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Proton chemical shifts in NMR: Part 17.[†] Chemical shifts in alkenes and anisotropic and steric effects of the double bond

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The ^{1}H NMR spectra of a number of alkenes of known geometry were recorded in $CDCl_3$ solution and assigned, namely ethylene, propene, 4-methylcyclohexene, 1,4-dimethylcyclohexene, methylene cyclohexane (in $CFCl_3-CD_2Cl_2$ at 153 K), 5-methylene-2-norbornene, camphene, bicyclopentadiene, styrene and 9-vinylanthracene. These results together with literature data for other alkenes, i.e. 1,3- and 1,4-cyclohexadiene, norbornene, norbornadiene, bicyclo[2.2.2]oct-2-ene and α- and β-pinene, and other data allowed the determination of the olefinic shielding in these molecules. The shielding was analysed in terms of the magnetic anisotropy and steric effects of the double bond together with a model (CHARGE7) for the calculation of the two- and three-bond electronic effects. For the aromatic alkenes ring current and π-electron effects were included. This analysis showed that the double bond shielding arises from both anisotropic and steric effects. The anisotropy is due to the perpendicular term only with a value of $\Delta\chi(C{=}C)$ of $-12.1 \times 10^{-6} cm^3 mol^{-1}$. There is also a steric deshielding term of $82.5/r^6$ (r in Å). The shielding along the π-axis changes sign from shielding at long range (>2.5 Å) to deshielding at short range (<2 Å). The model gives the first comprehensive calculation of the shielding of the alkene group. For the data set considered (172 proton chemical shifts) ranging from $\delta = 0.48$ to 8.39, the r.m.s. error of observed vs calculated shifts was 0.11 ppm. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{1}H NMR; ^{1}H chemical shifts; alkenes; C=C anisotropy; C=C shielding

INTRODUCTION

The proton resonance spectra of alkenes have been investigated for ~50 years but there is still controversy over the shielding effect of the double bond and no quantitative calculation of alkene proton chemical shifts has been given. Jackman[2] first suggested the anisotropic shielding of the olefinic bond from the enhanced shielding of one of the CMe_2 groups in α-pinene which was situated over the double bond. This led to the well-known shielding cone (Fig. 1) in which any nucleus situated above the double bond is shielded whereas any nucleus in the plane of the double bond is deshielded. In an authoritative review of this field, Bothner-By and Pople[3] noted that whereas Jackman's model is due to a large diamagnetism along the x-axis (Fig. 1), Conroy[4] had suggested a large diamagnetism in the y direction and Pople from theoretical calculations[5] a paramagnetism in the y direction centred on the carbon atoms rather than the centre of the C=C bond. Both Jackman's and Pople's theories give increased shielding in the x-axis and deshielding in the y-axis. They differ only in their predictions for shielding along the z (i.e. C=C) axis, which is not easy to observe.

The shielding cone hypothesis was implicated in an early controversy over the assignment of the bridge methylene protons in norbornene. Deuteration studies[6] unambiguously assigned the 7-*syn* protons in norbornene to lower field than the 7-*anti* proton, contrary to Jackman's theory. A later investigation of olefinic shielding was due to ApSimon *et al.*[7] They derived comparable values for the parallel ($\chi_z - \chi_y$) and perpendicular ($\chi_x - \chi_y$) anisotropies of the double bond but concluded that 'the conventional picture of a shielding cone around the C=C bond appears to require substantial modification. It would appear that deshielding is confined to a restricted region at the ends of the double bond: outside this region a nucleus is shielded whether it lies in the plane of the double bond or above it.'

The central problem of this early work was that the NMR instrumentation at this time was inadequate to analyse the complex proton spectra of the rigid molecules needed to examine olefinic shielding. ApSimon *et al.* could use only the C-18 and C-19 methyl groups of unsaturated steroids as probes, which was a major limitation in this investigation.

Recently, *ab initio* DFT-GIAO (density functional theory–gauge including atomic orbitals) calculations have been

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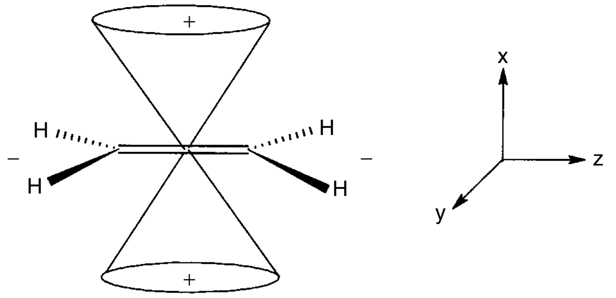


Figure 1. Classical shielding cone for ethylene.

applied to calculate the shielding effects of a double bond. Alkorta and Elguero,[8] using a probe methane molecule situated near to an ethylene molecule, calculated that the methane proton nearest the ethylene molecule was deshielded in every direction with the largest deshielding above the C=C bond. At 2.5 Å in the x direction (Fig. 1) the deshielding was 1.27 ppm and at 3.7 Å from the C=C bond in the y and z directions the deshielding was 0.11 and 0.06 ppm, respectively.

Martin *et al.*[9] using the same DFT-GIAO technique, again with a methane probe molecule but a different basis set, obtained more detailed information. They varied the orientation of the methane protons and averaged the results for the methane protons. They calculated the shielding over a box with $x = 2.5$, 3.0 and 3.5 Å and y and z varying from 0 to 2 Å in 0.5 Å steps from the centre of the C=C bond (Fig. 1). The resulting shielding increments were fitted by a quadratic equation in (x y z), which was only valid over the box dimensions, however. For $x = 3.5$ Å the methane protons were *shielded* by the double bond for all values of y and z, but for $x = 2.5$ Å the methane protons were *de*shielded. At $x = 3.0$ Å the shielding was positive or negative depending on the values of the other coordinates.

These authors also calculated the shielding increments of protons over a C=C bond in some rigid molecules. In norbornene the calculations reproduced the experimental result (δ 7-*syn* > δ 7-*anti*) but in α-pinene the calculations predicted that the *syn*-methyl group is deshielded compared with the *anti*-methyl group. Although the authors regarded this as agreeing with the experimental data, this is the reverse of the correct experimental value (see later).

It should be stressed that all such *ab initio* calculations are basis set dependent and also they do not give direct information on the mechanism responsible for the shielding. Thus in this case it is not possible to tell whether the results are due to C=C bond anisotropy or some other mechanism (e.g. van der Waals interactions). This is of importance as whereas anisotropy is independent of the probe nucleus, this series and others have shown that H–H van der Waals interactions are a function of both interacting atoms. In alkanes H$\cdots$H interactions are shielding but in aromatics deshielding. The *ab initio* calculations are very useful in visualizing the spatial dependence of the olefinic shielding. It is clear from these results that this must be a complex function of the distance as a simple $1/r^n$ term would not give both positive and negative shielding along one axis. This important aspect will be considered further subsequently.

No systematic attempt has yet been made to calculate the proton chemical shifts of alkenes and this is the subject of this investigation. We present the complete assignment of the proton spectra of a variety of aliphatic and aromatic alkenes. This provides a sufficient amount of data for a quantitative analysis of alkene shielding using a previous model (CHARGE) 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 more than three bonds away from the substituent in question. The model has been applied to a variety of saturated hydrocarbons,[10] haloalkanes,[11] ethers,[12] ketones[13] and aromatic compounds[14] and reviewed.[15] We shall use this model to perform a quantitative analysis of alkene shielding and show that the proton chemical shifts are influenced by both the magnetic anisotropy and steric effects of the double bond.

THEORY

As the theory has been given previously,[1,15] 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 a α effect from atom J given by the difference in the electronegativity of atoms I and J. A β effect from atom K proportional to both the electronegativity of atom K and the polarizability of atom I. There is also a γ effect from atom L given by the product of the atomic polarizabilities 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. CCCH) is parameterized separately and is given by the equation

$$\text{GSEF} = A + B\cos\theta \qquad (1)$$

where θ is the CCCH dihedral angle and A and B are empirical parameters.

The coefficients A and B vary if the proton is in a CH, CH_2 or CH_3 fragment and 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 the equation

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

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 were found to be shielding in alkanes and deshielding in aromatics and X$\cdots$H

(X = C, O, Cl, Br, I) interactions deshielding, according to a simple r^{-6} dependence:

$$\delta_{\text{steric}} = a_s/r^6 \quad (3)$$

Furthermore, any X $\cdots$ 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 the equation

$$\delta_{\text{el}} = A_z E_z \quad (4)$$

where A_z was 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 no symmetry was obtained from the general McConnell equation:[16]

$$\delta_{\text{an}} = [\Delta\chi_1(3\cos^2\theta_1 - 1) + \Delta\chi_2(3\cos^2\theta_2 - 1)]/3R^3 \quad (5)$$

where R is the distance from the perturbing group to the nucleus of interest in Å and $\Delta\chi$ is the molar anisotropy. $\Delta\chi_1 = \chi_x - \chi_y$ and $\Delta\chi_2 = \chi_z - \chi_y$, where χ_x, χ_y and χ_z are the susceptibilities along the x-, y- and z-axes and the angles θ_1 and θ_2 are defined as shown in Fig. 2. Note that the Jackman model (Fig. 1) is given by the first term in Eqn (5). This will be referred to henceforth as the perpendicular anisotropy and the second term as the parallel anisotropy.

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 from the Pauling theory and the equivalent dipole approximation is then used to calculate the ring current shifts.[14] This treatment reproduced the proton chemical shifts of a wide range of aromatic hydrocarbons and is incorporated unchanged here.

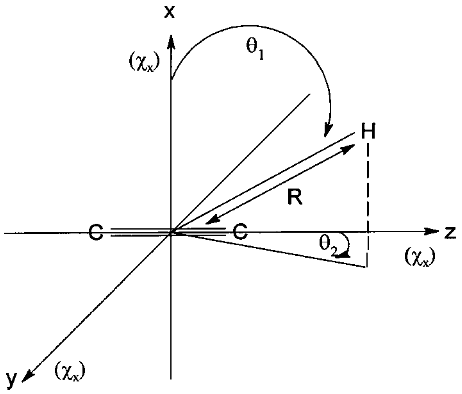


Figure 2. Principal axes of the C=C bond.

The π-electron densities are calculated from Hückel theory.[14] The standard coulomb and resonance integrals for the Huckel routine are given by the equation

$$\alpha_r = \alpha_0 + h_r\beta_0$$
$$\beta_{rs} = k_{rs}\beta_0 \quad (6)$$

where α_0 and β_0 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 substituted aromatics the appropriate values of the coefficients h_r and k_{rs} in Eqn (6) for the orbitals involving heteroatoms have to be found. These are obtained so that the π-electron densities calculated from the Hückel routine reproduce those 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 by the equation

$$\Delta\delta = a_1\Delta q_\alpha + a_2\Delta q_\beta \quad (7)$$

where Δq_α and Δq_β are the excess π-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.[14] The above contributions are added to the shifts of Eqn (1) to give the calculated shift:

$$\delta_{\text{total}} = \delta_{\text{charge}} + \delta_{\text{steric}} + \delta_{\text{anisotropy}} + \delta_{\text{el}} + \delta_\pi + \delta_{\text{rc}} \quad (8)$$

Application to alkenes

The olefinic group has γ effects on protons three bonds away and in principle steric, anisotropic and electric field effects on protons more than three bonds removed. All these need to be considered. There are a number of different γ effects as there are many different pathways in olefines alkenes, e.g. for the alkene protons there are CC=CH, CCC(sp^2)H, etc., and for the alkane protons C=CCH, CC(sp^2)CH, etc. For the saturated protons, the γ effects vary if the proton is in a CH, CH_2 or CH_3 fragment. The coefficients A and B in Eqn (1) for each γ effect need to be obtained to give the best fit with the observed data.

The π-electron densities were obtained from *ab initio* calculations, using Gaussian94 at the 6–31G* level.[17] This basis set gave the best agreement with the observed dipole moments (e.g. propene, observed 0.35 D, calculated 0.36 D). Subsequently the h_r and k_{rs} parameters in the Hückel calculation were varied in order to obtain the same π-electron densities as the *ab initio* calculations. Simple Hückel theory gives the same π-electron densities (= 1.0) for the olefinic carbon atoms in propene and butadiene. In order to obtain more realistic π-electron densities in these cases, two modifications were introduced. The hyperconjugative effect of a saturated substituent (e.g. CH_3) on the π-electron densities was modelled by the equation

$$\alpha_r = \alpha_r{}^0 + 0.06 - 0.13\,q_r \quad (9)$$

The coulomb integral (α_r) of the sp^2 carbon connected to an sp^3 carbon is modified in order to reproduce the increased charge on the attached sp^2 carbon. q_r is the charge on the attached sp^3 carbon atom. This gave excess π-electron densities on the olefinic atoms of propene as ±0.037electrons which compares reasonably with the *ab initio*-calculated values of -0.104 (C-1) and $+0.029$ (C-2).

A similar modification was made to the Coulomb integral of an alkene carbon attached to another alkene carbon via a single bond (e.g. C-2 —C-3 in butadiene). In this case the Coulomb integral was altered from 0.0 to 0.043. Again this gave reasonable agreement with the *ab initio* calculations. For butadiene the excess π-electron densities on the olefinic atoms were ±0.0154, which compare well with the *ab initio*-calculated value of ±0.0157.

The shielding or steric effect due to the carbons in a C=C bond has to be calculated with the C=C bond anisotropy as they are both an integral part of the total shielding. The C=C bond anisotropy is a complex function depending on the values of the perpendicular and parallel anisotropies [Eqn (5)]. If only the perpendicular anisotropy is present this gives the shielding cone of Fig. 1, i.e. shielding above the double bond, deshielding in the olefinic plane. The steric effects of all non-hydrogen atoms are deshielding and given by Eqn (3),[10–15] the only exception being the aromatic carbon for which no shielding term was required. The shielding effects of the olefinic carbon atoms may be assumed to be given by Eqn (3) with the appropriate value of the coefficient. Alternatively, the π-electrons may be considered as responsible for the shielding effects then as these electrons have a node in the *yz* plane (Fig. 1) the shielding term would include an orientation term:

$$\text{Shielding} = \cos^2\theta_1/R^6 \tag{10}$$

with R and θ_1 as shown in Fig. 2. Both of these alternatives need to be considered.

EXPERIMENTAL

The molecules studied are identified in Table 1 and shown with the atom numbering in Scheme 1. Compounds **1**, **2**, **11**, **13**, **14**, **18**, **19**, **20**, **22**, **24**, **25**, **26**, **27**, **28** and **29** and $CDCl_3$ solvent were obtained commercially (Aldrich Chemical). The data for compounds **3**, **4**, **6**, **8**, **9**, **10**, **12**, **15**, **16**, **17**, **21**, **33** and **34** was obtained from the Aldrich Library of FTNMR Spectra.[18] The assignments for all these spectra were straightforward and the proton chemical shifts are accurate to ±0.01 ppm. The data for the remaining compounds **5**, **7**, **23**, **30**, **31** and **32** are from the literature and the appropriate references are given in the tables.

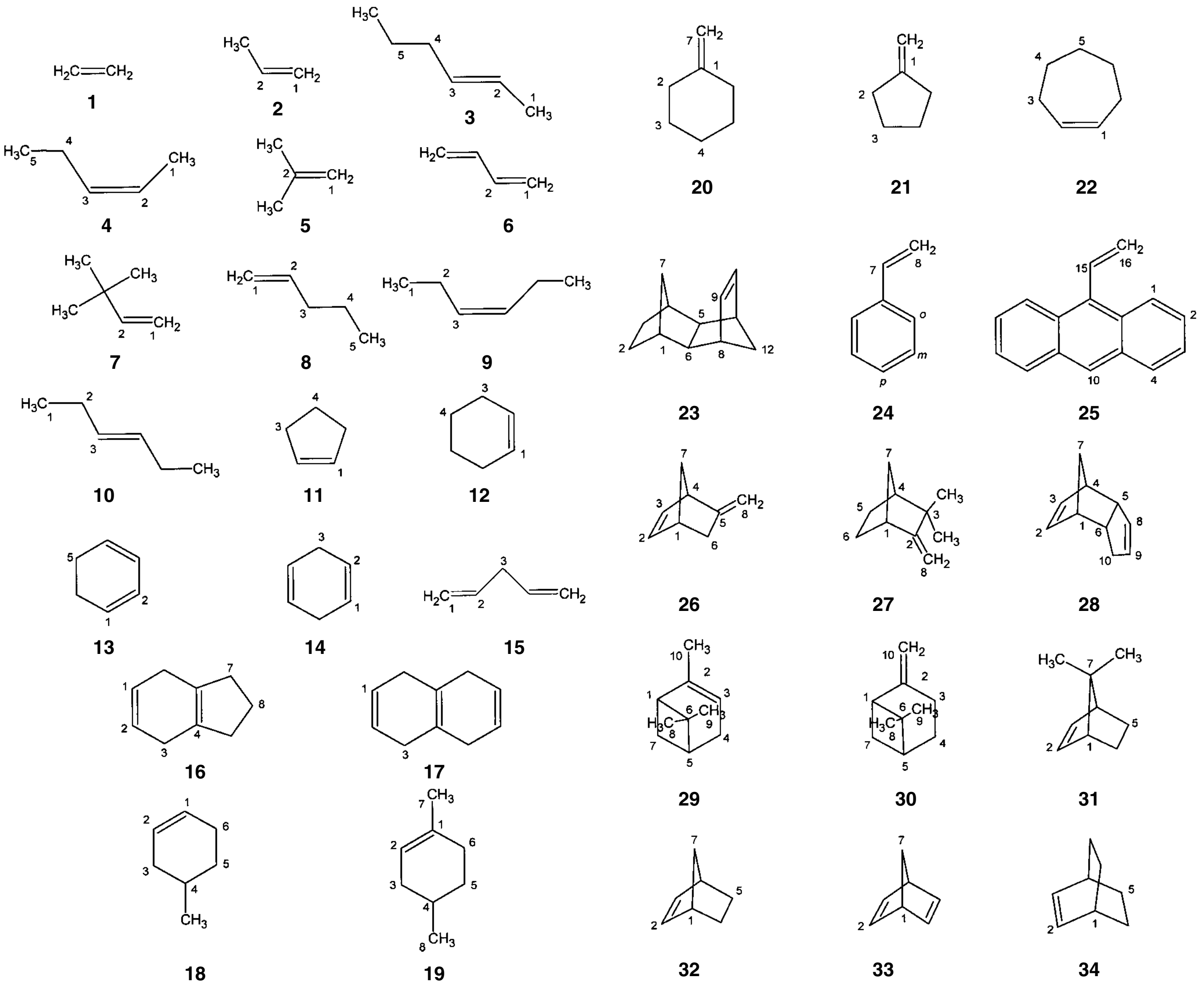
^1H and ^{13}C NMR spectra were obtained on a Bruker AMX400 spectrometer operating at 400.14 MHz for proton and 100.63 MHz for carbon. COSY and HETCOR experiments were performed on the same spectrometer. NOE experiments for camphene and bicyclopentadiene were obtained on a Bruker DPX500 spectrometer (AstraZeneca) operating at 500.13 MHz. Spectra were recorded in 10 mg cm^{-3} solutions (^1H) and ~50 mg cm^{-3} (^{13}C) with a probe temperature of ~25 °C in $CDCl_3$ and referenced to TMS. Typical ^1H conditions were 128 transients, spectral width 3300 Hz and 32 K data points, giving an acquisition time of 5 s and zero-filled to 128 K to give a digital resolution of 0.05 Hz.

Table 1. Compounds studied

No.	Compound
1	Ethylene
2	Propene
3	(*E*)-Pent-2-ene
4	(*Z*)-Pent-2-ene
5	Isobutene
6	Butadiene
7	*tert*-Butylethylene
8	Pent-1-ene
9	(*Z*)-Hex-3-ene
10	(*E*)-Hex-3-ene
11	Cyclopentene
12	Cyclohexene
13	Cyclohexa-1,3-diene
14	Cyclohexa-1,4-diene
15	Pent-1,4-diene
16	Tetrahydroindene
17	Isotetralin
18	4-Methylcyclohex-1-ene
19	1,4-Dimethylcyclohex-1-ene
20	Methylenecyclohexane
21	Methylenecyclopentane
22	Cycloheptene
23	*endo*-Norbornyl-5*n*,6*n*-norbornene
24	Styrene
25	9-Vinylanthracene
26	5-Methylene-2-norbornene
27	Camphene
28	Bicyclopentadiene
29	α-Pinene
30	β-Pinene
31	7,7-Dimethylnorbornene
32	Norbornene
33	Norbornadiene
34	Bicyclo[2.2.2]oct-2-ene

In order to quantify the olefinic shielding, the compounds must be of a known fixed geometry. The geometries of **1**, **2**, **5**, **6**, **7**, **20**, **21**, **22** and **33** were obtained by optimizations using the Gaussian94 program at the 6–31G* level.[17] The rest of the geometries were obtained by optimizations using the PCMODEL7 program.[19]

The acyclic alkenes **3**, **4**, **8**, **9** and **10** can exist in a number of rotational forms. The predominant form in these compounds is with the *trans (anti)* conformation of the carbon chain and this conformer is the one considered in these molecules. Similarly in butadiene only the stable s-*trans* conformer[20] was considered. In the cyclic series **18** and **19** can exist in a number of possible conformations. MM calculations showed that the preferred conformer in both cases is the half-chair with the 4-methyl group equatorial. The calculated axial–equatorial energy difference was 1.6 and 2.4 kcal mol^{-1} (1 kcal = 4.184 kJ) for **18** and **19**, respectively, thus the equatorial conformer is >90% populated in both



Scheme 1. Molecules studied and their numbering.

cases. In styrene the dihedral angle of the olefinic group was given as 30° by PCMODEL and 0° by Gaussian94 and both geometries were considered. However, in **25** both programs gave similar geometries with the vinyl group orthogonal to the anthracene ring.

Assignments

The assignments of the spectra of **1**, **2**, **11** and **14** were straightforward. Further experiments were performed to obtain the spectral assignment for those molecules whose assignment was either unknown or uncertain.

18

The ^1H and ^{13}C assignment was clarified by a HETCOR experiment as only a partial ^{13}C assignment was given previously.[21] Our results agree except that carbons C-4 and C-5 are exchanged. H-3,5eq and H-3,5ax were assigned on the basis that the equatorial protons are to low field. This was confirmed by the CHARGE calculations. The ^{13}C assignment is C-1 126.70, C-2 126.80, C-3 33.72, C-4 28.48, C-5 30.84, C-6 25.28, Me 22.02.

19

The same procedure was adopted. The ^{13}C assignment agreed with Senda *et al.*[22] and the ^1H assignment followed from the HETCOR plot. H-3,5 eq was assigned to low field of H-3,5ax as above but H-6eq was assigned to high field of H-6ax from the observed fine structure (a broad doublet).

13

The ^{13}C chemical shifts were assigned following Taskinen and Nummelin.[23] A HETCOR experiment plus decoupling experiments was performed to make the full ^1H assignment.

20

At room temperature only three signals appear in the spectrum, and the C-3, C-4 and C-5 protons overlap so a variable-temperature experiment was performed. At −120 °C in a 1 : 1 mixture of CD_2Cl_2 and $CFCl_3$ the ring inversion slowed sufficiently ($T_c = -80$ °C) to observe all the different protons. Lessard *et al.*[24] had previously observed this for some 2-substituted methylenecyclohexanes using ^{13}C NMR. In order to check for any solvent effects the ^1H spectrum at room temperature in the solvent mixture was compared with the spectrum in $CDCl_3$. No appreciable differences were observed so it was assumed that the low-temperature shifts could be used in the calculations.

The ^{1}H assignments of all these compounds are given in Table 4.

24 and 25

The ^{1}H spectrum for styrene was first order at 400 MHz and readily assigned. The ^{1}H spectrum for **25** was also first order but the assignment of H-1,8 and H-4,5 was not obvious. It was assumed that the more shielded protons were H-1,8 and this was confirmed from the calculated shifts. These assignments are given in Table 5.

26

The ^{1}H spectrum for this compound is first order but the assignment is not straightforward. A COSY plot gave a complete assignment with correlations between H-1 and H-2, H-6$_{exo}$, H-7$_{syn,}$, H-7$_{anti,}$, H-4 and even to H-8$_b$, at five bonds distant. Correlations between H-6$_{endo}$ and H-7$_{syn}$ distinguished H-7$_{anti}$ and H-7$_{syn}$ and confirmed the assignment of H-6$_{exo}$ and H-6$_{endo}$. H-2 and H-3 were assigned from their couplings to H-1 and H-4 respectively. H-8$_a$ (proton facing C-6) and H-8$_b$ (proton facing C-4) could not be differentiated unambiguously and NOE experiments were performed to distinguish between them. When H-4 was irradiated H-8$_b$ showed an NOE but when H-8$_a$ was irradiated no NOE was observed. This confirmed the assignment given in Table 6.

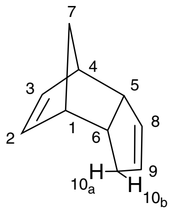
27

The ^{13}C assignment was from Grover and Stothers.[25] NOE experiments were then performed. The olefinic proton at 4.717 ppm was irradiated and the bridge proton at 2.670 ppm showed an NOE. This confirms that H-1 is at 2.670 ppm and that the olefinic proton is H-8$_a$. Thus H-8$_b$ occurs at 4.493 ppm. The methyl groups were assigned from an HMQC experiment as the carbon assignment is known. The *exo*-methyl group on irradiation gave an NOE at the olefinic proton at 4.493 ppm and also at the protons at 1.900 and 1.694 ppm. This confirms the assignment of the H-8$_b$ and also assigns H-4 at 1.900 ppm and H-7$_{syn}$ at 1.694 ppm. From the HMQC H-7$_{anti}$ occurs at 1.204 ppm, and this also distinguishes the H-5 and H-6 protons.

A COSY experiment helped to distinguish the *exo* and *endo* protons. H-4 showed a small cross peak with the proton at 1.70 ppm and a large common cross peak with the proton at 1.383 ppm. This identified H-5$_{exo}$ at 1.383 ppm H-5$_{endo}$ at 1.701 ppm. Using the same technique with H-1 identified H-6$_{exo}$ at 1.638 ppm and H-6$_{endo}$ at 1.236 ppm. (Table 6).

28

Ramey and Lini[26] assigned the proton spectrum at 60, 100 and 220 MHz. Even at the highest field H-2 and H-3 and H-8 and H-9 were unresolved. At 400 MHz. all the protons are resolved and the assignment follows. H-10$_a$ and H-10$_b$ can be identified from their HH couplings. H-10$_a$ has two large couplings (17.4 and 10.2 Hz), plus three small couplings of 2.01 Hz, whilst H-10$_b$ has only one large coupling (17.4 Hz) and four small couplings (two of 3.88 Hz and two of 1.95 Hz). NOE experiments were then performed in order to complete the ^{1}H assignment. H-10$_a$ was irradiated and H-10$_b$ and the protons at 2.526 ppm (H-6) and 5.465 ppm (H-9) showed NOE. In the second NOE experiment H-5 was irradiated and H-8, H-4, H-6 and H-7$_{anti}$ showed NOE. In the final NOE experiment, H-1 was irradiated and H-7$_{syn}$, H-7$_{anti}$, H-2 and H-3 showed an NOE. The assignment in Table 6 agrees with that in Ref. 26.



29

Although both the ^{1}H and ^{13}C spectra had been assigned previously, this spectrum was re-run to check the assignments. Abraham *et al.*[27] had originally assigned the 220 MHz ^{1}H spectrum of a number of bridged cyclobutanes including α- and β-pinene. A number of assignments of the ^{13}C spectra were given but Coxon *et al.*[28] used C—H coupling, ^{13}C and ^{2}H labelling and shift reagent studies to assign unambiguously the ^{13}C spectra of a number of pinanes. Thus a HETCOR experiment was performed to correlate the ^{13}C and ^{1}H assignments. This confirmed the previous assignment (Table 7).

30

The ^{1}H assignment of β-pinene given in Ref. 27 was recently confirmed by a complete analysis.[29] This assignment is given in Table 7.

Full details of all the assignment experiments and spectra are given in Ref. 30.

RESULTS AND DISCUSSIONS

Tables 3–7 comprise a large data set of alkene proton chemical shifts and this data set can now be used to test the various theories for alkene shielding detailed earlier in the context of the CHARGE model. In this model the parameters A and B in Eqn (1) for each γ effect have to be determined as well as the long-range shielding, i.e. the anisotropy and van der Waals effects. This was achieved by separating the γ effects into two groups. Those involving the olefinic protons were obtained first, and subsequently the remaining γ effects together with the anisotropy and the shielding were considered. This is because the alkane protons are affected by both the alkene γ effects and the C=C anisotropy and van der Waals shielding.

The values of the parameters were obtained by use of a non-linear least mean squares program, CHAP8,[31] which compares the observed and calculated chemical shifts. The values obtained for A and B are given in Table 2. Note that the $\cos\theta$ term averages to zero for a methyl group thus only the constant A is obtained.

Table 2. *A* and *B* values [Eqn (1)] for each γ effect

H···C fragment	*A*	*B*
$\mathrm{H-C=C-C-}$	−0.155	0.017
$\mathrm{H-C=C-C=}$	−0.428	−0.089
$\mathrm{H-\underset{\|}{C}-C=C}$	−0.006	−0.044
$\mathrm{H-\underset{\|}{C}-C-C-}$	0.175	−0.343
$\mathrm{H-\underset{\|}{C}-C-C=}$	0.131	−0.066
$\mathrm{H-C-C=C}$		
—CH	0.183	0.021
—CH_2	0.093	0.178
—CH_3	0.190	
$\mathrm{H-C-C-C=}$		
—CH	0.024	−0.362
—CH_2	−0.039	−0.294
—CH_3	0.026	

Both the anisotropy and van der Waals effects are considered as long-range effects in CHARGE as the effect of the C=C bond on protons up to three bonds distant is included in the γ effects above. The only protons that experience an anisotropy or shielding effect are those three bonds or more from the C=C bond in this model.

To determine the appropriate anisotropy and shielding functions a number of approaches were used. The first step was to decide whether the anisotropy was due to both parallel and perpendicular anisotropies or only one of them. The calculations were performed with both the parallel and perpendicular contributions. The result showed that the parallel anisotropy was almost zero. Indeed, the observed–calculated r.m.s. was the same whether two anisotropies were used or only the perpendicular one. Therefore, the anisotropy of a C=C bond is due to the perpendicular effect only, and the parallel effect can be neglected. The next step was to determine whether the anisotropy and the shielding have to be calculated from the middle of the C=C bond as suggested by Conroy[4] or at the carbon atoms as suggested by Pople.[5] In addition, the shielding term could either be the simple r^{-6} term of Eqn (3) or the more complex function of Eqn (10). Thus a number of different approaches were attempted and the results were as follows. The complex shielding function of Eqn (10) gave poorer results than the simple r^{-6} term and was eliminated. The remaining options gave very similar agreement with the observed data. It was more appropriate in the context of the CHARGE model to take the shielding at each carbon atom and the anisotropy at the middle of the C=C bond and this was the option employed. In this case the shielding of a γ proton (e.g. HCCC=C) is given by the γ effect of Table 2 from the olefinic carbon plus the anisotropy and steric effects from the C=C bond. Thus protons three bonds or more from the C=C bond have anisotropy from the bond and shielding effects from both the sp^2 carbons. This option on iterating the parameters gave values of $-20.09\ \text{Å}^3$ for the anisotropy (i.e. $-12.1 \times 10^{-6}\ \text{cm}^3\ \text{mol}^{-1}$) and $82.5\ \text{Å}^6$ for the shielding shifts together with the γ effects of Table 2. For the data set considered of 172 chemical shifts in Tables 3–7 spanning a range of ca 0.5–8.4δ the CHARGE7 scheme fits the experimental data to an r.m.s. error of 0.11 ppm. The generally very good agreement between the observed and calculated chemical shifts is encouraging.

The observed and the calculated chemical shifts for the acyclic alkenes (**1**–**10** and **15**, Fig. 3) are given in Table 3. The nomenclature *cis–trans* refers to the hydrogen, not to the alkane substituent. The calculated chemical shifts are in very good agreement with the observed data the majority of shifts being within 0.05 ppm. The CH proton in **7** is 0.3 ppm out (calculated 6.16 vs observed δ5.85. This chemical shift has the influence of the π electron density and a γ effect ($HC_{sp^2}CC$) from three methyl groups. In *tert*-butyl alkanes a similar enhanced γ effect was explicitly included but it was not felt necessary to include this here for only one chemical shift. The only other error larger than 0.2 ppm is for **8** and this could be due to conformational isomerism in this compound.

The observed and calculated chemical shifts for the cyclic alkenes are given in Table 4. The calculated chemical shifts are also in good agreement with the observed shifts although here both the spread of chemical shifts and the differences are greater than for the acyclic alkenes. Some of these differences may well be due to uncertainties in the calculated geometries of these molecules. This could be the case for H-5 in **22** in which the calculated shift is very different from the observed shift (δ 1.45 vs δ 1.72). It is generally stated that cycloheptene is largely in the chair form (conformer **1**, Fig. 3),[20,34] which was the conformer used in the calculations, but the literature is not unambiguous on this question.[35] The molecule can adopt up to five different conformations (Fig. 3) which are rapidly equilibrating by pseudorotation even at very low temperatures. However, the olefinic protons and the other methylene protons are in agreement with the observed data.

The observed and calculated chemical shifts for compounds **24** and **25** are presented in Table 5 and again the general agreement is very good. The calculated shifts for styrene are given for the non-planar PCMODEL geometry. These are in better agreement with the observed shifts than the planar geometry predicted by Gaussian94. In the latter the *ortho* protons and the near alkene protons experience additional downfield shifts due to H. . .H repulsion between the alkene and aromatic ring, but the *meta* and *para* proton shifts are the same as in Table 5. The available geometric

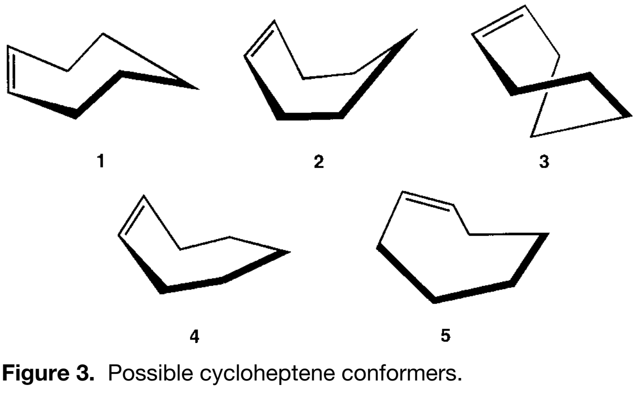


Figure 3. Possible cycloheptene conformers.

Table 3. Observed vs calculated chemical shifts (δ) for alkenes[a]

Compound	Proton	Observed	Calculated
1	—	5.405^{c}	5.407
2	1^{b}_{cis}	4.941^{c}	4.903
	1^{b}_{trans}	5.031	4.929
	2	5.834	5.841
	Me	1.725	1.667
3	2	5.42^{d}	5.345
	4	1.98	2.057
	Me_5	0.96	0.937
	Me_1	1.63	1.682
4	2	5.40^{d}	5.341
	4	2.05	2.006
	Me_5	0.96	0.919
	Me_1	1.60	1.622
5	1	4.65^{e}	4.712
	Me	1.72	1.702
6	1^{b}_{cis}	5.08^{d}	5.096
	1^{b}_{trans}	5.19	5.191
	2	6.31	6.310
7	1^{b}_{cis}	4.82^{f}	4.920
	1^{b}_{trans}	4.91	4.977
	2	5.85	6.172
	Me	1.00	1.092
8	1^{b}_{cis}	4.93^{d}	4.928
	1^{b}_{trans}	4.98	4.946
	2	5.80	5.809
	3	2.02	1.846
	4	1.41	1.228
	Me	0.90	0.897
9	Me	0.96^{d}	0.918
	2	2.02	2.051
	3	5.34	5.358
10	Me	0.97^{d}	0.938
	2	2.00	2.066
	3	5.43	5.335
15	1^{b}_{cis}	5.03^{d}	4.981
	1^{b}_{trans}	5.05	5.060
	2	5.84	6.009
	3	2.80	2.688

[a] See numbering in Fig. 3.
[b] See text.
[c] This work.
[d] Ref. 18.
[e] Ref. 32.
[f] Ref. 33.

evidence[20] does not preclude a slightly non-planar structure for styrene but our results support this structure.

In 9-vinylanthracene both programs give the same structure with orthogonal vinyl and aromatic groups. It is very encouraging that the model reproduces these shifts also to a very good degree of accuracy.

The observed and calculated chemical shifts for the norbornenes and bicyclooctene compounds (**23**, **26**–**28** and **31**–**34**) are given in Table 6. In **26**, H-8_b refers to the

Table 4. Calculated *vs* observed chemical shifts (δ) for monocyclic alkenes[a]

Compound	Proton	Observed	Calculated
11	1	5.74^{b}	5.765
	3	2.31	2.093
	4	1.82	1.721
12	1	5.68^{c}	5.747
	3	1.99	2.057
	4	1.61	1.555
13	1	5.894^{b}	5.879
	2	5.798	5.859
	5	2.151	2.245
14	1	5.70^{b}	5.650
	3	2.67	2.642
16	1	5.73^{c}	5.702
	3	2.63	2.602
	7	2.25	2.132
	8	1.82	1.892
17	1	5.71^{c}	5.729
	3	2.53	2.591
18	1	5.650^{b}	5.761
	2	5.650	5.758
	3_{eq}	2.080	2.091
	3_{ax}	1.640	1.503
	4	1.680	1.627
	5_{eq}	1.710	1.838
	5_{ax}	1.240	1.036
	6_{eq}	2.060	2.044
	6_{ax}	2.060	2.142
	Me	0.950	0.948
19	2	5.350^{b}	5.554
	3_{eq}	2.040	2.123
	3_{ax}	1.610	1.542
	4	1.610	1.666
	5_{eq}	1.700	1.856
	5_{ax}	1.200	1.084
	6_{eq}	1.900	1.921
	6_{ax}	1.980	1.937
	Me_7	1.650	1.714
	Me_8	0.950	0.955
20	2_{eq}	2.271^{b}	2.371
	2_{ax}	1.964	1.874
	3_{eq}	1.820	1.789
	3_{ax}	1.255	1.243
	4_{eq}	1.740	1.714
	4_{ax}	1.328	1.247
	7	4.571	4.725
21	2	2.250^{c}	2.264
	3	1.650	1.619
	6	4.820	4.733
22	1	5.794^{b}	5.622
	3	2.120	2.063
	4	1.504	1.429
	5	1.723	1.447

[a] See numbering in Fig. 3.
[b] This work.
[c] Ref. 18.

Table 5. Observed vs calculated chemical shifts (δ) for **24** and **25**[a]

Compound	Proton	Observed[b]	Calculated
24	*ortho*	7.414	7.620
	meta	7.328	7.432
	para	7.253	7.402
	7	6.722	6.727
	8_{trans}	5.758	5.723
	8_{cis}	5.246	5.251
25	1,8	8.320	8.079
	2,7	7.465	7.510
	3,6	7.465	7.537
	4,5	7.996	7.994
	10	8.386	8.517
	15	7.476	7.357
	16_{cis}	6.010	5.932
	16_{trans}	5.629	5.519

[a] See numbering in Fig. 3.
[b] This work.

proton facing C-4 and H-8_a is facing C-6. In **27**, H-8_a is facing C-1 and H-8_b is facing C-3. In **28**, H-10_a is facing C-1 and H-10_b is facing C-9 (Scheme 1). The calculated chemical shifts are generally in reasonable agreement with the observed data, but there are a number of exceptions. This is not surprising as the proton chemical shifts of the parent hydrocarbons have proved difficult to quantify in the CHARGE routine.[10,15] However there are some interesting points to note. Compound **23** is of particular interest as the 7_{syn} proton (*syn* to the olefinic group) is only ca 2 Å from and almost vertically above the olefinic group, thus it provides a crucial test of any shielding theory. Marchand and Rose[36] obtained the proton spectrum of this compound and identified the ab pattern of the H-7 protons from decoupling experiments. However they assigned the 7_{syn} proton to the more shielded resonance at 0.48δ based on the Jackman shielding cone for the C=C bond anisotropy (Fig. 1). We have reversed this assignment. The more shielded proton is the 7_{anti} and the 7_{syn} is the deshielded proton nearer to the C=C bond. This is strikingly confirmed by the calculated shifts in Table 6. Inspection of the CHARGE output shows that the 7_{syn} proton is strongly deshielded by the van der Waals deshielding due to the olefinic carbons whereas the anisotropy term is larger for the 7_{anti} proton. This clearly confirms the shielding pattern obtained here for the C=C group which alters sign along the x- axis (see later).

Table 6. Observed vs calculated chemical shifts (δ) for norbornanes and bicyclooctane[a]

Compound	Proton	Observed	Calculated
23	7_{syn}	1.970[b]	1.627
	7_{anti}	0.480	0.458
26	1	2.968[c]	3.247
	2	6.128	5.946
	3	6.073	5.861
	4	3.156	3.419
	6_{exo}	2.252	2.438
	6_{endo}	1.756	2.173
	7_{syn}	1.595	1.677
	7_{anti}	1.421	1.497
	8_a	4.717	4.717
	8_b	4.988	4.786

Table 6. (*continued*)

Compound	Proton	Observed	Calculated
27	1	2.670[c]	2.714
	4	1.900	2.106
	5_{exo}	1.383	1.305
	5_{endo}	1.701	1.795
	6_{exo}	1.638	1.605
	6_{endo}	1.236	1.501
	7_{syn}	1.694	1.504
	7_{anti}	1.204	0.999
	8_a	4.717	4.710
	8_b	4.493	4.736
	Me_{exo}	1.020	1.015
	Me_{endo}	1.050	0.979
28	1	2.878[c]	2.887
	2	5.984	5.786
	3	5.935	5.727
	4	2.785	2.945
	5	3.214	3.023
	6	2.729	2.693
	7_{syn}	1.478	1.425
	7_{anti}	1.301	1.389
	8	5.507	5.695
	9	5.476	5.547
	10_a	2.184	2.180
	10_b	1.622	2.037
31	2	5.900[d]	5.862
	Me_{syn}	0.900	0.901
	Me_{anti}	0.950	0.905
32	1	2.841[b]	2.788
	2	5.985	5.871
	5_{exo}	1.603	1.652
	5_{endo}	0.951	1.379
	7_{syn}	1.313	1.627
	7_{anti}	1.073	1.306
33	1	3.580[e]	3.553
	2	6.750	5.873
	7	2.000	1.749
34	1	2.480[e]	2.702
	2	6.230	5.773
	5_{exo}	1.230	1.445
	5_{endo}	1.500	1.596

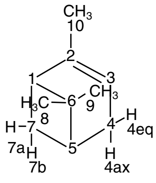
[a] See numbering in Fig. 3 and text.
[b] Ref. 36.
[c] This work.
[d] Ref. 38.
[e] Ref. 37

However, there are also additional shielding mechanisms in these molecules which are not included in the model. For example, the calculated shifts for the olefinic protons for **33** at δ5.87 are almost 1 ppm less than the observed shifts (δ6.75). Some years ago, Tori *et al.*[37] noted the unusual deshielding effects upon bridge methylenes of norbornadienes. They demonstrated a considerable transannular interaction between the two double bonds by UV spectroscopy. This transannular interaction could affect the proton chemical shifts of the olefinic protons involved in this interaction as well as the bridge methylenes, which are also not well calculated. However the calculated methine proton chemical shifts are in agreement with the observed data.

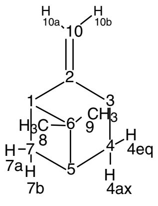
In **34**, the olefinic proton shifts are again not as well calculated as expected (observed δ6.23, calculated δ5.81). There will also be considerable transannular interactions in this compound between the olefinic group and the *endo* protons (Scheme 1) and this may be a reason for this deviation. However, the rest of the proton chemical shifts are calculated in good agreement with the observed data.

The calculated and observed chemical shifts for **29** and **30** are given in Table 7. The calculated shifts are generally in fair agreement with the observed data. There are some deviations which mainly concern the protons near the four-membered rings. The cyclobutane ring has not yet been included in the CHARGE model and there may be shielding effects from this fragment which are not covered. However, the general picture is reasonably well reproduced. In particular Me-9 is calculated as more shielded than Me-8, which is the observed assignment in both molecules.

Table 7. Observed vs calculated proton chemical shifts (δ) for α- and β-pinene



α-pinene (**29**)



β-pinene (**30**)

Compound **29**			Compound **30**		
Proton	Observed	Calculated	Proton	Observed	Calculated
1	1.931[a]	2.049	1	2.430[b]	2.631
7_a	2.333	2.414	7_a	2.310	1.886
7_b	1.151	1.101	7_b	1.420	1.531
5	2.067	2.522	5	1.970	2.072
4_{eq}	2.231	2.475	4_{eq}	1.820	1.675
4_{ax}	2.152	2.076	4_{ax}	1.850	1.893
3	5.185	5.564	3_{eq}	2.230	2.358
Me_8	1.264	1.042	3_{ax}	2.510	2.304
Me_9	0.835	0.984	10_a^c	4.500	4.736
Me_{10}	1.658	1.777	10_b	4.570	4.737
			Me_8	1.240	1.032
			Me_9	0.730	0.993

[a] This work.

[b] Refs. 27,29.

[c] See text.

CONCLUSIONS

The agreement between the observed and calculated proton chemical shifts is encouraging. The incorporation of the olefinic γ effects together with the calculation of the C=C anisotropy and shielding allow the prediction of the proton chemical shifts for alkenes, thus extending the CHARGE model to these important compounds.

The results demonstrate clearly that the parallel contribution to the anisotropy can be neglected and that the only anisotropic contribution is due to the perpendicular anisotropy.

The results also show that there is *deshielding* above the C=C bond at small distances due to the van der Waals term and *shielding* for large distances due to the bond anisotropy. On the other hand, there is always a *deshielding* effect in the plane of the C=C bond. The figures obtained here for the anisotropy and shielding show that along the *x*- axis (Fig. 1) the shielding is positive for distances <2.0 Å. At this distance the shielding changes sign to become negative. The maximum negative value of the shielding occurs at ca 2.5 Å. This is in good agreement with both the observed data and with the results from the *ab initio* calculations mentioned earlier which found a change in the sign of the shielding at ca 2.8 Å.

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