_{\mathrm{CC}}} E(\mathrm{C-C}) + \sum_{n_{\mathrm{CH}}} E(\mathrm{C-H}) \qquad (2)$$

At first glance, the above partitioning of atomization energy seems inappropriate for the systems we have chosen to illustrate the method, namely π-electron molecules with conjugated π-bonds, and aromatic hydrocarbons in particular. An extension of the HMO model due to Longuet-Higgins and Salem[7] predicts the following bond-energy contribution for any pair of neighboring carbon atoms *m* and *n*

$$E_{mn}\,(\mathrm{C{-}C}) = -\{U(r) + 2p_{mn}\,\beta(r)\} \qquad (3)$$

where *r* is the C–C distance, $U(r)$ and $\beta(r)$ are the σ-bond potential energy and the resonance integral, respectively, and p_{mn} represents the π-electron bond order for atoms *m* and *n*. The latter quantity depends on the LCAO-MO coefficients of all the occupied MOs, and thus is a function of the whole molecular geometry, not just the *m*–*n* distance *r*. On the other hand at the *equilibrium* molecular geometry there is a simple linear relationship between the bond order p^e_{mn} and the equilibrium bond distance r^e_{mn}:

$$p^e_{mn} = p(r^e_{mn}) = (R_1 - r^e_{mn})/(R_1 - R_2) \qquad (4)$$

where R_1 (R_2) is the length of a 'pure' single (double) C–C bond of the sp^2–sp^2 type. It follows from eqs. (3) and (4) that for π-electron hydrocarbons at *equilibrium* there is a *universal* function $E(r)$ which defines bond energies as dependent of equilibrium bond distances r^e_{mn},

$$E_{mn}\,(\mathrm{C{-}C}) = E(r^e_{mn}) \qquad (5)$$

The above result is valid providing that all the carbon atoms in the molecule are considered equivalent (a usual assumption in the HMO model). However, in aromatic molecules one finds two kinds of atoms: tertiary (with one hydrogen atom attached) and quaternary (with no hydrogen atom attached). Thus, up to three kinds of C–C bonds may be distinguished in these molecules (see below), with possible different bond-energy functions $E_i(r)$, (i = 1,2,3).

In our approach, the C–C bond energies are represented by one or more Morse functions, slightly modified to give E (C–C) = D_e at $r = r_e$ (rather than zero energy at $r = r_e$).

$$E_i\,(\mathrm{C{-}C}) = D_e^{\,i}\,\{1 - [1 - \exp\{-\alpha_i\,(r - r_e^{\,i})\}]^2\} \qquad (6)$$

slightly modified to give E (C–C) = D_e at $r = r_e$, rather than zero energy at $r = r_e$ (here r_e and D_e correspond to the minimum of the Morse function, not to some equilibrium bond distance). The subscript/superscript *i* labels the Morse function to be applied. In fact it would be equally feasible to parameterize E_i(C–C) with a three parameter harmonic model, *i.e.*

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† Electronic supplementary information (ESI) available: data for attempted fittings and exact and calculated atomisation energies for the final model. See http://www.rsc.org/suppdata/cc/b0/b007657k/

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$$E_i\,(\mathrm{C{-}C}) = D_e^{\,i}\ \{1 - \alpha_i\,(r - r_e^{\,i})^{\,2}\} \qquad (7)$$

but since the Morse function allows for anharmonicity without introducing any more parameters, we consider it superior for this application. At first, the bonds to terminal hydrogen atoms were also parameterized with Morse functions, but it was found essentially impossible to extract this data from the atomization energies (the optimized C–H bond lengths vary from just 1.084 to 1.086 Å over the whole data set). Thus the single value of E(C–H) for all such bonds was finally chosen as a parameter in the fitting procedure.

The next step is to define a normalized χ^2 statistic which will be minimized with respect to variations in the model parameters during the fitting procedure.

$$\chi^2 = \frac{\Sigma\{\Sigma D_e^{\mathrm{calc}} - \Sigma D_e\}^2}{n_{\mathrm{mols}}} \qquad (8)$$

This statistic is minimised in a simple iterative algorithm employing numerical partial first derivatives of eqn. (5) with respect to the model parameters in $\Sigma D_e^{\mathrm{calc}}$. This has been implemented as a *MATHEMATICA 4*[8] routine which is freely available from the authors, on request.

Topologically we can distinguish three types of C–C bond in polyacenes (see Fig. 1). These are (i) bonds between carbon atoms both bearing hydrogens; (ii) bonds between carbon atoms where only one of the carbons bears a hydrogen; and (iii) bonds between carbon atoms where neither bears a hydrogen. Thus it could be expected that the potential energy surface for these three types of bonds will differ, such that three independent Morse functions for each type of bond will be required to correctly describe all types of polyacene. However, we began the fitting procedure assuming that a single C–C potential energy surface might describe *all* types of C–C bonds, *i.e.* a four-parameter fit of $\{D_e, \alpha, r_e\}$ plus E(C–H) for all sixteen compounds. The result was quite poor reproduction of the 'exact' B3-LYP/6-311G** atomization energies by the model calculated ones: the average (percentage) accuracy $100(\chi^2/n_{\mathrm{mols}})^{\frac{1}{2}}$ being just 0.5%. Subsequent improvement of the model by distinguishing between chemically distinct types of C–C bond led to a final model with ten parameters (three Morse functions as described above) reproducing the atomization energies with 0.04% average accuracy over all sixteen compounds. The fitted model parameters are as follows (in units of kJ mol^{-1}, Å^{-1} and Å): type (i) C–C bonds $\{D_e, \alpha, r_e\}$ = {530.83, 5.052, 1.3549}; type (ii) C–C bonds $\{D_e', \alpha', r_e'\}$ = {498.45, 6.448, 1.3922}; type (iii) C–C bonds $\{D_e'', \alpha'', r_e''\}$ = {490.49, 4.102, 1.3642}; and E(C–H) = 431.47 kJ mol^{-1}. The data for all of the fits attempted and the exact and calculated atomization energies for the final model are supplied as ESI.†. Here we will just mention that by far the worst agreement between any ΣD_e and $\Sigma D_e^{\mathrm{calc}}$ is found for septacene (ΣD_e = 25212 kJ mol^{-1} and $\Sigma D_e^{\mathrm{calc}}$ = 25232 kJ mol^{-1}, a 0.08% error). It should be noted that an error of 20 kJ mol^{-1} on the atomization energy represents < 1 kJ mol^{-1} error on the average C–C bond energy, since septacene has 30 C–C bonds.

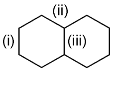

Fig. 1. Definition of C–C bond types.

The bond energies derived from the final model by substituting the optimized C–C bond lengths for r in eqn. (6) vary over a range of 438–531 kJ mol^{-1} in the sixteen compounds, with the C–C bond energy in benzene being at the upper end of this range. The complete distribution of C–C bonding energy is illustrated in Fig. 2 for just a few of the molecules: benzene, perylene and coronene. The values for perylene and coronene nicely demonstrate the Clar classification[9] of so-called 'empty rings' at the centre of composite polyacenes. The energies of innermost C–C bonds are much lower than those of the outermost bonds of the molecules, indicating that π-electron stabilization is concentrated in the peripheral rings (*e.g.* the difference in C–C bond energies between the peripheral rings and the central rings in perylene and coronene is 246 and 107 kJ mol^{-1}, respectively). It should also be mentioned that the bond energies reported here, and those derived by this method in general, will be slightly higher than any experimental estimates because by necessity we use ΣD_e values (*e.g.* the experimental ΣD_0 for benzene is 5464.8 kJ mol^{-1}, compared with our ΣD_e value of 5670 kJ mol^{-1}).

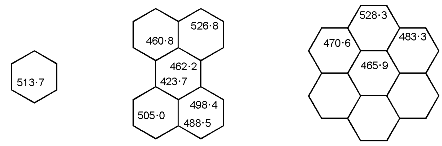

Fig. 2. C–C bond energies (kJ/mol^{-1}) for benzene, perylene and coronene.

To test whether the fitted parameters from our best model are sufficiently general to reproduce atomization energies and hence bond energies for polyacenes not in the fitting set of sixteen compounds, we have optimized four additional molecules at the same level of theory: benz[*a*]anthracene, benzo[*c*]-phenanthrene; benzo[*e*]pyrene and benzo[*g,h,i*]perylene. Indeed, we find that the ten-parameter Morse model reproduces the atomization energies of these compounds to the same accuracy obtained for the compounds present in the fit. So we may conclude that the parameters given here are sufficiently general to predict bond energies for most benzenoid hydrocarbons, with the possible exception of helicenes, where strong steric interactions may need to be explicitly treated in the model.

In addition to providing individual bond energy data, this parameterization procedure leads to a model of the molecules in question whose parameters also lend themselves to chemical interpretation. Consider the harmonic force constant $f = 2\alpha^2 D_e$ computed as the second partial derivative of eqn. (3) with respect to r. The model predicts f for type (i), (ii) and (iii) C–C bonds approximately in the ratio 1.6 : 2.5 : 1.0, information that probably has not been obtained before by any other method, experimental or theoretical.

In conclusion: the method for determining polyatomic molecule bond energies presented here should be applicable to essentially any series of related compounds (not only hydrocarbons); with the proviso that a more detailed treatment of the C–H bond and some types of steric or long-range interactions may be required for some families of compounds.

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