Visualization and Quantification of the Anisotropic Effect of C═C Double Bonds on ^{1}H NMR Spectra of Highly Congested Hydrocarbons-Indirect Estimates of Steric Strain

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The anisotropic effect of the olefinic C═C double bond has been calculated by employing the NICS (*nucleus independent chemical shift*) concept and visualized as an anisotropic cone by a through space NMR shielding grid. Sign and size of this spatial effect on ^{1}H chemical shifts of protons in norbornene, *exo*- and *endo*-2-methylnorbornenes, and in three highly congested tetracyclic norbornene analogs have been compared with the experimental ^{1}H NMR spectra as far as published. ^{1}H NMR spectra have also been calculated at the HF/6-31G* level of theory to get a full, comparable set of proton chemical shifts. Differences between $\delta(^1\text{H})$/ppm and the calculated anisotropic effect of the C═C double bond are discussed in terms of the *steric compression* that occurs in the compounds studied.

1. Introduction

The shielding constant at or above the center of aromatic ring systems (a *nucleus independent chemical shift*, NICS)[1] can be used to characterize the aromaticity of organic compounds. NICS values on a grid around molecules can be calculated, as well, to locate the diatropic and paratropic regions of the molecules involved.[2] These *through space NMR shieldings* (*TSNMRS*) were visualized[3] as *iso-chemical-shielding surfaces* (*ICSS*s) and employed not only to study the aromaticity of planar molecules[4a] and cross-conjugated fullvalenes[4b] as well as the aromaticity/antiaromaticity of spherical systems such as fullerenes[5a] or adamantyl/cubanyl derivatives[5b] but also to specify and quantitatively determine the stereochemistry of potential proximal nuclei; a number of their applications having already been published.[3,6–20] In addition to stereochemical assignments covering conformational, configurational and tautomeric aspects, some prevalent assertions in prescribed NMR textbooks that are in fact incorrect have also been addressed; *e.g.*, the ^{1}H chemical shift difference between *axial* and *equatorial* protons in cyclohexane *is not due to the anisotropic effect of the C−C single bond*[9] and the deshielding by 1.57 ppm of H-4 in 11-ethynylphenanthrene relative to the corresponding δ value in phenanthrene *does not arise from the anisotropic effect of the C≡C triple bond*.[14]

Similar approaches have been published by Alkorta and Elguero[21] (to estimate the TSNMRSs of the C−C single bond) and Martin *et al.*[22] to use a certain proton's distance dependence as a sensor for anisotropic effects of organic functional groups, including benzene, in *ab initio* calculations on supramolecules. In both cases shieldings of similar size and direction, comparable to the results of our model,[3] were obtained.

This method[3] is used in the present paper to calculate *the anisotropic effect of the C═C double bond* and to quantitatively determine the influence of this effect on the ^{1}H chemical shifts of proton NMR spectra of norbornene, two substituted norbornenes and three tetracyclic norbornene analogs. It can be applied to distinguish anisotropic effects from the steric effects that may also be present and clarify any uncertainties as to the relative contribution of these important effects in the interpretation of NMR spectra of unsaturated compounds. Besides steric effects, no other influences on the studied proton chemical shifts are expected. In the absence of polar groups there should be no electric field effects. There are no further intramolecular effects either, and the solvent is generally the same.

2. Results and Discussion

The proton NMR spectra of norbornane **1**[23,24] and norbornene **2**,[24] of *exo/endo*-2-methylnorbornanes and -norbornenes **3−6**,[25,26] and of tetracyclic analogs **7−9** and **11−12** (Scheme 1) have been published, at least partially.[27–30] Their respective ^{1}H chemical shifts are given in Tables 1 and 2 along with their values calculated at the HF/6 31G* level of theory (in parentheses). Proton chemical shifts of unsaturated tetracyclic norbornene derivative **10**, reported without NMR data,[31] were also calculated and included in Table 2 for the purpose of quantitatively determining the anisotropic effect of the C═C double bonds involved (*vide infra*).

Both experimental (as far as possible) and calculated ^{1}H chemical shifts of compounds **1−12** were studied and correlated, agreement being excellent ($\delta_{\text{exp}} = 1.25\delta_{\text{calc}} + 0.21$; $R^2 = 0.98$). Thus, a complete set of the proton chemical shifts of **1−12** is available for studies of the effect of additional double bond(s) on ^{1}H NMR spectra of the present bi- and tetracyclic structures that are subject to the anisotropic effect of this functional group and, in case of any ambiguity, to evaluate the influence of other structural distortions that could introduce *steric compression*[32] of C−H fragments, as reflected by variations in bond lengths and angles (steric compression shifts the corresponding proton chemical shift to low field).[29,30,33,34]

The anisotropic effect of the C═C double bond as visualized by iso-*chemical-shielding surfaces (ICSS) of −0.1 ppm (shielding, yellow) and 0.1 ppm (deshielding, red) is given in Figure 1*. The depicted TSNMRS cone proved to be in excellent

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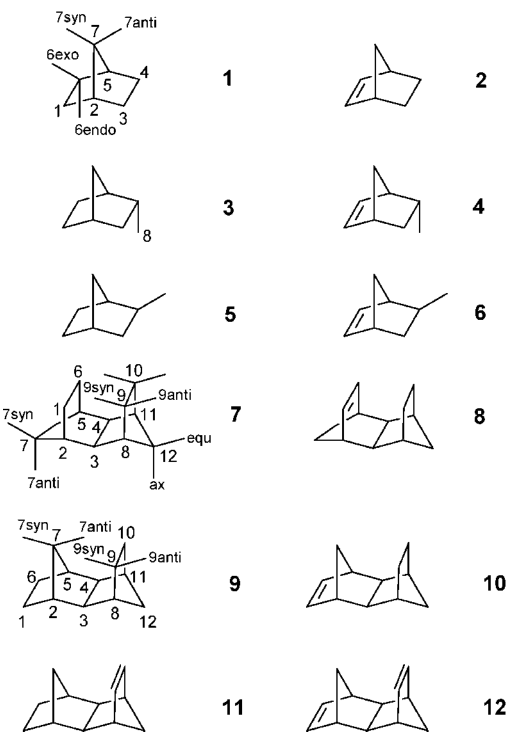
SCHEME 1



agreement with sketches that generally represent this effect in NMR spectroscopy textbooks (for example, ref 35) and result from the application of the classical model of Bovey and Johnson[36] and Haigh and Mallion.[37] In-plane, the effect on the chemical shift of potential proximal nuclei is deshielding (red ICSS = 0.1 ppm at 4 Å), but shielding (yellow ICSS = −0.1 ppm at 4.2 Å) *above and below this plane*. This anisotropy cone is now put into the unsaturated bi- and tetracyclic compounds studied (**2**, **4**, **6**, **8**, **10**−**12**) at the correct positions and the anisotropic effect on the ^{1}H chemical shifts of the protons in the corresponding molecules is determined quantitatively.

Norbornene 2 and 2-*exo*/*endo*-Methylnorbornenes 4 and 6. In Figure 2, the effect of C═C double bond anisotropy in norbornene **2** is visualized by different deshielding (0.15 ppm red, 0.10 ppm red-orange and 0.04 ppm orange) and shielding (−0.20 ppm green and −0.02 ppm yellow) ICSSs; in Figure 3 the anisotropic effect on the various protons of norbornene **2** is quantified. Using the same procedure, the anisotropic effects of the corresponding C═C double bonds on the ^{1}H chemical shifts of **4** and **6** were determined. The data thus obtained allow an estimate of both anisotropic and steric contributions to chemical shifts. They are given, together with both the experimental and theoretically calculated ^{1}H chemical shift differences between these olefins and their saturated analogs (*i.e.*, **2** and **1**, **4** and **3** and **6** and **5**, respectively) in Table 3. Because these differences include the contributions of the anisotropic effect of the C═C double bond together with their respective steric components, the following items are worth note: (i) The magnitudes of the anisotropic effects of the C═C double bond on the various protons in **2**, **4**, and **6** respectively, are relatively constant, as shown below:

H-3/4(*exo*): 0.08 ppm
H-3/4(*endo*): −0.14 to −0.16 ppm
H7(*syn*): 0.08 to 0.09 ppm
H-7(*anti*): 0.16 ppm

(**Note**: bridgehead protons H-2/5 are too close to the functional group, <3Å, and were not considered further for the bicyclic and polycyclic systems studied with respect to the anisotropic effect of the C═C double bond).[3] (ii) Differences in experimental and calculated ^{1}H chemical shifts correlate rather well with the anisotropy, except for H-7(*anti*) (*cf.* Table 3); H-7(*anti*) is found at 0.1−0.27 ppm higher field than would have been predicted solely from the anisotropic effect, indicating that steric strain is reduced in this part of the olefin compared to its saturated analog, as is borne out by the corresponding changes in molecular geometry: The introduction of a double bond into the norbornyl structure shortens the C-1−C-2 and C-5−C-6 bonds. This distortion is compensated by lengthening the C-2−C-3 and C-4−C-5 bonds of **2** relative to **1**. As a consequence, the respective C-7−H-7(*anti*) bond is longer and the H-7(*anti*)−C-7−C-2 bond angle is larger in **2** compared to **1** (*cf.* Scheme 2 and Supporting Information), corroborating this decrease in steric strain on H-7 (*anti*). Similar considerations apply to their respective effects on compression/distention of the corresponding bond lengths and angles.

Additionally, in **6**, (iii) H-7(*syn*) is found at a lower field than predicted from the isolated anisotropic effect, owing to increasing steric hindrance of this proton. Here it is evident that steric compression of H-7(*anti*) by the methyl group is transferred to H-7(*syn*).

Finally, (iv) *endo*-methyl in **4** is positioned in the shielding and *exo*-methyl in **6** in the deshielding region of the anisotropy cone of C═C, in agreement with experiment (*cf.* Figure 4). Support for this interpretation is also provided by the corresponding structural variation on olefin formation, as given in Scheme 3 (*cf.* also Table S1 in the Supporting Information).

Tetracyclic Norbornene Analogs 8 and 10−12. Structures **8** and **10**−**12** contain a second norbornyl moiety as an *endo* (**8**) or *exo* (**10**−**12**) "substituent" on norbonene. As this new part of the molecule introduces strong additional steric congestion into certain regions of the molecular framework, data for saturated structures **7** and **9** are given for the purpose of comparison (*cf.* Table 4).

***Effect of C═C Double Bond Anisotropy in* 8.** The anisotropic effect of the double bond in **8** on the bicyclo[2.2.1]heptane moiety may be calculated using the same approach that was applied to **2**, **4** and **6**. The anisotropy, visualized in Figure 5, proved to be of a magnitude similar to that of norbornene for H-3,4(*endo*) (which in this case correspond to the *exo* protons of norbornene) and stronger for H-7(*syn,anti*). It is worth noting that the second bicyclo[2.2.1]heptane moiety lies completely in the shielding cone:

H-3/4(*endo*): 0.09 ppm
H-7 (*syn*): 0.29 ppm
H-7 (*anti*): 0.16 ppm
H-8,11: −0.04 ppm
H-9 (*syn*): −0.36 ppm
H-9 (*anti*): −0.09 ppm
H-12 (ax,eq): only negligible

In case of tetracyclic derivatives **7** and **8** only tentative assignments of ^{1}H NMR spectra are published (*cf.* Table 2); thus only theoretically calculated values were used to verify the following: (i) The same effect on H-7(*anti)* as in **2**, **4** and **6** was observed (this proton, in terms of steric compression, is sterically released in the olefin compared with protons H-3,4 for which steric compression increases (*vide supra*, *cf.* Table 4)). (ii) The anisotropic effect on H-7(*syn*) is confirmed quantitatively and protons of the second bicyclo[2.2.1]heptane moiety are shifted to higher fields. (iii) There are differences, however, H-8−11, H-9,10(*anti*) and H-12(eq) are slightly more shielded (sterically released) but H-9,10(*syn*) and H-12(ax) are

TABLE 1: ^{1}H Chemical Shifts (δ/ppm) of Norbornane 1, Norbornene 2 and Methyl Substituted Derivatives 3−6[a]

compound	H-1,6	H-2	H-3$_{exo}$	H-3$_{endo}$	H-4$_{exo}$	H-4$_{endo}$	H-5	H-7$_{syn}$	H-7$_{anti}$	subst
1[b]	1.47^{x}/1.16^{n} (1.34^{x}/1.09^{n})	2.19 (1.91)	1.47 (1.34)	1.16 (1.09)	1.47 (1.34)	1.16 (1.09)	2.19 (1.91)	1.18 (1.09)	1.18 (1.09)	
2[b]	5.98 (6.34)	2.84 (2.46)	1.60 (1.46)	0.95 (0.99)	1.60 (1.46)	0.95 (0.99)	2.84 (2.46)	1.31 (1.33)	1.07 (1.01)	
3[c]	1.47^{x}/1.08^{n} (1.34^{x}/1.18^{n}/1.38^{x}/1.03^{n})	2.11 (1.85)	1.74 (1.56)	0.53 (0.61)	1.90 (1.58)		1.98 (1.77)	1.25 (1.15)	1.33 (1.20)	0.93 (1.05)
4[c]	6.19 (6.42/6.30)	2.74 (2.36)	1.87 (1.66)	0.41 (0.57)	2.10 (1.79)		2.66 (2.32)	1.25 (1.38)	1.39 (1.13)	0.78 (0.83)
5[c]	1.44^{x}/1.11^{n} (1.34^{x}/1.18^{n}/1.38^{x}/1.03^{n})	2.16 (1.89)	0.93 (0.91)	1.43 (1.33)		1.49 (1.28)	1.82 (1.65)	1.04 (0.98)	1.33 (1.19)	0.86 (0.96)
6[c]	6.00 (6.39/6.45)	2.78 (2.40)	1.03 (0.99)	1.29 (1.25)		1.45 (1.34)	2.39 (2.13)	1.37 (1.30)	1.29 (1.20)	1.07 (1.06)

[a] Calculated proton chemical shifts in parentheses. x = *exo* and n = *endo*. [b] Reference 24. [c] Reference 25.

TABLE 2: ^{1}H Chemical Shifts (δ/ppm) of Tetracyclic Norbonane and Norbornene Derivatives 7−12[a]

compound	H-1,6	H-2,5	H-3,4$_{endo}$	H-7$_{syn}$	H-7$_{anti}$	H-8−11	H-9 $_{syn}$	H-9$_{anti}$	H-12$_{ax}$	H-12$_{eq}$
7[b]	(1.69^{x}/1.20^{n})	(1.97)	(1.64)	(1.25)	(1.31)	(1.97)	(1.69)	(1.20)	(1.31)	(1.31)
8[c]	(6.26)	(2.29)	(1.96)	(1.57)	(1.26)	(1.81)	(1.47)	(1.05)	(1.37)	(1.21)
9[d]	1.45^{x}/0.95^{n} (1.32^{x}/0.90^{n})	2.05−1.35 (1.84)	1.55 (1.32)	0.95 (0.80)	1.55 (1.32)	2.20 (1.92)	1.45 (1.28)	1.25 (1.16)	1.25 (1.14)	1.15 (1.06)
10[e]	(6.50)	(2.26)	(1.48)	(1.22)	(1.36)	(1.90)	(1.32)	(1.24)	(1.35)	(1.22)
11[f]	1.40−0.94 (1.28^{x}/0.99^{n})	2.07−2.00 (1.79)	1.93 (1.61)	0.52 (0.47)	2.07−2.00 (1.77)	2.82 (2.44)	5.93 (6.25)	5.93 (6.25)	1.40−0.94 (1.03)	1.40−0.94 (1.25)
12[f]	6.20 (6.52)	2.47 (2.21)	2.19 (1.89)	0.95 (0.94)	2.55 (2.09)	2.67 (2.33)	6.02 (6.34)	6.02 (6.34)	1.62 (1.33)	1.50 (1.52)

[a] Calculated proton chemical shifts in parenthesas. x = *exo* and n = *endo*. [b] Only partially assigned.[28] m(10H) 2.33−1.88 1.82−1.22 m(8H). [c] Only partially assigned.[27] 2.55−2.38(4H) 1.98−1.17 (10H) 2.05. [d] References 29 and 30. [e] Not assigned.[31] [f] References 29 and 30.

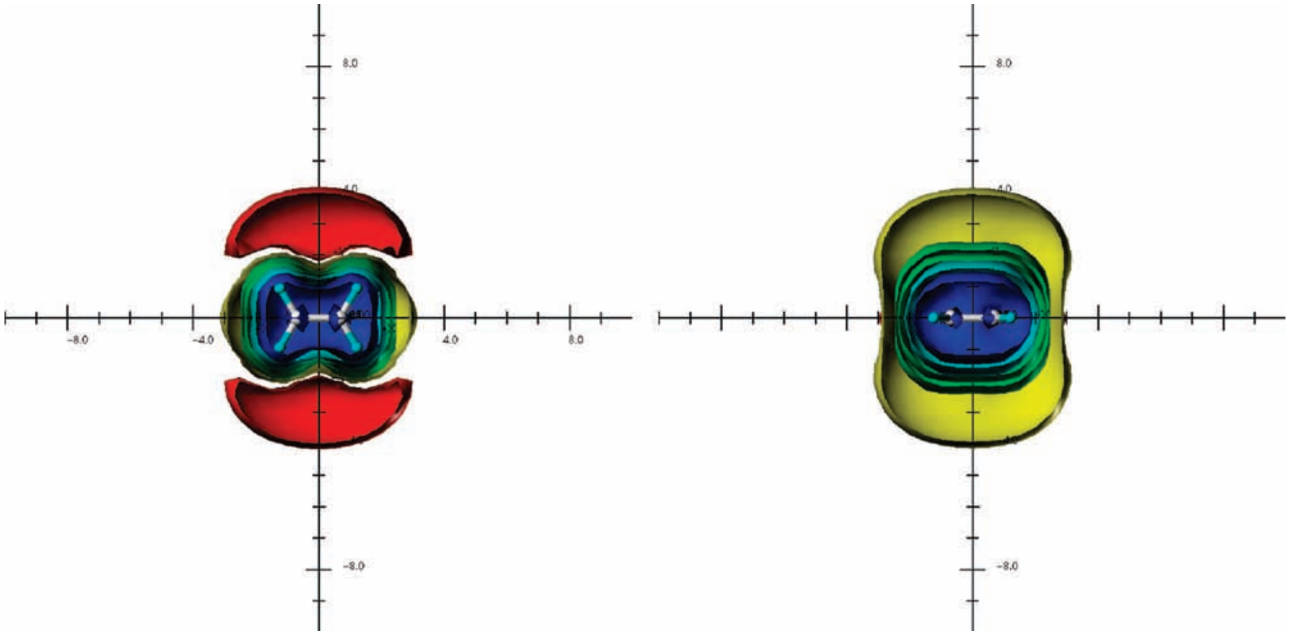


Figure 1. Calculated anisotropic effect of the C═C double bond (shielding ICSSs at −0.1 ppm yellow, at −0.5 ppm green, at −1 ppm green-blue, at −2 ppm cyan, at −5 ppm blue and deshielding ICSSs at 0.1 ppm red); view perpendicular to the molecule (left) and in the plane of the molecule (right).

slightly more deshielded (sterically a bit more compressed) as a result of the introduction of the additional double bond in **8** with respect to **7**.

The highest deviation from the anisotropic C═C double bond effect is observed for the H-3,4(*endo*) protons, as exemplified by the additional 0.22 low field shift of **8** relative to **7** (*cf.* Table 4). This must be the part of the molecule that undergoes the largest change in steric strain on introduction of the additional double bond. This interpretation is supported by the impressive change in the C-3/C-4-H-3/H-4(*endo*) bond length from 1.087 Å in **7** to 1.086 Å in **8** (*cf.* Supporting Information).

***Effect of C═C Double Bond Anisotropy in* 10, 11 *and* 12.** As was done with **2**, **4** and **6**, anisotropic effects of the double bond on the protons in the norbornene moiety of **10**, were obtained (*cf.* Figure 6 and Table 4). In the second saturated bicyclo[2.2.1]heptane moiety, protons are slightly deshielded due solely to the anisotropy of this C═C double bond (*cf.* Table 4):

H-3/4 (*endo*): −0.22 ppm
H-7 (*syn*): 0.06 ppm
H-7 (*anti*): 0.16 ppm

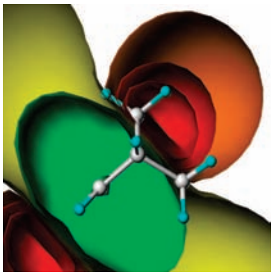


Figure 2. C═C double bond anisotropic effect in norbornene **2** as visualized by different deshielding (0.15 ppm red, 0.10 ppm red-orange and 0.04 ppm orange) and shielding (−0.20 ppm green and −0.02 ppm yellow) ICSSs.

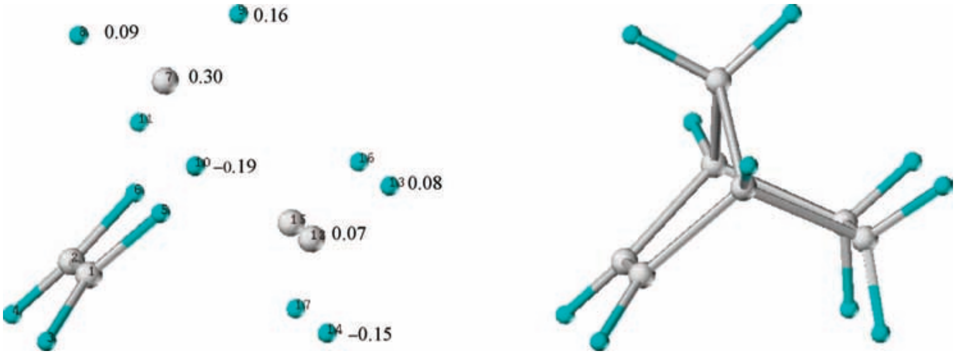


Figure 3. Quantification of the anisotropic effect of the 1,6-C=C double bond on the ^{1}H chemical shifts of norbornene **2**.

TABLE 3: Chemical Shifts (δ/ppm) and the Anisotropic Effect of the C=C Double Bond on Protons in Norbornene 2 and Methyl Substituted Derivatives 4 and 6

compound	H-1,6	H-2	H-3$_{exo}$	H-3$_{endo}$	H-4$_{exo}$	H-4$_{endo}$	H-5	H-7$_{syn}$	H-7$_{anti}$	subst
2										
exp		0.65	0.13	−0.21	0.13	−0.21	0.65	0.13	−0.11	
calc			(0.12)	(−0.10)	(0.12)	(−0.10)		(0.24)	(−0.08)	
anisotr		−0.19	0.08	−0.15	0.08	−0.15	−0.19	0.09	0.16	
4										
exp		0.63	0.13	−0.12	0.20		0.68	0.00	0.06	−0.14
calc			(0.10)	(−0.04)	(0.21)			(0.23)	(−0.07)	
anisotr		−0.19	0.08	−0.06	−0.16		−0.19	0.08	0.16	to high field
6										
exp		0.62	0.20	−0.14		−0.04	0.57	0.33	−0.04	0.21
calc			(0.08)	(−0.13)		(0.06)		(0.32)	(0.01)	
anisotr		−0.19	(0.08)	−0.14		−0.19	−0.19	0.08	0.16	to low field

SCHEME 2

	1	2
Bond lengths		
C-1–C-2/C-5–C-6	1.542	1.522
C-2–C-3/C-4–C-5	1.540	1.56
H-7(*anti*),C-7	1.086	1.087
Bond angles		
H-7(*anti*) –C-7–C-2	113.34	113.41

SCHEME 3

	5	6
Bond lengths		
C-7,H-7(*syn*)	1.086	1.083
C-7,H-7(*anti*)	1.085	1.086
Bond angles		
H-7(syn)–C-7–C-5	113.44	113.18
H-7(anti) –C-7–C-5	113.33	113.44

H-8,11: 0.01 ppm
H-9 (*syn*): 0.06 ppm
H-9 (*anti*): 0.03 ppm
H-12 (ax, eq): only negligible

In terms of steric hindrance in **10** with respect to **9** (comparing the proton chemical shifts of **9** and **10**), however, there are remarkable differences: (i) Although H-7(*anti*) is sterically released as usual (*vide supra*), the corresponding effect is smaller compared to **2**, **4** and **6**, but (ii) H-3,4(*endo*) and H-7(*syn*) are under strong steric compression in the olefin relative to the hydrocarbon.

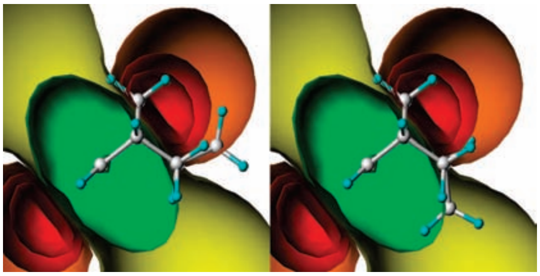


Figure 4. C=C double bond anisotropic effect in *exo*-4-Me-norbornene **6** and in *endo*-4-Me-norbornene **4** as visualized by different deshielding (0.15 ppm red, 0.10 ppm red-orange and 0.04 ppm orange) and shielding (−0.20 ppm green and −0.02 ppm yellow) ICSSs.

This increased steric compression in **10** is also felt (iii) by H-12(*ax*) but the steric effect on the other side of the molecule [H-8/11 and H-9(*syn*,*anti*)] is only negligible (*cf.* Scheme 4, Table 4 and the Supporting Information). Obviously, (iv) introduction of the double bond in **10** increases steric strain on H-7(*syn*), H-3,4(*endo*) and H-12(*ax*) whereas the rest of the molecule remains almost sterically unhindered (^{1}H chemical shift differences only reflect anisotropic effect influences).

Changes in geometry on comparison of the polycyclic hydrocarbon **9** and the corresponding olefin **10** are again completely in line with these ^{1}H chemical shift variations (*cf.* Scheme 4).

The types of interactions that are observed change when tetracyclic olefin **11** is compared with its saturated analog **9**. The anisotropic effect of the additional C=C double bond, visualized in Figure 7, is comparable to this effect in the compounds already studied:

H-1,6(*exo*): −0.05 ppm
H-1,6(*endo*): −0.03 ppm
H-3/4 (*endo*): 0.09 ppm
H-7(*syn*): −0.09 ppm
H-7(*anti*): −0.34 ppm
H-12x(ax): 0.16 ppm

TABLE 4: Chemical Shifts (δ/ppm) and the Anisotropic Effect of the C=C Double Bond on Protons in Tetracyclic Norbornene Derivatives 8 and 10−12[a]

compound	H-1,6	H-2,5	H-3,4$_{endo}$	H-7$_{syn}$	H-7$_{anti}$	H-8,11	H-9,10$_{syn}$	H-9,10$_{anti}$	H-12$_{ax}$	H-12$_{eq}$
8 comp with **7**										
calc		(0.32)	(0.32)	(0.32)	(−0.05)	(−0.16)	(−0.22)	(−0.15)	(0.06)	(−0.10)
anisotr		−0.20	0.09	0.29	0.16	−0.04	−0.36	−0.09	0.0	−0.03
10 comp with **9**										
calc		(0.42)	(0.16)	(0.42)	(0.04)	(0.02)	(0.04)	(0.08)	(0.21)	(0.16)
anisotr		−0.18	−0.22	0.06	0.16	0.01	0.06	0.03	0.01	−0.02
11 comp with **9**										
exp			0.38	−0.43	0.52−0.45				0.15−0.31	0.10−0.21
calc	(−0.04^x/−0.03^n)	−0.05	(0.29)	(−0.33)	(0.45)	(0.52)			(−0.11)	(0.19)
anisotr	−0.05^x/−0.03^n	−0.11	0.09	−0.09	−0.34	−0.20			0.16	0.07
12 comp with **9**										
exp			0.64	0.00	1.00				0.37	0.35
calc		(0.37)	(0.57)	(0.14)	(0.77)	(0.41)			(0.19)	(0.46)
anisotr		−0.28	−0.14	−0.04	−0.23	−0.18			0.13	0.08

[a] x = *exo* and n = *endo*.

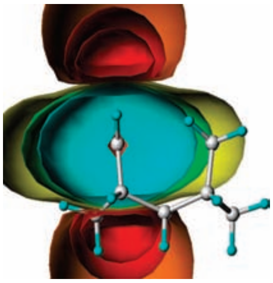


Figure 5. C=C double bond anisotropic effect in **8** as visualized by different deshielding (0.15 ppm red, 0.10 ppm red-orange and 0.04 ppm orange) and shielding (−0.20 ppm green and −0.02 ppm yellow) ICSSs.

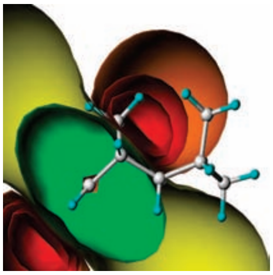
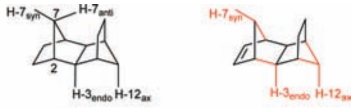


Figure 6. C=C double bond anisotropic effect in **10** as visualized by different deshielding (0.15 ppm red, 0.10 ppm red-orange and 0.04 ppm orange) and shielding (−0.20 ppm green and −0.02 ppm yellow) ICSSs.

SCHEME 4



	9	**10**
Bond lengths		
C-3–H-3(*endo*)	1.086	1.085
C-7–H-7(*syn*)	1.087	1.083
C-12–H-12(*ax*)	1.086	1.085
Bond angles		
H-3(*endo*) –C-3–C-2	108.91	108.64
H-7(syn) –C-7–C-5	111.78	111.78
H-12(*ax*)–C-12–C-8	113.51	113.47

As expected, the strongest effect is observed for H-7(*anti*), which is directly adjacent to the new C=C double bond and lies within the >3Å sphere. It usually would not be employed as a source of information on anisotropic effects[3] but, in this case, the effect of the double bond on the H-7(*anti*) chemical shift, 0.45 ppm calculated vs 0.52−0.45 ppm experimental (there are uncertainties in some assignments; see Table 2), proved to be very consistent in view of the geometry variations observed comparing **9** and **11** (*cf.* Scheme 5). In addition to the anisotropic effect, some increased steric strain which should shift H-7(*anti*) additionally to lower field can be detected. Thus, the *ca.* 0.5 ppm low field shift of H-7(*anti*) in **11** (with respect to **9**) can be attributed partly to the C=C double bond anisotropic effect and partly to the increasing steric strain in certain regions of the polycyclic olefin **11**.

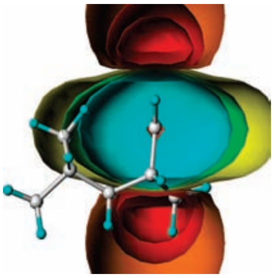
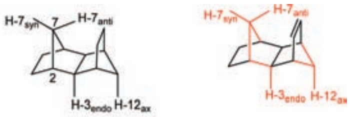


Figure 7. C=C double bond anisotropic effect in **11** as visualized by different deshielding (0.15 ppm red, 0.10 ppm red-orange and 0.04 ppm orange) and shielding (−0.20 ppm green and −0.02 ppm yellow) ICSSs.

SCHEME 5



	9	**11**
Bond lengths		
C-7–H-7(*anti*)	1.075	1.075
C-3–H-3(*endo*)	1.086	1.085
C-7–H-7(*syn*)	1.087	1.087
C-12–H-12(*ax*)	1.086	1.086
Bond angles		
H-7(*anti*)–C-7–C-5	115.38	115.40
H-3(*endo*)–C-3–C-2	108.91	109.09
H-3(*endo*)–C-3–C-8	106.61	106.56
H-7(*syn*)–C-7–C-2	111.79	111.48
H-12(*ax*)–C-12–C-8	113.52	113.67

Further, in terms of steric compression, H-3,4 (*endo*) are shifted to low field (thus are sterically more compressed) and H-7(*syn*) and H-12(*ax*) are additionally shielded (in terms of steric compression, sterically released); H-2,5 and H-1,6 reproduce the anisotropic effect quite well and hereby provide strong support for distance constraints when comparing ^{1}H chemical shifts of **11** and **9** (*cf.* Figure 7); variations in bond lengths and angles of **11** with respect to **9** are in agreement with this interpretation (*cf.* Scheme 5).

Finally, the introduction of two double bonds and their anisotropic effects and changes in steric compression, were studied with respect to the saturated analog **9**, in **12** (Figure 8).

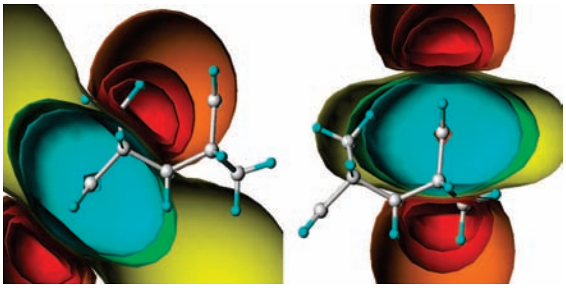
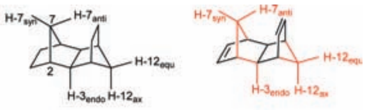


Figure 8. C═C double bond anisotropic effects in **12** as visualized by different deshielding (0.15 ppm red, 0.10 ppm red-orange and 0.04 ppm orange) and shielding (−0.20 ppm green and −0.02 ppm yellow) ICSSs.

SCHEME 6



9 **12**

Bond lengths	9	12
C-7–H-7(syn)	1.087	1.084
C-3–H-3(*endo*)	1.086	1.084
C-12–H-12(*eq*)	1.086	1.084
C-12–H-12(*ax*)	1.086	1.086
C-7–H-7(*anti*)	1.075	1.075

Here there are dramatic variations in the molecular framework (reflected by steric compression effects on ^{1}H chemical shifts and only H-12(*ax*) reproduces the double anisotropic effect; *cf.* Table 4):

H-3/4(*endo*): −0.14 ppm
H-7(*syn*): −0.04 ppm
H-7(*anti*): −0.23 ppm
H-12(*ax*): 0.13 ppm
H-12(*eq*): 0.08 ppm

The highly congested hydrocarbon with two double bonds presents several additional steric interactions. All proton chemical shifts relevant to the expected anisotropic effects are strongly deshielded (see Table 4) and hereby completely mask the anisotropic influences in **12**. The steric effect is strongest for H-7(*anti*) but can be also remarkable for H-7(*syn*), H-3,5(*endo*) and H-12(*eq*). The corresponding steric compression of these protons is illustrated in Scheme 6. For proton H-12(*ax*) only the calculated shift difference and anisotropic effect proved to be comparable; because this proton is slightly released (*cf.* Scheme 6) experimental assignments of H-12(*ax* and *eq*) for this compound should probably be inverted.

3. Experimental Section

Ab initio calculations were performed on SGI Octane and SGI Origin 2000 workstations or a Linux cluster using the *Gaussian03* program package.[38] Geometry optimizations were performed at the B3LYP/6-31G* level of theory[39] without restrictions. The chemical shieldings in the surroundings of the molecules were calculated on the basis of the NICS concept[1] whereby the molecule was placed in the center of a grid of ghost atoms ranging from −10.0 to +10.0 Å in all three dimensions with a step width of 0.5 Å, resulting in a cube of 68,921 ghost atoms. The chemical shielding calculations were performed using the GIAO[40,41] method at the HF/6-31G*//B3LYP/6-31G* level of theory.[42] Because GIAO is a coupled HF method that uses gauge-independent atomic orbitals for the calculation of shielding values, it can be used for the calculation of NICS values. When X-ray structures were available from the Cambridge crystallographic database,[43] they were employed as starting structures for the *ab initio* calculations; otherwise, starting structures were generated by SYBYL modeling software.[44] From the GIAO calculations, the coordinates and isotropic shielding values of the ghost atoms were extracted. After transformation of the tabulated chemical shieldings into a *SYBYL*[44] contour file, the TSNMRS of the molecules were visualized as ICSS, providing a 3-D view on the spatial extension, sign and scope of the anisotropic effects at each point in space.

4. Conclusions

The anisotropic effect of the C═C double bond has been calculated, visualized by iso-chemical-shielding surfaces (ICSSs) and employed to determine the magnitude of its effects on the proton chemical shifts of norbornene **2**, 4(*exo/endo*)Me−norbornenes **4** and **6**, and tetracyclic norbornene analogs **8** and **10**−**12**. ^{1}H chemical shift differences that can be attributed to the anisotropic effect were compared to differences between the corresponding ^{1}H chemical shifts of olefins **2**, **4**, **6**, **8** and **10**−**12** and their saturated analogs **1**, **3**, **5**, **7** and **9**. These differences were analyzed in terms of distortions in molecular geometry *via* steric compression as reflected by bond lengths and angles. Hereby differences in steric strain between the two groups of compounds could be readily evaluated. Even the part/moiety of the molecules undergoing strongest steric strain can be clearly identified using this approach. The magnitude of steric effects may be evaluated by changes in geometry of the polycyclic hydrocarbons containing double bonds compared to the corresponding saturated hydrocarbons as reflected by ^{1}H chemical shift differences.

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Supporting Information Available: Bond lengths and bond angles of **1**−**12**. This material is available free of charge *via* the Internet at http://pubs.asc.org.

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