Ab initio hybrid DFT–GIAO calculations of the shielding produced by carbon–carbon bonds and aromatic rings in ^{1}H NMR spectroscopy

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Theoretical calculations of ^{1}H shieldings by single, double and triple CC bonds as well as by aromatic rings (benzene, cyclopropenyl cation and hexafluorobenzene) have been performed using *ab initio* MO theory. As an illustration of the methodological approach, absolute chemical shieldings of ^{1}H-, ^{13}C-, ^{17}O- and ^{19}F-containing molecules have been calculated. The results, both inter- and intramolecular, range from good to excellent. The relative chemical shifts of some large molecules having strongly shielded protons are conveniently reproduced.

Calculs *ab initio* hybrides DFT-GIAO de l'effet d'écran produit par des liaisons carbone–carbone et par de noyaux aromatiques en RMN du ^{1}H. On rapporte les calculs théoriques *ab initio* des blindages de protons par des liaisons CC simple, double et triple ainsi par des noyaux aromatiques (benzène, cation cyclopropényle et hexafluorobenzène). Pour illustrer l'approche utilisée, les blindages des noyaux ^{1}H, ^{13}C, ^{17}O et 19^F ont été calculés. Les résultats tant inter- que intramoléculaires sont bons ou excellents. Les déplacements chimiques de quelques molécules de relativement grande taille sont reproduits de façon convenable.

In ^{1}H NMR spectroscopy, the anisotropy of the bonds affects the chemical shifts of the neighbours' protons;[1–3] a special case is that of aromatic rings since the shielding effects are related to ring currents and aromaticity.[4–6] We decided to use the London and Ditchfield GIAO (gauge including atomic orbitals) method to rationalize these effects.[7–9] We will present our results in the following order:

i Use of the hybrid DFT-GIAO approach on a number of small molecules, including ^{1}H, ^{13}C, ^{17}O and ^{19}F nuclei (DFT = density functional theory) to verify if the level of our calculations was adequate.[9,10]

ii Use of the hybrid DFT-GIAO calculations on a number of intermolecular situations with a methane molecule as a probe.

iii Hybrid DFT-GIAO calculations of some aromatic systems having strongly shielded protons.

Computational Details

All the calculations have been carried out using the Gaussian 94 set of programs.[11] The methodology followed can be divided into three steps.* (*a*) The small molecules described in the first section of this article have been fully optimized, whenever possible using their symmetry characteristics, with the hybrid Hartree Fock (HF)-density functional method (DFT) Becke 3LYP (B3LYP) method,[10] and the 6-311++G** basis set.[12] (*b*) The dimers discussed in the second section have been built using the geometries obtained in step (*a*) without further optimization. (*c*) Finally, the larger molecules of the third section have been fully optimized at the B3LYP/6-31G* level.[13] In all cases, the NMR properties of the molecules have been calculated at the B3LYP/6-311++G** level, using the GIAO magnetic perturbation methodology.[7]

* Fully optimized geometries and absolute shielding values for all atoms can be obtained from either of us (J.E. E-mail: jelguero@pinar1.csic.es; I.A. E-mail: ibon@pinar1.csic.es).

Results and Discussion

DFT-GIAO of small isolated molecules

We have summarized in Table 1 the results obtained and the experimental information available on the absolute chemical shifts of the four calculated nuclei, either directly determined or indirectly estimated (see Table 1 footnotes).

Since they are absolute values, the criteria of quality are the closeness of the slope to one and the intercept to zero rather than the correlation coefficients. The best experimental set is that formed by the carbon-13 absolute shieldings (σ) of the hydrocarbons methane, ethane, ethene, ethyne and benzene.[8,15] Considering that the data set is very small (five points), the only conclusion of the comparison of our B3LYP/6-311++G**-GIAO calculations [eqn. (1)] with those of Chesnut[8] using a HF/6-311**-GIAO basis set [eqn. (2)], is that both are of similar quality.

$$^{13}C_{calc} = (-10.7 \pm 1.5) + (1.03 \pm 0.01)\,^{13}C_{exp}, \quad n = 5,\ r^2 = 1.000 \quad (1)$$

$$^{13}C_{calc} = (3.1 \pm 1.4) + (1.00 \pm 0.01)\,^{13}C_{exp}, \quad n = 5,\ r^2 = 1.000 \quad (2)$$

In a second step, we plotted *all the values* of Table 1, mixing the ^{1}H, ^{13}C, ^{17}O and ^{19}F absolute shifts. The result is represented in Fig. 1, where the straight line corresponds to eqn. (3).

$$^{n}X_{calc} = (1.5 \pm 1.8) + (1.03 \pm 0.01)\,^{n}X_{exp}, \quad n = 18,\ r^2 = 0.999 \quad (3)$$

Again, the result is very satisfactory, taking into account that the values of Table 1 come from different authors and correspond to different experimental conditions. Since our final purpose is to study ^{1}H NMR effects, we have calculated the

Table 1 B3LYP/6-311++G**-GIAO calculated absolute chemical shifts of isolated molecules (all values in ppm)

	Calculated				Experimental (absolute values)			
Molecule	^{1}H	^{13}C	^{17}O	^{19}F	^{1}H	^{13}C	^{17}O	^{19}F
CH_4	31.74	190.43	—	—	30.61[a]	195.1[b]	—	—
H_3C-CH_3	31.02	174.59	—	—	29.26[a]	180.9[b]	—	—
$H_2C=CH_2$	26.24	54.13	—	—	25.43[a]	64.5[b]	—	—
$HC\equiv CH$	30.77	111.27	—	—	29.86[a]	117.2[b]	—	—
C_6H_6	24.40	49.65	—	—	24.20[c]	57.9[b]	—	—
$[C_3H_3]^+$	21.27	5.46	—	—	20.60[d]	9.1[e]	—	—
C_6F_6	—	35.59	—	336.87	—	47.9[f]	—	359[g]
H_2O	31.62	—	322.27	—	29.96[h]	—	334[i]	—
HF	30.24	—	—	407.95	28.4[h]	—	—	410[j]

[a] Ref. 14. [b] Ref. 15. [c] Ref. 16. [d] From the difference between benzene (7.27 ppm from TMS, ref. 1) and the cyclopropenyl cation (10.87 ppm, ref. 17) and the absolute value for benzene (this table). [e] From the difference between benzene (128.7 ppm from TMS, ref. 18) and cyclopropenium ion (176.8 ppm, ref. 18) and the absolute value for benzene (this table). [f] From the difference between benzene (128.7 ppm from TMS, ref. 18) and hexafluorobenzene (138.0 ppm from TMS, ref. 19) and the absolute value for benzene (this table). [g] From the difference between HF (−214 ppm from $CFCl_3$, ref. 20) and C_6F_6 (−163 ppm from $CFCl_3$, ref. 21) and the absolute value for hydrogen fluoride (this table). [h] Ref. 20. [i] Ref. 22, another value is 344 ppm (ref. 8). [j] Refs. 23 and 24.

regression equation (4) corresponding to protons:

$$^{1}H_{calc} = (1.5 \pm 1.8) + (1.03 \pm 0.01)^{1}H_{exp}, \quad n = 8, r^2 = 0.99 \tag{4}$$

This result, considering that the experimental range is much narrower, is still very good. Besides, the intercept and the slope of eqn. (3) and (4) are identical, showing that protons behave like the other nuclei.

DFT-GIAO of intermolecular dimers involving methane as a probe

We have explored a number of situations, which are represented in Scheme 1. In this second part we will use, for the discussion, chemical shifts relative to methane (^{1}H 31.74 ppm, ^{13}C 190.43 ppm, Table 1): $\Delta\delta = \delta_{dimer,\,calc} - \delta_{methane,\,calc}$; $\delta_{dimer,\,calc}$ is the chemical shift of the methane in the dimer. The results are reported in Table 2 ($\perp$ means perpendicular orientation and $\parallel$ means parallel orientation; in the case of ethene there are two perpendicular orientations, 1 is perpendicular to the π system and 2 is in the plane of the π system).

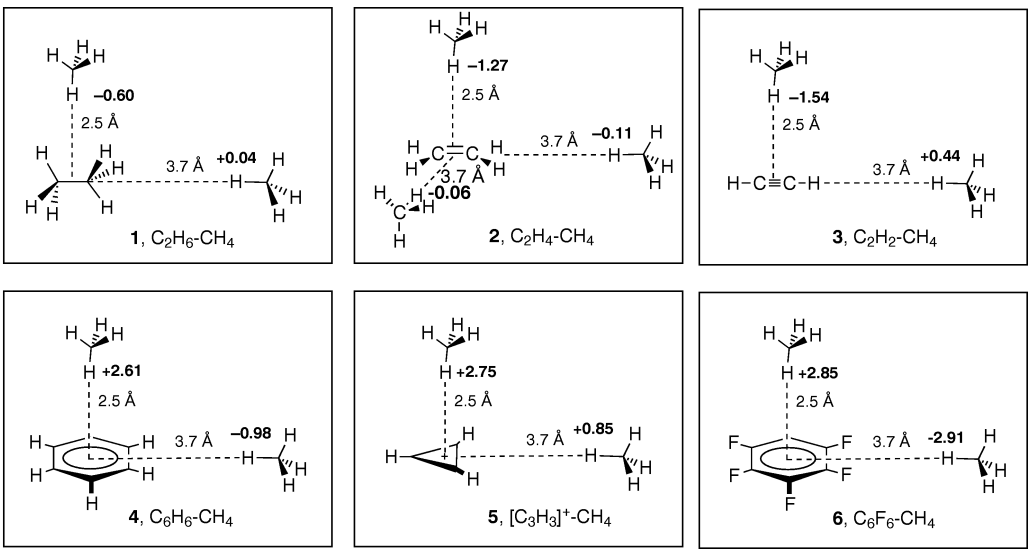
Although Table 2 contains a wealth of information we will concentrate on the problem of the Δδ values for the methane proton that is closest to the other molecule and see if it follows the classical ^{1}H NMR anisotropic shielding of bonds and rings (Fig. 2).[1,2] To facilitate the discussion, we have represented these Δδ values in Scheme 1.

The comparison of the upper part of Scheme 1 with Fig. 2 shows that in the case of the CC single bond, GIAO calculations reverse the classical picture; in the case of the CC double bond, the calculations reproduce the deshielding in the plane but not the shielding perpendicular to it; finally the more representative case of the CC triple bond is correctly reproduced. ApSimon and co-workers, and others, have discussed the possibility that some anomalies lie in the anisotropy of the CH bonds that often accompany the CC bonds.[3,25,26] For instance, in the case of ethane (Scheme 1) there are two classes of hydrogens close to the hydrogen of the methane probe: the 'eclipsed' one at 1.88 Å and the two staggered ones at 2.47 Å. To estimate the effect of a CH bond we have calculated some methane dimers **7a**–**c** which are represented in Scheme 2 (Δδ values).

The methane on the left side is the perturbating molecule and that on the right side is the 'probe' as in Scheme 1. The two distances, CC and HH, are trigonometrically related. The six values of the dimer (four ^{1}H and two ^{13}C) depend linearly ($n = 6$, $r^2 \sim 1.000$) on $1/d^6$, d being any of these two distances. For instance, the most interesting signal, the closest hydrogen of the 'probe', follows eqn. (5).

$$^{1}H(probe) = (0.09 \pm 0.05) + (-123 \pm 6)/d^6, \quad n = 3, r^2 = 0.998 \tag{5}$$

Thus, since in the case of ethane there is one hydrogen at 1.88 Å and two others at 2.47 Å, eqn. (4) predicts for the first a Δδ = −2.11 and for the second a Δδ = −0.31, that is, −0.91 on



Scheme 1

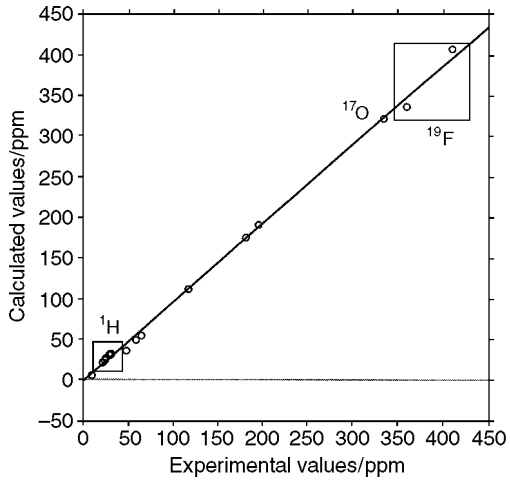


Fig. 1 Plot of calculated absolute chemical shifts against experimental absolute values (both in ppm) from Table 1 data (^{1}H, ^{13}C, ^{17}O and ^{19}F nuclei). The data corresponding to ^{1}H and ^{19}F shieldings are framed; the remaining ones are ^{13}C values and a ^{17}O value

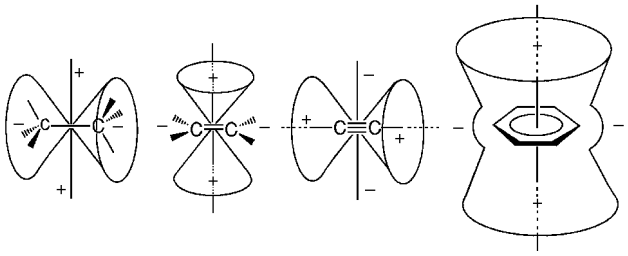


Fig. 2 Classical ^{1}H NMR anisotropic shielding of single, double and triple CC bonds and of the benzene ring

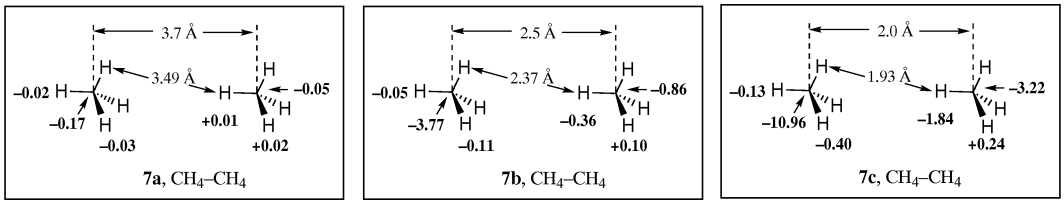
average. Since the hydrogen on dimer **1** is deshielded by −0.60 ppm (Scheme 1) it could be that the CC single bond produces, as expected (Fig. 2) a shielding of 0.3 ppm. Since the shielding properties of the CC double bond are ill defined[1,3,25,27] we decided not to carry out similar calculations.

We have selected three aromatic rings: benzene as the reference compound (for IGLO calculations of benzene see ref. 6), the cyclopropenyl cation and hexafluorobenzene. The cyclopropenyl cation having only two π electrons is the simplest aromatic system according to Hückel's rules,[28] while hexafluorobenzene has been selected in relation to ASIS (aromatic solvent-induced shifts).[29,30] In the case of benzene, the results reported in Scheme 1 (complex **4**) agree with all that is known about this ring, for both intramolecular and intermolecular effects (ASIS). It is possible to go a little further since the Johnson–Bovey values[31] have been tabulated.[2] For the perpendicular position, the table predicts +2.83 ppm (to

Table 2 B3LYP/6-311++G**-GIAO calculated absolute chemical shifts of molecule–methane dimers (all values in ppm; between parentheses values are relative to methane)

		^{1}H chemical shifts and Δδ values			^{13}C chemical shifts and Δδ values	
Dimer	Orientation	H-1[a]	H-2[b]	H-3[c]	C-1[d]	C-2[e]
[CH_4	—	31.74	31.74	—	190.43][f]	—
$H_3C{-}CH_3/CH_4$	⊥	31.14	31.71; 31.75	30.95, 31.08	188.77	173.95; 174.26
		(−0.60)	(≈0.00)	30.56, 31.05	(−1.66)	
$H_3C{-}CH_3/CH_4$	∥	31.78	31.82	31.01	190.15	174.49; 173.28
		(+0.04)	(+0.08)	30.98	(−0.28)	
$H_2C{=}CH_2/CH_4$	⊥(1)	30.47	31.98; 32.05	26.13	187.86	51.15
		(−1.27)	(≈0.30)		(−2.57)	
$H_2C{=}CH_2/CH_4$	⊥(2)	31.68	31.68		190.19	54.07
		(−0.06)	(−0.06)		(−0.24)	
$H_2C{=}CH_2/CH_4$	∥	31.63	31.71	26.19	189.96	53.01, 53.97
		(−0.11)	(−0.03)	26.24	(−0.47)	
$HC{\equiv}CH/CH_4$	⊥	30.20	31.84; 31.91	30.70	188.40	108.04
		(−1.54)	(≈0.15)		(−2.03)	
$HC{\equiv}CH/CH_4$	∥	32.18	31.63	30.80	188.70	111.35; 109.97
		(+0.44)	(−0.11)	30.48	(−1.73)	
C_6H_6/CH_4	⊥	34.35	32.64	24.39	190.77	48.88
		(+2.61)	(+0.90)		(+0.34)	
C_6H_6/CH_4	∥	30.76	31.49	24.14, 24.37	188.45	49.17, 49.63
		(−0.98)	(−0.25)	24.40	(−1.98)	49.61
$[C_3H_3]^+/CH_4$	⊥	34.49	31.52	21.27	185.97	3.68
		(+2.75)	(−0.22)		(−4.46)	
$[C_3H_3]^+/CH_4$	∥	32.59	31.17	21.26	189.15	4.92
		(+0.85)	(−0.57)	21.29	(−1.28)	5.45
C_6F_6/CH_4	⊥	34.59	32.25	—	191.04	35.59 (^{19}F: 336.9)
		(+2.85)	(+0.51)		(+0.61)	
C_6F_6/CH_4	∥	28.83	31.66, 31.81	—	187.46	37.27, 36.16, 36.13
		(−2.91)	(≈0.02)		(−2.97)	(^{19}F: 311.76, 335.92, 335.55)

[a] Methane hydrogen atom pointing towards the second molecule. [b] Other hydrogen atoms of methane. [c] Hydrogen atoms of the second molecule. [d] Methane carbon atom. [e] Carbon atoms of the second molecule in the complex. [f] Values for methane from Table 1.



Scheme 2

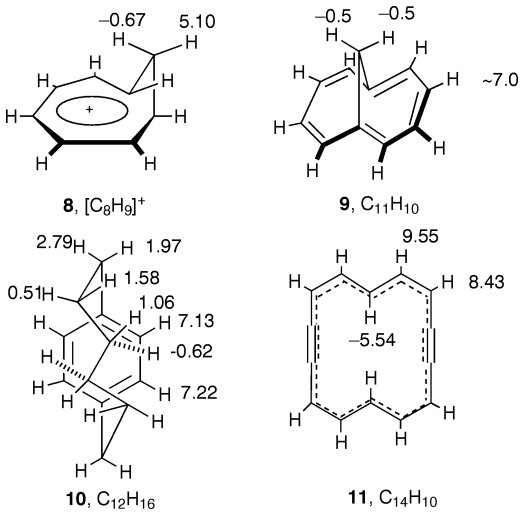


Fig. 3 ^{1}H NMR relative chemical shifts and molecular formulae of the four aromatic compounds **8**–**11**

compare with +2.61 ppm of Scheme 1) and for the parallel position, the table predicts −0.53 ppm (to compare with −0.98 ppm of Scheme 1), which is fairly good; the correction introduced by Farnum and Wilcox[32] improves the agreement (+2.53 and −0.58 ppm).

Having gained confidence in the GIAO calculations, we turned to the cyclopropenium ion where the calculations predict a similar effect over the plane of the ring (Scheme 1, **5**) but an opposite situation for a hydrogen situated in the plane, but since there is no experimental evidence of the latter situation we cannot confirm the accuracy of our calculations.

The last selected aromatic ring was hexafluorobenzene (Scheme 1, **6**) and it was selected because, compared with benzene, it seems to produce anomalous solvent effects[33] and because a recent study of their molecular electrostatic potential and electron density characteristics show important dissimilarities.[34] Other authors[35–38] note that the solvent effects of benzene and hexafluorobenzene (ASIS), both on ^{1}H and on ^{13}C NMR, are opposite in sign although much weaker in the latter. The results reported in Scheme 1 (complexes **4** and **6**) show that the perpendicular shielding effect is, for all purposes, identical. The different behaviour of both solvents may lie in a different nature of the interaction with the solute (both compounds differ markedly in this regard).[39,40] Note that in the parallel approach the proton is much more deshielded in **6** than in **4** and that aromatic fluoro derivatives are weak hydrogen-bond acceptors in the molecular plane.[19,41,42]

DFT-GIAO calculations in some aromatic systems having strongly shielded protons

We have selected for this last part four compounds, which are represented in Fig. 3. The absolute proton shielding of TMS, calculated with the same approximation, is 31.97 ppm. Similar

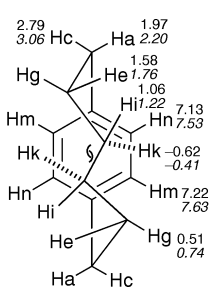


Fig. 4 Experimental and calculated (italic) ^{1}H NMR relative chemical shifts of [6]paracyclophane, **10**

values have been obtained for TMS using the GIAO method with different basis sets and levels of calculation.[43] It is interesting to note that the absolute value for the ^{13}C signal of TMS is about 192–193 ppm at the HF level while B3LYP calculations yield a value of 182.5 ± 0.1 ppm (in our case 184.75 ppm).[43] This difference of about 10 ppm roughly corresponds to the difference between the intercept in eqns. (2) and (3) and demonstrates that absolute values for ^{13}C signals are better reproduced with the simpler HF calculation.

The homotropylium cation **8** as the paradigm of homoaromaticity has been the subject of many theoretical studies.[44–49] Experimentally, one proof of its aromaticity is the difference in the chemical shielding of the inside and outside protons reported in Fig. 3.[50] The calculated values for these protons are (relative values between parentheses) 32.65 ppm (δ = −0.68) for the inside proton and 26.75 ppm (δ = 5.22) for the outside proton. Although the extraordinary coincidence is accidental (slightly different values are found in the literature)[51,52] the experimental difference, always Δδ = 5.8, is accurately reproduced (Δδ = 5.9).

1,6-Methano[10]annulene **9** has played a seminal role in the concept of aromaticity.[53] The shielding of the protons of the methane bridge (Fig. 3) is well reproduced by the calculations: 32.87 ppm (δ = −0.90). Compound **10**, [6]paracyclophane, belongs to the family of cyclophanes[54,55] and its ^{1}H-NMR signals are those reported by Tobe *et al.*[56,57] for $CDCl_3$ solutions at −50 °C. The calculations correspond to a molecule of symmetry C_2 with the benzene ring in a boat-like conformation [the out-of-plane deformation of the benzene ring, α,[57] is 22.4° (exp)[54] and 18.12° (calc)]. The chemical shifts relative to TMS, both the experimental ones (bold) and the calculated ones (bold, italic) are reported in Fig. 4.

The agreement is excellent: the relative order is exactly reproduced and for the eight different protons there exists a linear relationship between calculated and experimental values [note that the slope is the same as in eqn. (4)]:

$$^1H_{calc} = (0.18 \pm 0.02) + (1.030 \pm 0.005)^1H_{exp}, \quad n = 8, r^2 = 1.000 \quad (6)$$

The last compound studied is the annulene **11** (1,2,8,9-tetradehydro[14]annulene), a compound with complete electronic delocalization and with a difference of 14–15 ppm between the inner and outer protons (the chemical shifts reported in Fig. 3 are those of ref. 1).[58] The calculated structure of minimum energy has a planar D_{2h} geometry and the calculated chemical shifts with regard to TMS are (in parentheses the experimental values of Fig. 3): −9.07 (−5.54), +10.54 (+9.55) and +9.42 (+8.43 ppm). Here the agreement is less satisfactory, although the relative order is well reproduced as shown by eqn. (7):

$$^1H_{calc} = (1.80 \pm 0.17) + (1.13 \pm 0.02)^1H_{exp}, \quad n = 3, r^2 = 1.000 \quad (7)$$

The 14–15 ppm difference, characteristic of the inner/outer protons of aromatic compounds, is overestimated by the calculations (18.5–19.5 ppm).

Conclusions

In conclusion, the appraisal of the application of the DFT-GIAO methodology to problems related with bond anisotropies, ring currents and ASIS is clearly positive. A similar aproach (B3LYP/6-311 + G**-GIAO) has been used recently to compute succesfully the aromaticity and NMR chemical shifts of (benzene)$Cr(CO)_3$,[59] while DFT-IGLO has been shown to provide absolute chemical shifts close to those from GIAO-MP2 calculations.[60]

We are aware of the possibility of using GIAO calculations of the perpendicular proton shielding by rings as a measure of aromaticity and heteroaromaticity, at least, as the magnetic component of aromaticity.[59,61–63] This approach will be complementary to that of Schleyer *et al.*'s 'nucleus-independent chemical shifts'.[64] Nevertheless, we have postponed this application until more information has been gathered.

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