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An ab initio study of the NMR properties (absolute shieldings and NICS) of a series of significant aromatic and antiaromatic compounds

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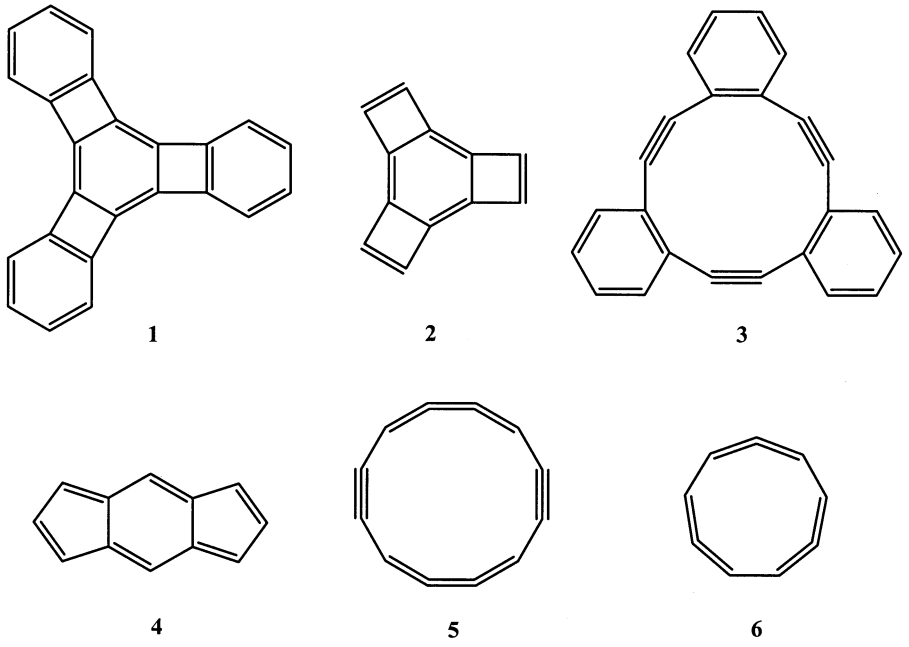
Abstract—The absolute shieldings of protons and the nuclear independent chemical shifts of six aromatic and antiaromatic hydrocarbons have been calculated at the GIAO/B3LYP/6-31G* level. In general, the results are in agreement with the experiment ones except in the case of 1,5,9-tridehydro[12]annulene **7**. Three possible explanations have been tested for this compound concluding that the anomaly (~14 ppm!) probably lies on the use of a DFT approach.

1. Introduction

Aromaticity, and its deformed mirror image, antiaromaticity, are capital concepts in chemistry although it is clear that more and clearer results are available for aromaticity than for antiaromaticity (for two recent reviews see Ref. 1).

There are some authors studying the foundations of aromaticity, for instance, compounds **1** and **2** (Scheme 1) related to the Mills–Nixon effect.[2] Initiated by Schleyer's pioneering research,[3] there has been a great interest in singlet vs triplet aromaticity.[4–6] Other authors have explored nonplanar aromatic compounds[7] concave π-electron systems,



Scheme 1. Structure of the compounds discussed in the introduction.

Keywords: aromaticity; antiaromaticity; annulenes; GIAO; NICS.

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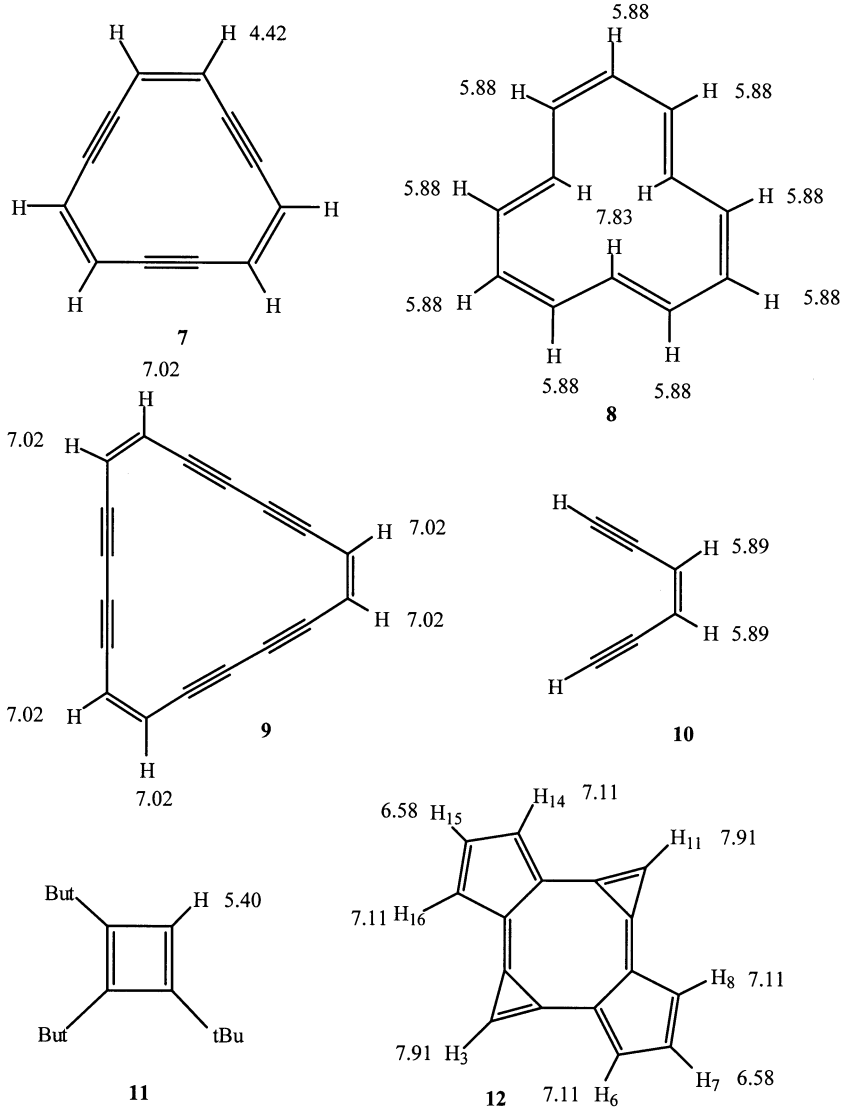
Table 1. Some typical aromatic [14] and [18] and antiaromatic [12] and [16]annulenes and their ^{1}H chemical shifts (in ppm)

Aromatic Systems			Antiaromatic Systems		
Annulene	Outer protons	Inner protons	Annulene	Outer protons	Inner protons
[14]	7.60	0.00	[12]	5.91	7.86
[18]	9.28	−2.99	[16]	5.40	10.43

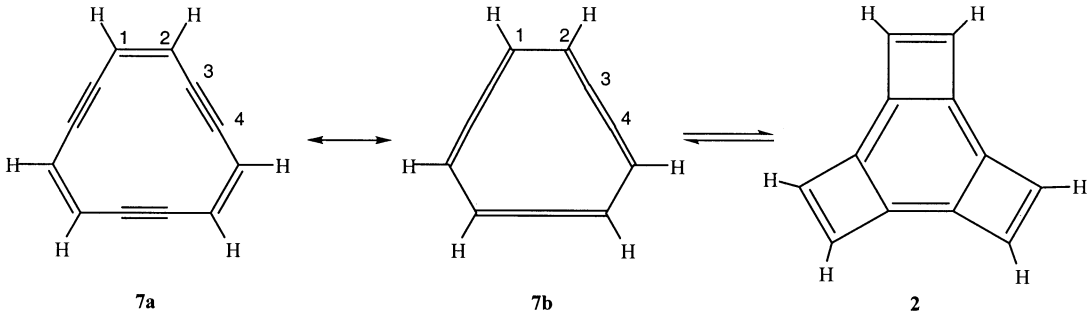
like the tetradehydroannulene **3**[8,9] and other dehydro[*n*]-annulenes,[9] as well as linear and angular polyacenes.[10] Compounds such as *s*-indacene **4** with mixed aromatic and antiaromatic character,[11] and ring carbomers, for instance **5** are very stimulating structures.[12] Rzepa has studied the effect of replacing one planar C═C unit in Hückel aromatic rings by a twisted C═C═C to obtain a Möbius ring, for instance **6** using NICS (nuclear independent chemical shifts) as criteria of aromaticity,[13] as well as the 'trimerous behaviour' of several annulenes.[14] The significance of the discovery of the isotope (H/D) perturbation character in [16] and [18]annulenes must be emphasized.[15] Finally, in our opinion, one of the most important consequences of the simple Hückel's rule has been the synthesis of a set of molecules of great beauty and interest prepared in order to test it.

Fully conjugated rings can be classified in two families: aromatic compounds which are diatropic and antiaromatic rings which are paratropic.[16] The first ones show deshielded outer protons and shielded inner (and over the plane) protons; the effects are of opposite sign in antiaromatic compounds but smaller in absolute value. Typical examples from Ref. 16 are given in Table 1.

Previously we have calculated (using the GIAO/B3LYP/6-31G* and 6-311+G** approaches) the ^{1}H chemical shifts of several aromatic compounds and found them in reasonable



Scheme 2. Compounds discussed in this work together with their ^{1}H chemical shifts.



Scheme 3. The valence isomer **2** of 1,5,9-tridehydro[12]annulene **7** (1,5,9-cyclododecatriene-3,7,11-triyne).

agreement with the experimental values.[17,18] Thus, we decided to attempt the calculation of some antiaromatic compounds and for comparative purposes also of several aromatic compounds, including the interesting Yoshida's derivative **12**.[19]

2. Methodology

Geometries of the studied stationary structures were fully optimized, with the internal 6-31G* basis set,[20] and at the B3LYP[21] theoretical level using procedures implemented in the Gaussian 98 set of programs.[22] Harmonic frequency calculations[23] verified the nature of the stationary points as minima (all real frequencies). The theoretical absolute NMR shieldings were calculated using the GIAO method[24] at the same computational level. For the NICS values, we followed the sign convention used by other authors, that is negative for aromatic compounds and positive for antiaromatic ones.[3,12–14]

3. Results and discussion

We have represented in Scheme 2 the six studied compounds **7**–**12**. The selection was based on the following reasons. First, we selected 1,5,9-tridehydro[12]annulene **7** (1,5,9-cyclododecatriene-3,7,11-triyne), an antiaromatic compound presenting a singlet at δ=4.42 ppm,[25] which was already examined by Pople in his classical paper of 1966 'Induced Paramagnetic Ring Currents'.[26] Compound **7**, according to Balaban[25] has 'two nonequivalent Kekulé structures: one with three cumulenic systems (**7b**), the other with three triple bonds and three double bonds (**7a**)' (Scheme 3). Moreover, there is a valence isomer (**2**) of this compound. Recently, AM1 calculations of **7a** (only geometry) have been reported.[9] Diederich, in a recent review has classified compound **7a**, based on electronic absorption and ^{1}H NMR spectra, as 'paratropic' i.e. antiaromatic.[27]

To our great surprise, GIAO/B3LYP/6-31G* calculations yield, for the protons of **7**, a value of σ=45.17 ppm, value that through an empirical relationship between δ and σ (see later on) yields δ^1H=−9.7 ppm!

Trying to understand the origin of this enormous discrepancy (13.2 ppm), we decided to study two other compounds, **8** and **9**. The [12]annulene **8** (the values of Scheme 2 are slightly different from Minkin's table)[16] is also antiaromatic. 1,3,7,9,13,15-Hexadehydro[18]annulene **9** is similar to annulene **7** but it is aromatic. The protons of the non-cyclic compound **10** appear at 5.89 ppm, i.e. at −1.13 ppm from **9** and +1.47 ppm relative to **7**.[28] Finally, there is the unknown compound **6** (C_9H_6: 1,2,4,5,7,8-cyclononahexaene), recently discussed[13,29] which deserves to be studied in the present context.

There is an abundant bibliography on the adequacy of B3LYP calculations coupled with the GIAO/NICS ones to describe aromatic compounds. We have found that GIAO/B3LYP calculations adequately reproduce the relative ^{1}H chemical shifts of a large variety of aromatic compounds,[17] although when any kind of nuclei are considered, RHF calculations are slightly preferable.[30] Schleyer has demonstrated that the B3LYP approximation is suitable for GIAO (^{1}H) and NICS for a variety of compounds including phenylenes, azaannulenes and a typical antiaromatic compound, cyclobutadiene.[31–33] Other groups have shown that B3LYP is comparable to MP2, coupled with GIAO, for calculating relative ^{17}O chemical shifts,[34] while for ^{19}F chemical shifts, RHF is better than B3LYP.[35] For ^{1}H some authors found RHF better (bowl shaped hydrocarbons)[36] while other authors found the opposite (heteroaromatic compounds).[37] For pyrene carbocations,[38] carbenes,[39] phospholes,[40] GIAO (NICS)/B3LYP perform reasonably well. To the best of our knowledge, nobody has described great anomalies when calculating either NICS or absolute shieldings based on B3LYP calculations. It was very recently, that Chauvin et al.[12] reported very large and negative NICS for the dehydroannulene **5** (singlet, −53 ppm at the center of the ring). The most recent papers show a tendency to use DFT/GIAO as the standard procedure to calculate absolute shieldings,[41,42] although for some nuclei, HF/GIAO produced best results.[41] Note that in the case of [10]annulene, Schaeffer has pointed out that both DFT and MP2 calculations yield an incorrect order of stability for the different isomers and that only CCSD(T) calculations are able to reproduce the experimental results.[43]

The optimized geometry of **7a**(**7b**) corresponds to a planar structure and has C–C distances of 1.476 (1–2), 1.329 (2–3) and 1.266 Å (3–4) and bond orders (NBO, natural bond orders) of 1.078, 1.706 and 2.070, respectively. Clearly, the compound is better described by resonance structure **7b**.

We have gathered in Table 2 the calculated absolute shieldings and the experimental ^{1}H chemical shifts for a series of

Table 2. GIAO/B3LYP/6-31G* calculated σ^1H and experimental δ^1H (Ref.)

Compound	σ^1H	δ^1H	Ref. δ^1H	NICS
Cyclobutadiene (C_4H_4)	26.80	5.40	[a]	+25.8
Cyclopentadienyl anion ($C_5H_5^-$)	27.37	5.57	44	
Benzene (C_6H_6)	24.96	7.34	45	
Cycloheptatrienyl cation[b] ($C_7H_7^+$)	22.96	9.25	46	
Cyclooctatetraenyl dianion ($C_8H_8^=$)	27.52	5.69	47	
Cyclononatetraenyl anion ($C_9H_9^-$)	25.43	7.13	48	
Compound **12** protons H-3,11	25.26	7.91	19	+4.1
Compound **12** protons H-6,8,14,16	25.43	7.11	19	+4.1
Compound **12** protons H-7,15	25.92	6.58	19	+4.1
Ethylene (C_2H_4)	26.72	5.41	45	
Compound **6**	27.15	–	–	−7.84[c]
Compound **7**	45.17	4.42	25	+106.1
Compound **8**, H outer[d]	26.66	5.88	25	+2.9
Compound **8**, H inner	22.52	7.83	25	+2.9
Compound **9**	23.35	7.02	28	−10.4
Model **10**	26.57	5.89	28	
TMS	32.18	0.00		

[a] Schleyer has commented that the presence of three *t*-butyl groups in **11** does not affect the chemical shift of the remaining proton.[33]
[b] Known as tropylium cation.
[c] According to Rzepa[13] compound **6** in its C_3 symmetry form has a NICS(0)=−6.6 ppm. We have calculated a σ^1H=27.15 ppm close to that of cyclopentadienyl anion (σ^1H=27.37 ppm). Compound **6** is unknown, but there exists another isomer of C_9H_6 formula, called the neocarzinostatin chromophore, with a CH_2 group in the nine-membered ring.[49]
[d] There are two kinds of outer protons, three central and six lateral ones, the calculated value corresponds to a weighted average.

aromatic and antiaromatic hydrocarbons as well as some reference compounds.

3.1. Proton chemical shifts

To compare absolute shieldings and chemical shifts, the following compounds have been excluded from Table 2 data (besides compound **6** where no experimental results were available): the anomalous compound **7**, the inner protons of compound **8** as well as compound **9** which is structurally related to **7**. A regression using the remaining thirteen values of Table 2 led to the plot represented in Fig. 1, where the calculated δ^1H values were referred to TMS ($\delta^1H_{calc}=32.18-\sigma^1H$). Since the line went almost through the point corresponding to TMS, we have imposed that the intercept should be 0. The resulting equation is

$$\delta^1H_{exp} = (1.055 \pm 0.017)\delta^1H_{calc}, \qquad n = 13, \tag{1}$$

$$R^2 = 0.997.$$

This equation predicts for δ^1H of the unknown compound **6** a value of 5.3 ppm.

Olefinic compounds (ethylene and model **10**) as well as aromatic compounds (except compound **9**) behave normally falling on the regression line. Amongst the antiaromatic compounds, only the inner protons of **8** would deviate clearly if they were included in the regression. We attribute this fact to the congestion in the inner core of the molecule, that possibly the calculations do not take into account conveniently. There are many reports on the anomalies in ^{1}H chemical shifts in sterically crowded molecules.[50] Nevertheless, none of the excluded compounds is comparable to compound **7** in its 'abnormal behaviour', this is not because of its potential antiaromaticity, since **8** and **11**, both antiaromatic behave normally. We have considered three possible reasons to explain why **7** is so different from the remaining compounds.

1. The experimental value (4.42 ppm) does not correspond to **7** but to its valence isomer **2** (also a planar compound, calculated to be 20.3 kJ mol^{-1} more stable). For this compound, the calculation yields σ^1H=25.49 ppm (δ^1H_{calc}=6.69 ppm) that through Eq. (1) could be transformed into δ^1H=7.06 ppm a typical aromatic value. Note that compounds related to **7** have been shown to be stable and not to isomerize into structures of type **2**.[51]
2. That the compound is not an antiaromatic singlet but an aromatic triplet. The aromatic triplet (calculated unrestricted) lies 32.3 kJ mol^{-1} below the singlet and its calculated σ^1H is 23.58 ppm very close to the aromatic compound **9** (23.350 ppm). Therefore a signal close to 7 ppm (experimental for **9**) or 9.0 ppm (model fitted for **9**) should be expected, which is not the case. Caution should be taken with this aspect of our work. For instance, Zilberg and Haas have shown that for antiaromatic hydrocarbons, the lowest lying triplet is always higher in energy than the distorted ground singlet state.[52] It is possible that high-level calculations, of the CAS type,[52] modify our conclusions, particularly the relative stabilities of the singlet and triplet states.
3. That the anomaly is due to the use of DFT calculations. Actually, a GIAO/RHF/6-31G* calculation for **7a**(**7b**) yield σ^1H=30.69 (δ^1H_{calc}=1.49 ppm), which according to Eq. [1], corresponds to 1.58 ppm.

3.2. Nuclear independent chemical shifts

We have calculated the NICS values at 0 Å [NICS(0)] in the plane of the ring of compounds of Schemes 2 and 3 as well as compound **6** (Table 2). Remember that, according to Schleyer's convention, aromatic compounds have negative

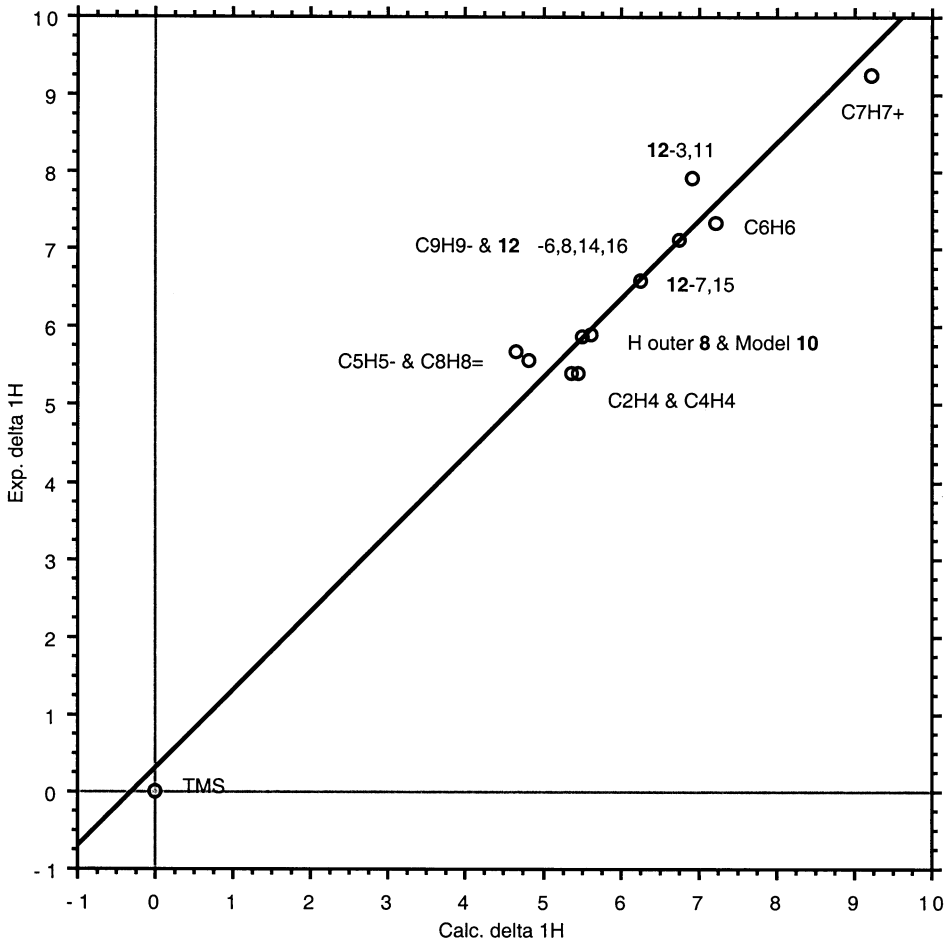
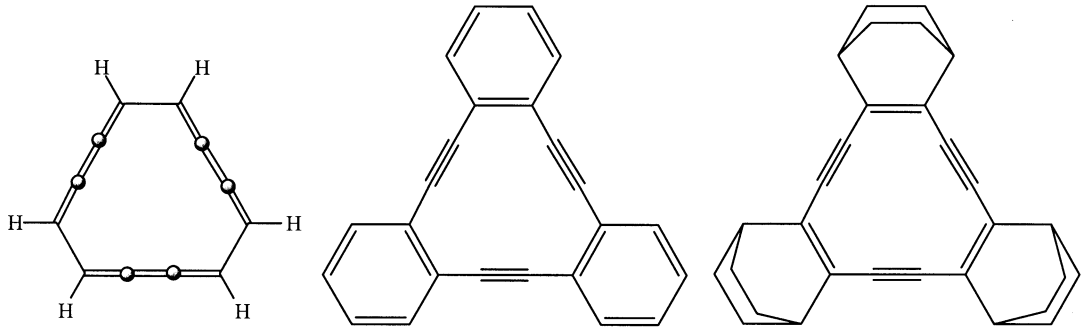


Figure 1. Plot of experimental δ^1H chemical shifts vs calculated σ^1H absolute shieldings (both in ppm).

NICS and antiaromatic compounds, positive ones, although the Gaussian series of programs used the opposite one. Schleyer reported for the NICS(0) of cyclobutadiene +27.6 ppm[3] and +25.9 ppm,[33] depending on the base used. If we take into account that the NICS(0) of benzene is about −10 ppm,[53] then, both **6** and **9** are typically aromatic. Compound **8** appears to be slightly antiaromatic, but the proximity of the inner H atoms could interfere with the calculation. The central ring of the aromatic Yoshida's hydrocarbon **12** is like a cyclooctatetraene (COT) and this results in an antiaromatic NICS(0).

Using this criteria compound **7** (+106.1 ppm) appears again completely different from all the others although consistent with the GIAO calculated σ^1H. A GIAO/RHF/6-31G* calculation of the NICS(0) of **7** yields a value of +23.3 ppm, comparable to cyclobutadiene (Table 2).

Substituted derivatives of **7**, which have been the subject of many studies, lack peripheral protons, but it is possible to compute their NICS(0) values. We have selected Tobe's benzannelated compound **3** and Komatsu's compound **13** (Scheme 4).[53] For the first one we have computed a



7 **3** **13**

Scheme 4. (*Z*,*Z*,*Z*)-1,5,9-Cyclododecatriene-3,7,11-triyne **7** and two derivatives.

NICS(0) value of +4.4 ppm, i.e. moderately antiaromatic, and for the second one +22.5 ppm, strongly antiaromatic. It seems that the periphery of **3** (18 π electrons) somewhat compensates the antiaromaticity of the center (12 π electrons). Fused derivative **13** is not so peculiar as **7**, may be it is difficult to accommodate a cumulenic structure similar to that of **7b**. An examination of the distances and NBO's of compounds **3** and **7** actually indicates that these compounds are better described as depicted in Scheme 4, i.e. **3a** and **13a**, instead of with the cumulene structures **3b** and **13b**.

4. Conclusions

Concerning compound **7**, the experimental value (4.42 ppm) can be compared to four situations: (i) to GIAO/B3LYP/6-31G* calculations that through Eq. (1) yield for **7**, −12.79 ppm; (ii) to GIAO/B3LYP/6-311++G** calculations for **7** that yield σ^1H=44.59 ppm and (via Eq. [1]] δ^1H=−12.20 ppm; (iii) to GIAO/B3LYP/6-31G* calculations for the valence isomer **2** that yield 7.06 ppm and (iv) to the triplet of **7** that corresponds δ^1H=8.98 ppm. Even if the triplet and the valence isomer were more stable than **7**, we are of the opinion that the experimental value corresponds to the ground state of the antiaromatic tridehydroannulene.

The valence isomer **2**, although more stable, must be separated from **7** by a high kinetic barrier to the isomerization. On the other hand, the triplet should be aromatic according to the calculated σ^1H.

Therefore, our conclusion of the anomaly of **7** lies mainly on the use of a DFT method, but also on the molecule itself. Curiously, the compound selected by Pople[26] in 1966 to study ring currents still deserves to be explored both in structural aspects and magnetic properties.

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References

1. Haley, M. M.; Pak, J. J.; Brand, S. C. *Top. Curr. Chem.* **1999**, *201*, 81–130. Krygowski, T. M.; Cyranski, M. K.; Czarnocki, Z.; Häfelinger, G.; Katritzky, A. R. *Tetrahedron* **2000**, *56*, 1783–1796. Cyranski, M. K.; Stepien, B. T.; Krygowski, T. M. *Tetrahedron* **2000**, *56*, 9663–9667.
2. Stanger, A. *J. Am. Chem. Soc.* **1991**, *113*, 8277–8280. Beckhaus, H.-D.; Faust, R.; Matzger, A. J.; Mohler, D. L.; Rogers, D. W.; Rüchardt, C.; Sawhney, A. K.; Verevkin, S. P.; Vollhardt, K. P. C.; Wolff, S. *J. Am. Chem. Soc.* **2000**, *122*, 7819–7820.
3. Gogonea, V.; Schleyer, P.vonR.; Schreiner, P. R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1945–1948.
4. Guihery, N.; Maynau, D.; Malrieu, J.-P. *New J. Chem.* **1998**, 281–286.
5. Lee, E. P. F.; Wright, T. G. *Phys. Chem. Chem. Phys.* **1999**, *1*, 219–225.
6. Krygowski, T. M.; Cyranski *Tetrahedron* **1999**, *55*, 11143–11148.
7. Bodwell, G. J.; Fleming, J. J.; Mannion, M. R.; Miller, D. O. *J. Org. Chem.* **2000**, *65*, 5360–5370.
8. Iyoda, M.; Fuchigami, K.; Kusaka, A.; Yoshida, T.; Yoshida, M.; Matsuyama, H.; Kuwatani, Y. *Chem. Lett.* **2000**, 860–861.
9. Tobe, Y.; Fujii, T.; Matsumoto, H.; Tsumuraya, K.; Noguchi, D.; Nakagawa, N.; Sonoda, M.; Naemura, K.; Achiba, Y.; Wakabayashi, T. *J. Am. Chem. Soc.* **2000**, *122*, 1762–1775.
10. Cyranski, M. K.; Stepien, B. T.; Krygowski, T. M. *Tetrahedron* **2000**, *56*, 9663–9667.
11. Nendel, M.; Goldfuss, B.; Houk, K. N.; Hafner, K. *THEOCHEM* **1999**, *461–462*, 23–28.
12. Godard, C.; Lepetit, C.; Chauvin, R. *Chem. Commun.* **2000**, 1833–1834. Lepetit, C.; Godard, C.; Chauvin, R. *New J. Chem.* **2001**, *25*, 572–580.
13. Martín-Santamaría, S.; Lavan, B.; Rzepa, H. S. *Chem. Commun.* **2000**, 1089–1090. Martín-Santamaría, S.; Rzepa, H. S. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2372–2377.
14. Martín-Santamaría, S.; Lavan, B.; Rzepa, H. S. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1415–1417.
15. Stevenson, C. D.; Kurth, T. L. *J. Am. Chem. Soc.* **2000**, *122*, 722–723.
16. Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Ya. *Aromaticity and Antiaromaticity*, Wiley: New York, 1994 p 71.
17. Alkorta, I.; Elguero, J. *New J. Chem.* **1998**, *22*, 381–385.
18. Schleyer, P.v.R.; Puchta, R.; Boggavarapu, K.; Mauksch, M.; Eikema Hommes, N.v.; Alkorta, I.; Elguero, J. Unpublished results.
19. Yoneda, S.; Shibata, M.; Kida, S.; Yoshida, Z.; Kai, Y.; Miki, K.; Kasai, N. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 63–64.
20. Hariharan, P. A.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222.
21. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789. (c) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*, Oxford: New York, 1989. (d) Bartolotti, L. J.; Fluchick, K. Reviews in Computational Chemistry, K.B., Lipkowitz, D.B., Boyd, Eds.; VCH: New York, 1996; Vol. 7, pp. 187–216.
22. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Zakrzewski, V.G.; Montgomery, J.A.; 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, Inc.: Pittsburgh, PA, 1998.
23. McIver, J. W.; Komornicki, A. K. *J. Am. Chem. Soc.* **1972**, *94*, 2625–2633.
24. (a) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789–807. (b) London, F. *J. Phys. Radium* **1937**, *8*, 397–409.

25. Balaban, A. T.; Banciu, M.; Ciorba, V. *Annulenes, Benzo-, Hetero-, Homo-Derivatives and their Valence Isomers*, Vol. I; CRC: Boca Raton, Florida, 1987 pp 92 and 103.
26. Pople, J. A.; Untch, K. G. *J. Am. Chem. Soc.* **1966**, *88*, 4811–4815.
27. Diederich, F.; Gobbi, L. *Topics in Current Chemistry*, Vol. 201; Springer: Berlin, 1999 pp 43–79.
28. Okamura, W. H.; Sondheimer, F. *J. Am. Chem. Soc.* **1967**, *89*, 5991–5992.
29. Yavari, I.; Norouzi-Arasi, H.; Nori-Shargh, D.; Fallah-Bagher-Shaidaei, H. *J. Chem. Res. (S)* **1999**, 154–155.
30. Alkorta, I.; Elguero, J. *Struct. Chem.* **1998**, *9*, 187–202.
31. Schulman, J. M.; Disch, R. L.; Jiao, H.; Schleyer, P. v. R. *J. Phys. Chem. A* **1998**, *102*, 8051–8055.
32. Bettinger, H. F.; Sulzbach, H. M.; Schleyer, P. v. R.; H.F., Schaefer *J. Org. Chem.* **1999**, *64*, 3278–3280.
33. Balci, M.; McKee, M. L.; Schleyer, P. v. R. *J. Phys. Chem. A* **2000**, *104*, 1246–1255.
34. Aminova, R. M.; Schamov, G. A.; Aganov, A. V. *THEOCHEM* **2000**, *498*, 233–246.
35. Tanuma, T.; Irisawa, J. *J. Fluorine Chem.* **1999**, *99*, 157–160.
36. Ferrer, S. M.; Molina Molina, J. *J. Comput. Chem.* **1999**, *20*, 1412–1431.
37. Dokalik, A.; Kalchhauser, H.; Mikenda, W.; Schweng, G. *Magn. Reson. Chem.* **1999**, *37*, 895–902.
38. Laali, K. K.; Hollenstein, S.; Galembeck, S. E.; Nakamura, Y.; Nishimura, J. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2129–2132.
39. Alder, R. W.; Blake, M. E.; Oliva, J. M. *J. Phys. Chem. A* **1999**, *103*, 11200–11211.
40. Delaere, D.; Dransfeld, A.; Nguyen, M. T.; Vanquickenborne, L. G. *J. Org. Chem.* **2000**, *65*, 2631–2636.
41. Eloranta, J.; Hu, J.; Suontamo, R.; Kolehmainen, E.; Knuutinen, J. *Magn. Reson. Chem.* **2000**, *38*, 987–993.
42. Corbally, R. P.; Mehta, L. K.; Parrick, J.; Short, E. L. *Magn. Reson. Chem.* **2000**, *38*, 1034–1036.
43. King, R. A.; Crawford, T. D.; Stanton, J. F.; Schaeffer, H. F. *J. Am. Chem. Soc.* **1999**, *121*, 10788–10793.
44. Fraenkel, G.; Carter, R. E.; McLachlan, A.; Richards, J. H. *J. Am. Chem. Soc.* **1960**, *82*, 5846–5850.
45. Abraham, R. J.; Canton, M.; Reid, M.; Griffiths, L. *J. Chem. Soc., Perkin Trans. 2* **2000**, 803–812.
46. Sebastian, J. F.; Grunwell, J. R. *Can. J. Chem.* **1971**, *49*, 1779–1781.
47. Katz, T. J. *J. Am. Chem. Soc.* **1960**, *82*, 3785–3786.
48. Boche, G.; Martens, D.; Danzer, W. *Angew. Chem., Int. Ed. Engl.* **1969**, *12*, 984–984.
49. Cramer, C. J.; Squires, R. R. *Org. Lett.* **1999**, *1*, 215–218.
50. Peeling, J.; Goodwin, B. W.; Schaefer, T.; Rowbotham, J. B. *Can. J. Chem.* **1973**, *51*, 2110–2117. Hon, F. H.; Tanida, H.; Tidwell, T. T. *J. Org. Chem.* **1972**, *37*, 1778–1782.
51. Nishinaga, T.; Kawamura, T.; Komatsu, K. *J. Org. Chem.* **1997**, *62*, 5354–5362.
52. Zilberg, S.; Haas, Y. *J. Phys. Chem. A* **1998**, *102*, 10851–10859.
53. Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.