Proton chemical shifts in NMR. Part 16.[1] Proton chemical shifts in acetylenes and the anisotropic and steric effects of the acetylene group

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The proton resonance spectra of a number of acetylenes of fixed geometry were recorded in dilute $CDCl_3$ solution and assigned. These were acetylene, equatorial- and axial-cyclohexylacetylene at −60 °C, 1,4-di-1-adamantylbutadiyne, 1-ethynyl-*t*- and -*c*-4-*tert*-butylcyclohexan-*r*-1-ol, 2-*exo*-ethynylnorbornan-2-ol† and 2,2′-ethyne-1,2-diyldibornan-2-ol. The aromatic acetylenes measured were phenylacetylene, *o*-ethynyltoluene, 2-ethynylnaphthalene and 9-ethynylanthracene. This data together with previous literature data for but-1-yne, but-2-yne, pent-1-yne, *tert*-butylacetylene, *p*-ethynyltoluene, 1-ethynylnaphthalene and 2-ethynylpropene allowed the determination of the acetylene substituent chemical shifts (SCS) in a variety of molecules. These SCS were analysed in terms of the magnetic anisotropy and steric effects of the acetylene group together with a model (CHARGE7) for the calculation of the two-bond and three-bond electronic effects. For the aromatic acetylenes ring current and π electron effects were included.

Analysis of the SCS showed that the acetylene SCS were due to anisotropic and steric effects plus electronic effects for near protons. A value of $\Delta\chi^{C\equiv C}$ of -11.1×10^{-6} cm^3 mol^{-1} was obtained together with a steric coefficient of 56.6 Å^6. Better results were obtained with both effects operating from the carbon atoms.

The model gives the first comprehensive calculation of the SCS of the acetylene group. For the data set considered of 88 proton chemical shifts spanning *ca.* 8.0 ppm the rms error of observed *vs.* calculated shifts was 0.074 ppm.

Introduction

The magnetic anisotropy of the C≡C bond was first proposed by Pople to explain the high-field shift of the acetylene proton compared to that of ethylene. He subsequently obtained an estimate of $\Delta\chi^{C\equiv C}$ of -19.4×10^{-6} cm^3 mol^{-1} from approximate MO theory. In a review of the early investigations Bothner-By and Pople[2] noted other values of $\Delta\chi^{C\equiv C}$. Reddy and Goldstein[3] obtained a value of -16.5×10^{-6} using the linear relationship they found between proton shifts and the corresponding ^{13}C–^1H couplings in compounds where the anisotropic effects were negligible. The anisotropic effects of other groups including the C≡C group were then extrapolated from these linear plots. In a similar manner Zeil and Buchert[4] examined the proton chemical shifts of a variety of acetylenes and nitriles. Assuming that the proton chemical shifts were linearly dependent on the substituent electronegativity plus a constant shift arising from the diamagnetic anisotropy gave a value of -36×10^{-6}. Subsequently Shoemaker and Flygare[5] obtained a value of the anisotropy of the acetylene group as -7.7×10^{-6} from the second-order Zeeman effect in the microwave spectra of propyne and its isotopic species.

Mallory and Baker[6] showed that regions of deshielding existed alongside C≡C bonds by the observation of low-field proton NMR chemical shifts in the aromatic compounds 4-ethynylphenanthrene, 5-ethynyl-1,4-dimethylnaphthalene and 5-ethynyl-1,4-diethylnaphthalene. They concluded that the deshielding effect of the C≡C bond fell off approximately as $1/r^3$.

No systematic attempt has yet been made to calculate the proton chemical shifts of acetylenic molecules and this is the subject of this investigation. We present the complete assignment of the proton spectra of a variety of aliphatic and aromatic acetylenes. This provides a sufficient amount of data for a quantitative analysis of acetylene SCS using a previous model for the calculation of proton chemical shifts. This model is based on simple charge calculations over one, two and three bonds and on steric, anisotropic and electric field contributions for protons greater than three bonds away from the substituent in question. The model has successfully been applied to a variety of saturated hydrocarbons,[7a,b] haloalkanes,[8] ethers,[9] ketones[10] and aromatic compounds.[11] We shall use this model to perform a quantitative analysis of C≡C SCS and show that the proton chemical shifts are influenced by both the magnetic anisotropy and steric effects of the acetylene group.

Theory

As the theory has been given previously[11,12] only a brief summary of the latest version (CHARGE7) will be 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. There is a β effect from atom K proportional to both the electronegativity of atom K and the polarisability of atom I. There is also a γ effect (GSEF) from atom L given by the product of the atomic polarisabilities of atoms I and L for I = H and L = F, Cl, Br, I, S. However for the second row atoms (C, O, *etc.*) the γ effect (*i.e.* C–C–C–H) is

† The IUPAC name for norbornane is bicyclo[2.2.1]heptane.

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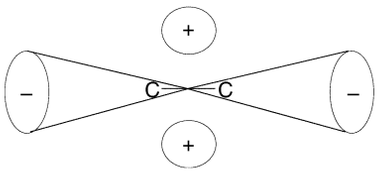


Fig. 1 Representation of the anisotropic shielding ($\Delta\delta$) in an axially symmetric molecule such as acetylene.

parametrised separately and is given by eqn. (1) where θ is the C–C–C–H dihedral angle and A and B empirical parameters.

$$\begin{aligned} \text{GSEF} &= A + B_1\cos\theta \quad 0° \le \theta \le 90° \\ &= A + B_2\cos\theta \quad 90° \le \theta \le 180° \end{aligned} \tag{1}$$

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).

$$\delta_{\text{charge}} = 160.84q - 6.68 \tag{2}$$

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

$$\delta_{\text{steric}} = a_S/r^6 \tag{3}$$

Furthermore any X···H steric contribution 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 determined as 3.67×10^{-12} esu units (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.

$$\delta_{\text{el}} = A_Z E_Z \tag{4}$$

The magnetic anisotropy of a bond with cylindrical symmetry such as C≡C was obtained using the McConnell equation[13] (eqn. (5)), where R is the distance from the perturbing group to the nucleus of interest in Å, ϕ is the angle between the vector R and the symmetry axis and $\Delta\chi^{C\equiv C}$ the molar anisotropy of the C≡C bond. ($\Delta\chi^{C\equiv C} = \chi^{C\equiv C}_{\text{parl}} - \chi^{C\equiv C}_{\text{perp}}$) where $\chi^{C\equiv C}_{\text{parl}}$ and $\chi^{C\equiv C}_{\text{perp}}$ are the susceptibilities parallel and perpendicular to the symmetry axis respectively. This is illustrated in Fig. 1.

$$\delta_{\text{anisotropy}} = \Delta\chi^{C\equiv C}(3\cos^2\phi - 1)/3R^3 \tag{5}$$

Aromatic compounds

For aromatic compounds it is necessary to include the shifts due to the aromatic ring current and the π electron densities in the aromatic ring. The aromatic ring current density is calculated in CHARGE from the Pauling theory and the equivalent dipole approximation is then used to calculate the ring current shifts.[11] This treatment reproduces the proton chemical shifts of a wide range of aromatic hydrocarbons and is incorporated unchanged here.

The π electron densities are calculated from Hückel theory.[14,15] The standard coulomb and resonance integrals for the Hückel routine are given by eqn. (6), where α_0 and β_0

$$\begin{aligned} \alpha_r &= \alpha_0 + h_r\beta_0 \\ \beta_{rs} &= k_{rs}\beta_0 \end{aligned} \tag{6}$$

are the coulomb and 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. For alternant aromatic hydrocarbons this gives π electron densities at every carbon equal 1.0 as in benzene and this agrees with the results of more sophisticated calculations.[1]

For substituted aromatics the appropriate values of the coefficients h_r and k_{rs} in eqn. (6) for the orbitals involving hetero atoms have to be found. These are now obtained in CHARGE so that the π densities calculated from the Hückel routine reproduce the π densities given from *ab initio* calculations.

The effect of the excess π electron density at a given carbon atom on the proton chemical shifts of the neighbouring protons is given in CHARGE by eqn. (7). Δq_α and Δq_β are the excess π

$$\Delta\delta = a_1\Delta q_\alpha + a_2\Delta q_\beta \tag{7}$$

electron density at the α and β carbon atoms and the values of the coefficients a_1 and a_2 were found to be 10.0 and 2.0 ppm per electron.[11]

The above contributions are added to the shifts of eqn. (2) to give the calculated shift of eqn. (8).

$$\delta_{\text{total}} = \delta_{\text{charge}} + \delta_{\text{steric}} + \delta_{\text{anisotropy}} + \delta_{\text{el}} + \delta_\pi \tag{8}$$

Application to the acetylene group

The acetylene group has in principle steric, electric field and anisotropic effects on protons more than three bonds away plus for aromatics an effect on the π electron densities. All these have to be incorporated into the model.

The major electric field of the acetylene group is due to the C–H bond as the C≡C bond is non-polar. The electric field calculation for any C–H bond is automatically included in the model. The C≡C group has cylindrical symmetry and eqn. (5) is used to calculate the anisotropy contribution. There is a possible steric effect of the acetylene group on the neighbouring protons and a possible steric effect of the near aliphatic protons on the acetylene proton. These are both given by eqn. (3) with different steric coefficients a_S which may be of either sign. Thus the unknowns to be obtained are $\Delta\chi$, the molar anisotropy of the C≡C bond and the steric coefficients a_S.

For protons of three bonds or less from the C≡C group it is necessary to determine the orientational dependence of the γ proton chemical shift with respect to the α acetylene carbon due to electronic effects. This is simulated by a γ substituent effect from the acetylene carbon (H–C–C–C≡) following eqn. (1), in which the coefficients A and B may differ for the C≡C group in aromatic *vs.* saturated compounds. Also in CHARGE the β effect is given by a simple general equation which was sufficient for the calculation of charge densities but not sufficiently accurate to reproduce the proton chemical shifts. Thus the β effect from the acetylene carbon atom (H–C–C≡) needs to be obtained. As there is no orientation dependence in this case only one coefficient is required.

For the aromatic acetylenes it is necessary to obtain the appropriate values of the factors h_r and k_{rs}, which are the Hückel integrals for the C≡C group (eqn. (6)). The π electron densities and dipole moments from *ab initio* calculations are very dependent on the basis set used. The 3-21G basis set gave the best agreement with the observed dipole moments (Table 1)

Table 1 Total and π (in parentheses) charges (*me*), and dipole moments (D) for propyne and phenylacetylene

Atom	Method				Observed
	STO-3G	3-21G	6-31G	CHARGE	
Propyne					
C_β	−136 (−21.7)	−419 (−22.0)	−488 (−24.7)	−106 (−22.4)	
C_α	−37 (11.3)	−47 (12.2)	−29 (13.9)	−62 (22.4)	
μ/D	0.50	0.69	0.68	0.50	0.75
Phenylacetylene					
C_β	−125 (−5.1)	−363 (−14.2)	−531 (−16.5)	−83 (−10.6)	
C_α	−40 (−0.9)	−60 (−0.1)	−155 (2.4)	−46 (−0.7)	
C-1	2 (−21.0)	−44 (−32.6)	−156 (−26.7)	−24 (−0.6)	
C-2	−54 (8.6)	−215 (18.5)	−148 (14.9)	−57 (4.5)	
C-3	−63 (0.3)	−230 (−1.3)	−209 (0.1)	−72 (−0.3)	
C-4	−59 (9.1)	−237 (12.6)	−188 (10.8)	−73 (3.6)	
μ/D	0.50	0.65	0.64	0.36	0.72

and the π densities from this basis set were used to parametrise the Hückel calculations. The CN group contains an sp hybridised carbon atom and the parameters for this group have already been derived.[1] Thus the values of h_r(Csp) and k_{rs}(Csp^2–Csp) used for nitriles were used for the acetylene calculations as the Hückel integrals for Csp operate for both of these functional groups. A value of k_{rs} of 1.60 (Csp–Csp) gave π electron densities for the aromatic acetylenes in reasonable agreement with those from the *ab initio* calculations.

The accuracy of the π densities calculated in the CHARGE program can be examined by calculating the dipole moments of some acetylenes. The calculated *vs.* observed (in parentheses) dipole moments[16] (D) of propyne, but-1-yne, *tert*-butylacetylene, phenylacetylene and *p*-ethynyltoluene are 0.50 (0.75), 0.50 (0.81), 0.52 (0.66), 0.36 (0.72) and 1.26 (1.02) and the general agreement is support for the π density calculations. The electron densities (total and π) and dipole moments calculated for propyne and phenylacetylene by CHARGE and GAUSSIAN94 are given in Table 1.

Values of h_r and k_{rs} for X–Csp have been determined for a number of different substituents C≡C–X. Values of h_r for F, Cl and O for olefins (C=C–X) were obtained previously from π electron densities calculated from GAUSSIAN94W at the 3-21G level for a range of olefinic compounds.[17]

These were left unchanged for the acetylenes and the values of k_{rs} for the ≡C–X bond varied for the best agreement with the *ab initio* π electron densities. Values of 0.74 (Csp–F), 0.57 (Csp–Cl) and 1.00 (Csp–O) gave reasonable agreement with those calculated from GAUSSIAN94W. Again, the accuracy of the calculated charges can be examined by calculating the dipole moments of these molecules. The calculated *vs.* observed (in parentheses) dipole moments (D) of fluoroacetylene, chloroacetylene, propynal and methoxyacetylene are 0.79 (0.75), 0.74 (0.44), 2.56 (2.46), and 1.62 (1.93). Note that the value of k_{rs} for the Csp–Csp^2 bond is already known from the phenylacetylene data. Also, the calculated *vs.* observed (in parentheses) chemical shifts of the acetylene proton in fluoroacetylene, chloroacetylene and propynal are 1.33 (1.63), 1.95 (1.80) and 3.61 (3.47). The good agreement of the calculated *vs.* observed chemical shifts for these molecules is strong support for the above treatment.

Experimental

The molecules studied here with the atom numbering are shown in Fig. 2.

Acetylene (**1**), cyclohexylacetylene (**10**), 1,4-di-1-adamantylbutadiyne (**11**) and phenylacetylene (**12**) were obtained commercially.[18–21] *o*-Ethynyltoluene (**13**) and 2-ethynylnaphthalene (**16**) were synthesised by double elimination of 1-(1,2-dibromoethyl)-2-methylbenzene and 1-(1-naphthyl)-1,2-dibromoethane.[22] 9-Ethynylanthracene (**17**) was synthesised by Sonogashira coupling[23] of 9-bromoanthracene and trimethylsilylacetylene. 1-Ethynyl-*t*- and -*c*-4-*tert*-butylcyclohexan-*r*-1-ol (**7**-*trans*, **7**-*cis*), 2-*exo*-ethynylbicyclo[2.2.1]heptan-2-ol (**8**) and 2,2′-ethyne-1,2-diylbis(1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol) (**9**) were synthesised by the addition of ethynylmagnesium bromide to the corresponding ketones in THF.[24]

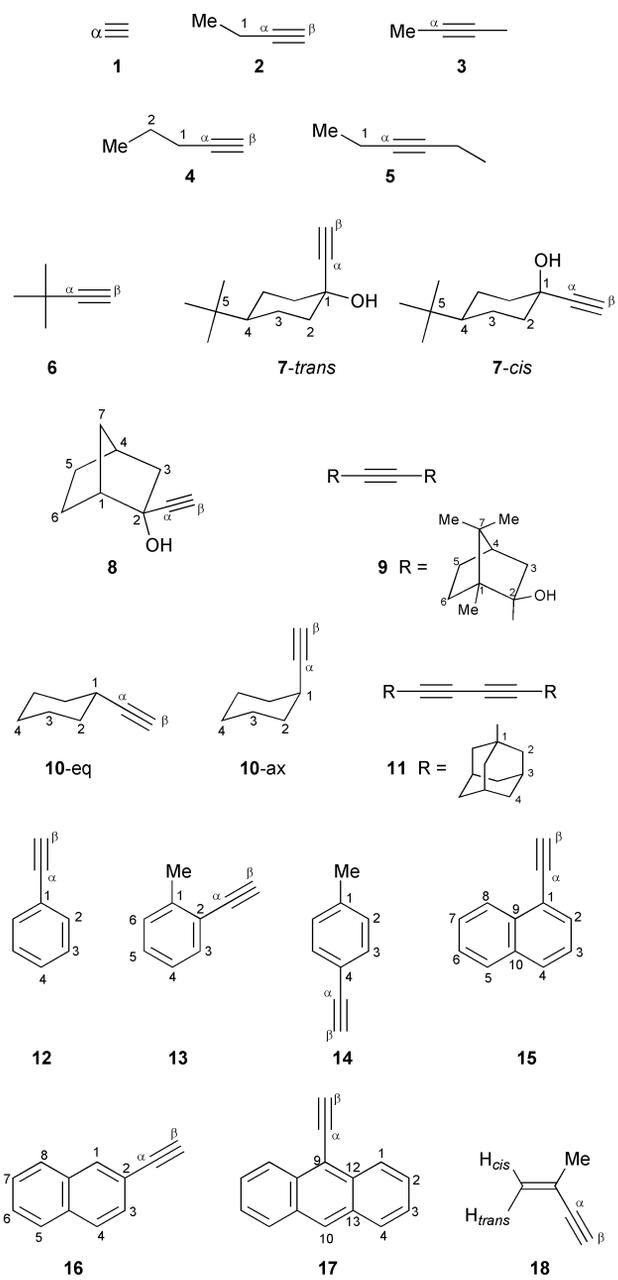


Fig. 2 Molecules studied and their numbering.

Table 2 Observed *vs.* calculated proton chemical shifts (δ) for acetylene[a] (**1**), but-1-yne (**2**), but-2-yne (**3**), pent-1-yne (**4**), *n*-hex-3-yne (**5**) and *tert*-butylacetylene (**6**)

	2		**3**		**4**		**5**		**6**	
Proton	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
H-1	2.25	2.18	—	—	2.18	2.02	2.15	2.23	—	—
H-2	—	—	—	—	1.57	1.55	—	—	—	—
Me	1.18	1.10	1.75	1.82	1.00	0.77	1.11	1.13	1.24[b]	1.24
C≡C–H	1.97	2.04	—	—	1.95	2.05	—	—	2.07	2.10

[a] Acetylene, obs. 1.91, calc. 1.91. [b] *tert*-Butyl.

^{1}H and ^{13}C NMR were obtained on a Bruker AMX400 spectrometer operating at 400 MHz for proton and 100.63 MHz for carbon. The spectra for **7**-*trans*, **7**-*cis*, **8** and **9** were recorded on a Varian 750 MHz spectrometer at Glaxo-Wellcome[25] which was used for the HMQC, HMBC and NOE experiments.

The spectra were recorded in 10 mg cm^{-3} (^{1}H) and *ca.* 50 mg cm^{-3} (^{13}C) solutions with a probe temperature of *ca.* 25 °C in $CDCl_3$ and referenced to TMS. Typical running conditions of the spectrometers were 128 transients, spectral width 3300 Hz and 32 k data points. This gave an acquisition time of 5 s and zero-filled to 128 k to give a digital resolution of 0.025 Hz.

The 2D experiments were conducted using the Bruker COSY-DQF and HXCO and the Varian HMQC and GHMQC-DA pulse sequences.[26,27] The geometry of the compounds investigated was obtained initially using GAUSSIAN94W at the RHF/6-31G* and MP2/6-31G* levels[28a] and later using GAUSSIAN98W[28b] at the DFT/B3LYP/ 6-31G** level. All the calculations were carried out using a PC.

Spectral assignments

The assignments of all the compounds investigated are given in Tables 2–6 together with the calculated proton chemical shifts. Letters e, a, x, n and s denote equatorial, axial (or *anti*), *exo*, *endo* and *syn* respectively.

The ^{1}H NMR data for but-1-yne (**2**), but-2-yne (**3**), pent-1-yne (**4**), hex-3-yne (**5**), *tert*-butylacetylene (**6**), *p*-ethynyltoluene (**14**), and 2-ethynylpropene (**18**) were from ref. 29 and that for 1-ethynylnaphthalene (**15**) from ref. 22.

Cyclohexylacetylene (10). The spectra of the separate conformers were obtained by recording the spectra at −60 °C at which temperature the rate of interconversion of the conformers was slow on the NMR time scale. The integral ratio for protons 1e and 1a was 1 : 6.2 with the equatorial conformer more favoured to give ΔG (eq–ax) 0.70 kcal mol^{-1}, in fair agreement with previous measurements of ΔG (eq–ax). Eliel[30] quotes 0.41–0.52 kcal mol^{-1}.

A ^{1}H COSY spectrum was recorded at −60 °C to fully assign the equatorial conformer. For **10**-eq protons 1a, 2e and 2a are readily assigned and examination of the ^{1}H COSY spectrum plus the integrals of the ^{1}H spectrum gave the assignments of the remaining protons. For **10**-ax only protons 1e, 2e and 2a were assigned by examination of the ^{1}H COSY spectrum. The remaining protons were hidden underneath the resonances of the protons in **10**-eq.

1,4-Di-1-adamantylbutadiyne (11). The ^{1}H spectrum of **11** was assigned from the integrals and fine structure. H-δ was easily identified at *ca.* 1.94 ppm, H-γ as a doublet with a coupling of *ca*. 4.5 Hz to H-δ at *ca.* 1.86 ppm. H-e and H-a with respect to the acetylene group were a single broad resonance at *ca.*1.67 ppm.

1-Ethynyl-*t*- and -*c*-4-*tert*-butylcyclohexan-*r*-1-ol (7-*trans*, 7-*cis*). The ^{1}H, ^{13}C and 2D spectra for these isomers were recorded at 750 MHz. The spectra for the pure *trans* isomer were recorded, but the spectra for the *cis* isomer were recorded from a mixture of the *cis* and *trans* conformers. This was not a problem as the resonances were easily distinguished.

7-*trans*. The ^{1}H spectrum consists of five separate resonances including the methyl resonances. These were assigned by use of a ^{1}H COSY spectrum. H-2e and H-3e were easily distinguished as only H-3e displayed a coupling to H-4a. H-3a and H-2a were identified by examination of the splitting pattern of the resonances. This assignment was further confirmed by examination of a HETCOR spectrum and the known ^{13}C spectral assignment.[31]

7-*cis*. The ^{1}H spectrum of this isomer again consisted of five resonances and was readily assigned in the same way as **7**-*trans*.

A lanthanide induced shift experiment using Yb(fod)$_3$‡ was conducted on the sample of the pure *trans* isomer to confirm that the configuration of Fig. 2 was correct. Yb(fod)$_3$ is known to bind to the OH group and therefore downfield shifts in the ^{1}H spectrum would be expected to be observed on H2e and H2a, as they are in close proximity to the Yb(fod)$_3$. This was observed and confirmed the characterisation of this isomer.

2-*exo*-Ethynylbicyclo[2.2.1]heptan-2-ol (8). The ^{1}H, ^{13}C, 2D and NOE spectra for this compound were recorded at 750 MHz. An X-ray crystal structure[25] of this compound was obtained which confirmed the configuration at C-2 (Fig. 2). The ^{1}H spectrum for this compound consisted of ten resonances. H-1 and H-4 were readily identifiable by examination of their splitting patterns, H-1 appearing as a doublet, H-4 as a triplet. The other proton groups were elucidated by examination of a HETCOR plot together with the known assignment of the ^{13}C spectrum.[32] By examination of the ^{1}H COSY spectrum H-5x and H-6x were identified by their strong coupling to H-4 and H-1 respectively. H-3x was identified by its strong coupling to H-4 and H-5x. H-7s was identified by ^{1}H COSY, HMBC and NOE experiments. H-7s has a W-coupling to H-6n and H-5n. A strong 3-bond HMBC coupling is also observed to C-6 and C-5, which is much less intense in H-7-anti. An NOE performed on H-3x also helped to elucidate H-7s.

With these assignments it was possible to assign the geminal partners of H-3x, 5x, 6x and 7s from the HETCOR plot. The assignments of these protons were confirmed by NOE and HMBC experiments.

2,2′-Ethyne-1,2-diylbis(1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol) (9). The ^{1}H, ^{13}C, 2D and NOE spectra for this compound were recorded at 750 MHz. An X-ray crystal structure[25] of this compound was obtained to confirm the configuration at C-2. This showed that the compound was as shown in Fig. 2.

The ^{1}H spectrum of this compound consisted of seven resonances plus the three methyl resonances. H-3x and H-3n were readily identified by examination of their splitting patterns, H-3x is a doublet of triplets and H-3n a doublet. H-4 was identified by examination of the ^{1}H COSY. Large couplings to H-3x and H-5x were observed giving the expected triplet pattern.

‡ The IUPAC name for fod is 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato.

Table 3 Observed *vs.* calculated proton chemical shifts (δ) for equatorial and axial ethynylcyclohexane (**10**-eq, **10**-ax) and 1,4-di-1-adamantylbutadiyne (**11**)

Compound	Proton	Obs.	Calc.
10-eq	1a	2.246	2.094
	2e	1.977	1.877
	2a	1.355	1.408
	3e	1.734	1.617
	3a	1.200	1.084
	4e	1.666	1.600
	4a	1.170	1.138
	C≡C–H	2.182	2.100
10-ax	1e	2.871	2.667
	2e	1.775	1.877
	2a	1.481	1.519
	C≡C–H	2.278	2.137
11	γ	1.861	1.810
	δ	1.941	1.943
	e	1.681	1.646
	a	1.681	1.639

Table 4 Observed proton chemical shift (δ) for 1-ethynyl-*t*- and -*c*-4-*tert*-butylcyclohexan-*r*-1-ol (**7**-*trans*, **7**-*cis*) and observed *vs.* calculated C≡C SCS

			SCS	
Compound	Proton	δ(Obs.)	Obs.	Calc.
7-*trans*	2e	2.040	0.033	0.293
	2a	1.514	0.297	0.328
	3e	1.762	-0.020	0.051
	3a	1.367	0.321	0.543
	4a	1.000	0.035	0.0
7-*cis*	2e	2.037	0.204	0.222
	2a	1.705	0.216	0.263
	3e	1.596	0.048	0.047
	3a	1.379	0.020	-0.038
	4a	1.010	0.017	0.026

Table 5 Proton chemical shifts (δ) for (**8**) and (**9**) and observed *vs.* calculated C≡C SCS

			SCS	
Compound	Proton	δ(Obs.)	Obs.	Calc.
8	1	2.407	0.155	0.229
	3x	2.140	0.269	0.255
	3n	1.360	0.334	0.406
	4	2.250	0.079	−0.006
	5x	1.561	−0.009	−0.003
	5n	1.318	−0.017	−0.091
	6x	1.380	−0.002	0.003
	6n	1.979	0.109	−0.142
	7s	1.802	0.462	0.493
	7a	1.389	0.099	−0.055
9	3x	2.228	0.489	0.336
	3n	1.822	0.083	0.195
	4	1.750	0.029	−0.059
	5x	1.695	0.020	0.056
	5n	1.180	0.222	0.159
	6x	1.468	−0.037	0.134
	6n	1.835	0.827	1.153
	Me (1)	0.940	0.034	0.110
	Me (7s)	1.057	0.039	−0.057
	Me (7a)	0.870	0.042	−0.016

H-5x was also identified from the ^{1}H COSY as large couplings are seen to H-3x and H-4. H-5n was assigned by examination of a HETCOR plot plus the known assignment of the ^{13}C spectrum [32] and this was confirmed by an NOE with H-5x.

H-6x was assigned from the ^{1}H COSY spectrum, with a large coupling to H-5x. HMBC spectra also revealed a large 3-bond coupling from H-6x to the 1-methyl carbon atom. H-6n was then assigned from the HETCOR plot and confirmed by an NOE to H-6x.

The methyls in the 7a and 7s positions were easily assigned by NOE experiments. The 7a methyl gave NOEs to H-5x, H-6x and H-4 and the 7s methyl gave NOEs to H-3x, H-3n and H-4. The C-1 methyl is then immediately assigned.

Phenylacetylene (12). Even at 400 MHz H-3 and H-4 are a strongly coupled multiplet. Decoupling H-2 gave an AB_2 pattern for H-3 and H-4 which was routinely analysed.

***o*-Ethynyltoluene (13).** The ^{1}H spectrum for *o*-ethynyltoluene consists of four aromatic resonances. H-3 and H-6 are doublets of doublets with H-6 split further by its coupling to the methyl protons. H-4 and H-5 are triplets easily identified by their roofing patterns.

2-Ethynylnaphthalene (16). The aromatic spectrum for 2-ethynylnaphthalene consists of seven resonances. The singlet at 8.02 is identified as H-1. H-3 and H-4 are also easily identified as a doublet of doublets and a doublet respectively. As the ^{13}C assignment of this compound is known,[33] a ^{13}C–^{1}H HETCOR spectrum confirmed the ^{1}H assignment.

9-Ethynylanthracene (17). The aromatic spectrum for this compound consists of five resonances. H-10 is easily identified as the singlet occurring at *ca.* 8.43 ppm. A ^{13}C–^{1}H-undecoupled spectrum was recorded to assign C-1 and C-4, as C-4 has a $^1J_{CH}$ coupling to H-4 (*ca.* 160 Hz) and two $^3J_{CH}$ couplings to H-2 and H-10 (*ca.* 6 Hz) to give a doublet of triplets. C-1 has one $^1J_{CH}$ coupling to H-1 and one $^3J_{CH}$ coupling to H-3 to give two doublets of triplets. The assignment of C-1 and C-4 allows the assignment of H-1 and H-4 in the proton spectra from a HETCOR plot.

A ^{1}H COSY spectrum identified H-2 and H-3 from their couplings to H-1 and H-4 respectively and the assignment of C-2 and C-3 followed from a ^{1}H–^{13}C HETCOR plot. The ^{13}C assignments are as follows. C-1 127.65, C-2 127.18, C-3 125.63, C-4 128.59, C-9 115.97, C-10 127.08, C-12 130.64, C-13 132.21, C-α 77.50, C-β 84.00.

Further details of all the assignments and spectra are given in ref. 34.

Results

The data for the acetylenes obtained here in dilute $CDCl_3$ solution is in excellent agreement with the earlier data obtained in various solvents. The value for acetylene (1.91 ppm) compares with previous literature values of 1.80 (CCl_4)[35] and 1.91 (CD_2Cl_2).[36] The proton chemical shift of benzene in $CDCl_3$ is 7.341 and this gives the *ortho*, *meta* and *para* proton SCS in phenylacetylene in $CDCl_3$ from the above data as 0.151, −0.030 and 0.000 ppm. These agree exactly with the comparable values in CCl_4 solution of 0.15, −0.02 and –0.01.[35] As found previously for other aromatic compounds[11] there is a small, almost constant shift to higher δ values in $CDCl_3$ compared to CCl_4 but the proton SCS for substituted benzenes obtained by earlier investigations may be used unchanged for the $CDCl_3$ solutions.

The data obtained here for the acetylenes may be combined with the proton chemical shifts of the parent compounds given previously[11,12] to give the acetylene SCS in these compounds. These are shown in Fig. 3 for eq-cyclohexylacetylene (**10**-eq), 1-ethynyl-*t*-4-*tert*-butylcyclohexan-*r*-1-ol (**7**-*trans*), 1- and 2-ethenylnaphthalene (**15**, **16**) and the norbornane (**8**) and bornane (**9**) derivatives. The SCS for **7**-*trans*, **8** and **9** are obtained as the chemical shifts for **7**, **8** and **9** minus the proton shifts of *t*-4-*tert*-butylcyclohexan-*r*-1-ol, *endo*-norborneol and isoborneol.[37] These SCS are of some interest. The SCS are both shielding and deshielding but the larger SCS are always deshielding. The γ effect of the C≡C group (*i.e.* H–C–C–C≡C) is

Table 6 Observed *vs.* calculated proton chemical shifts (δ) and observed *vs.* calculated C≡C SCS for acetylenes (**12**–**18**)

Compound	Proton	δ(Obs.)	δ(Calc.)	SCS(Obs.)	SCS(Calc.)
Phenylacetylene (**12**)	2,6	7.492	7.544	0.151	0.207
	3,5	7.311	7.337	−0.030	0.000
	4	7.341	7.343	0.0	0.006
	C≡C–H	3.069	3.191		
o-Ethynyltoluene (**13**)	3	7.460	7.484	0.200	0.178
	4	7.138	7.155	−0.027	−0.041
	5	7.245	7.289	−0.015	−0.017
	6	7.202	7.005	0.022	−0.022
	Me	2.454	2.494	0.111	0.252
	C≡C–H	3.271	3.156		
p-Ethynyltoluene (**14**)	2,6	7.100	7.016	−0.080	−0.011
	3,5	7.400	7.496	0.140	0.190
	Me	2.340	2.251	−0.003	−0.033
	C≡C–H	3.020	3.124		
1-Ethynylnaphthalene (**15**)	2	7.700	7.692	0.223	0.216
	3	7.340	7.478	−0.137	0.002
	4	7.760	7.856	−0.084	0.031
	5	7.760	7.814	−0.084	−0.011
	6	7.440	7.478	−0.037	0.002
	7	7.530	7.515	0.053	0.039
	8	8.350	8.340	0.506	0.515
	C≡C–H	3.430	3.298		
2-Ethynylnaphthalene (**16**)	1	8.028	8.067	0.184	0.242
	3	7.524	7.652	0.047	0.176
	4	7.788	7.810	−0.056	−0.015
	5	7.810	7.803	−0.034	−0.022
	6	7.500	7.467	0.023	−0.009
	7	7.500	7.462	0.023	−0.014
	8	7.810	7.832	−0.034	0.007
	C≡C–H	3.142	3.225		
9-Ethynylanthracene (**17**)	1	8.522	8.478	0.513	0.475
	2	7.602	7.598	0.135	0.043
	3	7.504	7.546	0.037	−0.009
	4	8.001	8.003	−0.008	0.0
	10	8.447	8.410	0.016	−0.022
	C≡C–H	3.990	3.594		
2-Ethynylpropene (**18**)	H_{trans}	5.300	5.233	0.359	0.337
	H_{cis}	5.390	5.479	0.359	0.553
	Methyl	1.900	1.788	0.175	0.149
	C≡C–H	2.870	3.164		

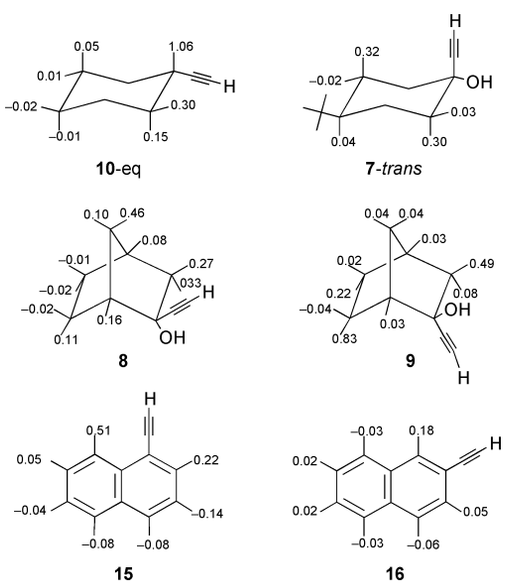


Fig. 3 Observed ethynyl SCS in aliphatic and aromatic molecules.

also deshielding with for the saturated compounds considerable orientational dependence without any obvious pattern, except that the γ SCS of the norbornane and bornane derivatives **8** and **9** is greater for the 120° orientation than for the eclipsed orientation for both the *exo* and *endo* compounds. This intriguing observation is valid for all norbornane substituents so far studied.[8,9]

The long range (>3 bonds) effects of the C≡C group are large but decrease rapidly with distance. For **10**-eq the C≡C SCS is almost zero for all long range protons. There is a large 1,3-diaxial interaction of the acetylene and H-3a in **7**-*trans*. Similar large effects are observed at the 7s protons in **8** and the 6n protons in **9**. All these protons are in a similar environment to the triple bond, *i.e.* essentially orthogonal to the C≡C bond. As there is no electric field effect of the C≡C bond these SCS can be due to either the C≡C anisotropy or a steric effect or both. Significantly the C≡C SCS at protons situated along the C≡C bond (*e.g.* the 3a and 3e protons in **10**-eq, the 7s proton in **9** *etc.*) is small but always deshielding. This would not be so if the SCS were solely due to the C≡C anisotropy. This suggestion will be shown to be verified by the detailed analysis in terms of the CHARGE model. Similar C≡C SCS are observed for the aromatic acetylenes **15** and **16** though in these compounds π electron effects will be present. Again the SCS are of either sign but the large effects are always deshielding, the largest being again due to the *peri* interaction in **15**.

The data in Tables 2–6 provide a rigorous test of the application of both the CHARGE model and also present theories of C≡C SCS. All the molecules considered are of fixed conformation and the geometries calculated by *ab initio* calculations, thus the only empirical parameters to be determined are those required for the model.

The *ab initio* geometries obtained were of some interest. GAUSSIAN94 at the MP2/6-31G* level gave values of the H–C≡ and C≡C bond lengths in acetylene of 1.061 and 1.203 Å respectively in complete agreement with the experimental values (1.061 and 1.203 Å).[38] The same basis set gave

corresponding values for phenylacetylene of 1.057 and 1.188 Å, but for *p*-tolylacetylene the values were 1.067 and 1.223 Å. This large change on the introduction of a *p*-methyl group seemed odd and these geometries did not give good results when used in CHARGE. In particular the acetylene proton shift is identical in these aromatic compounds (Table 6) but was not calculated to be so with these geometries. Using the recommended DFT/B3LYP[28c] routine with the 6-31G** basis set in GAUSSIAN98 gave bond lengths of 1.065 and 1.210 Å for both compounds and these values were used as standard for all the aromatic acetylenes. It is well known[28c] that the DFT technique treats electron correlation much better than the MP2 routine and this could be the explanation of the above result.

It is first necessary to consider how the acetylene (H–C≡) protons will be calculated. These could be reproduced in CHARGE by the appropriate values of the integral for the H–Csp bond. The near effects of anisotropic (or polar) bonds have been reproduced in this manner in previous parts of this series as attempting to calculate anisotropic (or polar) effects at such short distances by means of simple geometric functions (eqns. (3)–(5)) is not a feasible option. However if this procedure was adopted here the charge on the acetylene proton would be *ca.* equal to that in ethane, reflecting the near equality of their chemical shifts. This is obviously not the case as the acetylene proton is more acidic and the C–H bond more polar than even the olefinic proton. Thus the anisotropic contribution has been included in the chemical shift calculation for these protons. The procedure adopted was that the values of $\Delta\chi^{C\equiv C}$ and the steric coefficient together with the coefficients of the γ effects were obtained from the shifts of all the protons except the acetylene protons. The appropriate parameters for these protons were then included. This gave the correct chemical shift for the acetylene protons and an acceptable value of the proton charge (see later).

The parameters required for the calculations are the anisotropy of the C≡C bond, the sp carbon steric coefficient $a_S^{C\equiv C}$, the γ effect of the sp carbon atom *i.e.* H–C–C–C≡ (coefficients *A* and *B* eqn. (1)) and the β effect of the β acetylene carbon *i.e.* H–C–C≡. The γ effects may differ for aliphatic and aromatic acetylenes. This gives a total of five parameters for the aliphatic series plus a possible three more for the aromatic compounds. The acetylene proton chemical shifts were then fitted by the appropriate values of the ≡C–H exchange integral and the γ effect H–C≡C–X plus a second steric parameter a_S for the steric effect of neighbouring sp^3 protons on this proton.

The iterations were carried out on the observed chemical shift data of all protons by use of the non-linear mean squares programme (CHAP8[39]). The anisotropy of the C≡C bond was taken from both the centre of the C≡C bond and from each carbon atom, but the steric effect of the sp carbon atoms was taken as usual from the atom considered. The iterations gave better results when the anisotropy was taken from each carbon of the C≡C bond. Also both the values of the anisotropy, steric coefficent and the coefficients *A* and *B* (eqn. (1)) for the γ effects were identical when the iterations were performed with either the aliphatic compounds alone or the aromatic compounds, thus the final iteration was performed including all the compounds and using only five parameters. The values of these parameters were as follows. The anisotropy was −9.18 ppm $Å^3$ at each carbon atom, *i.e.* $\Delta\chi^{C\equiv C} = -18.36$ ppm $Å^3$ per molecule, *i.e.* -11.1×10^{-6} cm^3 mol^{-1}. The steric coefficient $a_S^{C\equiv C} = 56.6$ $Å^6$. The coefficients for the γ effects (H–C–C–C≡), (eqn. (1)), were *A* 0.423 and *B* −0.177 ppm. and the enhanced β effect (H–C–C≡) was 1.37. The acetylene protons were then considered. For these protons the iteration gave values of the C–H exchange integral of 42.8 (*cf.* 41.4), the γ effect (H–C≡C–C) coefficients were 0.22 and 1.20 for sp^3 and sp^2 carbons respectively and the steric coefficient (H–Csp^3 to H–C≡) was 46.5.

The iteration was over 124 chemical shift values of the compounds discussed previously excepting the acetylene alcohols as the parametrisation of the OH group has not been finalised in CHARGE. The rms error of the observed–calculated shifts was 0.074 ppm over a chemical shift range from *ca.* 1–8.5 ppm, a very satisfying result.

Discussion

The data of Tables 2–6 provide an examination of both the application of the CHARGE model to alkynes and of the influence of the acetylene group on proton chemical shifts. There is generally very good agreement between the observed and calculated proton chemical shifts. In the aliphatic compounds the model reproduces very well the sizeable low field shifts of protons situated at the side of the acetylene group; *e.g.* H-3a in axial cyclohexanes SCS (**7**-*trans*), obs. 0.32, calc. 0.43 ppm, H-7s in *exo*-ethynylnorbornanes (**8**), obs. 0.46, calc. 0.49 ppm, and H-6n in *endo*-ethynylbornanes (**9**), obs. 0.83, calc. 1.15 ppm (Fig. 2). The calculated values are due to both anisotropy and steric effects (see later). The smaller γ effects are again mostly to low-field and are also well reproduced by the combination of the anisotropy and the γ effect of eqn. (1).

In the aromatic acetylenes again the large SCS of the acetylene group due to the analogous periplanar interactions are also well reproduced; *e.g.* H-8 in 1-ethynylnaphthalene (**16**), obs. 0.51, calc. 0.51 ppm, H-1,5 in 9-ethynylanthracene (**17**), obs. 0.51, calc. 0.48 ppm. The other major SCS in the aromatic compounds are at the *ortho* protons and again these effects are due to the anisotropy plus γ effects. The SCS at the other ring protons due mainly to π effects are much smaller, reflecting the small interaction between the acetylene and the aromatic π systems.

There are some discrepancies in the calculated values of chemical shifts. Both the 1e proton in **10**-ax and the 1a proton in **10**-eq are *ca.* 0.2 ppm larger than the observed values (Table 3). These are the only methine (HC–C≡) protons in the data set and this may be a general result. Further data would be necessary to test this.

The observed and calculated shifts for H-2e in **10**-ax are in reasonable agreement (Table 3) as are the values for H-2e in **7**-*cis* (Table 4). In the analogous compound **7**-*trans* the corresponding SCS are obs. 0.03, calc. 0.29 ppm. It may be that in **7**-*trans* there is an interaction between the geminal hydroxy and acetylene groups. In this case the SCS for each group cannot be obtained simply by subtracting the shifts in this compound from those of the parent alcohol (or acetylene). There is a similar anomaly in the obs. *vs.* calc. SCS for H-3x and -3n in **9** but not for **8**. It is of interest that the anomalous results occur for compounds in which the acetylene group is sterically hindered. This intriguing possibility could be further tested once the OH group is included in the CHARGE parametrisation.

In the aromatic compounds an interesting anomaly occurs with H-3 in 1-ethynylnaphthalene (**15**). The observed SCS (−0.137 ppm) contrasts with the calculated value (0.002 ppm). The calculated SCS at this proton is as expected the same as the SCS for the *meta* proton in phenylacetylene and this agrees exactly with the observed value for this proton. An exactly similar effect was found for the cyano group. It would appear that both the C≡C and CN SCS operate differently in naphthalene and benzene.

There is generally very good agreement between observed and calculated shifts for the acetylene protons but the model does not fully account for the value in 9-ethynylanthracene (**17**), *cf.* obs. 3.99, calc. 3.59 ppm. This may be due to enhanced π effects at this position or to H (aromatic)–H (acetylene) steric effects which would be expected to give a low-field shift. As no other molecule in the data set experiences these interactions it was not felt necessary to include them.

It is of interest to consider the actual magnitudes of the contributions to the acetylene SCS. The acetylene proton has a partial atomic charge of +0.088 electrons which corresponds to

Table 7 Observed *vs.* calculated C≡C SCS with the electric field, steric and anisotropic contributions for equatorial- and axial-ethynylcyclohexane (**10**-eq and **10**-ax) and 1,4-di-1-adamantylbutadiyne (**11**)

Compound	Proton	Obs.	Calc.	C–H Electric field	C≡C-Anisotropy	C≡C-Steric	C-Steric	H-Steric	π-Shift
10-eq	1a	1.056	0.906	−0.053	−0.590	0.0	0.016	−0.046	
	2e	0.297	0.245	−0.019	−0.074	0.027	0.0	0.0	
	2a	0.145	0.225	−0.025	−0.072	0.028	0.0	−0.023	
	3e	0.054	−0.024	0.028	−0.059	0.0	0.0	0.0	
	3a	0.011	−0.110	0.011	−0.011	0.014	0.0	−0.019	
	4e	−0.014	−0.041	0.016	−0.056	0.0	0.0	0.0	
	4a	−0.020	−0.057	0.016	−0.062	0.0	0.0	−0.01	
	C≡C–H	—	—	−0.027	−5.556	0.0	0.05	0.031	−0.169
10-ax	1e	1.231	1.029	−0.045	−0.560	0.0	0.0	0.0	
	2e	0.095	0.244	−0.019	−0.072	0.028	0.0	0.0	
	2a	0.291	0.332	−0.033	−0.174	0.0	0.0	−0.034	
	C≡C–H	—	—	−0.064	−5.550	0.0	0.098	0.052	−0.170
11	γ	0.111	0.137	−0.024	−0.071	0.028	0.0	0.0	
	δ	0.071	−0.012	0.028	−0.059	0.0	0.0	0.0	
	e	0.069	−0.036	0.017	−0.062	0.0	0.0	0.0	
	a	0.069	−0.042	0.015	−0.056	0.0	0.0	0.0	

Table 8 Observed *vs.* calculated C≡C SCS, with the steric, anisotropy, electric field, ring current and π-shift contributions for phenylacetylene (**12**) and 1- and 2-ethynylnaphthalene (**15** and **16**)

Compound	Proton	Obs.	Calc.	C≡C-Steric	C≡C-Anisotropy	C–H Electric field	Ring current	π-Shift
12	2,6	0.151	0.207	0.029	−0.072	−0.020	−0.004	0.043
	3,5	−0.030	0.0	0.008	−0.068	0.045	0.005	0.013
	4	0.0	0.006	0.002	−0.063	0.033	−0.001	0.035
	C≡C–H	—	—	0.0	−5.582	−0.004	−0.108	
15	2	0.223	0.216	0.029	−0.080	−0.020	0.0	0.065
	3	−0.137	0.002	0.008	−0.070	0.046	0.0	0.023
	4	−0.084	0.031	0.002	−0.062	0.34	0.0	0.058
	5	−0.084	−0.011	0.0	−0.036	0.014	0.0	0.010
	6	−0.037	0.002	0.0	−0.010	0.010	0.0	0.003
	7	0.053	0.039	0.007	0.023	0.00	0.00	0.012
	8	0.506	0.515	0.326	0.210	0.084	0.0	0.0
	C≡C–H	—	—	0.0	−5.581	0.009	0.318	−0.136
16	1	0.184	0.242	0.032	−0.061	0.021	0.0	0.068
	3	0.047	0.176	0.027	−0.078	−0.020	0.0	0.024
	4	−0.056	−0.015	0.007	−0.069	0.045	0.0	0.006
	5	−0.034	−0.022	0.0	−0.038	0.012	0.0	0.004
	6	0.023	−0.009	0.0	−0.022	−0.001	0.0	0.013
	7	0.023	−0.014	0.0	−0.019	−0.001	0.0	0.006
	8	−0.034	0.007	0.005	−0.029	0.018	0.0	0.014
	C≡C–H	—	—	0.0	−5.581	−0.004	0.246	−0.123

a ≡C–H dipole moment of 0.45 D. This charge gives rise from eqn. (2) to a chemical shift of 7.47 ppm. Thus as expected the acetylene proton is more "acidic" than olefinic or aromatic protons. The difference between this value and the calculated shift (1.90 ppm) is due entirely to the C≡C anisotropic contribution (−5.65 ppm). In the other compounds other effects are present and Tables 7 and 8 give the observed *vs.* calculated C≡C SCS for the aliphatic and aromatic acetylenes respectively together with the calculated anisotropic, steric and electric field contributions.

For the alkylacetylenes (Table 7) the major contribution for the α and β protons is the C≡C anisotropy. All the other contributions (C–H electric field, C≡C steric, C-steric and H-steric) are very small for the compounds given with the exception of the acetylene protons in which there is a significant π-shift. (Note that this does not appear in acetylene itself as there is no π excess in acetylene.)

Note that in the SCS of the H-2e and H-2a protons of all the compounds in Table 7 the components do not add up to give the calculated value of the SCS. This is due to the electronic γ effects which are calculated separately and which affect protons that are three bonds or less from the C≡C group.

The large SCS for H-3a in axial-ethynylcyclohexane has been estimated from compound **7**-*trans* as 0.32 (obs.) and 0.43 ppm (calc.). The calculated SCS is made up of a C≡C steric contribution of 0.185 ppm plus an anisotropic contribution of 0.125 ppm plus some other very small contributions. For the other protons with large SCS a similar pattern is found; *e.g.* for H-7s in **8** the calculated SCS of 0.49 ppm is made up of 0.37 (steric) and −0.11 ppm (anisotropy) and for H-6n in **9** the corresponding values are 1.153, 0.57 and 0.27 ppm. The results show categorically that the largest contribution to these SCS is due to the C≡C steric term and not the C≡C anisotropy. Amazingly the C≡C steric term has not been considered in any previous investigation.

The aromatic acetylenes have other mechanisms which may affect the proton chemical shifts, in particular, the ring current and π electron effects and Table 8 gives the observed *vs.* calculated SCS for selected molecules with the electric field, ring current and π-shift contributions.

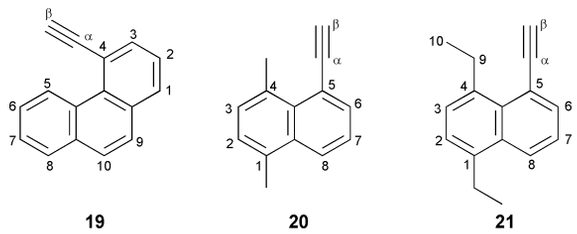
We have assumed in this investigation that the introduction of the acetylene group has no effect on the parent hydrocarbon ring current and thus there are no ring current effects on the C≡C SCS. The agreement obtained here is strong support for this assumption. In contrast the C≡C group does affect the π electron densities and this has a significant effect on the SCS.

The data of Table 8 show the similarities between the aromatic and aliphatic acetylenes. In particular the large periplanar interaction between the 1-acetylene and H-8 in **15** giving a calculated SCS of 0.49 ppm is predominantly due to the steric contribution (0.415 ppm) with only a small anisotropic term (0.10 ppm). The remaining SCS for the ring protons are quite small with the π-shifts and electric field effects roughly comparable. The ring current contribution to the SCS of the aromatic

protons is as stated above zero but Table 8 includes the actual ring current shift at the acetylene protons and the π-shifts which are both significant.

As stated previously, various values of the C≡C diamagnetic anisotropy have been given ranging from -7.7×10^{-6} to -36×10^{-6} cm^3 mol^{-1}. The value found here of -11.1×10^{-6} cm^3 mol^{-1} is a middle value which is in reasonable agreement with both Pople's original estimate of −19.4 and the value of −7.7 of Shoemaker and Flygare.

It is of some interest to see whether the large low-field shifts observed by Mallory and Baker in the proton NMR of 4-ethynylphenanthrene (**19**), 5-ethynyl-1,4-dimethylnaphthalene (**20**) and 5-ethynyl-1,4-diethylnaphthalene (**21**) are predicted by our model.



19 **20** **21**

They observed large low-field shifts for H-5 in **19** (1.63 ppm from H-5 in phenanthrene), the 4-methyl protons in **20** (0.49 ppm) and the methylene protons of the C-4 ethyl group of **21** (0.55 ppm) due to the deshielding effect of the C≡C group.

The calculated (CHARGE7) proton shifts *vs.* the observed δ values (in parentheses) for H-5 in **19**, the methyl protons in **20** and for the CH_2 protons in **21** are 9.38 (10.34), 2.90 (3.01) and 3.39 (3.62).

There is excellent agreement between the observed and calculated shifts for the methyl and methylene protons in **20** and **21**, but the calculated value for H-5 in **19** is too small by almost 1 ppm. This proton is in very close proximity to the triple bond. The distance between the center of the triple bond and H-5 is calculated as 2.208 Å from GAUSSIAN98. This compares with the values of 1.55 Å from Dreiding models and 2.408 Å from PC Model.[40] The GAUSSIAN98 geometry calculated at the B3LYP/6-31G** level may not be absolutely correct and small changes in bond lengths and angles at this close distance will have a very significant influence on the calculated proton chemical shifts. It would be of interest to obtain the crystal geometry and input this into CHARGE. However the simple eqns. (3) and (5) for the shielding and anisotropy of the C≡C bond are also likely to be less accurate for the close distances observed in this case. The major contribution to the low-field shift of this proton is again the steric term (0.71 *vs.* 0.34 ppm for the anisotropy) and a simple r^{-6} term would not be expected to be very accurate at these short internuclear distances.

Mallory and Baker concluded that the C≡C shielding was proportional to r^{-3} and that the shielding was from the centre of the triple bond. In the CHARGE scheme the steric term is proportional to r^{-6} but the anisotropy is proportional to r^{-3} and both terms are calculated at each carbon atom. Placing the anisotropy in the middle of the acetylene bond and using an r^{-3} steric term both gave poorer agreement for the data set considered here.

Conclusions

The proton chemical shifts of all the protons in the data set considered of 71 data points spanning a range of *ca.* 0.70 to 9.00 ppm are predicted with an rms error of 0.074 ppm. We may conclude that the C≡C SCS over more than three bonds is determined largely by the C≡C bond anisotropy and steric effect for both aliphatic and aromatic compounds. In all the compounds considered here the large SCS effects are due mainly to the steric term. The anisotropy is a significant, but smaller contribution. The protons <3 bonds from the triple bond require in addition the inclusion of electronic β and γ effects from the acetylene carbons in both aliphatic and aromatic acetylenes. The γ effect of the acetylene carbon atom has an orientational dependence.

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