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Remote Substituent Effects on Polar and Non-polar Covalent Bonds

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In this work the homolytic Z–X bond dissociation energies (BDE, E_d) for 48 molecules with the general formula 4-Y-C_6H_4-Z-X have been calculated by means of AM1 and PM3 semi-empirical quantum chemical methods. The BDEs and the remote substituent effects of Y on the Z–X BDEs have been compared with previously published data in terms of both relative and absolute accuracy. The relative accuracy is found to be rather good concerning the BDEs of the unsubstituted compounds calculated at the UHF level. At the RHF level, employing half-electron energies for the radicals, the absolute accuracy is also acceptable. The relative accuracy for the remote substituent effects is found to be rather poor. Both the substituent effects and the absolute BDEs are markedly weaker at the UHF level than those published in previous work. At the RHF level the absolute BDEs are close to the published data, but the substituent effect is still weaker.

The final part of this work deals with the experimentally established fact that remote substituent effects on Z–X BDEs change with the polarity of the Z–X bond. Relationships derived for simple molecules based on electronegativity have been used to explore this phenomenon qualitatively. This study shows that the change in remote substituent effect with bond polarity can very well be accounted for by relationships of this kind.

A key property of the chemical bond is the energy required for bond cleavage, the bond dissociation energy (BDE, E_d). Covalently bonded atoms or radicals can dissociate heterolytically [reaction (1)] or homolytically [reaction (2)] yielding an ion pair or a radical pair, respectively.

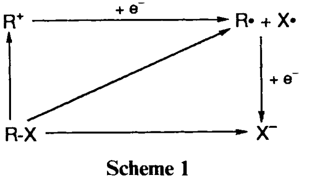
$$\text{R-X} \longrightarrow \text{R}^+ + \text{X}^- \qquad (1)$$

$$\text{R-X} \longrightarrow \text{R}^\bullet + \text{X}^\bullet \qquad (2)$$

The homolytic and heterolytic BDEs are related internally *via* the ionisation potential, *I*, and the electron affinity, *A*, of R$^\bullet$ and X$^\bullet$ [eqn. (3)].[1] This relationship is only valid under ideal

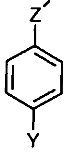
$$E_d(\text{R-X} \longrightarrow \text{R}^\bullet + \text{X}^\bullet) = E_d(\text{R-X} \longrightarrow \text{R}^+ + \text{X}^-) - I(\text{R}^\bullet) + A(\text{X}^\bullet) \qquad (3)$$

conditions, *i.e.* in the gas phase at low pressure. In solutions, however, the energy required for heterolysis is very much dependent on the solvent while that for homolysis is roughly invariable with the solvent. This is owing to the strong solvation of ions. Using solvation energies along with the reduction and oxidation potentials of the cation (R$^+$) and the anion (X$^-$), respectively, the BDE for homolysis can be calculated from heterolysis data (Scheme 1).[2,3] Employing thermodynamic cycles both electrochemical and radiation chemical methods have been made useful for BDE determinations. These methods have principally been used to determine R-H BDEs[4] of aromatic compounds, *e.g.* phenolic O–H bonds[5,6] and anilinic N-H bonds.[7,8]



Scheme 1

The increasing amount of experimental BDE data has served as a basis for structure–activity relationships useful both for predictions of unknown BDEs and for the understanding of the nature of chemical bonds.[5–12]



Remote substituent effects on BDEs have often been shown to follow linear free energy relationships. For several compounds with the general formula 4-Y-C_6H_4-Z-X, the Z-X BDEs have been shown to depend linearly on the Brown σ_p^+ constant[13] or the Hammett σ_p constant[13] of the substituent, Y [eqn. (4)]. BDE_0 is the bond dissociation energy for the

$$E_d = E_{d_0} + \rho^+\sigma_p^+ \qquad (4)$$

parent compound in a certain family of compounds, *i.e.* Y = H, and ρ^+ (or ρ) is a family specific constant.

For different Z and/or X the substituent dependence, ρ^+, on the Z-X BDE varies. This variation has been suggested to be dependent on the difference in electronegativity ($\chi_z - \chi_x$) between the two atoms involved in the covalent bond, *i.e.* the bonding atoms of Z and X.[11] Such a dependence was suggested to imply that the remote substituent affects mainly the parent rather than the radical product of homolysis. In a recent work we tested this hypothesis against experimental data.[8] The data agreed fairly well and the resulting equation [eqn. (5)] can thus be used to estimate the slopes, ρ^+, of the linear free energy relationships describing the substituent dependence.

$$\rho^+ = -11.3 + 30.3\,\Delta\chi_{\text{Pauling}} \qquad R^2 = 0.98 \qquad (5)$$

In this work we have employed AM1[14] and PM3[15] semiempirical quantum chemical calculations to determine the Z-X BDEs for a number of molecules with the general formula 4-Y-C_6H_4-Z-X. The resulting BDEs have been qualitatively and quantitatively compared with previously published data in terms of absolute values and remote substitution effects.

In addition, the Z-Z BDEs of some molecules with the

Table 1 Z–X Bond dissociation energies (kJ mol^{-1})

4-Y–C$_6$H$_4$–Z–X	E_d(UHF)$_{PM3}$	E_d(RHF)$_{PM3}$	E_d(UHF)$_{AM1}$	E_d(RHF)$_{AM1}$	$E_{d,lit}$
4-NH$_2$–C$_6$H$_4$–CH$_2$–H	321	378	314	373	
4-OH–C$_6$H$_4$–CH$_2$–H	320	378	316	374	
4-CH$_3$–C$_6$H$_4$–CH$_2$–H	323	379	313	376	
Ph–CH$_2$–H	325	379	316	375	368[16]
4-CF$_3$–C$_6$H$_4$–CH$_2$–H	326	380	321	376	
4-NO$_2$–C$_6$H$_4$–CH$_2$–H	321	381	321	377	
4-NH$_2$–C$_6$H$_4$–CH$_2$–CH$_3$	220	304	222	265	
4-OH–C$_6$H$_4$–CH$_2$–CH$_3$	236	303	246	309	
4-CH$_3$–C$_6$H$_4$–CH$_2$–CH$_3$	236	304	249	312	
Ph–CH$_2$–CH$_3$	239	304	249	312	318[17]
4-CF$_3$–C$_6$H$_4$–CH$_2$–CH$_3$	240	305	251	313	
4-NO$_2$–C$_6$H$_4$–CH$_2$–CH$_3$	235	306	251	314	
4-NH$_2$–C$_6$H$_4$–CH$_2$–Br	174	242	181	248	
4-OH–C$_6$H$_4$–CH$_2$–Br	174	242	182	248	
4-CH$_3$–C$_6$H$_4$–CH$_2$–Br	176	240	184	249	250[11]
Ph–CH$_2$–Br	177	239	184	248	248[11]
4-CF$_3$–C$_6$H$_4$–CH$_2$–Br	175	237	183	244	
4-NO$_2$–C$_6$H$_4$–CH$_2$–Br	174	236	182	245	
4-NH$_2$–C$_6$H$_4$–NH–H	322	362	331	351	354[8]
4-OH–C$_6$H$_4$–NH–H	324	376	334	388	
4-CH$_3$–C$_6$H$_4$–NH–H	326	373	339	411	365[8]
Ph–NH–H	327	370	342	383	367[8]
4-CF$_3$–C$_6$H$_4$–NH–H	321	391	323	410	385[8]
4-NO$_2$–C$_6$H$_4$–NH–H	342	380	357	397	
4-NH$_2$–C$_6$H$_4$–S–H	332	371	313	348	
4-OH–C$_6$H$_4$–S–H	334	370	318	355	
4-CH$_3$–C$_6$H$_4$–S–H	337	374	321	360	
Ph–S–H	339	375	324	362	330[18]
4-CF$_3$–C$_6$H$_4$–S–H	346	384	331	373	
4-NO$_2$–C$_6$H$_4$–S–H	350	390	334	379	
4-NH$_2$–C$_6$H$_4$–S–CH$_3$	250	296	240	279	
4-OH–C$_6$H$_4$–S–CH$_3$	251	295	244	287	
4-CH$_3$–C$_6$H$_4$–S–CH$_3$	256	299	234	292	
Ph–S–CH$_3$	256	300	250	294	279[19]
4-CF$_3$–C$_6$H$_4$–S–CH$_3$	266	310	259	306	
4-NO$_2$–C$_6$H$_4$–S–CH$_3$	268	317	264	313	
4-NH$_2$–C$_6$H$_4$–O–H	308	347	312	346	316[5]
4-OH–C$_6$H$_4$–O–H	309	348	320	356	336[5]
4-CH$_3$–C$_6$H$_4$–O–H	316	359	327	369	360[5]
Ph–O–H	320	365	331	376	369[5]
4-CF$_3$–C$_6$H$_4$–O–H	333	377	342	387	
4-NO$_2$–C$_6$H$_4$–O–H	340	384	346	392	394[5]
4-NH$_2$–C$_6$H$_4$–O–CH$_3$	177	218	194	231	254[10]
4-OH–C$_6$H$_4$–O–CH$_3$	180	225	201	241	
4-CH$_3$–C$_6$H$_4$–O–CH$_3$	186	236	207	255	258[10]
Ph–O–CH$_3$	191	242	211	262	266[10]
4-CF$_3$–C$_6$H$_4$–O–CH$_3$	203	254	221	274	
4-NO$_2$–C$_6$H$_4$–O–CH$_3$	210	261	227	279	271[10]

general formula (4-Y–C$_6$H$_4$–Z)$_2$ have been determined using the PM3 method. This was done to estimate qualitatively the effects of remote substitution on non-polar Z–Z bonds.

Finally, we have discussed the possibility of incorporating remote substituent effects into established empirical methods for prediction of BDEs, based on the concepts of electronegativity and hardness. We have also explored the potential of these equations in reproducing the variation of remote substituent dependence with bond polarity.

Methods

The semiempirical quantum chemical calculations were performed on a VAX 6000-310 running MOPAC version 6.0. The starting geometries were created graphically and roughly optimised, using molecular mechanics. The MOPAC calculations were performed at the UHF level. However, since one of the referees pointed out the benefits of using half-electron energies rather than UHF energies for the radicals we also performed most calculations accordingly. The Z–X and Z–Z BDEs were calculated from the heats of formation of the parent compound and the corresponding radicals according to eqn. (6).

$$E_d = H_f(Z^\bullet) + H_f(X^\bullet) - H_f(Z\text{–}X) \qquad (6)$$

The following Z–X and Z–Z couples were treated: CH$_2$–H, CH$_2$–CH$_3$, CH$_2$–Br, NH–H, S–H, S–CH$_3$, O–H and O–CH$_3$ and NH–NH, CH$_2$–CH$_2$ and S–S, respectively. The 4-substituents, Y, were NH$_2$, OH, CH$_3$, H, CF$_3$ and NO$_2$. The calculated heats of formation are available as supplementary material.*

Results and Discussion

Z–X Bonds.—Table 1 compiles the resulting Z–X BDEs, based on the MOPAC calculations, and the corresponding values found in the literature.

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* For details of the Supplementary Publications Scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1 [Supp. Pub. No. 57030 (6 pp.)].

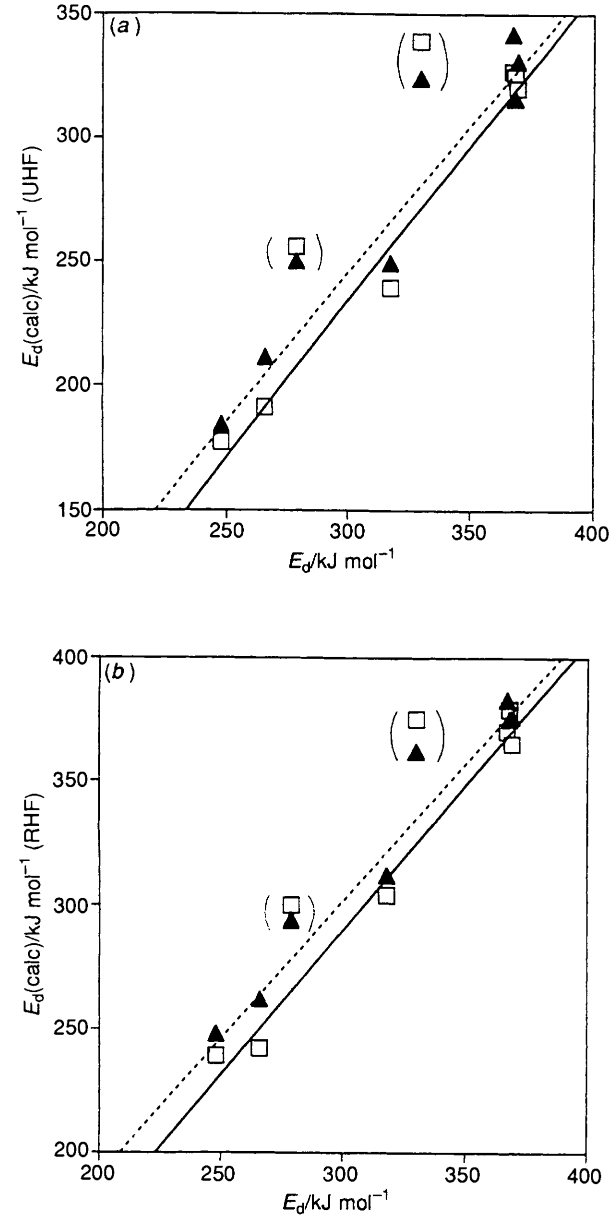

Fig. 1 BDEs for (from left to right in the figure) Ph-CH_2-Br, Ph-O-CH_3, Ph-S-CH_3, Ph-CH_2-CH_3, Ph-S-H, Ph-NH-H, Ph-CH_2-H and Ph-O-H calculated using (*a*) UHF AM1 (▲) and PM3 (□); (*b*) RHF AM1 (▲) and PM3 (□) semiempirical quantum chemical methods plotted against the corresponding literature data. The symbols for sulfur containing bonds in (*a*) and (*b*) are bracketed.

The quantitative and qualitative accuracies in estimating the absolute BDEs of Z-X bonds were checked by comparing the results of the parent compounds, Y = H, with the corresponding experimentally established data found in the literature [Fig. 1(*a*) (UHF) and 1(*b*) (RHF)]. As can be seen in Fig. 1(*a*) the results from the UHF AM1 and PM3 calculations qualitatively agree fairly well with the previously published BDEs. The BDEs calculated from the results of the RHF AM1 and PM3 calculations (half-electron energies used for the radicals) agree much better quantitatively. For instance, the C-Br BDE of benzylbromide calculated using the AM1 method at the RHF level is identical to the experimentally found value. However, calculated BDEs, where sulfur (S) is one of the binding atoms, seem to deviate from the general trend by being much closer to published values at the UHF level and by being higher than the published values at the RHF level. The linear least-squares fits given in Fig. 1(*a*) and 1(*b*) are based on the non-sulfur containing bonds and, as can be seen, the lines fit very well to the remaining data [eqns. (7a) (UHF), (7b) (RHF), (8a) (UHF) and (8b) RHF)].

$$E_{d,PM3} = -144.11 + 1.26\,E_{d,lit} \quad (\text{kJ mol}^{-1}) \quad (R^2 = 0.98) \qquad (7a)$$

$$E_{d,PM3} = -61.0 + 1.17\,E_{d,lit} \quad (\text{kJ mol}^{-1}) \quad (R^2 = 0.98) \qquad (7b)$$

$$E_{d,AM1} = -114.95 + 1.20\,E_{d,lit} \quad (\text{kJ mol}^{-1}) \quad (R^2 = 0.97) \qquad (8a)$$

$$E_{d,AM1} = -31.3 + 1.11\,E_{d,lit} \quad (\text{kJ mol}^{-1}) \quad (R^2 = 0.99) \qquad (8b)$$

The absolute values of the BDEs based on the UHF calculations are much lower than the experimental values with the exception of sulfur containing bonds. This can be accounted for by the relatively low radical heats of formation (due to spin contamination) calculated by the MOPAC program at the UHF level. The $\hat{S}^2$ values for the UHF calculations on the radicals were in the order of 0.93 to 1.24 indicating spin contamination ($\hat{S}^2 = 0.75$ if no spin contamination).

In Figs. 2(*a*) and 2(*b*) the resulting remote substituent effects, ρ^+, based on the Brown $\sigma_p{}^+$ constant are plotted against experimentally derived effects of remote substitution on O-H,[12] C-H,[16] C-Br,[11] N-H[8] and C-O[10] bonds. The UHF PM3 BDE of 4-NO_2-C_6H_4-CH_2-H was excluded when estimating the substituent dependence on benzylic C-H bonds, since it deviated markedly from the general trend.

The trends are similar for both the AM1 and the PM3 method at both levels but the linear fits between calculated and experimental values are very poor, as can be seen [eqns. (9a) (UHF), (9b) (RHF), (10a) (UHF) and (10b) (RHF)].

$$\rho^+_{PM3} = 5.91 + 0.29\,\rho^+_{lit} \quad (\text{kJ mol}^{-1}) \quad (R^2 = 0.64) \qquad (9a)$$

$$\rho^+_{PM3} = 8.08 + 0.47\,\rho^+_{lit} \quad (\text{kJ mol}^{-1}) \quad (R^2 = 0.61) \qquad (9b)$$

$$\rho^+_{AM1} = 7.35 + 0.31\,\rho^+_{lit} \quad (\text{kJ mol}^{-1}) \quad (R^2 = 0.76) \qquad (10a)$$

$$\rho^+_{AM1} = 9.33 + 0.50\,\rho^+_{lit} \quad (\text{kJ mol}^{-1}) \quad (R^2 = 0.69) \qquad (10b)$$

The relatively low calculated difference in ρ^+ between molecules with the same Z, *e.g.* phenols and anisoles, shows that the polar effects on the remote substituent dependencies are reproduced badly by the two methods used in this work. The use of half-electron energies in order to avoid spin contamination does not improve the correlation to experimental data, however the ρ^+ interval is somewhat increased. Note, in particular, that the negative remote substituent effect found experimentally for 4-substituted benzylbromides[11] was not reproduced at the UHF level by the methods used in this work. At the RHF level a weak negative substituent effect on the C-Br BDE was obtained. However, for Z-X bonds where $(\chi_z - \chi_x)$ is positive the AM1 and PM3 methods could probably be employed to estimate remote substituent effects if they are calibrated against experimental data.

We have also used this method to estimate substituent effects on C-H bonds of molecules with the general formula $(R^1)(R^2)(R^3)$C-H with promising results.

Focusing on phenolic O-H bonds, which show the strongest positive remote substituent dependence, we find it interesting to compare our results with some recently published BDEs based on STO-3G *ab initio* calculations by Tomiyama *et al.*[20] These calculations resulted in a negative remote substituent dependence ($\rho^+ \approx -5$) and a BDE for the unsubstituted phenol of 273.09 kJ mol^{-1}. This value is almost

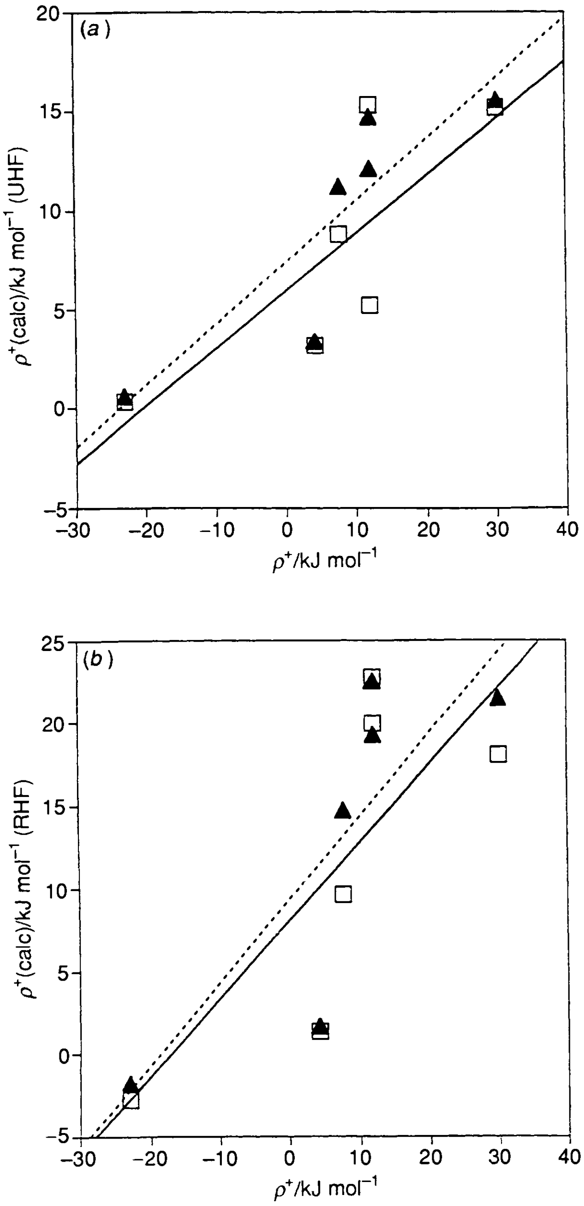

Fig. 2 Remote substituent effects on Z–X BDEs of (from left to right in the figure) benzylbromides, toluenes, anilines, anisoles and phenols based on (*a*) UHF AM1 (▲) and PM3 (□); (*b*) RHF AM1 (▲) and PM3 (□) calculations plotted against the corresponding literature data.

100 kJ mol^{-1} lower than the corresponding experimental value[5] and almost 50 kJ mol^{-1} lower than the lowest value calculated in this work.

Z–Z Bonds.—Table 2 compiles the Z–Z BDEs calculated using the PM3 method at the UHF level.

Comparable experimental data are sparse in the literature. However, a value of 230 ± 6 kJ mol^{-1} for (Ph–S)$_2$ is given in ref. 21. This value should be compared with our calculated value of 193 kJ mol^{-1} (Table 2). The BDEs in Table 2 were not primarily calculated to give absolute BDEs but to study the remote substituent effects on purely covalent bonds. In order to do this we have plotted the relative BDEs against the Brown $\sigma_p{}^+$ constants of the 4,4′-substituents (Fig. 3). The rather deviating values for (4-CF$_3$-C$_6$H$_4$-NH)$_2$ and (4-NO$_2$-C$_6$H$_4$-NH)$_2$ are excluded, since we do not believe them to be reliable.

As can be seen the remote substituent effects are positive. The substituent dependencies on these BDEs are probably due mainly to substituent effects on the corresponding radicals rather than on the parent molecules. The overall linear least square fit is given in eqn. (11).

$$\Delta E_{d,z\text{-}z} = -2.0 + 6.2\,\sigma_p^+ \quad (\text{kJ mol}^{-1}) \quad (R^2 = 0.73) \qquad (11)$$

Remote Substituent Effects on Z–X BDEs.—We find it interesting to relate, on a qualitative basis, the observed change in substituent dependence with bond polarity to some equations for BDE estimations derived for simpler molecules. These methods all have in common that, they are functions of the electronegativity and, in one case, the hardness of the bonded atoms.

The primary hypothesis, on which the final part of this work rests, is that the electronegativity, χ, and hardness, η (or rather the electronegativity and hardness indices[22] of Z, as will be explained later) of radicals with the general formula 4-Y-C$_6$H$_4$-Z$^\cdot$ are linearly dependent on the substituent constant of Y. This dependence would thus be described by Hammett equations ($\chi = C_\chi + \rho_\chi{}^+\sigma_p{}^+$; $\eta = C_\eta + \rho_\eta{}^+\sigma_p{}^+$). Since the absolute electronegativity[23] and the absolute hardness[23] have the operational definitions $(I + A)/2$ and $(I - A)/2$, respectively, we simply calculated the ionisation potentials, I, and the electron affinities, A, for some 4-substituted phenoxyl- and anilino-radicals (Table 3), using the AM1 method in MOPAC.

The results showed that the substituent dependence for the electronegativity is linear and between five and six times stronger than for the hardness ($\rho_\chi{}^+ \approx 0.8$ and $\rho_\eta{}^+ \approx 0.15$). No significant difference in remote substituent dependence for the electronegativity of phenoxyl- and anilino-radicals could be found. We thus assume $\rho_\chi{}^+$ and $\rho_\eta{}^+$ to be invariant with radical type. It should be stressed though, that the electronegativities used in eqn. (5) are for the binding atoms of Z and X. Electronegativities for radicals and molecules are global parameters owing to the electronegativity equalisation principle.[24] The electronegativity of a phenoxyl radical[25] and a hydrogen atom does not give the same picture of the polarity of the O–H bond in phenol as the atomic electronegativities of O and H do. To avoid the use of global electronegativities one can use the previously mentioned electronegativity indices for bonded atoms.[22] These should give a better picture of bond polarity. Electronegativity indices, as well as hardness indices, of bonded atoms are dependent on the atoms to which the atoms of interest are bonded.[22] Thus, for radicals with the general formula 4-Y-C$_6$H$_4$-Z$^\cdot$, the substituent dependence on the electronegativity indices of Z should be qualitatively similar to the previously estimated effects on the global electronegativity of the radicals.

The equations to be discussed further on all have the same general construction [eqn. (12)].

$$E_{d,AB} = E_{d,AB}^{cov} + E_{d,AB}^{ion} \qquad (12)$$

The first term on the right side denotes the full covalent contribution to the BDE and the second term is the ionic contribution. The full covalent contribution is approximated by either the arithmetic $(E_{d,AA} + E_{d,BB})/2$, or the geometric mean, $(E_{d,AA}E_{d,BB})^{\frac{1}{2}}$, or a combination of both.[26] Ghanty and Ghosh have derived an equation for calculation of BDEs for homonuclear diatomic molecules, A–A, which is based on the electronegativity and hardness of atom A and the A–A bond distance.[27] We shall, however, focus on the ionic part of eqn. (12), assuming the remote substituent dependence on non-polar bonds to be more or less invariant with the nature of Z. This may of course be a rather rough assumption but the results from the PM3 calculations of Z–Z BDEs indicate the differences to be rather small. Furthermore, this assumption is justified by the previously described experimental relation between sub-

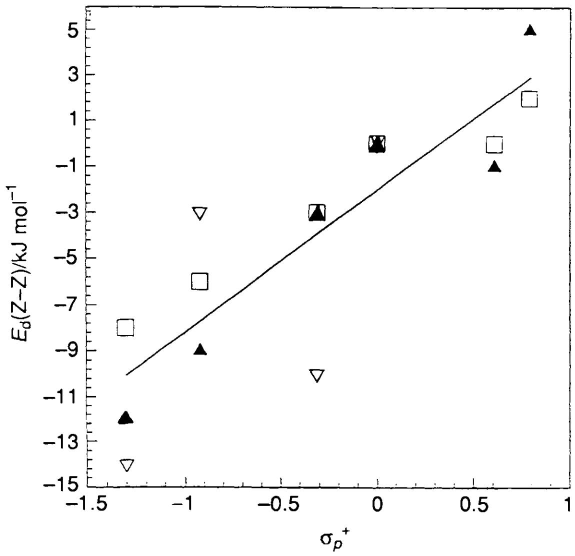

Fig. 3 Relative S–S (▲), N–N (▽) and C–C (□) BDEs of molecules with the general structure $(4\text{-}Y\text{-}C_6H_4\text{-}Z)_2$ calculated using the PM3 method plotted against the Brown substituent constants of the 4,4′-substituents

Table 2 Z–Z Bond dissociation energies (kJ mol^{-1})

$(4\text{-}Y\text{-}C_6H_4\text{-}Z)_2$	$E_d(\text{UHF})_{\text{PM3}}$
$(4\text{-}NH_2\text{-}C_6H_4\text{-}CH_2)_2$	168
$(4\text{-}OH\text{-}C_6H_4\text{-}CH_2)_2$	170
$(4\text{-}CH_3\text{-}C_6H_4\text{-}CH_2)_2$	173
$(Ph\text{-}CH_2)_2$	176
$(4\text{-}CF_3\text{-}C_6H_4\text{-}CH_2)_2$	176
$(4\text{-}NO_2\text{-}C_6H_4\text{-}CH_2)_2$	178
$(4\text{-}NH_2\text{-}C_6H_4\text{-}NH)_2$	62
$(4\text{-}OH\text{-}C_6H_4\text{-}NH)_2$	73
$(4\text{-}CH_3\text{-}C_6H_4\text{-}NH)_2$	66
$(Ph\text{-}NH)_2$	76
$(4\text{-}CF_3\text{-}C_6H_4\text{-}NH)_2$	92
$(4\text{-}NO_2\text{-}C_6H_4\text{-}NH)_2$	94
$(4\text{-}NH_2\text{-}C_6H_4\text{-}S)_2$	181
$(4\text{-}OH\text{-}C_6H_4\text{-}S)_2$	184
$(4\text{-}CH_3\text{-}C_6H_4\text{-}S)_2$	190
$(Ph\text{-}S)_2$	193
$(4\text{-}CF_3\text{-}C_6H_4\text{-}S)_2$	192
$(4\text{-}NO_2\text{-}C_6H_4\text{-}S)_2$	198

Table 3 Calculated hardness and electronegativity

	Ph-O$^\bullet$		Ph-NH$^\bullet$	
4-Subst.	η/eV	χ/eV	η/eV	χ/eV
NH_2	2.96	5.53	3.12	5.21
OH	3.15	5.99	3.25	5.59
CH_3	3.33	6.05	3.42	5.63
H	3.48	6.18	3.56	5.73
CF_3	3.40	7.00	3.45	6.53
NO_2	3.13	7.41	3.29	6.96

stituent dependence and bond polarity.[8,11] The equations to be discussed are eqns. (13)–(16).

$$E_{\text{d,AB}} = E_{\text{d,AB}}^{\text{cov}} + K_1(\chi_A - \chi_B)^2 \qquad (13)$$

$$E_{\text{d,AB}} = E_{\text{d,AB}}^{\text{cov}} + K_2\left\{1 - \exp\left[-\frac{30}{K_2}(\chi_A - \chi_B)^2\right]\right\} \qquad (14)$$

$$E_{\text{d,AB}} = E_{\text{d,AB}}^{\text{cov}} + K_3|\chi_A - \chi_B| \qquad (15)$$

$$E_{\text{d,AB}} = E_{\text{d,AB}}^{\text{cov}} + K_4\frac{(\chi_A - \chi_B)^2}{(\eta_A + \eta_B)} \qquad (16)$$

K_1–K_4 are empirical constants which are depending on the unit of the bond dissociation energies. Eqn. (13) was proposed by Pauling,[28] eqn. (14) by Matcha,[29] eqn. (15) by Reddy *et al.*[30] and eqn. (16) by Ghanty and Ghosh.[26] Note that the ionic part of eqn. (16) is simply the energy change due to the charge transfer between bonded atoms as originally derived by Parr and Pearson.[23]

To assess the compatibility between the experimentally found remote substituent effects on BDEs for molecules with the general formula $4\text{-}Y\text{-}C_6H_4\text{-}Z\text{-}X$ and eqns. (13)–(16) we had to find the derivative of these functions with respect to the substituent constant, σ_p^+ (or σ_p). Since the electronegativity and the hardness, or more correctly their indices, have been replaced by first-order polynomials, the derivatives of these properties are simply ρ_χ^+ and ρ_η^+, respectively where ρ_χ^+ and ρ_η^+ are the coefficients of the first-order terms. The derivatives of the ionic parts of eqns. (13)–(16), $\partial E_{\text{d,ion}}/\partial\sigma_p^+$, would thus be [eqns. (17)–(20)].

$$\frac{\partial E_{\text{d,(13)}}^{\text{ion}}}{\partial\sigma_p^+} = 2\rho_\chi^+K_1(\chi_A - \chi_B) \qquad (17)$$

$$\frac{\partial E_{\text{d,(14)}}^{\text{ion}}}{\partial\sigma_p^+} = 60\rho_\chi^+(\chi_A - \chi_B)\exp\left[-\frac{30}{K_2}(\chi_A - \chi_B)^2\right] \qquad (18)$$

$$\frac{\partial E_{\text{d,(15)}}^{\text{ion}}}{\partial\sigma_p^+} = K_3\rho_\chi^+ \qquad (19)$$

$$\frac{\partial E_{\text{d,(16)}}^{\text{ion}}}{\partial\sigma_p^+} = K_4\left[2\rho_\chi^+\frac{(\chi_A - \chi_B)}{(\eta_A + \eta_B)} - \rho_\eta^+\frac{(\chi_A - \chi_B)^2}{(\eta_A + \eta_B)^2}\right] \qquad (20)$$

As can be seen, the only derivative that does not account for the observed change in substituent dependence with difference in electronegativity, is that of eqn. (15), [eqn. (19)]. The remaining three derivatives are all functions of electronegativity differences.

Since the derivative of eqn. (14) is an exponential function including the unknown constant K_2, we focus on the simpler derivatives of eqns. (13) and (16). In Fig. 4 we have plotted the experimentally found remote substituent dependencies against the derivatives† of eqns. (13) and (16), calculated using the electronegativity and hardness indices of bonded atoms found in ref. 22. The derivative of eqn. (13) was taken simply as the difference in electronegativity and the first term of the derivative of eqn. (16) was multiplied by a factor of 10 and the second term by a factor of 1 according to the previously estimated ratio between ρ_χ^+ and ρ_η^+ (5/1). All other constants were taken as unity.†

As can be seen, both the derivative of eqns. (13) and (16) qualitatively satisfy the experimentally observed differences in remote substituent dependence. The linear least square fits are given in eqns. (21) and (22).

$$\rho_{\text{lit}}^+ = -8.4 + 6.2\frac{\partial E_{\text{d(13)}}^{\text{ion}}}{\partial\sigma_p^+} \quad (R^2 = 0.99) \qquad (21)$$

$$\rho_{\text{lit}}^+ = -8.3 + 10.5\frac{\partial E_{\text{d(16)}}^{\text{ion}}}{\partial\sigma_p^+} \quad (R^2 = 1.00) \qquad (22)$$

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† What is being calculated and plotted as abscissa in Fig. 4 is a quantity proportional to $\partial E_{\text{d}}^{\text{ion}}/\partial\sigma_p^+$; *i.e.* the constants K_1 and K_4, as well as ρ_χ^+ are set to unity. However, for notational simplicity, we refer to this quantity as $\partial E_{\text{d}}^{\text{ion}}/\partial\sigma_p^+$ throughout the text.

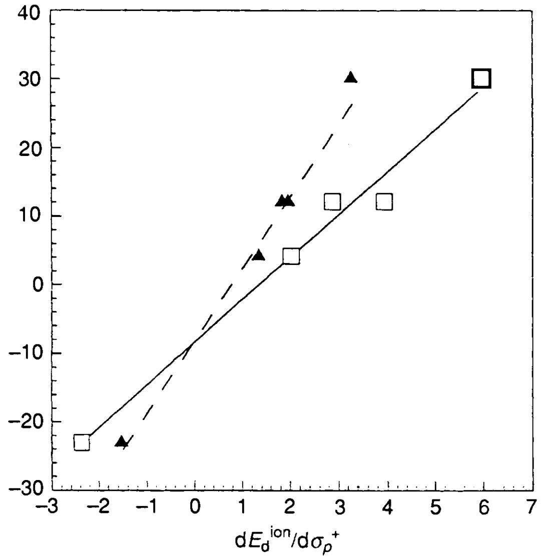

Fig. 4 Literature values of remote substituent effects on Z–X BDEs of (from left to right in the figure) benzylbromides, toluenes, anilines, anisoles and phenols plotted against the derivatives of eqns. (13) (□) and (16) (▲)

Conclusions

This work shows that 'user friendly', non-expert, semiempirical quantum chemical methods can be used for BDE estimates. Trends in remote substituent effects on BDEs can also be reproduced qualitatively. However, the accuracy is very low. If calibrated, the AM1 and PM3 methods could probably also be used quantitatively [eqns. (7)–(10)].

The final part of this work shows that the experimentally observed change in remote substituent dependence with bond polarity can be accounted for by relationships similar to those derived for simple molecules. Thus, a general structure–activity relationship for Z–X BDEs of molecules with the general formula 4-Y-C_6H_4-Z-X should be within reach.

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