

Separation of Anisotropic and Steric Substituent Effects—Nuclear Chemical Shielding Analysis of H-4 and C-4 in Phenanthrene and 11-Ethynylphenanthrene

Erich Kleinpeter* and Sabrina Klod

Contribution from the University of Potsdam, Department of Chemistry, P.O. Box 60 15 53, D-14415 Potsdam, Germany

Received September 8, 2003; E-mail: kp@chem.uni-potsdam.de

Abstract: The anisotropic effect of a proximally introduced ethynyl group on the chemical shifts of H-4 and C-4 of the phenanthrene skeleton was calculated using GIAO-HF/NICS methodology. The anisotropic effect, long considered to be the source of the considerable downfield shift of H-4 in 11-ethynylphenanthrene in comparison to the chemical shift value of the corresponding proton in phenanthrene, was determined to be only negligible in magnitude on the basis of these calculations. Partitioning of the natural chemical shieldings of H-4 and C-4 by the NCS–NBO method into various contributions from the C–C and C–H bonds present in each molecule revealed that steric compression was able to account for the large downfield shifts of both H-4 and C-4 in 11-ethynylphenanthrene relative to phenanthrene. Thus, the substituent effect is almost totally permeated by this latter interaction and not by the aforementioned process, which was previously presumed to be the sole underlying cause.

Introduction

Calculations at the ab initio level of the ring current effects of arenes and the anisotropic effects of multiple bonds¹ together with application of the nucleus independent chemical shielding (NICS) concept² have recently been employed^{1,3–9} to successfully solve a number of stereochemical problems. For such analyses, it was found to be convenient to elicit a tangible appreciation of the ring current/anisotropic effects by displaying the results pictorially as isochemical-shielding surfaces (ICSS),¹ usually to demonstrate the presence and consequence of such an effect, although the method is truly quantitative. But the application has also been used to argue against the influence of an anisotropic effect. For example, a detailed investigation of the effects of C–C and C–H bonds on the shieldings of the axial and equatorial hydrogens in cyclohexane by natural chemical shielding—natural bond orbital (NCS–NBO) analysis¹⁰ has clearly demonstrated the various magnetic contributions of the C–C and C–H bonds to the chemical shieldings of these two chemically distinct protons present in the chair conformation

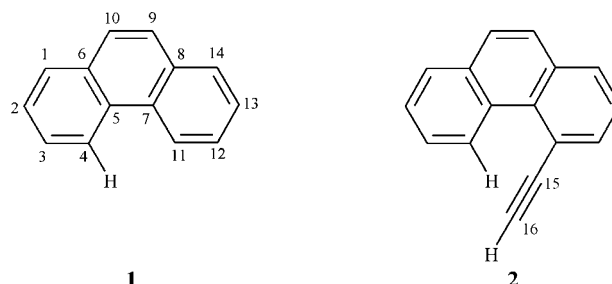


Figure 1. Structures of phenanthrene (1) and 11-ethynylphenanthrene (2).

of cyclohexane.¹¹ It was conclusively determined in that study that it was not the anisotropic effect of the C–C single bonds which was responsible for the chemical shift difference between the axial and equatorial protons, and indeed the ab initio calculations actually reversed the classical notion regarding the anisotropic effect of the C–C single bond. Rather, it was the magnetic contributions from the C₂–C₃ and C₅–C₆ bonds to the NCS of the axial and equatorial protons at C-1 which essentially determined the chemical shift difference between these two protons.¹¹

In the present study, the substituent effect of a C≡C triple bond on the chemical shift of both proton and carbon was examined by employing the same precise and quantitative methods of investigation. In comparison to phenanthrene (1, see Figure 1), the introduction of an ethynyl group at C-4 (11-ethynylphenanthrene, 2) shifts the remaining proton corresponding to H-4 to lower field by 1.57 ppm. This deshielding has repeatedly been cited¹² as a prime example of the anisotropic

- (1) Klod, S.; Kleinpeter, E. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1893.
- (2) Schleyer, P. v. R.; Maerker, C.; Dansfield, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.
- (3) Kleinpeter, E.; Holzberger, A. *Tetrahedron* **2001**, *57*, 6941.
- (4) Germer, A.; Klod, S.; Peter, M. G.; Kleinpeter, E. *J. Mol. Model.* **2002**, *8*, 231.
- (5) Toth, G.; Kovacs, J.; Levai, A.; Koch, A.; Kleinpeter, E. *Magn. Reson. Chem.* **2001**, *39*, 241.
- (6) Kovacs, J.; Toth, G.; Simon, A.; Levai, A.; Koch, A.; Kleinpeter, E. *Magn. Reson. Chem.* **2003**, *41*, 193.
- (7) Seidl, P. R.; Carneiro, J. W. M.; Tostes, J. G. R.; Koch, A.; Kleinpeter, E. *Chem. Eur. J.* **2003**, submitted.
- (8) Hausmann, J.; Käss, St.; Kersting, B.; Klod, S.; Kleinpeter, E. *J. Chem. Soc., Chem. Commun.* **2003**, submitted.
- (9) Miklos, F.; Kanizsai, I.; Thomas, St.; Kleinpeter, E.; Sillanpää, R.; Stájer, G. *Heterocycles* **2004**, *63*, 63.
- (10) Bohmann, J. A.; Weinhold, F.; Farrar, T. C. *J. Chem. Phys.* **1997**, *107*, 1173.

- (11) Klod, S.; Koch, A.; Kleinpeter, E. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1506.

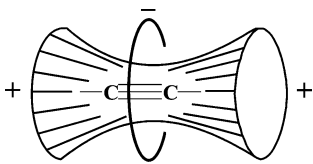


Figure 2. Depiction of the shielding and deshielding zones normally considered to be in effect due to the anisotropy of the triple bond.

effect of the triple bond and can be considered to be almost the quintessential textbook case of this phenomenon. Figure 2 portrays the generally accepted construct of the shielding and deshielding zones arising from the anisotropy of the triple bond. This supposition, accepted almost without dispute for this particular example, has been tested by Martin et al.²⁷ by theoretical means and found to be correct only for large distances between the triple bond and the corresponding protons.

Computational Method

Ab initio quantum-mechanical calculations were performed on SGI Octane and SGI Origin 2000 work stations using the Gaussian 98 program.¹³ Geometry optimization was performed at the HF/6-31G* level of theory without constraints.¹⁴ Shieldings were calculated using the gauge-independent atomic orbital (GIAO) method^{15,16} as incorporated in Gaussian 98¹³ at the same level of theory. The quality of the basis set (6-31G**, 6-31+G**, 6-311G**) was found to be of no influence on both shape and size of the anisotropic effect.¹ Since the GIAO approach is gauge-invariant, it can be used² for NICS calculations. This was done by placing the triple bond of **2** at the center of a grid of lattice points ranging from -10 to $+10$ Å (step width 0.5 Å) in all three dimensions, resulting in a cube consisting of 68 921 lattice points. The symmetry of the compound was taken into account for this process to simplify matters. The coordinates and shielding values of the lattice points around the triple bond were transformed into SYBYL¹⁷ contour files and the anisotropic effect visualized as ICSS, thereby providing a three-dimensional map of the spatial extension, sign, and scope of the anisotropic effect of the C≡C triple bond at each point in space.¹

The NBO 5.0 program¹⁰ was utilized by linking it directly to the Gaussian 98 program.¹³ The NCS–NBO analyses partitioned quantitatively the shielding of a particular nucleus into magnetic contributions from all bonds and lone pairs present in the

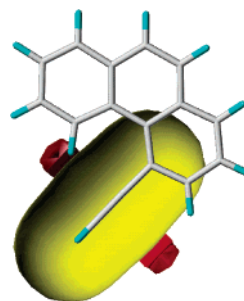


Figure 3. Shielding (yellow) and deshielding (red) ICSS of **2** as calculated by NICS analysis. In this depiction, the red surface pertains to 0.1 ppm of deshielding. The calculated depiction does resemble the classical construct taking into account that ICSS are displayed rather than zone boundaries. Although it is clearly evident that H-4 experiences some degree of deshielding, it lies on the waning side of the 0.1 ppm surface and the magnitude of deshielding emanating solely from the anisotropic effect of the triple bond is minimal (precisely, $\Delta\sigma = -0.06$ ppm).

structures, the shielding and deshielding contributions being divided into Lewis and non-Lewis components.

Results and Discussion

First, the anisotropic effect of the C₁₅≡C₁₆ triple bond in **2** was calculated and the result portrayed as ICSS (see Figure 3). The proton H-4 which is positioned in the deshielding zone of the C₁₅≡C₁₆ triple bond is certainly deshielded by this anisotropic effect, but the predicted shift to lower field is clearly much smaller (less than 0.1 ppm) than what is actually observed.¹² Thus, a re-evaluation of the source of the downfield shift of H-4 in **2** is warranted as the experimentally observed chemical shift difference of H-4, 1.57 ppm, between **1** and **2** suggests that there is at least an additional deshielding substituent effect of 1.51 ppm that needs to be accounted for that does not originate from the anisotropic effect of the C₁₅≡C₁₆ triple bond, as has long been suggested.

Following GIAO calculation of the chemical shifts of H-4 and C-4 for both **1** and **2**, the theoretical NMR shieldings of H-4 and C-4 in both compounds were partitioned into magnetic contributions from the various C–C and C–H bonds present in the structures by employing NCS analysis¹⁰ based on the NBO method.¹⁰ Both localized (Lewis) and nonlocalized (non-Lewis) contributions to the shielding of H-4 and C-4 in these two compounds were calculated and are presented in Table 1. However, for the purposes of this discussion, only the net magnetic partitions of each particular bond to the NCS of H-4 and C-4 need actually be considered, i.e., not only are the Lewis and non-Lewis components summed, but also the total contributions of multiple bonds.

Excellent reproduction of the experimental chemical shift difference between H-4 in **1** and **2** was obtained by these GIAO calculations: $\Delta\delta_{\text{exp}} = +1.57$ ppm vs $\Delta\sigma_{\text{calc}} = -1.66$ ppm (deshielding: δ -scale, positive sign; σ -scale, negative sign). Although an experimental value for the chemical shift difference between C-4 for **1** and **2** is currently unavailable, numerous studies using the GIAO method for the calculation of ¹³C chemical shifts in aromatic and heteroaromatic compounds have provided¹⁸ very precise results such that the shifts of C-4 in **1** and **2** as obtained by these GIAO calculations can be used with confidence. Thus, C-4 was also predicted to be strongly shifted to lower field: $\Delta\delta_{\text{calc}} = +4.18$ ppm. This deshielding of C-4 is

(12) For example: (a) Kemp, W. In *NMR in Chemistry: A Multinuclear Introduction*; Macmillan: London, 1986. (b) Friebolin, H. In *Basic One- and Two-Dimensional NMR Spectroscopy*; Wiley-VCH: Weinheim, 1998; or (c) Günther, H. In *NMR-Spektroskopie*; Georg Thieme Verlag: Stuttgart, 1992.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(14) Hehre, W. J.; Random, L.; Schleyer, P. v. R.; Pople, J. A. In *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(15) Ditchfield, R. J. *Mol. Phys.* **1974**, *27*, 789.

(16) Cheeseman, J. P.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497.

(17) SYBYL 6.7; Tripos, Inc.: St. Louis, 2001.

(18) Kleinpeter, E.; Koch, A. *J. Phys. Org. Chem.* **2001**, *14*, 566.

Table 1. Partitions of the Natural Chemical Shieldings of H-4 and C-4 in 1 and 2

source	L (Lewis)/ NL (non-Lewis)	1		2		$\Delta\sigma$ (H-4)	$\Delta\sigma$ (C-4)
		H-4	C-4	H-4	C-4		
C ₁ –C ₂	L	0.16	1.03	0.19	1.14	0.03	0.11
	NL	-0.10	-1.00	-0.10	-0.99	0.00	0.01
C ₁ –C ₂	L	1.02	1.89	1.16	2.20	0.14	0.31
	NL	0.10	2.70	-0.03	2.53	-0.13	-0.17
C ₁ –C ₆	L	-0.23	-0.29	-0.22	-0.28	0.01	0.01
	NL	0.14	0.05	0.15	0.08	0.01	0.03
C ₁ –H ₁	L	-0.14	-0.41	-0.16	-0.45	-0.02	-0.04
	NL	0.13	0.24	0.14	0.27	0.01	0.03
C ₂ –C ₃	L	0.26	-4.69	0.17	-4.12	-0.09	0.57
	NL	-0.49	4.06	-0.40	3.58	0.09	-0.48
C ₂ –H ₂	L	-0.07	-1.27	-0.10	-1.18	-0.03	0.09
	NL	0.06	1.02	0.09	0.95	0.03	-0.07
C ₃ –C ₄	L	-3.47	-50.25	-3.33	-51.55	0.14	-1.30
	NL	1.06	-0.43	0.99	-0.59	-0.07	-0.16
C ₃ –C ₄	L	0.12	-1.98	0.22	-2.14	0.10	-0.16
	NL	0.47	2.06	0.45	1.78	-0.02	-0.28
C ₃ –H ₃	L	-0.41	-4.88	-0.50	-5.44	-0.09	-0.56
	NL	0.22	2.70	0.30	3.35	0.08	0.65
C ₄ –C ₅	L	-0.06	-34.26	-0.22	-35.27	-0.16	-1.01
	NL	-1.05	-6.69	-0.96	-6.37	0.09	0.32
C ₄ –H ₄	L	28.38	-32.25	27.74	-32.74	-0.64	-0.49
	NL	-0.98	5.12	-1.15	4.51	-0.17	-0.61
C ₅ –C ₆	L	-0.51	-3.37	-0.55	-3.41	-0.04	-0.04
	NL	0.12	1.31	0.14	1.25	0.02	-0.06
C ₅ –C ₆	L	-0.26	1.99	-0.38	2.01	-0.12	0.02
	NL	0.52	-2.81	0.59	-2.96	0.07	-0.15
C ₅ –C ₇	L	-0.67	-3.04	-0.58	-3.28	0.09	-0.24
	NL	0.11	1.21	0.10	1.57	-0.01	0.36
C ₆ –C ₁₀	L	-0.06	0.32	-0.08	0.37	-0.02	0.05
	NL	0.06	-0.60	0.08	-0.70	0.02	-0.10
C ₇ –C ₈	L	-0.19	0.00	-0.25	-0.22	-0.06	-0.22
	NL	0.08	-0.05	0.12	0.10	0.04	0.15
C ₇ –C ₈	L	-0.23	-0.20	-0.35	-0.34	-0.12	-0.14
	NL	0.14	0.15	0.12	0.16	-0.02	0.01
C ₇ –C ₁₁	L	-0.09	-0.17	-0.39	-0.32	-0.30	-0.15
	NL	-0.18	-0.21	0.08	-0.04	0.26	0.17
C ₈ –C ₉	L	-0.06	-0.12	-0.08	-0.14	-0.02	-0.02
	NL	0.07	0.11	0.08	0.11	0.01	0.00
C ₈ –C ₁₄	L	-0.13	-0.12	-0.12	-0.14	0.01	-0.02
	NL	0.09	0.10	0.09	0.11	0.00	0.01
C ₉ –C ₁₀	L	0.10	0.08	0.13	0.12	0.03	0.04
	NL	-0.06	-0.07	-0.08	-0.08	-0.02	-0.01
C ₉ –C ₁₀	L	0.27	0.41	0.27	0.41	0.00	0.00
	NL	-0.07	-0.12	-0.07	-0.11	0.00	0.01
C ₉ –H ₉	L	-0.10	-0.14	-0.11	-0.16	-0.01	-0.02
	NL	0.09	0.12	0.10	0.13	0.01	0.01
C ₁₀ –H ₁₀	L	-0.10	-0.13	-0.12	-0.15	-0.02	-0.02
	NL	0.10	0.14	0.11	0.16	0.01	0.02
C ₁₁ –C ₁₂	L	-0.29	-0.27	-0.28	-0.24	0.01	0.03
	NL	0.14	0.17	0.12	0.14	-0.02	-0.03
C ₁₁ –C ₁₂	L	-0.37	-0.23	-0.54	-0.34	-0.17	-0.11
	NL	0.12	0.07	0.36	0.27	0.24	0.20
C ₁₁ –C ₁₅	L	-0.04	-0.83	-0.13	0.00	-0.09	0.83
	NL	-0.21	0.76	0.52	0.40	0.73	-0.36
C ₁₂ –C ₁₃	L	0.03	0.01	0.04	0.08	0.01	0.07
	NL	0.01	0.04	0.02	-0.01	0.01	-0.05
C ₁₂ –H ₁₂	L	-0.10	-0.08	-0.11	-0.13	-0.01	-0.05
	NL	0.08	0.09	0.09	0.11	0.01	0.02
C ₁₃ –C ₁₄	L	0.10	0.09	0.10	0.09	0.00	0.00
	NL	-0.05	-0.04	-0.04	-0.03	0.01	0.01
C ₁₃ –C ₁₄	L	0.47	0.45	0.44	0.43	-0.03	-0.02
	NL	-0.07	-0.12	-0.01	-0.07	0.06	0.05
C ₁₃ –H ₁₃	L	-0.08	-0.08	-0.08	-0.09	0.00	-0.01
	NL	0.07	0.08	0.08	0.08	0.01	0.00
C ₁₄ –H ₁₄	L	-0.09	-0.10	-0.09	-0.09	0.00	0.01
	NL	0.09	0.10	0.10	0.09	0.01	-0.01
C ₁₅ –C ₁₆	L			-0.51	-0.43	-0.51	-0.43
	NL			0.24	0.18	0.24	0.18
C ₁₅ –C ₁₆	L			-1.93	-1.97	-1.93	-1.97
	NL			0.06	0.80	0.06	0.80
C ₁₅ –C ₁₆	L			0.70	0.30	0.70	0.30
	NL			0.17	0.05	0.17	0.05

Table 1. (Continued)

source	L (Lewis)/ NL (non-Lewis)	1		2		$\Delta\sigma$ (H-4)	$\Delta\sigma$ (C-4)
		H-4	C-4	H-4	C-4		
C ₁₆ -H ₁₆	L			-0.37	-0.17	-0.37	-0.17
	NL			0.69	0.33	0.69	0.33
C-1 core	L	-0.11	-0.22	-0.13	-0.25	-0.02	-0.03
	NL	0.03	0.06	0.04	0.07	0.01	0.01
C-2 core	L	-0.14	-0.35	-0.15	-0.37	-0.01	-0.02
	NL	0.03	0.12	0.04	0.12	0.01	0.00
C-3 core	L	-0.15	-0.88	-0.17	-0.87	-0.02	0.01
	NL	0.01	0.12	0.01	0.10	0.00	-0.02
C-4 core	L	0.87	203.84	0.65	203.86	-0.22	0.02
	NL	-0.26	0.03	-0.19	0.03	0.07	0.00
C-5 core	L	0.09	0.16	0.04	0.07	-0.05	-0.09
	NL	-0.04	-0.13	-0.03	-0.11	0.01	0.02
C-6 core	L	-0.06	-0.10	-0.07	-0.12	-0.01	-0.02
	NL	0.01	0.02	0.02	0.03	0.01	0.01
C-7 core	L	0.01	-0.02	-0.01	-0.03	-0.02	-0.01
	NL	-0.01	0.00	0.00	0.00	0.01	0.00
C-8 core	L	-0.05	-0.06	-0.05	-0.07	0.00	-0.01
	NL	0.01	0.02	0.01	0.02	0.00	0.00
C-9 core	L	-0.07	-0.10	-0.08	-0.11	-0.01	-0.01
	NL	0.02	0.03	0.02	0.03	0.00	0.00
C-10 core	L	-0.07	-0.09	-0.08	-0.10	-0.01	-0.01
	NL	0.02	0.03	0.02	0.03	0.00	0.00
C-11 core	L	0.03	-0.02	-0.07	-0.09	-0.10	-0.07
	NL	-0.01	0.00	0.02	0.02	0.03	0.02
C-12 core	L	-0.07	-0.08	-0.07	-0.08	0.00	0.00
	NL	0.01	0.02	0.01	0.02	0.00	0.00
C-13 core	L	-0.08	-0.08	-0.07	-0.08	0.01	0.00
	NL	0.02	0.02	0.02	0.02	0.00	0.00
C-14 core	L	-0.07	-0.07	-0.07	-0.07	0.00	0.00
	NL	0.02	0.02	0.02	0.02	0.00	0.00
C-15 core	L			-0.18	-0.06	-0.18	-0.06
	NL			0.07	0.04	0.07	0.04
C-16 core	L			-0.29	-0.15	-0.29	-0.15
	NL			0.08	0.04	0.08	0.04
Σ Lewis		23.30	69.03	18.80	63.84	-4.50	-5.19
Σ non-Lewis		0.69	10.60	3.52	11.62	2.83	1.02
Σ total		23.99	79.64	22.33	75.46	-1.66	-4.18
σ_{H} TMS		32.90		32.90			
σ_{C} TMS			201.69		201.69		
δ_{calc}		8.91	122.05	10.57	126.23		
		(exp 8.70) ²⁸	(exp 122.6) ²⁸	(exp 10.27) ²⁹	(no exp value)		

actually consistent with the δ effect in ¹³C NMR, which results in resonances being shifted to lower field due to this effect, even if the steric strain is greater than what is experienced due to γ substituents; in the latter case, the resultant effect is to shift the resonances to higher field.¹⁹ It is notable that while the mechanism responsible for the shielding of the γ effect is well understood,^{20–22} the mechanism responsible for the deshielding arising from the δ effect is still under discussion.²³

From Table 1, it can be seen that although to some degree all of the bonds in **1** and **2** contribute to the NCS of H-4 and C-4 in their respective structures, only a few bonds are of significance, especially in consideration of those partitions that result in a chemical shift difference between the two compounds. Careful examination of these crucial bonds that contribute to the chemical shift differences of H-4 and C-4 revealed some interesting features, and these notable partitions are collected in Tables 2 and 3 for H-4 and C-4, respectively.

For the contributions to the NCS of H-4, only the bonds directly associated with the C₄-H₄ system (C₃-C₄, C₄-C₅, and C₄-H₄) and the proximal C₁₅≡C₁₆ and C₁₆-H₁₆ bonds are significant, altogether deshielding H-4 by $\Delta\sigma = -1.67$ ppm (cf. the overall total of $\Delta\sigma = -1.66$ ppm), and thus account well for the experimental chemical shift difference. Martin et al.²⁴ similarly used one methane proton as a probe above π bonds and calculated the shielding contributions of the individual localized orbitals employing the IGLO method;²⁵ also in his case, the net absolute shielding of the methane proton corresponds to the individual contributions from methane but also from the π systems.

Hence, there is an inference of strong steric interaction between H-4 and the ethynyl group in **2**, which is conveyed by the chemical shifts of H-4 (theoretically and experimentally on the basis of comparison of **1** and **2**) and supported by the structural distortions present in the geometry-optimized structure of **2**. For example, the C₄-H₄ bond is significantly shortened (see Figure 4 and Table 4) while the adjacent C-C bonds (C₃-C₄, C₄-C₅, and C₅-C₇) are all lengthened in agreement with

(19) Pihlaja, K.; Kleinpeter, E. In *Carbon-13 NMR Chemical Shifts in Structural and Stereochemical Analysis, Methods in Stereochemical Analysis*; VCH: New York, 1994.

(20) Seidl, P. R.; Leal, K. Z.; Costa, V. E. U.; Stapelbroek-Mollmann, M. E. *Magn. Reson. Chem.* **1998**, *36*, 261.

(21) Seidman, K.; Maciel, G. E. *J. Am. Chem. Soc.* **1977**, *99*, 659.

(22) Mann, G.; Kleinpeter, E.; Werner, H. *Magn. Reson. Chem.* **1978**, *11*, 561.

(23) Kleinpeter, E.; Seidl, P. R. *J. Phys. Org. Chem.*, in press.

(24) Martin, N. H.; Brown, J. D.; Nance, K. H.; Scharfer, H. F., III; v. R. Schleyer, P.; Wang, Z.-X.; Woodcock, H. L. *Org. Lett.* **2001**, *3*, 3823.

(25) Fleischer, U.; Kutzelnigg, W.; Lazzaretti, P.; Muehlenkamp, V. *J. Am. Chem. Soc.* **1994**, *116*, 5298.

Table 2. Partitions of Selected Bonds to the Natural Chemical Shielding of H-4

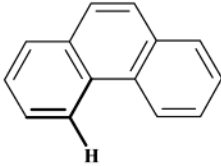
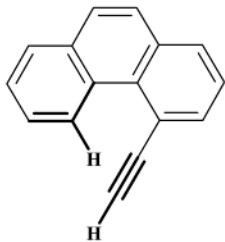
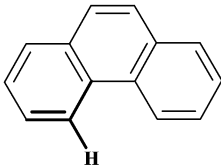
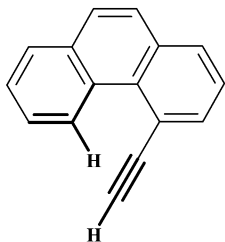
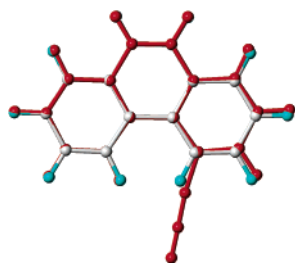
Bond			$\Delta\sigma$ (partition difference between 1 and 2)
C ₃ -C ₄	-1.82	-1.67	0.15
C ₄ -C ₅	-1.11	-1.18	-0.07
C ₄ -H ₄	27.40	26.59	-0.81
C ₁₅ -C ₁₆	-	-1.27	-1.27
C ₁₆ -H ₁₆	-	0.33	0.33
			$\Delta\sigma = -1.67$ ppm (i.e. H-4 in 2 is deshielded relative to H-4 in 1 , $\Delta\delta_{\text{exp}} = +1.57$ ppm)

Table 3. Partitions of Selected Bonds to the Natural Chemical Shieldings of C-4

Bond			$\Delta\sigma$ (partition difference between 1 and 2)
C ₂ -C ₃	-0.63	-0.54	0.09
C ₃ -C ₄	-50.60	-52.25	-1.69
C ₄ -C ₅	-40.95	-41.64	-0.69
C ₄ -H ₄	-27.13	-28.23	-1.10
C ₅ -C ₆	-2.88	-3.11	-0.23
C ₅ -C ₇	-1.83	-1.71	0.12
C ₁₅ -C ₁₆	-	-1.07	-1.07
			$\Delta\sigma = -4.57$ ppm (i.e. C-4 in 2 is deshielded relative to C-4 in 1)

**Figure 4.** Overlaid geometry-optimized structures of **1** (light-blue framework) and **2** (red framework).

considerable steric compression being experienced within the C₃-C₄H₄-C₅ moiety of **2**.

The outer C₂-C₃ bond, though, is slightly shortened in **2** in comparison with **1**. Furthermore, the bond angles C₄-C₅-C₇, C₅-C₇-C₁₁, and C₇-C₁₁-H₁₁/C₁₅ are all increased (by 1.2, 3.1, and 6.2°, respectively), again in line with the greater strain experienced by **2**. However, the bond angle C₃-C₄-H₄ (and in a complementary manner, the bond angle C₅-C₄-H₄) varies by only a negligible amount. Thus, overall the structure of **2** is widened and opened up in comparison to the structure of **1**.

This structural evidence for the presence of considerable strain in **2** extends to distortions that are apparent in the σ (C₄-H₄)

Table 4. Bond Lengths and Angles of Selected Bonds

	1	2
bond		
C ₄ -H ₄	1.072	1.065
C ₂ -C ₃	1.402	1.399
C ₃ -C ₄	1.368	1.369
C ₄ -C ₅	1.411	1.412
C ₅ -C ₇	1.461	1.474
angle		
C ₃ -C ₄ -H ₄	118.45	118.04
C ₅ -C ₄ -H ₄	120.17	120.07
C ₄ -C ₅ -C ₇	122.99	124.21
C ₅ -C ₇ -C ₁₁	123	126.12
C ₇ -C ₁₁ -H ₁₁ /C ₁₅	120.16	126.37
C ₁₁ -C ₁₅ -C ₁₆		173.55

and π (C₁₅≡C₁₆) orbitals of **2** and which are depicted in Figures 5 and 6, respectively. These structural perturbations clearly indicate the presence of great steric strain, which undoubtedly must have an influence on the chemical shifts of H-4 and C-4 and must be accounted for. Distortions of the π cloud were reported previously by Martin et al.^{26,27} along with short

(26) *Modeling NMR Chemical Shifts: Gaining Insights into Structure and Environment*; Facelli, J. C., de Dios, A. C., Eds. ACS Symposium Series 732; American Chemical Society: Washington, DC, 1999; pp 207–219.

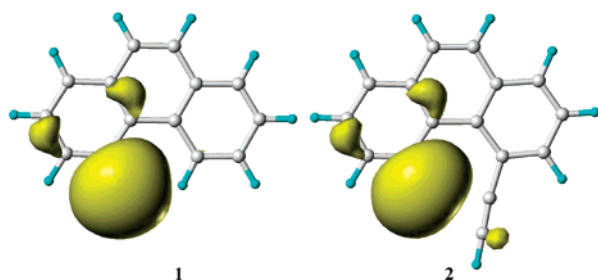


Figure 5. $\sigma(\text{C}_4\text{--H}_4)$ orbitals of **1** and **2**. The distortion in the $\sigma(\text{C}_4\text{--H}_4)$ orbital in **2** due to the steric interaction with the ethynyl group is clearly evident.

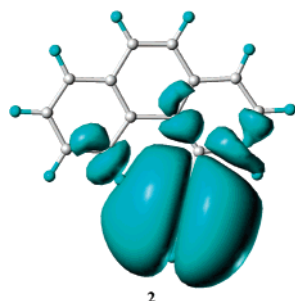


Figure 6. $\pi(\text{C}_{15}\equiv\text{C}_{16})$ orbital of **2**. The distortion in the $\pi(\text{C}_{15}\equiv\text{C}_{16})$ orbital due to the steric interaction with H-4 is also clearly evident.

distances of one methane proton above π systems in supermolecules, supporting the suggestion of van der Waals orbital compression effects to be the cause of deshielding.

A similar conclusion results from analysis of the chemical shift of C-4. In this case again it is the bonds directly associated with the $\text{C}_4\text{--H}_4$ system ($\text{C}_3\text{--C}_4$, $\text{C}_4\text{--C}_5$, and $\text{C}_4\text{--H}_4$) and the spatially near $\text{C}_{15}\equiv\text{C}_{16}$ triple bond that are of real significance in terms of their influence on the chemical shift of C-4. The next nearest C–C bonds, $\text{C}_2\text{--C}_3$, $\text{C}_5\text{--C}_6$, and $\text{C}_5\text{--C}_7$, contribute slightly to the NCS of C-4, but their influence is only minor and they essentially cancel each other out. Altogether, the aforementioned bonds deshield C-4 by $\Delta\sigma = -4.57$ ppm, accounting for the vast majority of the overall calculated chemical shift difference of $\Delta\delta = +4.18$ ppm. These partitions to the NCS of C-4 also indicate explicitly that strong steric interaction must be present in **2**. It must be emphasized that the carbon chemical shift analysis is more difficult, not because

experimental values are not available, but because the substituent is introduced at the δ position. It is consistent with the δ effect that C-4 is shifted to lower field upon introduction of the $\text{C}\equiv\text{C}$ triple bond. However, in contrast to the introduction of substituents at the γ position, the partitions of the NCS do not shield the carbon nucleus but rather deshield it, even if the structural modification results in even stronger steric compression than what may be experienced by a γ substitution.²³ Thus, for NCS analysis of the various partitions to the shieldings of a particular carbon atom, careful assessment is required in order to draw conclusions regarding not only the magnitude but indeed also the very sign of the chemical shift in the case of substituents effecting considerable steric strain.

Conclusions

On one hand, evidence was not forthcoming for an anisotropic effect giving rise to the observed large downfield shift of H-4 using NICS analysis. On the other hand, there is clear structural evidence in the form of distorted geometries and misshapen orbitals for steric strain that manifests itself as downfield shifts for both C-4 and H-4 in **2** relative to the corresponding nuclei in **1**. Partitioning of the magnetic contributions from the bonds present in the structures using NCS–NBO analysis accounts well for this in a quantitative and thoroughly consistent manner for both H-4 and C-4, thus lending credence to the supposition that the downfield shifts emanate from steric strain and not from an anisotropic effect. Thus, it is not the anisotropic effect of the triple bond that deshields H-4 by $\Delta\delta = +1.57$ ppm but rather the steric nonbonding interaction (steric substituent effect) of the ethynyl substituent and the $\text{C}_3\text{--C}_4\text{H}_4\text{--C}_5$ fragment of **2** that is responsible for the shift to lower field of H-4 in **2** in comparison to H-4 in **1**. This study thus illustrates how a long-held belief, though intuitively sound, can be erroneous. However, although it is simply the case that the anisotropic effect is ineffective, this can only be assessed by adequate quantification using an appropriate level of theory.

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Supporting Information Available: The x , y , z coordinates, bond lengths, and bond angles of the geometry-optimized structures for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA038395K

(27) Martin, N. H.; Nance, K. H. *J. Mol. Graph. Model.* **2002**, *21*, 51.

(28) DBS; Tsukuba, Ibaraki; National Institute of Advanced Industrial Science and Technology, Japan. <http://www.aist.go.jp/RIODB/SDBS/>.

(29) Mallory, F. B.; Baker, M. B. *J. Org. Chem.* **1984**, *49*, 1323.