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Studies of Magnetic Anisotropy. 2. NMR Evidence for the Existence of Deshielding Regions alongside Carbon–Carbon Triple Bonds[1]

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The existence of the regions of magnetic deshielding that are predicted to occur alongside carbon–carbon triple bonds is confirmed experimentally by the observation of unusually low-field proton NMR chemical shifts for the H-5 proton in 4-ethynylphenanthrene (**1**) and also for the three benzylic protons of the C-4 methyl group in 5-ethynyl-1,4-dimethylnaphthalene (**2**) and the two benzylic protons of the C-4 ethyl group in 5-ethynyl-1,4-diethylnaphthalene (**3**).

Acetylenic hydrogen atoms have proton NMR chemical shifts at higher fields than would be expected solely on the basis of the electronegativity of the sp-hybridized carbon atoms to which they are bonded. It is widely accepted[2] that this effect arises because of anisotropy in the magnetic susceptibility of the carbon–carbon triple bond. This magnetic anisotropy, $\Delta\chi$, is defined as $\chi_{\parallel} - \chi_{\perp}$, where $\chi_{\parallel}$ and $\chi_{\perp}$ are the magnetic susceptibilities parallel and perpendicular, respectively, to the triple-bond axis. A value of $\Delta\chi = -7.70$ (in units[3] of 10^{-6} erg Gauss^{-2} mol^{-1}) has been determined experimentally for methylacetylene from a study of the high-field molecular Zeeman effect on its microwave spectrum.[4] An alternative determination by a complementary experimental method based on the Cotton–Mouton effect gave a value[3] of -7.9 for methylacetylene.[5] A value[3] of -8.39 has been calculated theoretically for acetylene itself.[6] From these various results, a value[3] of $\Delta\chi$ near -8 now seems to be reliably established for the carbon–carbon triple bond.[7-12]

As a consequence of the negative sign of $\Delta\chi$, the ethynyl hydrogen atom of a terminal acetylene that is tumbling freely in an external magnetic field finds itself in a region of special magnetic *shielding* as illustrated in Figure 1. That is, the external magnetic field acting at the acetylenic hydrogen atom is opposed by the small magnetic field generated as the net result of the circulation of electron density within the ethynyl group that is induced by the external field. As a corollary, regions of special magnetic *deshielding* are predicted to exist alongside the carbon–carbon triple bond as shown in Figure 1. Surprisingly, however, compelling NMR spectral evidence regarding this predicted deshielding was lacking. In fact, in the only previous systematic study of which we are aware,[13] the series of cyclic acetylenes from cyclononyne through cyclododecyne failed to show appreciable deshieldings for any of the cross-ring methylene groups. A small but positive indication of acetylene deshielding can be found, however, in the proton NMR spectra of a series of 2,4,6-tri-*tert*-butylphenylacetylenes, in which the chemical shifts of the ortho *tert*-butyl groups are downfield from those of the para *tert*-butyl groups by 0.20–0.25 ppm.[14] Also

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[1] (a) Part 1: Penn, L.; Mallory, F. B. *J. Magn. Reson.* **1975**, *18*, 6–11. (b) This paper has been presented in part, see: "Abstracts of Papers", First Chemical Congress of the North American Continent, Mexico City, Dec 2, 1975; American Chemical Society: Washington, DC, 1975; Abstr ORGA 46. (c) Taken from the Ph.D. Thesis of M. B. Baker, Bryn Mawr College, 1976.

[2] (a) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. "High-resolution Nuclear Magnetic Resonance"; McGraw-Hill: New York, 1959; p 179. (b) Pople, J. A.; Untch, K. G. *J. Am. Chem. Soc.* **1966**, *88*, 4811–4815. (c) Macomber, R. S. *J. Org. Chem.* **1972**, *37*, 1205–1209. (d) Charrier, C.; Dorman, D. E.; Roberts, J. D. *Ibid.* **1973**, *38*, 2644–2650.

[3] Throughout this discussion, susceptibilities and anisotropies are expressed in units of 10^{-6} erg Gauss^{-2} mol^{-1}.

[4] Shoemaker, R. L.; Flygare, W. H. *J. Am. Chem. Soc.* **1969**, *91*, 5417–5421.

[5] Geschka, H.; Pferrer, S.; Häussler, H.; Hüttner, W. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 790–795.

[6] Kato, Y.; Fujimoto, Y.; Saika, A. *Chem. Phys. Lett.* **1972**, *13*, 453–456.

[7] Earlier experimental measurements of $\Delta\chi$ based on proton NMR chemical shifts led to values[3] of -11.8,[8] -16.5,[9] -31.6,[10] and -34.1;[11] it is now recognized that several factors mitigate against obtaining accurate evaluations of $\Delta\chi$ from proton chemical-shift data.[4,6,12]

[8] Castellano, S.; Lorenc, J. *J. Phys. Chem.* **1965**, *69*, 3552–3564.

[9] Reddy, G. S.; Goldstein, J. H. *J. Chem. Phys.* **1963**, *39*, 3509–3512.

[10] Heel, H.; Zeil, W. *Z. Elektrochem.* **1960**, *64*, 962–971.

[11] Zeil, W.; Buchert, H. *Z. Phys. Chem. (Frankfurt/Main)* **1963**, *38*, 47–55.

[12] Appleman, B. R.; Dailey, B. P. *Adv. Magn. Reson.* **1974**, *7*, 231–320.

[13] Nordlander, J. E.; Hanish, J. M.; Mollenshott, J. E.; Sheeler, L. R. "Abstracts of Papers", 151st Meeting of the American Chemical Society, Pittsburgh, Mar 31, 1966; American Chemical Society: Washington, DC, 1966; Abstr ORGN 112.

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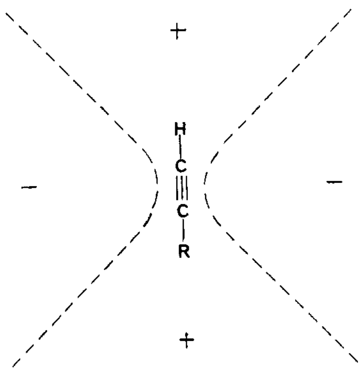
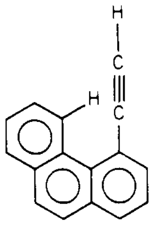


Figure 1. Expected regions of net magnetic shielding (+) and deshielding (−) around a freely tumbling acetylene resulting from circulations of the triple-bond electrons induced by an external magnetic field.

the proton NMR chemical shift of the peri hydrogens in 1,5-bis(phenylethynyl)naphthalene[15] is about 0.7 ppm downfield from that of the peri hydrogens in naphthalene itself, although part of this downfield shift may result from the deshielding effect of the phenyl groups. In order to provide what we hoped would be a definitive test of the existence of the deshielding regions indicated in Figure 1, we undertook the preparation of a sample of 4-ethynylphenanthrene (1) to determine, by proton NMR spectroscopy, whether or not the hydrogen at C-5 exhibits an unusually large downfield chemical shift; subsequently, we extended our studies to include 5-ethynyl-1,4-dimethylnaphthalene (2) and 5-ethynyl-1,4-diethylnaphthalene (3).



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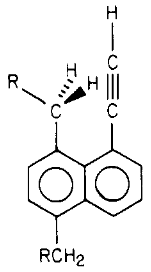

2, R = H
3, R = CH_3

Results

Acetylenes 1–3 were synthesized, and their proton NMR spectra were measured in CCl_4 solution. The chemical shift of H-5 in 4-ethynylphenanthrene (1) is 10.27 ppm, which is 1.63 ppm downfield from the chemical shift of 8.64 ppm for H-5 (and H-4) in phenanthrene itself. The proton NMR spectrum of 5-ethynyl-1,4-dimethylnaphthalene (2) shows two methyl peaks at 2.52 and 3.01 ppm; the peak at 2.52 ppm is assigned to the C-1 methyl group because a similar chemical shift of 2.48 ppm is found for the methyl groups of 1,4-dimethylnaphthalene as a reference compound, and, consequently, the peak at 3.01 ppm is assigned to the C-4 methyl group. Similarly, the quartet signals at 3.07 and 3.62 ppm in the proton NMR spectrum of 5-ethynyl-1,4-diethylnaphthalene (3) are attributed to the methylene groups of the C-1 and C-4 ethyl groups, respectively. These chemical-shift measurements establish that the H-5 proton in acetylene 1 is deshielded by 1.63 ppm, that the C-4 methyl protons in acetylene 2 are deshielded by 0.49 ppm, and that the C-4 methylene protons in acetylene 3 are deshielded by 0.55 ppm.

Discussion

Our results fully confirm the existence of the deshielding regions shown in Figure 1 that are predicted on the basis of the magnetic anisotropy of the carbon–carbon triple bond.[16–18] These results not only demonstrate that acetylenic deshielding exists but also show that the magnitude of this deshielding, as expected, falls off with distance. For example, as a consequence of the rapid rotation of the C-4 methyl group in acetylene 2, each of the three methyl protons spends only a fraction of its time in the location close to the triple bond that is analogous to the location in which the H-5 proton of acetylene 1 spends all of its time. Because of this rotational averaging, the C-4 methyl group is, in effect, probing the deshielding effect at the position of the center of gravity of the three methyl protons, which is a point lying about 0.5 Å beyond the methyl carbon atom along the extension of the line passing from the C-4 ring carbon atom through the C-4 methyl carbon atom.[19] This accounts for the observation that the deshielding effect in acetylene 2 (0.49 ppm) is smaller than that in acetylene 1 (1.63 ppm).

We are unable to make a reliable judgment about the form of the distance dependence of the deshielding effect because we do not have accurate values for the distances from the center of the triple bond to H-5 in acetylene 1 or from the center of the triple bond to the center of gravity of the C-4 methyl protons in acetylene 2. But if we use as a first approximation for these two distances the values of 1.54 and 2.44 Å, respectively, measured from Dreiding models,[20] our chemical-shift results provide a hint that the deshielding of the carbon–carbon triple bond falls off approximately as $1/r^3$. Thus, the ratio of the deshielding effect in acetylene 2 compared to that in acetylene 1 predicted on the basis of a $1/r^3$ distance dependence is $(1.54/2.44)^3 = 0.25$, which is close to our observed ratio of $0.49/1.63 = 0.30$. Such a distance dependence would be consistent with the well-known models for bond anisotropy based on the approximation of a magnetic point dipole located at the midpoint of the bond.[21] This apparent consistency should be viewed with caution, however, considering our uncertainty about the actual distances in acetylenes 1 and 2 and also the questionable accuracy of the point dipole approximation at these short distances.

The effective point in space in which the deshielding effect is being probed by the two benzylic protons of the C-4 ethyl group in acetylene 3 lies slightly closer to the triple bond than that being probed by the three benzylic protons of the C-4 methyl group in acetylene 2. This is because severe van der Waals repulsions raise the energy

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(14) Zimmerman, H. E.; Dodd, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 6507–6515.

(15) Bossenbroek, B.; Shechter, H. *J. Am. Chem. Soc.* **1967**, *89*, 7111–7112.

(16) Steric compression, another factor thought to produce deshielding,[17] probably does not contribute significantly to the observed downfield shift of H-5 in acetylene 1 relative to phenanthrene. In 4-methylphenanthrene as a model compound, for example, the methyl group causes a downfield shift for H-5 of only 0.23 ppm relative to phenanthrene, and at least part of that small effect has been ascribed to magnetic anisotropy of the methyl group.[18]

(17) (a) Regan, T. H.; Miller, J. B. *J. Org. Chem.* **1967**, *32*, 2789–2794. (b) Dickerman, S. C.; Haase, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 5458–5459. (c) Cheney, B. V. *Ibid.* **1968**, *90*, 5386–5390. (d) Mallion, R. B. *J. Chem. Soc. B* **1971**, 681–686.

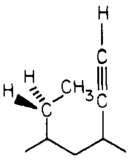
(18) Bartle, K. D.; Smith, J. A. S. *Spectrochim. Acta Part A* **1967**, *23A*, 1689–1714.

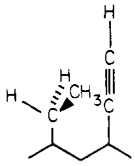
(19) Ouellette, R. J.; Sinha, B. K.; Stolfo, J.; Levin, C.; Williams, S. *J. Am. Chem. Soc.* **1970**, *92*, 7145–7148.

(20) These estimated distances are surely too short, because Dreiding models fail to take into account the molecular distortions that are caused by van der Waals crowding.

(21) (a) McConnell, H. M. *J. Chem. Phys.* **1957**, *27*, 226–229. (b) Pople, J. A. *Proc. R. Soc. (London), Ser. A* **1957**, *A239*, 550–556.

and, hence, lower the equilibrium population of those conformations of acetylene **3** in which the terminal methyl group of the C-4 ethyl group is crowded against the triple bond; this conformational bias limits the excursions that the two benzylic protons of that ethyl group make into the regions remote from the triple bond. This accounts for the observation that the deshielding effect in acetylene **3** (0.55 ppm) is larger than that in acetylene **2** (0.49 ppm).





The absence of detectable downfield proton NMR chemical shifts in the series of C_9 through C_{12} cycloalkynes[13] probably means that the distances between the cross-ring methylene groups and the triple bonds in these flexible molecules are too large[22] for appreciable deshielding to occur. In a rigid acetylene like **1**, in contrast, the probing H-5 proton cannot escape from the region of strong deshielding close to the triple bond.

The studies of the Zeeman effect on the microwave spectrum of methylacetylene cited above[4] led to the following values for the separate diamagnetic and paramagnetic contributions to the magnetic susceptibilities both parallel and perpendicular to the triple-bond axis:[3] $\chi_{\parallel}{}^{d} = -46.1$; $\chi_{\parallel}{}^{p} = 9.5$; $\chi_{\perp}{}^{d} = -187.3$; $\chi_{\perp}{}^{p} = 158.4$. The observed magnetic anisotropy is the algebraic sum of these four terms: $\Delta\chi = (\chi_{\parallel}{}^{d} + \chi_{\parallel}{}^{p}) - (\chi_{\perp}{}^{d} + \chi_{\perp}{}^{p}) = -46.1 + 9.5 + 187.3 - 158.4 = -7.7$. This dissection of $\Delta\chi$ into its four individual terms clearly demonstrates the inadequacy of the simple pictorial explanation that is commonly advanced to try to account for the existence of the shielding and deshielding regions indicated in Figure 1. In that simple picture, the overall effect is attributed to diamagnetic circulation of the four π electrons around the triple-bond axis induced by the component of the external magnetic field acting along that axis; the problem with this picture is that it relates to only one of the four terms, namely $\chi_{\parallel}{}^{d}$. Although this term has the same sign as $\Delta\chi$, and therefore qualitatively predicts the correct shielding and deshielding behavior shown in Figure 1, it is obvious that this agreement is fortuitous because the other three terms, $\chi_{\parallel}{}^{p}$, $\chi_{\perp}{}^{d}$, and $\chi_{\perp}{}^{p}$, are of such magnitudes that they cannot justifiably be ignored. If one felt obliged to verbalize the situation for methylacetylene, one might say that the negative sign for $\Delta\chi$ results from the fact that the paramagnetic term $\chi_{\parallel}{}^{p}$ is small, owing to the nearly axial symmetry of the molecule ($\chi_{\parallel}{}^{p}$ would be zero for a molecule with perfect axial symmetry such as acetylene itself), and therefore the diamagnetic term $\chi_{\parallel}{}^{d}$ is not counteracted by $\chi_{\parallel}{}^{p}$ to quite the same extent as the diamagnetic term $\chi_{\perp}{}^{d}$ is counteracted by $\chi_{\perp}{}^{p}$.

As one would expect, the cyano group exhibits a deshielding effect similar to that of the ethynyl group, as indicated by the reports that the proton NMR chemical shift of H-5 in 4-cyanophenanthrene in $CDCl_3$ lies either 1.0 ppm[23] or 1.3 ppm[24] downfield from that of H-5 (and H-4) in phenanthrene itself.[18]

The proton NMR spectra of the series of 4-halophenanthrenes in CCl_4 have been reported to show the following downfield shifts for H-5 relative to phenanthrene itself: 0.56 ppm in 4-fluorophenanthrene; 1.16 ppm in 4-chlorophenanthrene; 1.39 ppm in 4-bromophenanthrene; 1.46 ppm in 4-iodophenanthrene.[25] Although these downfield shifts may result in part from steric effects, we believe they are best explained by invoking the existence of a region of magnetic deshielding alongside halogen substituents like that alongside ethynyl groups. Presumably, the circulation of the four lone-pair electrons in the two mutually perpendicular valence-level p orbitals of a halogen is analogous to the circulation of the four bond-pair electrons in the two mutually perpendicular valence-level π orbitals of an acetylene.

Experimental Section

General Methods. Melting points were measured with a Thomas-Hoover oil-bath apparatus and are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Garden City, MI. Proton NMR spectra were obtained at 60 MHz with a Varian A-56/60A spectrometer. Mass spectra were determined with a Hitachi Perkin-Elmer RMS-4 spectrometer interfaced with a Perkin-Elmer 990 gas chromatograph.

4-Ethynylphenanthrene (1). Naphthalene was transformed by a sequence of known reactions to 4-phenanthreneethanol.[26–31] This alcohol was dehydrated by a method described previously for preparing styrenes.[32] A 50-mL two-necked flask containing 13 g (0.23 mol) of potassium hydroxide and a trace of picric acid (to inhibit polymerization) was equipped with an addition funnel and a distillation head with a vacuum take-off and a receiver. This system was evacuated to about 15 torr, and the flask was heated in an oil bath at 225 °C while 3.8 g (0.017 mol) of 4-phenanthreneethanol was added dropwise. The product distilled from the reaction mixture as it was formed. The 3.4 g (97%) of crude product was redistilled to give 2.6 g (70%) of 4-vinylphenanthrene: bp 110–112 °C (2 torr); ^{1}H NMR ($CDCl_3$) δ 8.89 (m, 1 H, H-5), 7.94–7.27 (m, 9 H, H-1 to H-3, H-6 to H-10, α-vinyl), 5.90–5.27 (m, 2 H, β-vinyl); IR (neat) 3080 and 1615 (vinyl) cm^{-1}; MS, *m/e* 204 (M^+).

Bromine was added dropwise to a solution of 2.6 g (0.013 mol) of 4-vinylphenanthrene in 10 mL of glacial acetic acid until the bromine color persisted. Water was then added, and the resulting crystals were collected by suction filtration and recrystallized from ethanol[33] to give 3.1 g (67%) of 4-(1,2-dibromoethyl)phenanthrene: mp 110–112 °C; ^{1}H NMR ($CDCl_3$) δ 8.91 (m, 1 H, H-5), 8.03–7.45 (m, 8 H, H-1 to H-3, H-6 to H-10), 6.39 (t, 1 H, *J* = 8 Hz, CHBr), 4.17 (d, 2 H, *J* = 8 Hz, CH_2Br). Anal. ($C_{16}H_{12}Br_2$) C, H.

4-(1,2-Dibromoethyl)phenanthrene (0.32 g, 0.88 mmol) was heated under reflux for 1 h in a mixture of 5 mL of dimethyl sulfoxide and 10 mL of ethanol containing excess sodium ethoxide. Then the mixture was cooled, diluted with water, and extracted with diethyl ether. The ether extract was washed with water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure to give a residue that was recrystallized twice from ethanol to give 0.10 g (40%) of a monobromo compound with mp 106.5–106.6 °C. Anal. ($C_{16}H_{11}Br$) C, H.

This material (0.10 g, 0.35 mmol) was treated with excess potassium *tert*-butoxide in 5 mL of *tert*-butyl alcohol at 80 °C for 30 min. The solution was then cooled, diluted with water, and extracted with diethyl ether. The ether extract was washed with water, dried over anhydrous magnesium sulfate, and evap-

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(22) (a) Anet, F. A. L.; Yavari, I. *Tetrahedron* **1978**, *34*, 2879–2886. (b) Allinger, N. L.; Meyers, A. Y. *Ibid.* **1975**, *31*, 1807–1811.

(23) Kreher, R.; Köbler, W. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 264–265.

(24) Gore, P. H.; Kamonah, F. S. *Synth. Commun.* **1979**, *9*, 377–382.

(25) Beringer, F. M.; Chang, L. L.; Fenster, A. N.; Rossi, R. R. *Tetrahedron* **1969**, *25*, 4339–4345.

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(27) Wilds, A. L.; Werth, R. G. *J. Org. Chem.* **1952**, *17*, 1154–1161.

(28) Snyder, H. R.; Werber, F. X. In "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. 3, pp 798–800.

(29) Newman, M. S. *J. Org. Chem.* **1951**, *16*, 860–862.

(30) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 1285.

(31) Bendas, H.; Djerassi, C. *J. Am. Chem. Soc.* **1956**, *78*, 2474–2476.

(32) Frank, R. L.; Adams, C. E.; Allen, R. E.; Gander, R.; Smith, P. V. *J. Am. Chem. Soc.* **1946**, *68*, 1365–1368.

(33) On prolonged treatment with boiling ethanol, this dibromide undergoes solvolysis to give a monobromo monoethoxy compound, mp 113.0–113.5 °C. Anal. ($C_{18}H_{17}BrO$) C, H.

orated under reduced pressure to give a brown oil. This oil was dissolved in petroleum ether (bp 35–60 °C) and filtered through a column of alumina. Evaporation of the eluate under reduced pressure gave 4-ethynylphenanthrene (1) as a colorless oil: ^{1}H NMR (CCl_4) δ 10.27 (m, 1 H, H-5), 8.03–6.96 (m, 8 H, H-1 to H-3, H-6 to H-10), 3.54 (s, 1 H, C≡CH); IR (neat) 3265 (≡CH), 2095 (C≡C) cm^{-1}; MS, *m/e* 202 (M$^+$).

5-Ethynyl-1,4-dimethylnaphthalene (2). A Reformatsky reaction[29] of 13 g (0.075 mol) of 3,4-dihydro-5,8-dimethyl-1-(2*H*)-naphthalenone[34] with an excess of ethyl bromoacetate and activated zinc[30] gave, after dehydration of the initial hydroxy ester with phosphorus pentoxide in refluxing benzene and distillation at reduced pressure, a mixture of two isomeric unsaturated esters, bp 80–150 °C (1 torr). This mixture was treated with an excess of sulfur at 210 °C for 3 h. Distillation of the crude dehydrogenation product at reduced pressure gave 8.5 g of material with a boiling range of 120–190 °C (1 torr). This distillate was saponified with excess sodium hydroxide in refluxing ethanol. The ethanol was evaporated under reduced pressure, and the residue was acidified with dilute HCl. The resulting mixture was extracted with diethyl ether, and the ether extract was dried over anhydrous magnesium sulfate and evaporated under reduced pressure to give a residue that was recrystallized twice from ethanol to give 2.5 g (16% overall) of 5,8-dimethyl-1-naphthaleneacetic acid: mp 190.8–191.4 °C; ^{1}H NMR ($CDCl_3$) δ 7.59–6.99 (m, 5 H, H-2, H-3, H-6, H-7, H-8), 4.37 (s, 2 H, CH_2), 2.85 (s, 3 H, CH_3), 2.67 (s, 3 H, CH_3). Anal. ($C_{14}H_{14}O_2$) C, H.

Reduction of 1.8 g (8 mmol) of 5,8-dimethyl-1-naphthaleneacetic acid with excess lithium aluminum hydride in diethyl ether[31] gave 1.1 g (65%) of 5,8-dimethyl-1-naphthaleneethanol as an oil: ^{1}H NMR ($CDCl_3$) δ 8.14–7.11 (m, 5 H, H-2, H-3, H-6, H-7, H-8), 3.84 (t, 2 H, J = 6 Hz, CH_2), 3.63 (t, 2 H, J = 6 Hz, CH_2), 2.90 (s, 3 H, CH_3), 2.67 (s, 3 H, CH_3); MS, *m/e* 200 (M$^+$).

This material (1.0 g, 5 mmol) was dehydrated[32] by adding it dropwise to a mixture of 4 g (71 mmol) of potassium hydroxide and a trace of picric acid maintained at 225 °C and 1 torr. The product distilled out as it was formed, giving 0.4 g (44%) of 1,4-dimethyl-5-vinylnaphthalene as an oil: ^{1}H NMR ($CDCl_3$) δ 8.04–7.16 (m, 6 H, H-2, H-3, H-6, H-7, H-8, α-vinyl), 5.61–5.14 (m, 2 H, β-vinyl), 2.80 (s, 3 H, CH_3), 2.61 (s, 3 H, CH_3); IR (neat) 3050, 3005, 1618 (vinyl) cm^{-1}; MS, *m/e* 182 (M$^+$).

Bromination of 0.1 g of 1,4-dimethyl-5-vinylnaphthalene, followed by dehydrobromination with potassium *tert*-butoxide as described above for the synthesis of 1 gave 5-ethynyl-1,4-dimethylnaphthalene (2) as an oil: ^{1}H NMR (CCl_4) δ 7.93–7.05 (m, 5 H, H-2, H-3, H-6, H-7, H-8), 3.25 (s, 1 H, C≡CH), 3.01 (s, 3 H, C-4 CH_3), 2.52 (s, 3 H, C-1 CH_3); IR (neat) 3260 (≡CH), 2080 (C≡C) cm^{-1}; MS, *m/e* 180 (M$^+$).

5-Ethynyl-1,4-diethylnaphthalene (3). 5,8-Diethyl-3,4-dihydro-1(2*H*)-naphthalenone[35] was subjected to a series of procedures very similar to those described above for the preparation of 5,8-dimethyl-1-naphthaleneacetic acid to give, after recrystallization of the crude product from petroleum ether (bp 35–60 °C), 5,8-diethyl-1-naphthaleneacetic acid: mp 129.6–130.4 °C; ^{1}H NMR ($CDCl_3$) δ 8.29–7.26 (m, 5 H, H-2, H-3, H-6, H-7, H-8), 4.29 (s, 2 H, C-1 CH_2), 3.15 (q, 2 H, J = 7.5 Hz, C-5 or C-8 CH_2), 3.11 (q, 2 H, J = 7.5 Hz, C-5 or C-8 CH_2), 1.36 (t, 3 H, J = 7.5 Hz, CH_3), 1.29 (t, 3 H, J = 7.5 Hz, CH_3). Anal. ($C_{16}H_{18}O_2$) C, H.

Reduction of 1.1 g (5 mmol) of 5,8-diethyl-1-naphthaleneacetic acid with excess lithium aluminum hydride in diethyl ether gave 1.0 g (96%) of 5,8-diethyl-1-naphthaleneethanol as an oil: ^{1}H NMR (CCl_4) δ 8.23–7.27 (m, 5 H, H-2, H-3, H-6, H-7, H-8), 3.76 (t, 2 H, J = 6 Hz, hydroxyethyl CH_2), 3.51 (t, 2 H, J = 6 Hz, hydroxyethyl CH_2), 3.17 (q, 2 H, J = 7.5 Hz, ethyl CH_2), 3.05 (q, 2 H, J = 7.5 Hz, ethyl CH_2), 1.33 (t, 3 H, J = 7.5 Hz, CH_3), 1.26 (t, 3 H, J = 7.5 Hz, CH_3); MS, *m/e* 228 (M$^+$).

This material (1.0 g, 4 mmol) was dehydrated[32] by adding it dropwise to a mixture of 4 g (71 mmol) of potassium hydroxide and a trace of picric acid maintained at 225 °C and 1 torr. The product distilled out as it was formed, giving 0.7 g (76%) of 1,4-diethyl-5-vinylnaphthalene as an oil: ^{1}H NMR ($CDCl_3$) δ 8.22–7.26 (m, 6 H, H-2, H-3, H-6, H-7, H-8, α-vinyl), 5.70–5.18 (m, 2 H, β-vinyl), 3.24 (q, 2 H, J = 7.5 Hz, CH_2), 3.08 (q, 2 H, J = 7.5 Hz, CH_2), 1.36 (t, 3 H, J = 7.5 Hz, CH_3), 1.26 (t, 3 H, J = 7.5 Hz, CH_3); MS, *m/e* 210 (M$^+$).

Bromination of 0.6 g of 1,4-diethyl-5-vinylnaphthalene, followed by dehydrobromination with potassium *tert*-butoxide as described above for the synthesis of 1, gave 5-ethynyl-1,4-diethylnaphthalene (3) as an oil: ^{1}H NMR (CCl_4) δ 8.11–7.20 (m, 5 H, H-2, H-3, H-6, H-7, H-8), 3.62 (q, 2 H, J = 7.5 Hz, C-4 ethyl CH_2), 3.28 (s, 1 H, C≡CH), 3.07 (q, 2 H, J = 7.5 Hz, C-1 ethyl CH_2), 2.32 (t, 6 H, J = 7.5 Hz, methyls); IR (neat) 3260 (≡CH), 2085 (C≡C) cm^{-1}; MS, *m/e* 208 (M$^+$).

Conclusions

By observing downfield proton NMR chemical shifts, relative to appropriate references, of 1.63 ppm for H-5 in 4-ethynylphenanthrene (1), 0.49 ppm for the C-4 methyl group in 5-ethynyl-1,4-dimethylnaphthalene (2), and 0.55 ppm for the benzylic hydrogens of the C-4 ethyl group in 5-ethynyl-1,4-diethylnaphthalene (3), we have confirmed that acetylenes exert a deshielding effect alongside the carbon–carbon triple bond. Through these measurements, we have essentially mapped the magnitude of this effect as a function of distance from the center of the triple bond at three points along a line approximately perpendicular to the triple-bond axis and have found that the deshielding falls off sharply with this distance r, perhaps approximately as $1/r^3$.

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Registry No. 1, 69320-05-4; 2, 64524-88-5; 3, 88916-60-3; 4-phenanthreneethanol, 88916-61-4; 4-vinylphenanthrene, 41498-39-9; 4-(1,2-dibromoethyl)phenanthrene, 88916-62-5; 4-(bromoethenyl)phenanthrene, 88916-59-0; 5,8-dimethyl-1-naphthaleneacetic acid, 25178-70-5; 5,8-dimethyl-1-naphthaleneethanol, 88916-63-6; 1,4-dimethyl-5-vinylnaphthalene, 88916-64-7; 5,8-diethyl-1-naphthaleneacetic acid, 88916-65-8; 5,8-diethyl-1-naphthaleneethanol, 88916-66-9; 1,4-diethyl-5-vinylnaphthalene, 88916-67-0.

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