Proton chemical shifts in NMR. Part 14.[1] Proton chemical shifts, ring currents and π electron effects in condensed aromatic hydrocarbons and substituted benzenes

Raymond J. Abraham,*[a] Marcos Canton,[a] Matthew Reid[a] and Lee Griffiths *[b]

[a] *Chemistry Department, The University of Liverpool, PO Box 147, Liverpool, UK L69 3BX*
[b] *AstraZeneca, Mereside, Alderley Park, Macclesfield, Cheshire, UK SK10 4TG*

The proton resonance spectra of a variety of condensed aromatic compounds including benzene, naphthalene, anthracene, phenanthrene, pyrene, acenaphthylene and triphenylene were obtained in dilute CDCl₃ solution. Comparison of the proton chemical shifts obtained with previous literature data for CCl₄ solution shows small but significant differences. A previous model (CHARGE6) for calculating the proton chemical shifts of aliphatic compounds was extended to aromatic compounds. This was achieved by including an automatic identification of both five- and six-membered aromatic rings based on atomic connectivities plus a dipole calculation of the aromatic ring current. The ring current intensity in the molecules was calculated by two alternative methods. a) The ring current intensity in the individual benzenoid rings was a function of the number of adjoining rings and b) the molecular ring current was proportional to the molecular area divided by the molecular perimeter. This, plus the inclusion of deshielding steric effects for the crowded protons in these molecules, gave a good account of the observed chemical shifts. The model was also applied successfully to the non-alternant hydrocarbons of fulvene and acenaphthylene and to the aliphatic protons near to and above the benzene ring in tricyclophane and [10]cyclophane.

The Huckel calculation of the π electron densities in CHARGE6 was used to calculate the π electron densities in substituted benzenes. The π-inductive effect was used to simulate the effect of CX_3 groups (X = H, Me, F) on the benzene ring. These together with the long range effects of the substituent groups identified previously allowed a precise calculation of the SCS of a variety of substituents on all the benzene ring protons.

The model gives the first accurate calculation of the proton chemical shifts of condensed aromatic compounds and of the proton SCS in the benzene ring. For the data set of 55 proton chemical shifts spanning 3 ppm the rms error of the observed *vs.* calculated shifts was *ca.* 0.1 ppm. The model also allows the interpretation of the shifts in terms of the separate interactions calculated in the programme, *i.e.* π electron densities and steric, anisotropic and electric field effects. Previous correlations of the proton SCS with π electron densities and substituent parameters are shown to be over simplified. The relative proportions of these different interactions are very different for each substituent and for each ring proton.

Introduction

The influence of the π electron densities and ring currents of aromatic compounds on their proton chemical shifts have been investigated since the beginning of proton NMR spectroscopy.[2] Thus it is all the more surprising that despite this wealth of investigation there is still no authoritative calculation (even a semi-empirical one) of the proton chemical shifts of aromatic compounds and the structural chemist still has to rely on proton data banks for the identification of aromatic compounds by NMR.

Pauling[3] introduced the concept of an aromatic ring current to explain the diamagnetic anisotropy of crystalline benzene. Pople[4] later extended this to explain the difference in the proton chemical shifts of benzene and ethylene and he further showed that the equivalent dipole model of this ring current gave a surprisingly good account of this difference. More sophisticated ring current models for benzene were then developed. The classical double-loop[5] and double dipole models[6] mimic the π electron circulation by placing the current loops (and equivalent dipoles) above and below the benzene ring plane. A value of ±0.64 Å was found to be most appropriate. The equations of Haigh and Mallion[7] give the shielding ratios directly from quantum mechanical theory. Schneider *et al.*[8] have recently presented a detailed experimental examination of the double-loop and Haigh and Mallion ring current

models, though not the simple equivalent dipole model (see later). The calculations gave good agreement with the experimental data, thus the effect of the benzene ring current on the chemical shifts of neighbouring protons is reasonably well understood.

However, the proton chemical shifts in condensed aromatic compounds and substituted benzenes have not yet been well calculated and this is the subject of this investigation. Bernstein *et al.*[9] in their initial calculations of the proton chemical shifts of condensed aromatic compounds assumed the same ring current for each benzenoid ring but this was subsequently considered to be an over simplification. Thus it is first necessary to calculate the π electron current density for each benzenoid ring and then to calculate the effects of these currents on the chemical shifts of the ring protons. The quantum mechanical method for calculating the π electron current densities was first given by Pople[10] and McWeeny[11] subsequently extended the London–Pople theory. McWeeny's work gives not only the circulating current density but also the effect of this circulating current at the proton in question. It should be noted that all these theories were based on simple Huckel theory.

Early experimental investigations to test these theories were not helped by the complex proton spectra of many condensed aromatic hydrocarbons at the low applied magnetic fields then in use and also by the quite large concentration effects on the proton chemical shifts due to the propensity of these

large planar rings to stack in solution. However three systematic investigations attempted to overcome these difficulties. Jonathan et al.[12] analysed the proton spectra of several condensed aromatics at infinite dilution in CCl_4 or CS_2. They then used the Pople–London theory to calculate the current intensity in the benzenoid rings and the Johnson–Bovey tables[5] to obtain the ring current shifts. They also estimated C–C and C–H anisotropic effects and found that these could be ignored. They obtained "only fair agreement" with the observed shifts. Varying the separation of the π-electron loops gave a poorer fit with the observed shifts. They noted that other interactions were affecting the proton shifts and in particular noted a high frequency shift for close protons which was suggested to be due to van der Waals contact but did not attempt to quantify this.

Subsequently Cobb and Memory[13] and Haigh and Mallion[7] performed two similar but more extensive investigations. The proton spectra of several condensed aromatic compounds in dilute solution were analysed and the McWeeny equation used to obtain the ring current densities and shielding ratios. They both ignored σ bond anisotropies in this calculation. Both investigations obtained reasonable correlations for "non overcrowded protons" between the observed proton shifts and the ratio of the π electron shielding for a given proton compared to benzene (H'/H'_b in the nomenclature of ref. 7). The more comprehensive data of ref. 7 when converted to the δ scale may be written as $\delta_{obs} = 1.56\ (H'/H'_b) + 5.66$ with an rms error of 0.06 ppm over a range of ca. 1.6 ppm. However the differences between the calculated and observed data for the "crowded" protons were ca. 0.5–0.7 ppm with one of 1.2 ppm, all to high frequency of the calculated value. Again they attributed these shifts to steric effects but did not quantify or define these effects.

More recently Westermayer et al.[14] used a double dipole model to test the observed shifts. They correlated the resulting geometric factors with the observed shifts to obtain a value for the benzene diamagnetic susceptibility anisotropy. They stated that superior results for the sterically crowded protons were obtained but it is not clear why this should be the case as no steric term was introduced.

Although it is obvious which protons are crowded (e.g. H4,5 in phenanthrene) it is not obvious whether this interaction is also present in the other "less crowded" protons. Thus the simple question of whether the difference between the α and β proton chemical shifts in naphthalene is due to ring currents, π-electron densities or steric effects has still not been satisfactorily answered. Although Pople in his original studies[10] calculated the ring current intensities in the five- and seven-membered rings of azulene, to our knowledge there has not been any calculation of the proton chemical shifts in non-alternant hydrocarbons.

The influence of the substituents on the proton chemical shifts in the benzene ring has also been investigated for many years and again there is still no quantitative calculation of these effects. Following the classic work of Castellano et al.[15] and Hayamizu and Yamamoto[16] who completely analysed the complex proton spectra of a wide range of monosubstituted benzenes in dilute solution in CCl_4 the proton substituent chemical shifts (SCS) are known accurately and tables of these SCS are an integral part of any text on NMR spectroscopy.[17–19] The theoretical interpretations of these effects have concentrated on the correlation between the SCS and the calculated π (and also σ) electron densities on the adjacent carbon atoms following the excellent correlation found between the ^{13}C SCS and the π electron densities at the para carbon atom in monosubstituted benzenes.[20] Correlations with π electron densities calculated by various methods have been reported, the most recent being the ab initio calculations of Hehre et al.[21] They used the STO-3G basis set and showed that the ^{13}C SCS could be well interpreted on the basis of calculated electron densities but this was not the case for the proton SCS. The para proton SCS could be correlated with the total charge density at

the para carbon atom but the meta proton SCS did not correlate well with the calculated meta carbon charge densities but with the sum of the charges at the hydrogen and attached carbon atoms. They stated that "this lack of consistency indicates either that the calculations are unrealistic or that the ^{1}H SCS depend to a very significant extent on factors other than electron densities at the H and attached C atoms". They omitted the ortho proton SCS presumably on the grounds that these other effects are even more important at these protons. They also noted that strongly electronegative substituents caused polarisation of the π system without charge transfer, leading to changes in the π densities around the ring and this is termed the π-inductive effect. They also found various correlations between the calculated charge densities and the Taft σ_I and σ_R values. This reflects the results of other investigators who have attempted to correlate substituent parameters with the proton SCS.[16,22,23] Despite all these endeavours there is still no calculation of proton SCS in substituted benzenes reliable enough to be of use to the structural chemist.

We give here the proton chemical shifts of a selection of condensed aromatic compounds in $CDCl_3$ and show that these differ by a small but significant amount from the earlier data in CCl_4 solution. These provide sufficient data for an analysis of the proton chemical shifts based on the CHARGE model for calculating proton chemical shifts.[1] In previous parts of this series this model has been applied successfully to a variety of saturated hydrocarbons,[24] haloalkanes,[25] ethers[26] and ketones.[1] We shall show that this model can be extended to provide a quantitative calculation of the proton shifts in condensed aromatic compounds, including two non-alternant hydrocarbons and the SCS of monosubstituted benzenes. We give two alternative calculations of the ring current intensity in the benzenoid rings together with a dipole model of the benzene ring current. In model A the ring current intensity in the individual benzenoid rings is a function of the number of adjoining rings whereas in model B the molecular ring current is given by the classical Pauling treatment as proportional to the molecular area divided by the molecular perimeter. All the protons in the condensed aromatic compounds are considered and the "crowded" proton chemical shifts reproduced by a simple steric effect. The effects of substituents in monosubstituted benzenes are well reproduced for the ortho, meta and para protons on the basis of calculated π electron densities plus the steric, anisotropic and electric field effects of the substituents. We show also that the model reproduces the high field shifts of protons situated over the benzene ring thus providing a general calculation of proton chemical shifts of condensed aromatic compounds. A preliminary account of this work has been presented.[27]

Theory

As the theory has been detailed previously only a brief summary of the latest version (CHARGE6)[28] is given here. The theory distinguishes between substituent effects over one, two and three bonds which are attributed to the electronic effects of the substituents and longer range effects due to the electric fields, steric effects and anisotropy of the substituents. The CHARGE scheme calculates the effects of atoms on the partial atomic charge of the atom under consideration, based upon classical concepts of inductive and resonance contributions.

If we consider an atom I in a four atom fragment I–J–K–L the partial atomic charge on I is due to three effects. There is an α effect from atom J given by the difference in the electronegativity of atoms I and J and a β effect from atom K proportional to both the electronegativity of atom K and the polarisability of atom I. There is also a general γ effect from atom L given by the product of the atomic polarisabilities of atoms I and L. For the second row atoms (C, O, etc.) the γ effect (i.e. C–C–C–H) is parameterised separately and is given by eqn. (1) where θ is the C–C–C–H dihedral angle and A and B empirical parameters.

$$\text{GSEF} = A + B_1\cos\theta \qquad 0° \le \theta \le 90°$$
$$= A + B_2\cos\theta \qquad 90° \le \theta \le 180° \qquad (1)$$

There are also routines for the methyl γ effect and for the decrease in the γ effect of the electronegative oxygen and fluorine atoms for CX_2 and CX_3 groups.

The total charge is given by summing these effects and the partial atomic charges (q) converted to shift values using eqn. (2).

$$\delta = 160.84q - 6.68 \qquad (2)$$

The effects of more distant atoms on the proton chemical shifts are due to steric, anisotropic and electric field contributions. $H \cdots H$ steric interactions in alkanes were found to be shielding and $X \cdots H$ (X = C, F, Cl, Br, I) interactions deshielding according to a simple r^{-6} dependence [eqn. (3)].

$$\delta_{\text{steric}} = a_S/r^6 \qquad (3)$$

Furthermore any $X \cdots H$ steric contributions on a methylene or methyl proton resulted in a push-pull effect (shielding) on the other proton(s) on the attached carbon.

The effects of the electric field of the C–X bonds (X = H, F, Cl, Br, I, O) were calculated from eqn. (4) where A_Z was

$$\delta_{\text{el}} = A_Z E_Z \qquad (4)$$

determined as 3.67×10^{-12} esu (63 ppm au) and E_Z is the component of the electric field along the C–H bond. The electric field for a univalent atom (*e.g.* fluorine) is calculated as due to the charge on the fluorine atom and an equal and opposite charge on the attached carbon atom. The vector sum gives the total electric field at the proton concerned and the component of the electric field along the C–H bond considered is E_Z in eqn. (4). This procedure is both simpler and more accurate than the alternative calculation using bond dipoles.

The magnetic anisotropy of a bond with cylindrical symmetry (*e.g.* CN) was obtained using the McConnell equation [eqn. (5)], where R is the distance from the perturbing group to

$$\delta_{\text{an}} = \Delta\chi^{\text{CN}} (3\cos^2\varphi - 1)/3R^3 \qquad (5)$$

the nucleus of interest in Å, φ is the angle between the vector R and the symmetry axis and $\Delta\chi^{\text{CN}}$ the molar anisotropy of the CN bond. ($\Delta\chi^{\text{CN}} = \chi^{\text{CN}}_{\text{parl}} - \chi^{\text{CN}}_{\text{perp}}$) where $\chi^{\text{CN}}_{\text{parl}}$ and $\chi^{\text{CN}}_{\text{perp}}$ are the susceptibilities parallel and perpendicular to the symmetry axis respectively.

For a non-cylindrically symmetric group such as a carbonyl group eqn. (5) is replaced by the full McConnell eqn. (6). The

$$\delta_{\text{an}} = [\Delta\chi_1(3\cos^2\theta_1 - 1) + \Delta\chi_2(3\cos^2\theta_2 - 1)]/3R^3 \qquad (6)$$

C=O group has different magnetic susceptibilities (χ_1, χ_2 and χ_3) along the principal axes (X_1, X_2 and X_3) and thus two anisotropy terms are required.

In eqn. (6) θ_1 and θ_2 are the angles between the radius vector R and χ_1 and χ_3 respectively and $\Delta\chi_1$ ($\chi_1 - \chi_2$) and $\Delta\chi_2$ ($\chi_3 - \chi_2$) are the two anisotropies for the C=O bond which may be termed the parallel and perpendicular anisotropy respectively.

These contributions were added to the shifts of eqn. (2) to give the calculated shift of eqn. (7).

$$\delta_{\text{total}} = \delta_{\text{charge}} + \delta_{\text{steric}} + \delta_{\text{anisotropy}} + \delta_{\text{el}} \qquad (7)$$

Application to aromatic compounds

Ring current shifts. There are a number of modifications to be made to CHARGE6 to calculate the proton shifts of aromatic compounds. It was necessary to include the effect of the aromatic ring current and for this to be achieved the programme has to automatically recognise an aromatic ring. A routine was written based on the atomic connectivities in the rings and the programme now recognises both five- and six-membered aromatic rings including the heterocyclic rings of pyrrole, furan and thiophene. The aromatic ring current at any proton was then calculated from the equivalent dipole model [eqn. (8)].

$$\delta_{\text{rc}} = fc\mu(3\cos^2\theta - 1)/R^3 \qquad (8)$$

In eqn. (8) R is the distance of the proton from the benzene ring centre, θ the angle of the R vector from the benzene ring symmetry axis, μ is the equivalent dipole of the benzene ring and fc the π electron current density for the benzenoid ring. (For benzene $fc = 1$.)

It was next necessary to calculate the value of fc for any given compound and two alternative methods are presented. The first method (model A) was based on inspection of the calculated ring current intensities of refs. 7 and 12. Haigh and Mallion[7] did not publish the calculated ring current intensities for the common aromatic compounds, but a selection of their calculated values for some less common condensed aromatic compounds is given in Table 1.

Inspection of this data shows that the changes in the ring current intensity are a function of the number and orientation of the rings attached to the benzenoid ring. In model A the ring current intensity in any given benzenoid ring is assumed to be only a function of the number and orientation of the rings attached to the benzenoid ring considered. This may be quantified by the number and orientation of the substituent sp^2 carbon atoms attached to the ring in question (R_0). Thus we define a) the number of attached sp^2 carbons on each ring carbon atom and b) the relative position of these attached atoms in the benzene ring. Thus for benzene each carbon atom has two carbon neighbours thus $R_0 = 12$. For either ring in napthalene two of the carbon atoms have three carbon neighbours thus $R_0 = 14$. The middle rings of anthracene and phenanthrene both have $R_0 = 16$ but the relative positions of the substituent carbons differ in the two cases. These are defined as R_0 equals 16a and 16b. This analysis gives seven different ring systems (Table 1) of which six are present in the molecules indicated in Fig. 1. Only the molecules with the rings itemised A, B in Fig. 1 are included in Table 1 as these are the only molecules for which the ring current intensities were given in ref. 7. However all the molecules measured were included in the iteration (see later).

Inspection of Table 1 shows that with few exceptions the separation of the ring current densities into the different ring types gives a reasonably constant value for each ring type. The only serious exception is the calculated values for ring type 18 (*i.e.* all substituted carbons) of ref. 12 which are very different for perylene and coronene. The values from ref. 7 for the similar molecules benzo[*ghi*]perylene and naphtho[1,2,3,4-*def*]chrysene are much more consistent.

It would be possible to average the calculated values of ref. 7 for each ring type and use these averages in our calculation. In view of the approximations inherent in these calculations it was decided to parametrise the current density for each ring type separately to obtain the best agreement with the observed shifts. These optimised values are given in Table 1 (column 5) and will be considered later.

An alternative method of calculating the molecular ring current (model B) is to use the Pauling model[3] in which the carbon skeleton is considered as a conducting electrical network in which for any current loop the emf is proportional to the area enclosed and the resistance proportional to the number of bonds. On this basis if the condensed aromatics are considered to be made up of a number of regular hexagons the ring current for any molecule is simply proportional to the number of hexagons in the molecule divided by the number of bonds in the

Table 1 Calculated ring current intensities in condensed aromatic hydrocarbons

Molecule	Ring type[a]	(R_0)	Ring current intensity (fc)			
			[b]	[c]	Model A	Model B[d]
Benzene (**1**)		12	1.00	1.00	1.00	1.00
Naphthalene (**2**)		14	1.093	1.048,[e] 1.094,[f] 1.121[g]	0.950	0.925
Anthracene (**3**)	Ring A	14	1.085	1.119,[h] 1.197,[i] 1.104[j]		0.943
	Ring B	16a	1.280	1.291,[e] 1.311,[f] 1.299,[g] 1.298,[h] 1.170[j]	0.818	
Phenanthrene (**4**)	Ring A	14	1.133			0.943
	Ring B	16b	0.975	0.877,[g] 0.876[h]	0.745	
Triphenylene (**5**)	Ring A	14	1.111			0.876
	Ring B	18	0.747			
Pyrene (**6**)	Ring A	15	1.329	1.337,[k] 1.292[l]	0.786	0.878
	Ring B	16b	0.964			
Perylene (**7**)	Ring A	15	0.979			0.681
	Ring B	18	0.247	0.603,[f] 0.606[m]	0.173	
Coronene (**8**)	Ring A	16b	1.460		1.06[a]	1.008
	Ring B	18	1.038	0.745,[n] 0.684[l]		
		17	—	1.297,[k] 1.226,[m] 1.310[i]		

[a] See text. [b] Ref. 12. [c] Ref. 7. [d] This work. [e] Hexacene. [f] Dibenzo[*a,c*]naphthacene. [g] Dibenzo[*a,j*]naphthacene. [h] Dibenzo[*a,l*]naphthacene. [i] Dibenzo-[*def,mno*]chrysene. [j] Benzo[*h*]pentaphene. [k] Dibenzo[*def,mno*]chrysene. [l] Benzo[*ghi*]perylene. [m] Naphtho[1,2,3,4-*def*]chrysene. [n] Dibenzo[*b,def*]-chrysene.
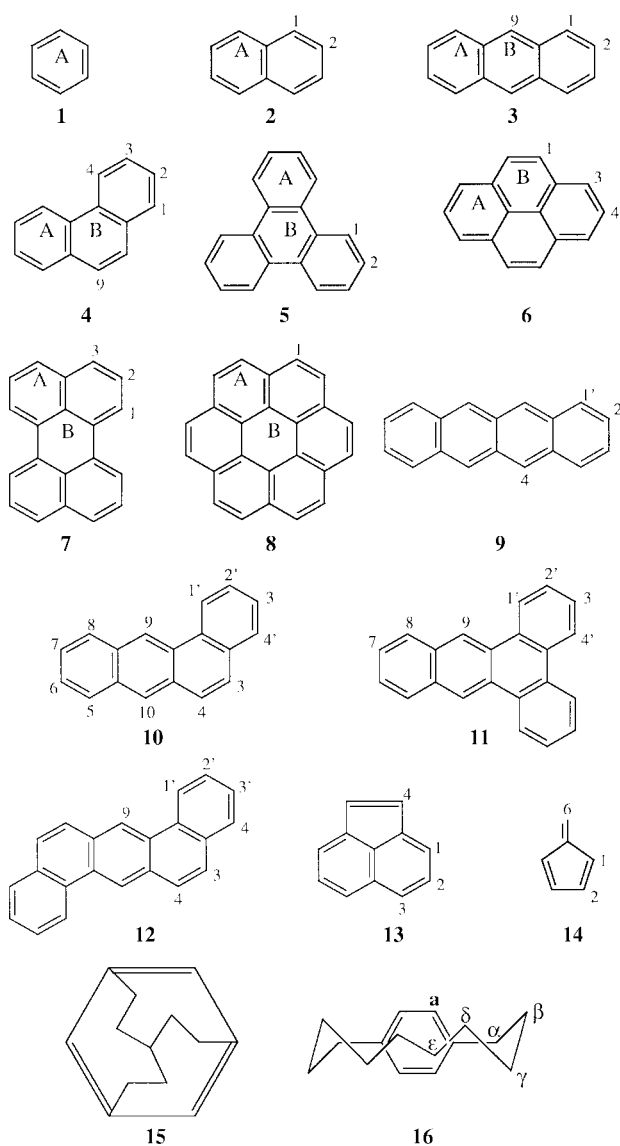
Fig. 1 Molecules studied and their nomenclature.

perimeter of the molecule. Thus for benzene, naphthalene and anthracene the ring current ratio is 1 : 6/5 : 9/7. The Pauling model gives too large a value for the diamagnetic anisotropy of condensed aromatics[6a] so that as in method A the Pauling

model was used to separate the various molecular types and the ring current for each molecular type was parametrised against the experimental data. Although the same experimental data are used in both models the different selectivities give different answers. For example in model B anthracene and phenanthrene have identical ring currents which is not the case in model A.

Conversely in model A the fully substituted benzenoid rings in perylene (**7**) and coronene (**8**) have identical ring currents whereas in model B they differ as the molecular area/perimeter ratio differs for the two compounds.

π Electron densities. The π electron densities are calculated in the CHARGE programme from Huckel theory.[29] The standard coulomb and resonance integrals for the Huckel routine are given by eqn. (9), where a_0 and β_0 are the coulomb and

$$a_r = a_0 + h_r\beta_0$$
$$\beta_{rs} = k_{rs}\beta_0 \qquad (9)$$

resonance integrals for a carbon $2p_z$ atomic orbital and h_r and k_{rs} the factors modifying these integrals for orbitals other than sp^2 carbon. The Huckel routine was modified by the ω technique to model the very polar π systems of the nucleic acid bases.[30] The ω technique involves varying the coulomb integral for each atom according to the charge on that atom. This is shown in eqn. (10) where a_r is the coulomb integral, a_r^0 the

$$a_r = a_r^0 - q_r\omega \qquad (10)$$

initial coulomb integral, q_r the excess π charge on atom r and ω a constant. Eqn. (10) "cuts in" at a given value of the excess π charge on atom r. For the nucleic acid bases the appropriate value of ω was 1.40 and and the cut-in threshold 0.2 electrons.[30]

For alternant aromatic hydrocarbons this calculation gives π electron densities at every carbon equal to 1.0 as in benzene. Thus the excess π electron density is zero. This is in agreement with the results of more sophisticated calculations. *E.g.* the excess π electron densities at the α and β carbons of naphthalene are calculated as −0.8 and −4.1 me (millielectrons) from *ab initio* calculations with the 6-31G* basis set.

For the non-alternant hydrocarbons fulvene and acenaphthylene the Huckel routine gives large excess π densities at certain carbon atoms which are much larger than those calculated by *ab initio* methods in which iteration procedures restrict the tendency in the Huckel routine to separate the π charges. The ω technique was modified to correct this by decreasing the "cut in" point of eqn. (10) from 0.2 electrons to 0.01 electrons and

increasing the value of ω to 6.0. This simple modification gave reasonable results for these two compounds, though the dipole moments are still on the high side (*e.g.* fulvene 0.92 D (calc.) *vs.* 0.44 D (obs.)[31] and acenaphthylene 0.93 D (calc.) *vs.* 0.3 D (obs.)[31]). As these hydrocarbons have quite different π densities and geometries from the alternant hydrocarbons both the ring current of the five-membered ring and the ring current density of the attached six-membered ring were parametrised separately.

For the substituted benzenes the appropriate values of the coefficients h_r and k_{rs} in eqn. (9) for the orbitals involving hetero atoms have to be found. In ref. 29 two procedures were considered. One was to obtain those values which gave the best agreement with the experimental dipole moments of the compounds investigated, the alternative was to find values which best reproduced the π densities obtained by *ab initio* calculations. Both sets of coefficients were given, but the first set was adopted in the CHARGE programme as the simplest method of obtaining reasonable dipole moments of unsaturated compounds. However later developments of the CHARGE method, in which a more flexible method of reproducing observed dipole moments was adopted, meant that the dipole moments of unsaturated compounds could be reproduced with either set of Huckel parameters. We now use the later set so that the π densities calculated from the Huckel routine reproduce the π densities given from *ab initio* calculations.

The only other modification necessary to the Huckel routine concerns the effect of saturated substituents (*e.g.* CX_3) on the π electron densities in the benzene ring which is usually termed hyperconjugation. It is simple to reproduce this effect in a Huckel calculation if it is regarded as an example of the π-inductive effect mentioned earlier. In this case an equation corresponding to eqn. (10) was used to vary the Coulomb integral of the aromatic carbon atom connected to an sp^3 carbon. In this way changes to the π electron density of the benzene ring due to both electron donating substituents such as CH_3 and electron withdrawing substituents such as CF_3 can be handled by the same procedure.

Having obtained the π electron density in the benzene ring it is then necessary to determine the effect of the π electron density at a given carbon atom on the proton chemical shifts. An experimental determination of this factor is due to Gunther *et al.*[32] They measured the proton chemical shifts of a variety of cyclic charged molecules (tropylium cation, cyclopentadienyl anion, *etc.*) and compared them with benzene. From this data they obtained a value of the coefficient a_1 [eqn. (11)] of 10.0

$$\Delta\delta = a_1\Delta q_\alpha + a_2\Delta q_\beta \qquad (11)$$

between the proton shift $\Delta\delta$ and the excess π charge Δq_α on the attached carbon atom.

It has also been recognised that there is an influence of the excess π charge on the carbon atom β to the proton considered and a related effect gives rise to the phenomenon of negative spin density in EPR spectroscopy.[33] The hyperfine couplings to the α and β protons in alkyl radicals, in which the radical carbon atom is planar and sp^2 hybridised, are quoted as $a^H_\alpha = -22$ G and $a^H_\beta = 4 + 50\cos^2\theta$ where θ is the dihedral angle between the free radical 2p-orbital and the proton considered.[33] These considerations suggest that in aromatic compounds in which the CH bond is orthogonal to the π orbital, θ is 90° and the value of a_2 in eqn. (11) is negative and *ca.* 1/5th of a_1, *i.e.* -2.0.

These modifications were the only ones needed to apply the CHARGE routine to aromatic compounds. However it is still necessary to calculate the charge densities at the aromatic protons in CHARGE and thus to quantify the appropriate α, β and γ effects. Also the long range interactions present in the aliphatic molecules (*i.e.* steric, electric and anisotropic) must also be included and where necessary evaluated. These will be considered subsequently.

The steric effects of both the aromatic carbon and hydrogen atoms are not known and must be determined. We shall show (see later for a full discussion) that an aromatic carbon atom has no steric effect on a close aromatic proton but that an aromatic proton has a *de*shielding effect on a close aromatic proton. We assume that this can be represented by a simple r^{-6} term [eqn. (3)] thus only the appropriate value of a_S in eqn. (3) for the aromatic proton to proton steric shift needs to be obtained. The electric field and anisotropies of the polar and anisotropic groups involved are calculated in an identical manner to that for any aliphatic C–H bond and thus no further parameterisation is necessary.

Experimental

Ethylene, benzene, toluene, *tert*-butylbenzene, naphthalene, anthracene, phenanthrene, pyrene, triphenylene, benz[*a*]anthracene, benzo[*b*]triphenylene and dibenzo[*ah*]anthracene and the $CDCl_3$ solvent were obtained commercially (Aldrich Chem. Co.). The solvent was stored over molecular sieves and used without further purification.

^{1}H NMR spectra were obtained on a Bruker AMX400 spectrometer operating at 400.14 MHz. Spectra were recorded in 10 mg cm^{-3} solutions (^{1}H) with a probe temperature of *ca.* 25 °C in $CDCl_3$ and referenced to TMS. Typical ^{1}H conditions were 128 transients, spectral width 3300 Hz, 32K data points, giving an acquisition time of 5 s and zero-filled to 128K to give a digital resolution of 0.025 Hz.

The geometries of the compounds were obtained by optimisations using the GAUSSIAN94 programme at the RHF/ 6-31G* level.[34] For molecules too large to be handled conveniently by GAUSSIAN at the 6-31G* level, *e.g.* perylene, smaller basis sets were used, *e.g.* 3-21G. For the largest molecules, *e.g.* coronene and the two cyclophanes (**15**) and (**16**), the molecular mechanics PCMODEL programme was used.[35] The geometry and CHARGE computations were performed on a PC.

Results

The proton spectra of the compounds all consisted of well separated peaks at 400 MHz (except for toluene) thus the proton chemical shifts could be obtained immediately and the assignments of the compounds followed previous investigations. For toluene the proton spectrum of toluene-d_8 was first obtained. The dilute ^{1}H spins only couple to the [2]D nuclei and the spectrum consists of three broad singlets at 7.165, 7.170 and 7.254 δ. This gave sufficient information to identify the coupling patterns in the ^{1}H spectrum of toluene and hence the slightly more accurate proton chemical shifts given in Table 2.

The data obtained in $CDCl_3$ solution are given and compared with that of previous investigations in CCl_4 solution in Table 2. In ref. 12 the authors only reported the shift differences from benzene and we have added 7.27 ppm (the benzene value in CCl_4) to them. The shift values in Table 2 are of interest. There is generally good agreement between the data sets but it is noteworthy that there is a small but almost constant difference in the proton chemical shifts in $CDCl_3$ solution compared to CCl_4. Averaging over all the aromatic compounds in Table 2 gives a value of 0.086 ppm (± 0.01) to low field in $CDCl_3$ solution. This is also the case for ethylene but here the difference is slightly less. The aliphatic protons of the methyl groups in toluene and *tert*-butylbenzene do not show this effect but have the same shifts in the two solvents. The constant value of this difference means that data in CCl_4 solution can be converted directly to $CDCl_3$ solution by merely relating the shifts to benzene. Furthermore this suggests that the accurate SCS values reported earlier for the monosubstituted benzenes in CCl_4 solution may be used with confidence to investigate the application of the CHARGE model to these compounds and

Table 2 Observed and calculated proton chemical shifts (δ) for aromatic compounds

Compound	Proton	Observed			Calculated	
		CDCl$_3$[a]	CCl$_4$[b,c]		Model A	Model B
Ethylene		5.405	5.352[d]	—		5.407
Benzene (**1**)		7.341	7.27[b]	(7.27)[c]	7.331	7.342
Naphthalene (**2**)	1	7.844	7.73	7.81	7.931	7.829
	2	7.477	7.38	7.46	7.524	7.493
Anthracene (**3**)	1	8.009	7.93	8.01	7.948	8.009
	2	7.467	7.39	7.39	7.524	7.577
	9,10	8.431	8.36	8.31	8.495	8.485
Phenanthrene (**4**)	1	7.901	7.80	un	7.930	7.968
	2	7.606	7.51	un	7.509	7.544
	3	7.666	7.57	un	7.566	7.600
	4,5	8.702	8.62	8.51	8.455	8.433
	9,10	7.751	7.65	7.71	7.839	8.085
Triphenylene (**5**)	1	8.669	8.61	8.56	8.587	8.707
	2	7.669	7.58	7.61	7.613	7.654
Pyrene (**6**)	1	8.084	8.00	8.06	7.976	8.253
	3	8.190	8.10	8.16	7.930	8.156
	4	8.010	7.93	7.99	7.546	7.785
Perylene (**7**)	1	8.196	8.11	8.09	8.361	8.250
	2	7.466	7.38	7.41	7.515	7.404
	3	7.656	7.57	7.60	7.845	7.630
Coronene (**8**)	1	8.90[e]	8.82	8.84		8.900
Benz[a]anthracene (**9**)	1′	8.840	8.77		8.698	8.553
	2′	7.685	7.59		7.708	7.627
	3′	7.651	7.525		7.638	7.557
	4′	7.849	7.755		8.102	8.004
	3	7.616	7.55		7.987	8.117
	4	7.800	7.72		8.027	8.200
	5	8.048	8.03		8.101	7.977
	6	7.540	7.465		7.637	7.544
	7	7.564	7.47		7.647	7.553
	8	8.133	8.03		8.169	8.038
	9	9.174	9.08		9.125	9.052
	10	8.370	8.275		8.561	8.572
Benz[b]anthracene (**10**)	1′	8.00[f]			8.082	7.947
	2′	7.39			7.619	7.522
	4	8.67			8.581	8.546
Benzo[b]triphenylene (**11**)	1′	8.791	8.675		8.685	8.758
	2′	7.670	7.54		7.649	7.634
	3′	7.651	7.53		7.636	7.618
	4′	8.592	8.475		8.637	8.674
	7	7.568	7.455		7.641	7.521
	8	8.097	7.965		8.134	8.008
	9	9.097	9.075		9.103	9.238
Dibenzo[ah]anthracene (**12**)	1′	8.874	8.805		8.708	8.502
	2′	7.719	7.625		7.721	7.583
	3′	7.646	7.55		7.649	7.511
	4′	7.914	7.82		8.113	7.944
	3	7.760	7.67		8.016	8.077
	4	7.963	7.88		8.121	8.230
	10	9.155	9.075		9.170	9.107
Acenaphthylene (**13**)	1	7.812			7.829	7.826
	2	7.548			7.474	7.519
	3	7.692			7.708	7.701
	5,6	7.083			7.070	7.024
Fulvene (**14**)	1,4	6.228[g]			6.384	6.317
	2,3	6.531			6.421	6.404
	6	5.892			6.015	5.960
Toluene ortho		7.180	7.061[h]			7.080
meta		7.260	7.140			7.284
para		7.165	7.042			7.172
Me		2.343	2.337[i]			2.343
tert-Butylbenzene ortho		7.390	7.281[h]			7.279
meta		7.297	7.180			7.358
para		7.165	7.052			7.218
Me		1.325	1.319[i]			1.332

[a] This work except where stated. [b] Ref. 7. [c] Ref. 12. [d] Ref. 36. [e] Ref. 37. [f] Ref. 38. [g] Ref. 39. [h] Ref. 16. [i] Ref. 2, vol. 2, Appendix B. un = unresolved.

these data are reproduced in Table 3. Also given in Table 3 are the SCS values obtained in our laboratory for selected compounds in dilute CDCl$_3$ solution. The excellent agreement between the sets of SCS values confirms this assumption.

The data collected in Tables 2 and 3 provide a rigorous test of the application of both the CHARGE model and also of present ring current theories to these compounds. The compounds listed in the tables are all of fixed conformation. The GAUSSIAN94 (6-31G*/3-21G) and the PCMODEL calculations gave molecular geometries for the aromatic

Table 3 Observed[a] vs. calculated proton SCS ($\Delta\delta_H$) of substituted benzenes

| | Proton substituent chemical shifts ($\Delta\delta_H$) | | | | | |
| | ortho | | meta | | para | |
Substituent	Obs	Calc	Obs	Calc	Obs	Calc
H	0.00	0.00	0.00	0.00	0.00	0.00
CH$_3$	−0.20	−0.27	−0.12	−0.06	−0.22	−0.17
	−0.16		−0.08		−0.18[b]	
t-Bu	0.02	−0.06	−0.08	0.02	−0.21	−0.12
	0.05		−0.04		−0.19[b]	
F	−0.29	−0.23	−0.02	0.02	−0.23	−0.21
Cl	0.03	−0.04	−0.02	0.07	−0.09	−0.08
Br	0.18	0.07	−0.08	0.09	−0.04	−0.02
I	0.39	0.18	−0.21	0.08	0.00	0.01
OH	−0.56	−0.53	−0.12	−0.13	−0.45	−0.42
OCH$_3$	−0.48	−0.44	−0.09	−0.12	−0.44	−0.41
NH$_2$	−0.75	−0.62	−0.25	−0.24	−0.65	−0.65
CF$_3$	0.32	0.28	0.14	0.18	0.20	0.20
	0.29		0.14		0.21[c]	
CHO	0.56	0.54[d]	0.22	0.20[d]	0.29	0.26
C(O)CH$_3$	0.62	0.61[d]	0.14	0.21[d]	0.21	0.28
C(O)OCH$_3$	0.71	0.91[d]	0.11	0.21[d]	0.21	0.26
CN	0.36	0.35	0.18	0.21	0.28	0.24
	0.32		0.14		0.27[e]	
NO$_2$	0.95	0.81	0.26	0.23	0.38	0.25

[a] Ref. 16 unless stated otherwise. [b] This work (CDCl$_3$ soln.). [c] Ref. 42. [d] Averaged, see Table 5 and text. [e] Ref. 43.

hydrocarbons in excellent agreement with the experimental geometries, where known (e.g. benzene C–C 1.397, C–H 1.087 Å (MP2/6-31G*), vs. 1.395 and 1.087 Å (PCMODEL) and 1.396 and 1.083 Å (experimental)[40]).

In the CHARGE model the α, β and γ effects of the substituents are considered to be due to electronic effects and therefore they are modelled on a simple empirical basis. The α effect of an sp^2 carbon is given from the difference in the electronegativities of the carbon and hydrogen atoms divided by the appropriate exchange integral. The value of this integral was chosen to reproduce the observed chemical shift of ethylene (Table 2). This gives a partial atomic charge for the ethylene protons of +0.075 e which corresponds to a C–H bond dipole of 0.4 D. This is in reasonable agreement with the usual quoted range (ca. 0.6–0.7 D).[41] The β effect is calculated directly from the carbon electronegativity and proton polarisability,[28] thus the only other electronic effect to be considered is the γ effect (H–C–C–C) of the unsaturated carbon atoms in the aromatic compounds. For the condensed aromatic compounds considered here the only values of the CCCH dihedral angle θ are 0° and 180° (Table 2) and thus eqn. (1) may be simplified to $A + B\cos\theta$ with the coefficients A and B to be obtained from the observed data.

Long-range effects

The interactions considered to be responsible for the long range effects of the aromatic ring have been documented earlier as steric plus magnetic anisotropy (i.e. ring current) effects. (There is also a small electric field effect due to the C–H dipoles. This is calculated by CHARGE directly from the partial atomic charges as the coefficient A_Z in eqn. (4) has already been determined). Thus we are now in a position to test the theoretical treatment given earlier against the observed data presented in the tables.

In previous investigations in this series which were concerned with substituted alkanes the steric effect of all non-hydrogen atoms was deshielding on the near protons, but proton–proton interactions gave a shielding effect. This was confirmed both experimentally and theoretically. In contrast it is immediately obvious from both the results of previous investigations[7,13] and the data presented here that proton–proton steric interactions in the aromatic systems considered here give rise to deshielding

Table 4 Observed vs. calculated proton chemical shifts (δ) in [10]para-cyclophane (**16**)

Carbon atom (CH$_2$)	Observed (CH$_2$)	Calculated (average)	
α	2.62	2.453	2.606
		2.759	
β	1.54	1.806	1.699
		1.592	
γ	1.08	1.631	1.270
		0.909	
δ	0.73	1.133	0.894
		0.655	
ε	0.51	0.626	0.525
		0.424	
Aromatic	7.04	7.102	7.088
		7.074	

effects on the proton chemical shifts. A further unambiguous demonstration that steric effects on proton chemical shifts in aromatic systems are totally different from those in saturated systems came from the observation of the proton chemical shift of the unique CH proton in the cyclophane (**15**). This proton occupies a position along the symmetry axis of the benzene ring and occurs at −4.03 δ. Because of its proximity to the benzene ring plane (it is ca. 1.9 Å above the ring plane) it is an excellent test of any ring current theory and was used by Schneider et al. in their investigation of the different ring current models.[8] It is also in close proximity to the benzene ring carbon atoms, the average C···H distance being ca. 2.20 Å. Any deshielding effect from the aromatic carbon atoms comparable to that found for saturated carbon atoms would have a pronounced deshielding effect on this proton. For example using the steric coefficient found previously for saturated carbon atoms (a_s in eqn. (3) = 220.0 ppm Å^6) would give a value for the CH proton chemical shift of +6.0 δ! Clearly there is no significant deshielding steric effect from the aromatic carbon atoms at this proton. Schneider et al.[8] termed this a "soft" steric effect in contrast to the "hard" steric effect of proton–proton interactions. This is supported by the results for [10]paracyclophane (Table 4) in which there is good agreement between the observed and calculated shifts again with no sp^2 carbon steric effect. This result was adopted in the CHARGE routine so that

there is no steric effect on the proton chemical shifts from any aromatic carbon atom. Note that this may not be the case for olefinic carbon atoms and work is currently in place in our laboratory to further define this interesting result.[42]

Thus the parameters to be determined from the observed results in Table 2 are the coefficients A and B for the carbon γ effect [eqn. (1)], the appropriate $H \cdots H$ steric coefficient [eqn. (3)], the ring current equivalent dipole μ [eqn. (8)] and the factors fc [eqn. (8)] for the condensed rings. There are six factors for both model A and model B (Table 1) making a total of 10 unknown parameters. The values of the unknown parameters were achieved using a non-linear least mean squares programme (CHAP8)[44] to give the best fit with the observed data. The data set used comprises all the condensed aromatics of Table 2, a total of 57 proton shifts thus the iteration is over-determined. The initial iteration for model A clearly showed that coronene was an exception and this was removed from the subsequent iteration. With this amendment the programme iterated satisfactorily with reasonable rms error and definition. For model B coronene is a separate case and the iteration performed satisfactorily. The iteration gave $A = -0.107$, $B = 0.143$, the $H \cdots H$ steric coefficient a_S [eqn. (3)] = $+24.55$ ppm Å^6, μ [eqn. (8)] = 26.2 ppm Å^3 and the fc values in Table 1. In fulvene and acenaphthylene both the ring current of the five-membered ring (μ_P) and also the factors (fc) for the benzenoid rings in acenaphthylene were parametrised separately. This gave $\mu_P = 11.6$ ppm Å^3 and $fc = 0.81$. These iterations are for two unknowns and seven observed shifts, thus the iterations are still overdetermined.

The determination of these unknown parameters also allows the calculation of the proton SCS of the monosubstituted benzenes in Table 3 as the electric field and anisotropic effects of the substituents have already been determined previously. The appropriate values of the coefficients in eqn. (10) needed to model the effect of the alkyl substituents on the π densities were $a_r^0 = a_r + 0.15$, $\omega = -0.50$. The only other effect to consider is the steric effect of the side-chain protons on the *ortho* protons of the benzene ring. The steric effect of alkane protons on olefinic protons was determined from a general investigation involving a variety of olefinic molecules[42] to be deshielding and this result was used here. The steric effect of the OH and NH protons in alcohols and amines has been shown to be zero[45] and again this result was incorporated into the present calculations. This allowed the determination of the proton SCS of all the monosubstituted benzenes of Table 3 and these results are given with the observed data in the table. There is generally excellent agreement between the observed and calculated shifts in Table 3 and this good agreement allows the SCS in the benzene ring to be analysed further in terms of the constituent interactions (see discussion).

Finally it was felt to be of interest to determine whether the equivalent dipole ring current calculation given here could be used to determine the benzene ring current effect for protons at the side and over the benzene ring. This data was used by Schneider[8] in determining the accuracy of the various ring current models. We consider here two illustrative examples: the unique CH proton in the tribridged cyclophane (**15**)[8] and the protons in [10]paracyclophane (**16**).[46] The proton chemical shifts for both compounds have been recorded in dilute CDCl$_3$ solution. The geometries of both compounds were modelled by PCMODEL and GAUSSIAN. **15** is a rigid strained molecule but in **16** the methylene chain exists in two equivalent rapidly interconverting staggered conformations. Thus the two protons on each methylene group in the alkyl chain have the same observed shift and the calculated shifts for the two methylene protons have to be averaged. The calculations used eqn. (8) to determine the ring current shifts with the value of the equivalent dipole obtained above. The CH proton of **15** is observed at -4.03 δ (calc. -4.03 δ) and the corresponding data for **16** are given in Table 4.

Discussion

The general agreement of the observed *vs.* calculated shifts in Tables 2 and 4 and the observed *vs.* calculated SCS of Table 3 is very good. Although the calculated values for models A and models B for the individual protons vary appreciably (Table 2), the overall agreement for both models is similar. For the 57 data points of Table 2 the rms error (obs. *vs.* calc. shifts) is 0.13 ppm (model A) and 0.12 ppm (model B) over a range of 3.3 ppm. The analogous calculation using only the benzene ring current (*i.e.* all fc values = 1.0) gives much poorer agreement (rms = 0.28 ppm) showing that it is necessary to take account of the variation in the ring current density for a proper description of the proton chemical shifts. Although for convenience the SCS are given in Table 3, as the proton chemical shift of benzene is calculated accurately (Table 2) obviously the actual chemical shifts of all the substituted benzenes are calculated to the same accuracy as the SCS values in Table 3. It can be seen that the great majority of the observed shifts are reproduced to <0.1 ppm, though there are some exceptions (see later). This is the first quantitative calculation of this data and it implies that the latest CHARGE programme (CHARGE7) can be applied with some confidence to the prediction of the proton chemical shifts of virtually any substituted benzenoid compound.

The calculation also provides new insight into the interpretation of these proton chemical shifts as the different interactions responsible for the calculated values are separately identified and quantified in the CHARGE programme. The ring current calculations provide further evidence for the accuracy of the simple equivalent dipole model of the benzene ring current. The value of μ of 26.2 ppm Å^3 is very similar to that obtained from the classical circulating current model (27.6).[17,47] The calculations also confirm previous studies[47] in demonstrating that the ring current effect is not the only factor responsible for the difference between the ethylene and benzene proton shifts. The experimental difference of 1.93 ppm (Table 2) is made up of 1.77 ppm from the ring current and 0.17 ppm from the electronic effects of the β and γ carbon atoms of benzene. This was allowed for in some previous ring current calculations by using cyclohexadiene rather than ethylene as the appropriate olefinic model[47] and the above calculations support this approach. It is also pertinent to note the excellent agreement obtained with the simple equivalent dipole model. On this basis the use of the more complex double dipole and double-loop models does not appear to be justified. Interestingly Mallion[48] came to exactly the same conclusion many years ago.

It is of interest to compare the values of the separate ring current factors (fc) in Table 1 with the values obtained previously.[7,12] The trends are similar, supporting the original compartmentalisation of these factors, though the values obtained here are mostly much nearer to the benzene value ($fc = 1$) than the previous calculations. This is exactly to be expected as Huckel theory usually over estimates any electron separation. The only exception is the value for coronene. In model A the outer rings are of type 16b (*i.e.* analogous to the middle ring of phenanthrene) but this value of the ring current density (0.745, Table 1) gives a much too low value for the proton chemical shift. A value of fc of 1.06 reproduces the experimental proton chemical shift. In model B this problem does not arise as coronene is a separate case, and the iteration gives a value of $fc = 1.008$, very close to the benzene value and the Huckel calculated value.

It is encouraging that the calculated shifts for the non-alternant hydrocarbons of fulvene and acenaphthylene are in very good agreement with the observed shifts (Table 2) as this suggests that the approach adopted here can be extended to these systems. The value of the ring current of the five-membered ring obtained here (11.6 ppm Å^3) may be used to obtain the current density in the five-membered ring as the equivalent dipole $\mu = iA$ where A is the area of the current loop.

Table 5 Calculated contributions to proton SCS ($\Delta\delta_H$) in substituted benzenes

Substituent			Calculated contribution				
			γ-Effect	Steric	Anisotropic	Electric field	π Shift
CH₃	*ortho*		−0.144	—	—	—	−0.064
	meta		—	—	—	—	−0.132
	para		—	—	—	—	−0.183
F	*ortho*		0.128	—	—	—	−0.360
	meta		—	—	—	0.115	−0.137
	para		—	—	—	0.088	−0.332
OH	*ortho*		−0.128	—	—	—	−0.494
	meta		—	0.011	—	—	−0.188
	para		—	0.005	—	—	−0.456
CHO	*ortho*	H-2	0.144	—	−0.125	0.360	0.195
		H-6	0.144	—	0.767	0.153	0.195
	meta	H-3	—	—	−0.043	0.062	0.073
		H-5	—	—	0.107	0.069	0.073
	para		—	—	0.010	0.049	0.181
CN	*ortho*		−0.230	—	—	0.372	0.151
	meta		—	—	—	0.127	0.056
	para		—	—	—	0.097	0.138
NO₂	*ortho*		0.096	—	—	0.606	0.105
	meta		—	—	—	0.143	0.043
	para		—	—	—	0.105	0.115

After allowing for the area of the five-membered ring compared to benzene this gives a current density of $0.63i_b$, much less than benzene. More data on similar systems would be necessary to confirm this result.

Proton SCS in substituted benzenes

The good agreement between the observed and calculated SCS in Table 3 together with the separation of the different interactions in CHARGE allows us to determine these interactions for the different substituents and Table 5 gives the contributions to the proton SCS for selected substituents in Table 3.

In Table 5 for the anisotropic substituents (*e.g.* C=O) the contributions are given for each separate proton (*e.g.* H2 and H6) although these are averaged in Table 3 to compare with the observed (averaged) data. The large effect of the carbonyl anisotropy is clearly apparent in these figures. The orientation of the carbonyl is such that the oxygen atom is *syn* to H6. The calculations are supported by and also show very clearly the origin of the large *ortho* proton deshielding in *o*-methoxybenzaldehyde (H6 7.82 δ)[37] compared to *o*-hydroxybenzaldehyde (H6 7.50 δ) where the carbonyl group is now hydrogen bonded to the hydroxy group.

Table 5 also shows that the carbonyl anisotropy is the major factor in the *meta* proton SCS of benzaldehyde (*cf.* H3 and H5). This demonstrates the importance of these "other" effects, which are of course not included in any of the correlations of electron densities *etc.* with the proton SCS. Indeed it is important to stress the difference between the present calculations and the correlations with Hammett σ,[22] the Swain–Lupton F and R values[49] *etc.* The CHARGE calulations are ground state calculations whilst the other parameters are derived from pH and rate constants and therefore reflect energy differences between the anion or the transition state and the ground state of the molecule, a totally different quantity.

Nevertheless in view of the numerous correlations of these quantities with the proton SCS it is useful to consider these correlations together with the present calculations. The correlation between the proton SCS and Hammett σ_I and σ_R^0 values was given as eqn. (12)[21] for a similar set of substituents to those

$$\text{SCS (}para\text{)} = 0.27\sigma_I + 1.25\sigma_R^0$$
$$\text{SCS (}meta\text{)} = 0.24\sigma_I + 0.446\sigma_R^0 \qquad (12)$$

in Table 5 and a similar analysis of the SCS in terms of the Swain–Lupton F and R values gives eqn. (13).

$$\text{SCS (}para\text{)} = 0.142F + 0.926R$$
$$\text{SCS (}meta\text{)} = 0.098F + 0.376R \qquad (13)$$

These equations are reasonably consistent implying in general a much greater resonance effect on the *para* proton SCS than on the *meta* proton SCS. Inspection of the data in Table 5 shows a much more diverse pattern. Indeed the major disadvantage of such correlations is that they obscure the large differences in the SCS components of the various groups which all need to be considered individually. *E.g.* the OH group has no anisotropic or steric effect and both the *meta* and *para* SCS are dominated by the π electron shift. This is much greater in the *para* position but the *meta* SCS is still dominated by the π effect. In contrast, in benzaldehyde the electric field and anisotropy contributions equal the π shift for the *meta* proton and are a significant but minor contribution for the *para* proton. The nitro and cyano groups differ from both of these in that they appear to have no anisotropic effect but the electric field effect is predominant at the *meta* proton and equal to the π shift at the *para* proton. Further investigations in our laboratory have confirmed this result for the cyano group[43] and it would be of interest to perform similar investigations for the nitro group. Clearly each substituent group must be considered separately in order to evaluate the separate steric, electric and anisotropic contributions at the various protons.

Finally it is of interest to consider the discrepancies in the observed *vs.* calculated data of Table 3. The most interesting systematic deviation is that due to Br and I. The calculated values for the *para* SCS for all the halogens are in excellent agreement with the observed data and the *ortho* and *meta* SCS for F and Cl are in reasonable agreement. However the *ortho* SCS for Br and I are more deshielding than calculated and the *meta* SCS much more shielding than calculated. The *ortho* SCS are given by the γ effect, which is a function of the polarisability

of the γ atom *i.e.* the halogen. The value of the polarisability was taken from data on alkyl halides[24] thus this may not be appropriate for substituted benzenes. In contrast the *meta* SCS are of interest as similar exceptional behaviour was observed for the 3-protons in equatorial halocyclohexanes.[50] Again there is a large deviation from the calculated value for the Br and I substituents. The equatorial proton is in a similar W orientation to the halogen atom as the *meta* proton in the substituted benzenes and it may be that there is an additional long range (four bond) mechanism for the halogen atoms in this specific orientation. Further studies would be necessary to confirm this.

Acknowledgements

References

1 Part 13, R. J. Abraham and N. J. Ainger, *J. Chem. Soc.*, *Perkin Trans. 2*, 1999, 441.
2 (*a*) J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution NMR Spectroscopy*, Pergamon Press, Oxford, 1965; (*b*) R. C. Haddon, V. R. Haddon and L. M. Jackman, *Top. Curr. Chem.*, 1971, **16**, 103.
3 L. Pauling, *J. Chem. Phys.*, 1936, **4**, 673.
4 J. A. Pople, *J. Chem. Phys.*, 1956, **24**, 1111.
5 (*a*) J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, 1957, **79**, 846; (*b*) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.
6 (*a*) R. J. Abraham, *Mol. Phys.*, 1961, **4**, 145; (*b*) R. J. Abraham and C. J. Medforth, *Magn. Reson. Chem.*, 1987, **25**, 432.
7 (*a*) C. W. Haigh and R. B. Mallion, *Mol. Phys.*, 1970, **18**, 737 and 767; (*b*) C. W. Haigh, R. B. Mallion and E. A. G. Armour, *Mol. Phys.*, 1970, **18**, 751.
8 H. J. Schneider, V. Rudiger and U. Cuber, *J. Org. Chem.*, 1995, **60**, 996.
9 H. J. Bernstein, W. G. Schneider and J. A. Pople, *Proc. R. Soc. London, Ser. A*, 1956, **236**, 515.
10 J. A. Pople, *Mol. Phys.*, 1958, **1**, 175.
11 R. McWeeny, *ibid.*, 1958, **1**, 311.
12 N. Jonathan, S. Gordon and B. P. Dailey, *J. Chem. Phys.*, 1962, **36**, 2443.
13 T. B. Cobb and J. D. Memory, *J. Chem. Phys.*, 1967, **47**, 2020.
14 M. Westermayer, G. Hafelinger and C. Regelmann, *Tetrahedron*, 1984, **40**, 1845.
15 (*a*) S. Castellano and C. Sun, *J. Am. Chem. Soc.*, 1966, **88**, 4741; (*b*) S. Castellano, C. Sun and R. Kostelnik, *Tetrahedron Lett.*, 1967, **46**, 4635 and **51**, 5205; (*c*) M. P. Williamson, R. J. Kostelnik and S. M. Castellano, *J. Chem. Phys.*, 1968, **49**, 2218.
16 K. Hayamizu and O. Yamamoto, *J. Mol. Spectrosc.*, 1968, **28**, 89 and 1969, **29**, 183.
17 R. J. Abraham, J. Fisher and P. Loftus, *Introduction to NMR Spectroscopy*, J. Wiley, New York, 1988.
18 J. B. Lambert, H. B. Shurvell, D. A. Kightner and R. G. Cooks, *Organic Structural Spectroscopy*, Prentice-Hall, New Jersey, 1998.
19 E. Pretsch, J. Seibl, T. Clerc and W. Simon, *Tables of Spectral Data for Structure Determination of Organic Compounds*, 2nd Edn., Springer-Verlag, Berlin, 1989.
20 G. C. Levy and G. L. Nelson, *Carbon-13 NMR for Organic Chemists*, J. Wiley, New York, 1972.
21 W. J. Hehre, R. W. Taft and R. D. Topsom, *Prog. Phys. Org. Chem.*, 1976, **12**, 159.
22 R. T. C. Brownlee and R. W. Taft, *J. Am. Chem. Soc.*, 1970, **92**, 7007.
23 G. K. Hamer, I. R. Peat and W. F. Reynolds, *Can. J. Chem.*, 1973, **51**, 897 and 915.
24 R. J. Abraham, L. Griffiths and M. A. Warne, *J. Chem. Soc.*, *Perkin Trans. 2*, 1997, 31.
25 R. J. Abraham, L. Griffiths and M. A. Warne, *J. Chem. Soc.*, *Perkin Trans. 2*, 1997, 203, 881.
26 R. J. Abraham, L. Griffiths and M. A. Warne, *ibid.*, 1998, 1751.
27 13th International NMR Conference, Edinburgh, July, 1999.
28 R. J. Abraham, L. Griffiths and M. A. Warne, *Magn. Reson. Chem.*, 1998, **S179**, 36.
29 (*a*) R. J. Abraham and P. E. Smith, *J. Comput. Chem.*, 1987, **9**, 288; (*b*) R. J. Abraham and P. E. Smith, *J. Comput. Aided Mol. Des.*, 1989, **3**, 175.
30 (*a*) R. J. Abraham and P. E. Smith, *Nucleic Acids Res.*, 1988, **16**, 2639; (*b*) A. Streitweiser, *Molecular Orbital Theory for Organic Chemists*, J. Wiley, New York, 1961.
31 A. L. McClellan, *Tables of Experimental Dipole Moments*, vol. 1, Freeman, London, 1963; vols. 2 and 3 Rahara Enterprises, California, vol. 2, 1974, vol. 3, 1989.
32 H. Gunther, *NMR Spectroscopy*, 2nd edn., J. Wiley, Chichester, 1995, p. 71.
33 P. B. Ayscough, *Electron Spin Resonance in Chemistry*, Methuen, London, 1967.
34 GAUSSIAN94, Gaussian Inc., Pittsburgh, PA, 1994, J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople.
35 PCMODEL version 7, Serena Software Ltd., PO Box 3076, Bloomington, Indiana, 1998.
36 U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon and S. Sternhell, *Tetrahedron*, 1969, **25**, 691.
37 C. J. Puchert and J. Behnke, *Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*, Aldrich Chemical Company Inc., Milwaukee, USA, 1993.
38 J. Netka, S. L. Crump and B. Rickborn, *J. Org. Chem.*, 1986, **51**, 1189.
39 U. Nuchter, G. Zimmermann, V. Francke and H. Hopf, *Liebigs Ann. Rec.*, 1997, 1505.
40 Landholt-Bornstein, vol. 7, *Structure Data of Free Polyatomic Molecules*, ed. K. H. Hellwege and A. M. Hellwege, Springer, New York, 1976.
41 (*a*) O. Exner, *Dipole Moments in Organic Chemistry*, George Thieme Pub., Stuttgart, 1975; (*b*) V. I. Minkin, O. A. Osipov and Y. A. Zhdanov, *Dipole Moments In Organic Chemistry*, Plenum Press, New York, 1970.
42 R. J. Abraham and M. Canton, unpublished work.
43 R. J. Abraham and M. Reid, *Magn. Reson. Chem.*, in the press.
44 S. S. Kuo, *Computer Applications of Numerical Methods*, ch. 8, Addison-Wesley, London, 1972.
45 R. J. Abraham, unpublished work.
46 A. Agarwal, J. A. Barnes, J. L. Fletche, M. J. McGlinchey and B. G. Sayer, *Can. J. Chem.*, 1973, **51**, 897.
47 R. J. Abraham and W. A. Thomas, *J. Chem. Soc. B*, 1966, 127.
48 R. B. Mallion, *J. Chem. Phys.*, 1980, **75**, 793.
49 C. G. Swain and E. P. Lupton, *J. Am. Chem. Soc.*, 1968, **90**, 4328.
50 R. J. Abraham, L. Griffiths and M. A. Warne, *J. Chem. Soc.*, *Perkin Trans. 2*, 1997, 2151.

Paper a907830d