Substituent Effects and the Strengths of Chemical Bonds

By **Vincenzo Barone** * and **Giuseppe Del Re**, Cattedra di Chimica Teorica, Università di Napoli, via Mezzocannone 4, I–80134 Napoli, Italy
Sàndor Fliszàr, Department of Chemistry, University of Montreal, Montreal, Quebec, Canada

The dependence of bond strengths on substituent effects is studied with special reference to organic chemistry, on the basis of a theoretical definition of bond energies obtained from a molecular electronic state represented by one Slater determinant over bond orbitals. Two rules appear to hold: (1) the more negative the sum of the charges on the neighbours of an atom X, the more positive the charge on X, and *vice versa*; (2) the larger the electron populations of the atoms of a bond, the greater the strength of that bond. Values for the energies of a variety of bonds (CC, CO, CN, NN, NO, OO, *etc.*) in different environments have been derived using a semi-empirical version of the general definition, with the two-electron integrals evaluated by a population-dependent formula. The correlation with experimental bond energies is excellent. The possibility of evaluating bond energies in a rather simple way opens up the interesting opportunity of summarizing the theoretical description of a system of localized bonds by a charge and bond-energy diagram. Applications to bond cleavage and protonation problems are illustrated for ketones and polyamines, respectively.

THE chemical and physical behaviour of organic molecules is currently analysed in terms of additive properties of bonds, inductive effects, steric effects, and conjugation. Although this kind of analysis has been used for years especially at an intuitive level, there remains much room for improvement. One problem is to find some specific quantity to represent substituent effects and to see how the properties of bonds are related to changes in that quantity. We are interested in particular in ' inductive effects ' regarded as polarization and charge alternation effects in systems of localized bonds.

In fact, additive rules for the electric dipole moment, the molar refraction, and the heat of formation of a saturated molecule, where the contribution of each bond is assumed to be the same as in any other molecule containing the same bond, make comparison of different molecules very straightforward. Unfortunately, as is well known, such rules hold only in the first order; therefore corrections must be introduced, in particular to allow for inductive effects. This recognizes that, because of some charge transfer from neighbouring atoms, a given bond is not exactly the same in varying environments. More specifically, the ' electronegativities ' of the atoms A and B involved in a bond are affected by their neighbours.

Inductive effects can be incorporated in a very simple quantum-chemical formalism permitting evaluation of charge distributions and *in situ* bond dipole moments for saturated molecules.[1] This provides a picture where the notion of inductive effect is translated into a bond polarization scheme easily amenable at least to semi-quantitative considerations.[2,3] The validity of that point of view has been extensively studied.[4-7]

The relationship between the net charges of the atoms of a bond and quantities other than bond moments, in particular bond energies, has been studied in a series of papers [8-10] where it was shown that the total energy could be split into a sum of charge-dependent bond contributions plus a conformational term. The present paper is devoted to the practical application of this partitioning. In particular we shall treat our theoretical bond energies as measures of bond strengths, in accordance with ideas (discussed in detail by Cottrell [11a] and Sanderson [11b]) associating the strength of a bond with the amount of energy required to break it.[12]

A rigorous theoretical determination of quantities corresponding exactly to bond dissociation energies is complicated because it involves comparison between a molecule and its fragments, in addition to a number of thermodynamic considerations.[13] However, for many purposes, it is enough to require from theory a partitioning of molecular energies that provides some theoretical characterization of each bond of a molecule from the energetic point of view. Comparison with experimental quantities will have to be made in the same spirit as for bond orders and the like, the advantage being that one is dealing with quantities whose physical nature is clear and which are well defined parts of a physical observable.

The required theoretical expression for ' bond strengths ' has been given elsewhere,[8-10] and hence is only briefly summarized in the next section. In the main body of this paper, we show that it is possible to associate in a simple manner specific features of the structure of a molecule with its chemical behaviour.

Good numerical agreement can be obtained; however, attention has been focused on the general trends which can be inferred from the theoretical expression of bond energies, because their identification with experimental bond dissociation energies (considered as a measure of bond strengths) is reasonable, but not free from difficulties. Among other things, considerations of trends has led to simple rules concerning the role of vicinal effects on bond strengths.

Protonation of polyamines and photochemical dissociation of ketones are discussed to illustrate the applications of the general rules and concepts.

Outline of the Theoretical Approach.—The energy of a Slater determinant $|\psi\rangle$ corresponding to a closed shell state with doubly occupied localized molecular orbitals, in the zero differential overlap approximation for the two-electron integrals,[14] is given by equation (1) [8] where

Z_A and Z_B indicate the 'effective core charges' of atoms A and B and R_{AB} their distance, $\boldsymbol{F}$ is the matrix of two-centre Coulomb integrals, and $\boldsymbol{P}_{kl}$ is a column vector, whose μth element is given by equation (2) if the elements $C_{\mu k}$ of $\boldsymbol{C}_k$ are real.

$$\langle\psi|H|\psi\rangle = \sum_{XY}\frac{Z_X Z_Y}{R_{XY}} + 2\sum_{K}\boldsymbol{C}_K{}^{+}\boldsymbol{H}^{\text{core}}\boldsymbol{C}_K + \sum_{Kl}(2\boldsymbol{P}_{KK}{}^{+}\boldsymbol{F}\boldsymbol{P}_{ll} - \boldsymbol{P}_{Kl}{}^{+}\boldsymbol{F}_{PKl}\boldsymbol{P}_{Kl}) \quad (1)$$

$$(\boldsymbol{P}_{kl})_\mu = C_{\mu l}C_{\mu k} \quad (2)$$

Equation (1) can be transformed into an equation where suitable 'bond energies' appear if one uses a localized bond-orbital scheme where the bond orbitals are obtained from an appropriate effective Hamiltonian $\boldsymbol{H}^{\text{eff.}}$, which replaces the $\boldsymbol{H}^{\text{core}}$ of equation (1). The effective Hamiltonian consists: (i) of the part of the core Hamiltonian which relates to the AB bond minus the potential energy terms associated with atoms other than A and B (which go into the non-bonded interaction term), and (ii) of a term representing the shielding effect of the electrons on the nuclei A and B; it incorporates part of the electron repulsion and exchange term of equation (1).[15,16]

TABLE 1

Parameters used in the calculation of charge distributions

Atom	$\delta_A{}^\circ$	m_A	Reference
H	0	1	1
C	0.07	4	1
N	0.24	3	1
O	0.40	2	1
F	0.45	1	3
Cl	0.35	1	1
Br	0.30	1	17
I	0.28	1	3

Bond	η_{AB}	$\gamma_{A(B)}$	$\gamma_{B(A)}$	Reference
HC	1.00	0.40	0.30	1
CC	1.00	0.10	0.10	1
CO	0.95	0.10	0.10	1
OO	0.41	0.10	0.10	
CN	1.0	0.10	0.10	1
NN	1.0	0.10	0.10	
NH	0.45	0.30	0.40	1
CF	0.63	0.20	0.40	3
CCl	0.60	0.20	0.40	1
CBr	0.60	0.20	0.40	17
CI	0.55	0.20	0.40	3

In principle $H^{\text{eff.}}$ could be computed; in practice, we construct it according to the so-called Del Re method.[1] The whole set of parameters adopted here is collected in Table 1 (with the same notation as ref. 1). The correction to the orbital energies to be introduced for obtaining the total energy can be calculated from the eigenvectors of $\boldsymbol{H}^{\text{eff.}}$. Both the term containing $\boldsymbol{H}^{\text{eff.}}$ and the other term can then be partitioned into bond contributions, with the exception of a small part. More precisely, we can write equation (3). Here, the quantity $E^{(AB)}$, written in the form (4), can be interpreted as the

$$\langle\psi|H|\psi\rangle \simeq \sum_{\text{bonds}} E^{(AB)} + \text{n.b.} \quad (3)$$

$$E^{(AB)} \simeq 2\varepsilon^{(AB)} + B_0{}^{(AB)} \quad (4)$$

contribution of the bond AB to the energy of the molecular framework. This contribution consists of two parts: the customary orbital energy term and an 'effective nuclear repulsion' term $B_0{}^{(AB)}$. The latter arises from the core-repulsion and from the repulsion of the electron clouds associated with the atoms participating in the bond. If our calculations were of the Hückel π-electron type, $B_0{}^{(AB)}$ could be practically neglected; with σ bonds, on the contrary, it may have fairly large values. From a formal analysis[18] the 'effective nuclear repulsion' term appears to have the form (5) where Q_A

$$B_0{}^{(AB)} = Z_A Z_B/R_{AB} - (Q_A{}^2/2m_A - P_{A(B)}{}^2)F_{AA} + (Q_B{}^2/2m_B - P_{B(A)}{}^2)F_{BB} + (Q_A Q_B - P_{A(B)}P_{B(A)})F_{AB} \quad (5)$$

and Q_B are the total electron population of the atoms A and B, and $P_{A(B)}$ and $P_{B(A)}$ are the 'bond population' for a single electron occupying the appropriate bond orbital. The quantities F_{AA}, F_{BB}, and F_{AB} are effective two-electron integrals; Z_A and Z_B are 'effective core charges'; m_A and m_B are the numbers of bonds formed by A and B respectively. The term n.b. in equation (3) can be approximately expressed by (6) and is a typical

$$\text{n.b.} \simeq \tfrac{1}{2}\sum_{\substack{XY\\\text{non-bonded}}} q_X q_Y/R_{XY} \quad (6)$$

electrostatic non-bonded interaction term, where the q_X terms are net atomic charges. Additional overlap-dependent terms (standard non-bonded interactions[18]) may be important, especially when the q values are small.

RESULTS AND DISCUSSION

General Rules.—It is now possible to describe the vicinal effect on bond energies in terms of factors governing charge distributions. Two simple rules govern the effect of substituents on the electron populations Q and the effect of Q on the strengths of the corresponding bonds.

Rule 1. As a consequence of 'charge alternation'[1] the electron density on an atom is lowered by electron-richer neighbours. An outcome of the inductive effect is thus that *the more negative the weighted sum of the charges on the neighbours of an atom A, the more positive the charge on A, and conversely*, or, in more familiar terms, *a positive site is favoured when embedded in negative neighbours*. The first three columns of Table 2 illustrate this rule. Substitution of hydrogen atoms on A by methyl groups, whose carbon atoms possess net negative charges, reduces the electron population of A. Therefore, the central carbon atom of the t-butyl group is electron-deficient with respect to a methyl carbon atom. Similarly, the nitrogen atoms of amines and hydrazines are less populated as they are increasingly substituted by methyl groups. This is equivalent to saying, 'avoid, as much as possible, charges of the same sign on neighbouring atoms'. This effect is also apparent on the charges on oxygen when comparing HOOH to CH_3OOCH_3.

TABLE 2

Charges on C–C, O–O, N–N, C–O, and C–N bond-forming atoms and corresponding bond dissociation energies (in kJ mol^{-1})

Molecule A–B	Q_A	Q_B	$D_{calc.}^{(AB)}$	$D_{exp.}^{(AB)}$	Reference *
$H_3C–CH_3$	4.116 57	4.116 57	362.7	358.6	19
$C_2H_5–CH_3$	4.072 58	4.117 57	353.5	354.4	19
i-$C_3H_7–CH_3$	4.029 11	4.118 32	343.9	350.2	19
$C_2H_5–C_2H_5$	4.073 61	4.073 61	343.9	343.9	19
i-$C_3H_7–C_2H_5$	4.030 15	4.073 47	334.7	336.8	19
i-C_3H_7–i-C_3H_7	4.030 94	4.030 94	325.1	325.1	19
HO–OH	2.323 49	2.323 49	213.4	213.4	20
$CH_3O–OCH_3$	2.147 16	2.147 16	150.6	150.6	21, 22
$(CH_3)_3CO–OC(CH_3)_3$	2.158 74	2.158 74	154.4	154.8	21, 23
$C_2H_5O–OH$	2.105 63	2.369 07	182.0	179.9	20
$H_2N–NH_2$	3.471 19	3.471 19	238.9	238.9	19
$CH_3NH–NH_2$	3.287 28	3.479 86	222.2	217.1	19
$(CH_3)_2N–NH_2$	3.124 76	3.486 62	207.5	207.5	19
$CH_3NH–NHCH_3$	3.297 31	3.297 31	206.3	198.3	19
$(CH_3)_2N–NHCH_3$	3.135 88	3.305 16	192.0	187.4	19
$(CH_3)_2N–N(CH_3)_2$	3.144 84	3.144 84	177.8	175.7	19
$H_3C–OH$	4.013 26	2.453 90	386.2	382.8	20
$H_3C–OCH_3$	4.024 86	2.269 17	335.1	334.7	20
$(CH_3)_3C–OCH_3$	3.884 30	2.277 16	318.0	326.3	20
$CH_3–OOC_2H_5$	4.016 40	2.148 32	298.7	301.2	20
$H_3C–NH_2$	4.058 47	3.525 74	329.7	329.7	19
$H_3C–NHCH_3$	4.066 10	3.352 00	307.5	305.0	19
$H_3C–N(CH_3)_2$	4.072 66	3.197 76	287.0	288.3	19

If Q is in atomic units and $F_{AA}°$, $F_{BB}°$, and $F_{AB}°$ in eV, we have K_C 42.68, $N'^{(CC)}$ $-1\,453.1$; K_O 21.05, $N'^{(OO)}$ -613.4; and K_N 14.27, $N'^{(NN)}$ -407.1.

* In the references bond energies are given in kcal mol^{-1}.

The central carbon atom of the t-butyl group is electron-deficient with respect to that of a methyl carbon atom; therefore an atom attached to a t-butyl group is electron richer than when attached to an electron richer methyl carbon atom. Hence, the oxygen atoms in di-t-butyl peroxide are electron richer than in dimethyl peroxide.

Comparison of the results confirms the intuitive notion that the main effect of substitution in compounds R-A-B is found at A and that a much smaller perturbation of charge density is experienced by B, so that, knowledge of the effect of α-substitution turns out to be generally sufficient for an estimate of the overall substituent effect on ' bond strength '.

Rule 2. The *energy of a bond is greater the higher the electron population of the atoms forming the bond.* In other words, an increasingly positive character on the bonded atoms lowers the bond strength, as the nuclear repulsion term becomes more important. This is in line with commonsense chemistry whose basic tenet could be expressed as follows: ' insert (shielding) electrons between nuclei in order to form bonds '.

The above rule can be translated into numerical results by further developing equations (3)—(5). For practical applications of equation (4), it may be useful to refer to ' bond atomization energies ' $D_{\text{bond}}^{(AB)}$ which correspond to $E_{\infty}^{(AB)}$ (the value which $E_{\text{bond}}^{(AB)}$ would have for infinite separation of the nuclei) minus $E_{\text{bond}}^{(AB)}$. This quantity is given by the equation (7) where $N^{(AB)}$ is the

$$\begin{aligned} D_{\text{bond}}^{(AB)} = N^{(AB)} + (Q_A{}^2/2m_A - P_{A(B)}{}^2)F_{AA} + \\ (Q_B{}^2/2m_B - P_{B(A)}{}^2)F_{BB} + \\ (Q_AQ_B - P_{A(B)}P_{B(A)})F_{AB} - 2\varepsilon^{(AB)} \end{aligned} \quad (7)$$

value of $E_{\text{bond}}^{(AB)}$ at infinity minus the core repulsion term.

Calculation of the orbital energies $\varepsilon^{(AB)}$, using the method of ref. 1, indicates no major variations in that term for a given bond under different environments. Hence, the term $2\varepsilon^{(AB)}$ may be incorporated into the constant term. Furthermore, for small charge separation, $P_{A(B)} = P_{B(A)} \simeq 0.5$. In molecules which are

TABLE 3

Electron population of C–C bond-forming atoms and corresponding bond dissociation energies. The charges are calculated following ref. 1 with the parameters of Table 1. The $D_{\text{exp}}^{(CC)}$ values are extracted from ref. 19 *

Molecule				Method 1		Method 2		Method 3		Method 4	
A–B	Q_A	Q_B	$D_{exp.}^{(CC)}$	$D^{(CC)}$	$\Delta\%$	$D^{(CC)}$	$\Delta\%$	$D^{(CC)}$	$\Delta\%$	$D^{(CC)}$	$\Delta\%$
$H_3C–CH_3$	4.116 57	4.116 57	358.6	358.6	0	358.6	0	358.6	0	358.6	0
$C_2H_5–CH_3$	4.072 58	4.117 57	354.4	351.5	−0.83	354.8	0.08	354.4	0	352.3	−0.59
$C_2H_5–C_2H_5$	4.073 61	4.073 61	343.9	351.5	2.19	351.0	2.10	350.6	1.93	346.9	0.85
i–$C_3H_7–C_2H_5$	4.030 15	4.073 47	336.8	333.9	−0.87	337.2	0.17	336.8	0	335.1	−0.50
i–C_3H_7–i–C_3H_7	4.030 94	4.030 94	325.1	323.4	−0.51	323.8	−0.36	323.8	−0.36	325.1	0

Q_A, Q_B in atomic units; $D^{(CC)}$ in kJ mol^{-1}; F_{AA} and F_{AB} in eV, $\Delta\% = [(D_{calc.}^{(CC)} - D_{exp.}^{(CC)})/D_{exp.}^{(CC)}] \times 100$.

Method 1, $F_{AA}° = I_V - A_V$ of ref. 25*a*, $F_{AB}°$ from ref. 24*b*, K_A 44.48
Method 2, $F_{AA}°$ from ref. 24*a*, $F_{AB}°$ from ref. 24*b*, K_A 38.24
Method 3, $F_{AA}°$ from ref. 28, $F_{AB}°$ from ref. 24*b*, K_A 34.52
Method 4, $F_{AA}°$ from ref. 28, $F_{AB}°$ from ref. 25*b*, K_A 31.05

$$F_{AA} = F_{AA}° - K_Aq_A$$

* In ref. 19 the experimental bond energies are given in kcal mol^{-1}.

symmetric about the bond under consideration $P_{A(B)} = P_{B(A)} = 0.5$ With these approximations, equation (7) becomes (8) where $N'^{(AB)} = N^{(AB)} - 2\varepsilon^{(AB)} - (F_{AA} + F_{BB} + F_{AB})/4$.

$$D_{\text{bond}}^{(AB)} = N'^{(AB)} + (Q_A{}^2F_{AA}/2m_A + Q_B{}^2F_{BB}/2m_B + Q_AQ_BF_{AB}) \quad (8)$$

The variable term in equation (8) describes the major charge effect on chemical bonds. For numerical tests the one- and two-centre two-electron integrals for neutral atoms $F_{AA}°$, $F_{BB}°$, and $F_{AB}°$ have been estimated according to a wide variety of well known semi-empirical recipes.[24,25] The necessary bond lengths have been taken as follows: C–C 154, C–O 145, C–N 150, O–O 144, N–N 147 pm. Especially for polar molecules, an explicit dependence of one-centre two-electron integrals on atomic charges allows an improvement in semi-empirical SCF procedures.[26,27] Two formulae (9) and (10) were tested here. In Table 3 are summarized the

$$F_{AA}(q) = F_{AA}° - K_Aq_A \quad (9)$$

$$F_{AA}(q) = F_{AA}°K_A/Q_A \quad (10)$$

results obtained for C–C bonds by equation (9) with a variety of choices for $F_{AA}°$ and $F_{AB}°$. Despite the good correlation between experimental and theoretical bond energies, equation (10) was found to be preferable in the case of heteronuclear bonds and allows further simplification of equation (8).

In fact, assuming for the two-centre two-electron integrals F_{AB} the form (11a) suggested by equation (10)

$$F_{AB} = F_{AB}°\sqrt{K_AK_B/Q_AQ_B} \quad (11a)$$

$$N'^{(AB)} = \sqrt{N'^{(AA)}N'^{(BB)}} \quad (11b)$$

and for the constant $N'^{(AB)}$ the form (11b) equation (8) becomes (12). In equation (12) there are two parameters for each kind of atom ($N'^{(AA)}$ and K_A); if these parameters are chosen so as to fit experimental bond energies for homonuclear bonds, no further parameters are needed for heteronuclear bonds. This is, thus, a decisive test for the reliability of the approximations introduced in deriving formula (12).

$$D_{\text{bond}}^{(AB)} = \sqrt{N'^{(AA)}N'^{(BB)}} + Q_AK_AF_A°/2m_A + Q_BK_BF_B°/2m_B + \sqrt{Q_AQ_BK_AK_BF_{AB}°} \quad (12)$$

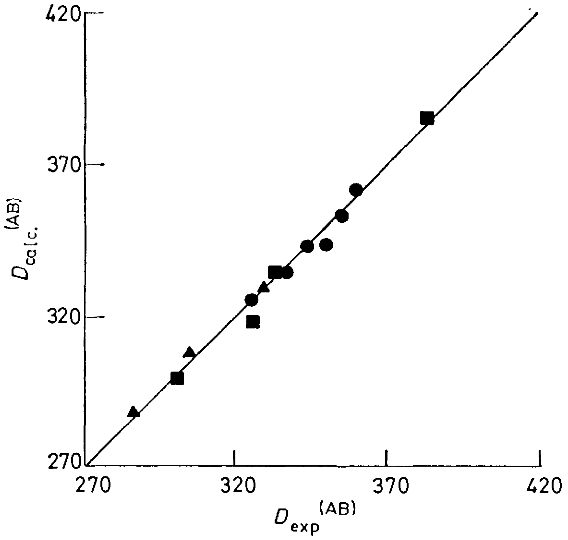

FIGURE 1 A comparison between theoretical bond energies ($D_{calc.}^{(AB)}$) and experiment ($D_{exp.}^{(AB)}$) for ●, C–C; ■, C–O; and ▲, C–N bonds. All values are in kJ mol^{-1}

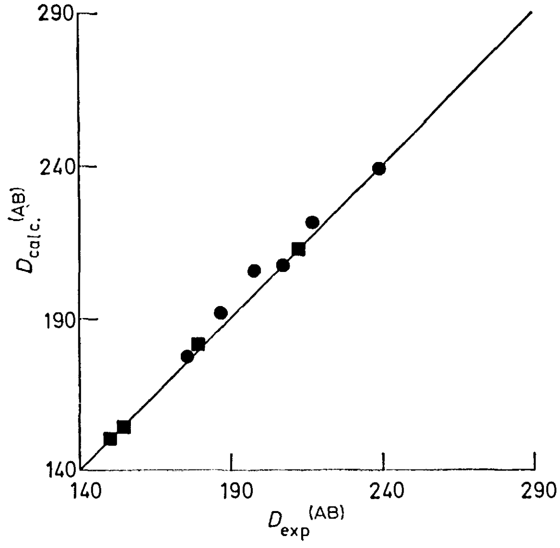

FIGURE 2 The same comparison as in Figure 1 for ●, N–N and ■, O–O bonds

Bonds formed by C, N, *and* O *Atoms*.—The results obtained by use of equations (12) are summarized in Table 2 for a large variety of C–C, C–O, C–N, O–O, and N–N bonds. The $F_{AA}°$ and $F_{AB}°$ values adopted are taken from refs. 24*a* and 24*b*, but the results are largely insensitive to the particular choice of two-electron integrals. As one might expect, the calculated and experimental values are different, but the correlation is good. Its quality is perhaps better evidenced in Figure 1 for C–C, C–O, and C–N bonds. The straight line in the Figure has slope 1, which corresponds to a perfect correlation between calculated and experimental results. It is encouraging that the correlation is as good for C–N and C–O (heteronuclear bonds, no adjustable parameters) as for C–C bonds.

Figure 2 is the analogue of Figure 1 for O–O and N–N bonds. The results are in line with the assumed smallness of terms between non-bonded atoms and approximate transferability of bond properties. The changes shown in Figures 1 and 2 may be viewed as resulting from ' fine tuning ' by the substituents attached to the atoms forming the bonds.

It is interesting to note that in all the examples studied equation (12) is practically equivalent to (8) with F_{AA}, F_{BB}, and F_{AB} equal to $F_{AA}°$, $F_{BB}°$, and $F_{AB}°$, but with net charges reduced to 15% of the values obtained by direct use of the parameters of Table 1. This rule of thumb may be useful when experimental data for calibrating the adjustable parameters of equation (12) are not available. This recipe has already been used with encouraging results.[29]

Straightforward application of rules 1 and 2 permits a quick qualitative evaluation of substituent effect on bond energies. For example, multiple substitution of H by CH_3 in hydrazines (Table 3) decreases the charges Q on the nitrogen atoms (rule 1) and, consequently, lowers the N–N bond energy (rule 2). In di-t-butyl peroxide, as compared with dimethyl peroxide, the relatively lower charge on the carbon atoms attached to oxygen raises the charge on O (rule 1) and, hence, the O–O bond strength (rule 2).

Carbon–Hydrogen Bonds.—In alkanes R–H (where R = CH_3, C_2H_5, i-C_3H_7, and t-C_4H_9), rule 1 predicts that the charge on the carbon atom attached to H decreases in the order CH_3 . . . t-C_4H_9. Hence $D^{(CH)}$ is expected to decrease in the same order. This expectation is confirmed by the experimental results: $D^{(CH)}$ 435.1 (R = CH_3),[30] 410.0 (R = C_2H_5),[31] 395.4 (R = i-C_3H_7),[32] and 380.3 kJ mol^{-1} (R = t-C_4H_9).[33] The replacement of a hydrogen atom of methane by chlorine reduces Q_C^1 and consequently (rule 2) the C–H bonds weaken from 435.1 (CH_4) to 410.0 kJ mol^{-1} in chloromethane.[34]

Photochlorination experiments[34] indicate a monotonic decrease in the C–H bond dissociation energies in the order CH_2Cl–H > $CHCl_2$–H > CCl_3–H. Similarly, photobromination experiments[35] indicate a lower bond dissociation energy in tribromomethane than in bromomethane. Finally, Q_C decreases when going from H–CH_2OH to H–$CH(CH_3)OH$[1] as predicted by rule 1. Rule 2 thus explains the concurrent decrease in the C–H bond dissociation energies by *ca.* 17 kJ mol^{-1}.[36]

Nitrogen–Hydrogen Bonds.—Rule 1 predicts that the charge on a nitrogen atom attached to hydrogen decreases as the number of methyl substituents is increased. Experimental bond dissociation energies[19] confirm the trend predicted by rule 2, as $D^{(CH)}$ decreases in the order 430.5 (NH_3), 381.2 (NH_2CH_3), and 362.8 kJ mol^{-1} [$NH(CH_3)_2$].

Carbon–Halogen Bonds.—From an analysis of the effect of fluorine atoms as substituents on the strength of various bonds in organic molecules, Vedenejev *et al.*[37] concluded that the strength of C–F bonds in monofluoroalkanes R–F decreases in the order R = CH_3 > C_2H_5 > i-C_3H_7 > t-C_4H_9 from *ca.* 494 to 435 kJ mol^{-1}. This ordering is in line with the above rules, since the central carbon atom in the t-butyl group is electron deficient with respect to the methyl carbon atom, thus giving rise (rule 2) to a stronger C–F bond when R = CH_3 than for R = t-C_4H_9. For the same reasons, the C–Cl bond is weaker in i-C_3H_7Cl (306.7 ± 9.6 kJ mol^{-1})[38] than in CH_3Cl (336.8 ± 12.6 kJ mol^{-1}).[39] Similar trends are also described by Cottrell[11a] for the iodine analogues R–I, for which the C–I bond dissociation energy decreases in the order R = CH_3 > . . . > t-C_4H_9 from *ca.* 226 to *ca.* 188 kJ mol^{-1}. The effect of replacing a hydrogen atom by an electron-withdrawing phenyl group is also interesting in connection with the present discussion. In $PhCH_2$–I the phenyl group is expected to decrease the electron density at the atom attached to iodine, hence to weaken the C–I bond with respect to methyl iodide. This is indeed observed, as the bond dissociation energy drops from *ca.* 226 in CH_3I to *ca.* 163 kJ mol^{-1} in $PhCH_2I$.[39,40] A similar effect is also observed for C–Cl bonds when the hydrogen atoms of chloromethane are replaced by phenyl groups. The electron density at the carbon atom attached to chlorine is expected to decrease as the number of electron-withdrawing phenyl substituents is increased. The trends in bond dissociation energies thus anticipated are confirmed by experimental results: 336.8 (CH_3Cl),[39] 252.7 ($PhCH_2Cl$),[39] 234.3 (Ph_2CHCl),[39] and 200.8 kJ mol^{-1} (Ph_3CCl).[40] Of course, the observed trends may also be ascribed to stabilization of free radicals by the phenyl groups; here we do not pause on that point, for a discussion of the relative importance of bond weakening and resonance stabilization of free radicals is outside our present scope.

Results similar to those just discussed for phenyl substitution in chloromethanes are also observed for replacement of hydrogen atoms by halogens (other than fluorine). Thus, when the hydrogen atoms in CH_3Cl are replaced by chlorine, the C–Cl bonds weaken with increasing substitution from 336.8 (CH_3Cl)[39] to *ca.* 280 kJ mol^{-1} in CCl_4.[36]

The same trends are also shown by C–Br bonds whose bond dissociation energies decrease monotonically from *ca.* 280 for CH_3Br to *ca.* 205 kJ mol^{-1} for CCl_3Br,[41] with increasing bromine substitution. All the substituent effects reported hitherto for bond dissociation energies obey rules 1 and 2: only fluorine substitution seems to provide an exception. Thus, investigations by Rabinowitsch and Reed[42] suggest that $D^{(CF_3-Cl)} \simeq D^{(CH_3-Cl)} \simeq 335$ kJ mol^{-1}. This remark, however, does not affect conclusions regarding C–F bond strengths in monofluoroalkanes R–F, where C–F bond strengths apparently depend mainly on the properties of the alkyl groups, and follow rules 1 and 2.

Further Applications of Bond Energies.—The possibility of evaluating bond energies in a rather simple way opens up the interesting opportunity of summarizing the theoretical description of a system of localized bonds by a charge and bond-energy diagram. In such diagrams bond orders are replaced by bond energies, to which the standard interpretation of bond orders can be extended, with a gain in physical significance. Figure 3 shows some examples.

In Figure 4, the role of substituents in the photodissociation of ketones is considered: the weakest bond is found to be one involving the C=O carbon atom, in agreement with experiment.[43] The bond energy diagrams also allow prediction of the specific bond which will be cleaved in asymmetric ketones.[44]

Bond energies can also be used to predict enthalpies

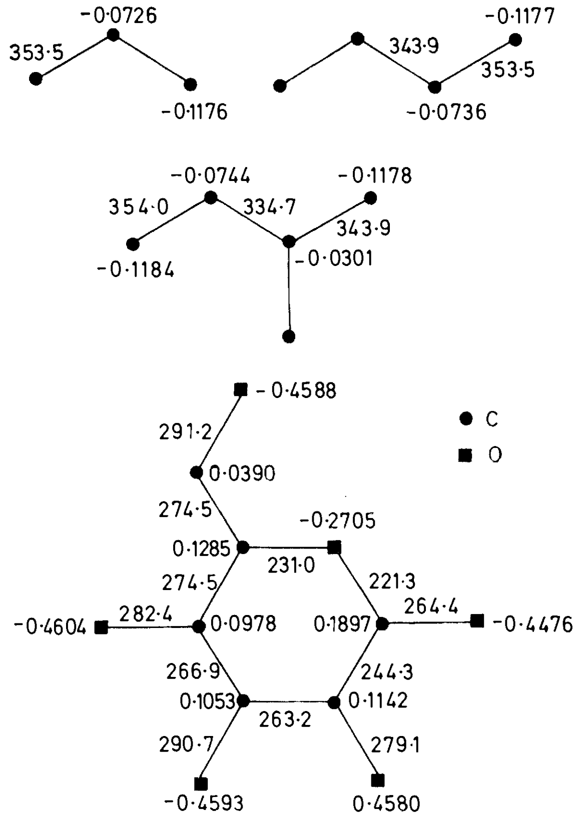

FIGURE 3 Three simple and one less simple example of application of charge and bond energy diagrams

of formation. A discussion of the trend of protonation ΔH° of diamines illustrates this remark. Table 4 summarizes the experimental protonation enthalpies of some diamines.

If one accepts the reasonable assumption that ΔH° values are related to $\overset{+}{\mathrm{N}}$–H bond energies, it is possible to explain the trend of enthalpies by rules 1 and 2. Thus, rule 1 predicts that the charge on a nitrogen atom attached to a proton decreases as the number of methyl substituents is increased. Experimental enthalpies confirm the trend predicted by rule 2, as $|\Delta H^\circ|$ (and hence $D^{(\mathrm{NH})}$) decreases in going from example 1 to 4 in Table 4. The same happens for nitrogen atoms with more electronegative neighbours (*cf.* examples 1, 2, 4 respectively with 5, 3, 6 in Table 4). Finally, removal of the electronegative group NH_2 increases the $\overset{+}{\mathrm{N}}$–H bond energy (*cf.* examples 1 and 2).

TABLE 4

Experimental protonation enthalpies of some diamines (in kJ mol^{-1}). $\Delta H_{\mathrm{exp}}^\circ$ refers to the reaction $L + H^+ \longrightarrow LH^+$

	Ligand (L)	$-\Delta H_{\mathrm{exp}}^\circ$ *	Reference
1	$H_2N(CH_2)_2NH_2$	50.96	46
2	$H_2N(CH_2)_5NH_2$	57.99	46
3	$H_2N(CH_2)_2O(CH_2)_2NH_2$	50.67	47
4	$(H_3C)NH(CH_2)_2NH_2$	47.07	48
5	$H_3{}^+N(CH_2)_2NH_2$	45.61	46
6	$H_3{}^+N(CH_2)_2NHCH_3$	43.26	48

* In the references the ΔH° values are given in kcal mol^{-1}.

Limitations and Extensions.—The application of the bond energy concept suffers from the well known difficulty that activation energies (not to speak of entropies) often play a major role in the observed reactive behaviour of molecules. That difficulty is not specific to our theoretical analysis and a discussion of it is outside the scope of this paper.

On the other hand, examples of situations where bond energies are significant for elucidating reaction mechanisms are known; in particular they may be useful in analysing proposed (or known) transition complexes. In such cases the present treatment takes inductive effects and structural features into account through a sort of ' fine tuning ' of bond energies.

The theoretical method adopted to define bond energies is applicable even to a sophisticated *ab initio* scheme, provided a set of bond orbitals is used to construct the final Slater determinant (or determinants). Such a set can always be defined over a basis of hybrid orbitals obtained by some convenient method. The *ab initio* version of PCILO,[49,50] however delicate in practical use, is an example of a very general theoretical *ab initio* scheme within which our definitions hold. Of course, after optimization of bond orbitals, the PCILO method would also take into account bond-bond charge transfers and correlation. These effects are higher order corrections to the bond energy concept. In particular the role of correlation energies remains somewhat un-

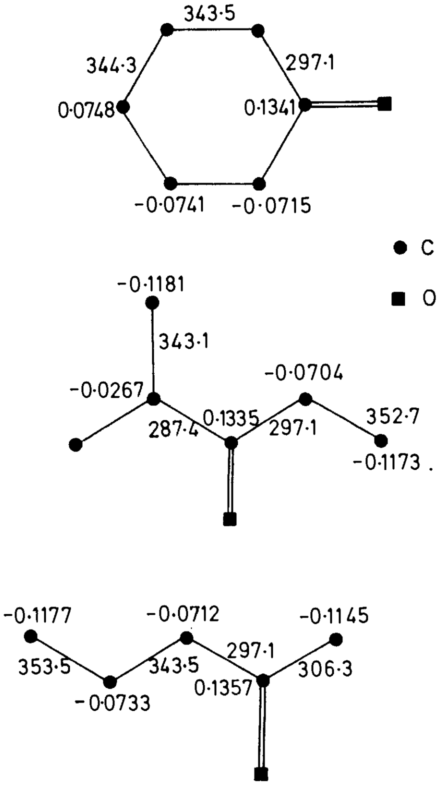

FIGURE 4 Charge and bond energy diagrams for different ketones. The π contributions to charges are not included, but they can be easily computed by a suitable method [45]

certain. The intra-bond correlation energy can, of course, be included in the definition; the inter-bond contributions are by definition outside the scope of the bond model. Published studies on the correlation problem[51] suggest that the former is very much constant for a given type of bond in different environments; moreover, our procedure for estimating two-electron integrals corresponds to using a reduced bond polarity for evaluating bond energies which is precisely what would result from explicit inclusion of an intra-bond correlation.

However, the limitation inherent in the use of a strict localized-bond description is there: direct bond–bond coupling can be responsible for very important aspects of the behaviour of a molecule. Nevertheless the present model has two decisive advantages: conceptually it allows (at least in principle) a clear-cut distinction between what can be explained in terms of a pure localized scheme and delocalization effects; practically it usually gives a satisfactory description of many features of the molecular reality because for most molecules direct (through-space) bond–bond coupling is really a minor correction.

In view of the above considerations and of the fact that analyses of *ab initio* results in terms of partial contributions to energy have been published,[52,53] it might be interesting to carry out in practice an *ab initio* version of the present study; it remains to be seen whether or not it would add to the validity and significance of the general conclusions.

Conclusions.—This study has shown that it is possible to combine quantum mechanical considerations and the chemical bond concept to define theoretical bond energies based on a simple orbital scheme and to rationalize their dependence on substituent effects in terms of very simple rules. The excellent numerical agreement between experiment and theory supports the validity of the definition and the intuitive expectation that direct bond–bond interactions are negligible in most unconjugated molecules.

The rules suggested above can play the role of general guidelines, as *e.g.* Taft's rules, for they permit a quick qualitative prediction of environment effects on the charges and strengths of a number of bonds; the charge and bond energy diagrams proposed appear to compete very effectively in information content with the standard charge and bond-order diagrams.

The examples of protonation of polyamines and photochemical fragmentation of ketones suggest that the scope of the theoretical considerations is quite broad. The very short computing times needed for obtaining reliable results indicate that even extension of the quantitative aspects to very large molecules presents no difficulty.

Further elaboration of the theoretical scheme is certainly possible: however, it is not certain that it would be especially useful. Indeed, the most important conclusion that should perhaps be drawn from the above results is that there remains much room for attempts to apply quantum theoretical schemes to shape simple tools for interpretive and predictive purposes.

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