

# Are nucleus-independent (NICS) and $^1\text{H}$ NMR chemical shifts good indicators of aromaticity in $\pi$ -stacked polyfluorenes?

Sílvia Osuna <sup>a</sup>, Jordi Poater <sup>b,\*</sup>, Josep M. Bofill <sup>c</sup>, Pere Alemany <sup>d</sup>, Miquel Solà <sup>a,\*</sup>

<sup>a</sup> Institut de Química Computacional and Departament de Química, Universitat de Girona, Campus de Montilivi, 17071 Girona, Catalonia, Spain

<sup>b</sup> Afdeling Theoretische Chemie, Scheikundig Laboratorium der Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands

<sup>c</sup> Departament de Química Orgànica and Centre de Recerca en Química Teòrica (CeRQT), Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Catalonia, Spain

<sup>d</sup> Departament de Química Física and Centre de Recerca en Química Teòrica (CeRQT), Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Catalonia, Spain

Received 26 May 2006

Available online 6 July 2006

## Abstract

We have analyzed the change of local aromaticity in a series of polyfluorene compounds with the increase of the number of  $\pi$ -stacked layers. The local aromaticity of the aromatic and non-aromatic rings of polyfluorenes remains unchanged when going from one to four layers of  $\pi$ -stacked rings according to HOMA, PDI, and FLU aromaticity descriptors. On the contrary, experimental  $^1\text{H}$  NMR chemical shifts indicate a reduction of the aromaticity of  $\pi$ -stacked rings with the increase of the number of layers. Calculated NICS also show a change of aromaticity, but opposite to the tendency given by the  $^1\text{H}$  NMR chemical shifts. We show that this increase (decrease) of local aromaticity in superimposed aromatic rings indicated by NICS ( $^1\text{H}$  NMR) is not real but the result of the coupling between the magnetic fields generated by the  $\pi$ -stacked rings.

© 2006 Elsevier B.V. All rights reserved.

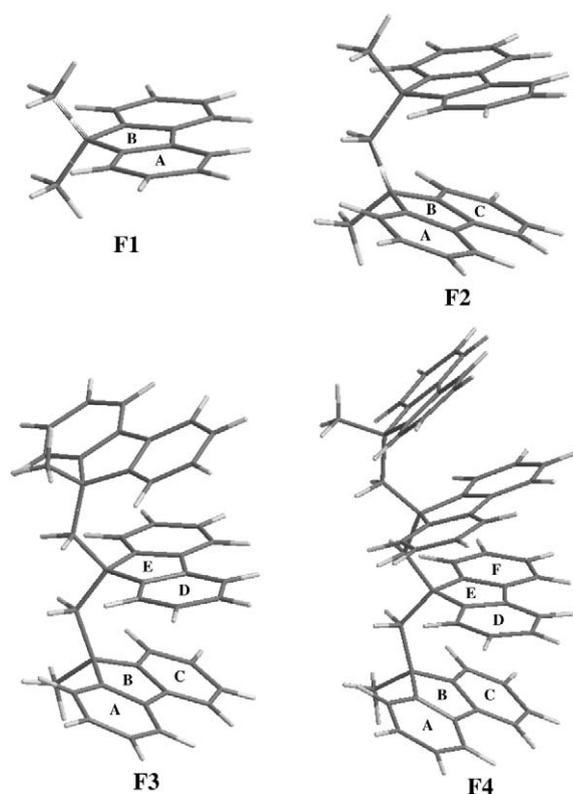
$\pi$ -Stacking interactions are present in important organic and biological systems, i.e. stacked DNA Watson–Crick bases [1]. Structural and functional modeling of  $\pi$ -stacked species has been a subject of great interest in bioorganic chemistry in the quest for a better comprehension of the origin of the  $\pi$ -stacking interactions between aromatic rings [2]. Model compounds play a key role in the understanding of the structural, electronic, magnetic, and spectroscopic properties of  $\pi$ -stacked species. Up to now only very few  $\pi$ -stacked molecules with multiple layers that can be used as experimental models of these interactions have been synthesized [3]. Among them, one of the most important is a versatile class of  $\pi$ -stacked polyfluorenes (see Scheme 1) whose syntheses have been recently reported

[4,5]. The appearance of these novel experimental compounds [6] has prompted the theoretical and computational research. In this context, Kim et al. [7], by means of *ab initio* methods, have analyzed the stacking effect of polyfluorenes on the  $^1\text{H}$  NMR chemical shifts and have successfully reproduced the experimental structures obtained both in solution and in crystal.

An interesting aspect of these  $\pi$ -stacked polyfluorenes that has not been analyzed yet is the change in aromaticity of the five- and six-membered rings (five- and six-MRs) with the increase in the number of layers. The local aromaticity of the five- and six-MRs of polyfluorenes may be modified by the  $\pi$ -electron transfer occurring between the multiple layers. Aromaticity is related to the energy stabilization due to the  $\pi$ -electron delocalization governed by both the connectivity of the molecular graph and cyclic effects. This energy stabilization is considered with respect to an ideal ‘dendrimer of the same connectivity’ [8]. As

\* Corresponding authors. Fax: +34 972 418356.

E-mail addresses: [J.Poater@few.vu.nl](mailto:J.Poater@few.vu.nl) (J. Poater), [miquel.sola@udg.es](mailto:miquel.sola@udg.es) (M. Solà).



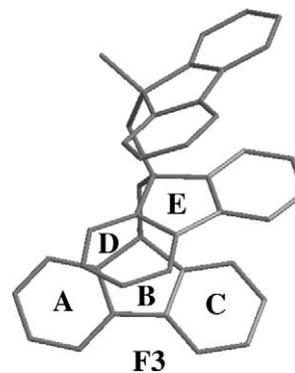
Scheme 1.

shown by several authors [9], the local aromaticity of a given aromatic ring can be analyzed from the values of the chemical shifts of the  $^1\text{H}$  NMR spectra. Thus, according to the experimental  $^1\text{H}$  NMR spectra of polyfluorenes F1–F4 (see Scheme 1) reported by Rathore et al. [4], there is a reduction of aromaticity of the five- and six-MRs when going from F1 to F4. The  $^1\text{H}$  NMR chemical shifts of the F2 (6.81–7.12 ppm) aromatic protons are upfielded with respect to F1 (7.31–7.80), and consecutively for F3 (6.27–7.12) and F4 (6.09–6.99) systems [4]. It is also observed in the experimental  $^1\text{H}$  NMR spectra that those protons of F3 and F4 belonging to the intermediate fluorene moiety are more upfielded than those of the external layers. These upfielded  $^1\text{H}$  NMR chemical shifts when going from F1 to F4 prove the existence of  $\pi$ -stacking between the fluorene moieties [7]. Nevertheless, it should be pointed out that, very recently, two works [10,11] have shown that  $^1\text{H}$  NMR chemical shifts are not always reliable aromaticity indicators, especially for polycyclic systems, like in this case. In particular, it has been found that traces of magnetizability and of magnetic shielding at the hydrogen nuclei are biased due to parallel  $\pi$ -ring currents also affecting the in-plane components. Consequently, some authors suggest using only the out-of-plane shielding component for aromaticity analyses [12,13].

Because of the drawbacks of  $^1\text{H}$  NMR chemical shifts as indicators of aromaticity, we have decided to reexamine the local aromaticity of these interesting systems by using four

aromaticity descriptors based on different manifestations of aromaticity. Moreover, the use of more than a single indicator in aromaticity analysis has been recommended [14–17] because of the multidimensional character of this property [18,19]. In particular, we have applied the geometry-based harmonic oscillator model of aromaticity (HOMA) [20] index, the magnetic-based nucleus-independent chemical shift (NICS) [16,21], and the electronic-based *para*-delocalization (PDI) [14] and aromatic fluctuation indexes (FLU) [22]. For the indexes used, we have that the more negative the NICS values, the lower the FLU index, and the higher the HOMA and PDI results, the more aromatic the rings are.

We have first obtained the optimized geometries of the four  $\pi$ -stacked polyfluorenes (F1–F4), at the B3LYP/6-31G\* level, with *syn* conformation and without symmetry constraints. We are aware that density functional density methods do not work properly for describing the energetics of the  $\pi$ - $\pi$  stacking interactions [23], as being the electron correlation very important for obtaining accurate interaction energies [24]. However, the geometries obtained with B3LYP are in line with previous X-ray [4] and *ab initio* [7] structures, with a clear helical shape (see Scheme 2 for F3). In addition, since  $^1\text{H}$  NMR chemical shifts obtained at the B3LYP/6-31G\* level of theory are reasonable [7] as compared to experimental data [4], we also expect that our B3LYP/6-31G\* NICS calculations are within acceptable limits. As both B3LYP/6-31G\* geometrical parameters and stabilities of these species have been already discussed [7], no further insight into the structures or energies will be done. The following local aromaticity analysis performed on optimized systems has been carried out with the help of the GAUSSIAN 03 [25] and AIMPAC [26] software packages using the B3LYP/6-31G\* level of theory. The latter program has been used to compute the delocalization indices (DIs) needed to calculate the PDI and FLU indices. Calculation of DIs at the DFT level of theory cannot be performed exactly because the electron-pair density is not available at this level of theory. As a reasonable approximation, we have used the Kohn–Sham orbitals obtained from DFT to calculate HF-like DIs [15].



Scheme 2.

Table 1  
B3LYP/6-31G\* PDI (in electrons), FLU, HOMA, and NICS (in ppm) for F1–F4 polyfluorenes

System	Ring	PDI <sup>a</sup>	FLU	HOMA	NICS(0) <sup>b</sup>	NICS(1) <sup>b</sup>	NICS(-1) <sup>b</sup>
F1	A <sup>1</sup>	0.093	0.001	0.956	-8.67	-10.34	-10.34
	B <sub>5</sub> <sup>1</sup>	-	0.055	-1.421	1.45	-1.98	-1.98
F2	A <sup>1</sup>	0.092	0.002	0.966	-8.95	-10.70	-10.61
	B <sub>5</sub> <sup>1</sup>	-	0.055	-1.453	0.62	-2.84	-3.08
	C <sup>1</sup>	0.092	0.002	0.963	-9.46	-11.29	-11.04
F3	A <sup>1</sup>	0.091	0.002	0.966	-9.08	-10.82	-10.72
	B <sub>5</sub> <sup>1</sup>	-	0.056	-1.460	0.26	-3.64	-3.17
	C <sup>1</sup>	0.092	0.002	0.963	-9.71	-11.53	-11.28
	D <sup>2</sup>	0.090	0.002	0.967	-9.73	-11.32	-11.54
	E <sub>5</sub> <sup>2</sup>	-	0.055	-1.459	0.10	-3.70	-3.65
F4	A <sup>1</sup>	0.091	0.002	0.967	-9.43	-11.26	-10.99
	B <sub>5</sub> <sup>1</sup>	-	0.056	-1.468	0.06	-3.83	-3.32
	C <sup>1</sup>	0.091	0.002	0.963	-9.83	-11.68	-11.39
	D <sup>2</sup>	0.090	0.002	0.964	-10.59	-12.44	-12.30
	E <sub>5</sub> <sup>2</sup>	-	0.055	-1.460	-0.27	-4.24	-3.89
	F <sub>5</sub> <sup>2</sup>	0.090	0.002	0.970	-9.72	-11.66	-11.32

Superscripts 1 and 2 refer to the fluorene layer to which the ring correspond, and subscript 5 refers to five-MRs.

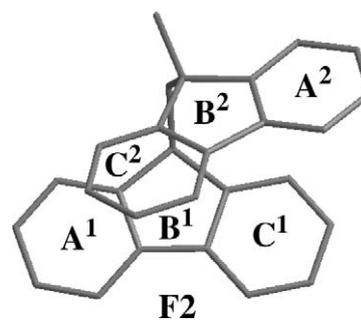
<sup>a</sup> PDI can only be calculated for six-MRs.

<sup>b</sup> NICS(0) corresponds to NICS calculated at the center of the corresponding rings, whereas NICS(1) is calculated at 1 Å above the rings towards the center of the helix structure, and NICS(-1) is calculated at 1 Å towards outside the helix.

All aromatic data obtained for the four molecules under study is enclosed in Table 1. Only non-equivalent rings with respect to symmetry operations have been included (see Scheme 1 for labeling). First of all, six-MRs are shown to present a noticeable aromatic character by all criteria. The values of all indices do not differ much from those of benzene at the same level of theory (PDI = 0.105 electrons, FLU = 0.000, HOMA = 0.984, NICS(0) = -9.67 ppm, and NICS(1) = -11.20 ppm), although all of them indicate an expected somewhat smaller aromaticity for the six-MRs of F1 as compared to that of benzene. PDI, FLU, and HOMA consider that local aromaticity of six-MRs is kept almost constant with the increase of the size of the systems for both internal and external rings with very minor changes. However, NICS(0) shows an increase of aromaticity from F1 to F4. And the same trend is also given by NICS(1), which in principle should better reflect the  $\pi$  aromaticity [13]. This change in local aromaticity indicated by NICS is unexpected taking into account the identical connectivity of the molecular graph in all six-MRs of polyfluorenes that should lead to similar  $\pi$ -electron delocalization and magnetic properties.

The NICS results indicate a larger increase of aromaticity when going from F1 to F2 for ring C than A. This difference can be qualitatively explained by the empirical model of shielding for benzene proposed and determined by Johnson and Bovey using a current loop model [28]. As previously observed in [*n*]helicenes [17] and [2.2]paracyclophane [29], the reduction of NICS(0) upon  $\pi$ -stacking is caused by the coupling between, i.e. the sum of, the magnetic fields created by the current densities of the rings of a given fluorene moiety placed over or below the other. Since the center of ring C of one layer has the centers of rings A

(4.184 Å) and C (4.675 Å) of the other layer at closer distances than ring A (at 6.578 and 4.192 Å from A and C rings, respectively), the couplings are more important for ring C than A (see Scheme 3). Therefore, the increase of local aromaticity in aromatic rings of  $\pi$ -stacked polyfluorenes indicated by NICS is not real but the result of the coupling between the magnetic fields generated by the two stacked moieties. The opposite trend given by NICS as compared to <sup>1</sup>H NMR chemical shifts cannot be considered unexpected, as, first, the corresponding chemical shifts are in both cases upfielded and, second, they are calculated at two different points of the system [30]. Moreover, as found experimentally for the <sup>1</sup>H NMR chemical shifts [4], the change of NICSs is more accused for six-MRs closer to the rotation axis, especially those belonging to middle layers of polyfluorenes F3 and F4 that have a superimposed ring above and another below, which accentuates the coupling between the magnetic field created by the ring



Scheme 3.

under study and those fields generated by the superimposed rings, thus causing an extra artificial increase of the local aromaticity according to NICS values. In line with these results, it is also worth noticing that there are five rings with a NICS higher (more negative) than that of benzene itself ( $-9.67$  ppm), even though benzene is considered to be the most aromatic system among polycyclic aromatic hydrocarbons. Finally, as expected, NICS(1) values are always more negative than NICS(-1) ones, as the former are calculated in points inside the helix, thus being more influenced by the magnetic fields of rings from other layers.

On the other hand, it must be noticed that five-MRs are considered non-aromatic by all aromaticity criteria, in line with previously analyzed systems also containing five-MRs [14]. As stated for the six-MRs, the values of FLU and HOMA of these five-MRs remain almost constant all along the series, from F1 to F4. And again, NICS shows a slight increase of aromaticity with the size of the system. Indeed, the five-MRs change from slightly antiaromatic in F1 to slightly aromatic in F4 according to NICS(0). This increase of aromaticity as before is fictitious and has to be attributed to the magnetic coupling of the induced magnetic fields of the five-MR and the superimposed rings of the adjacent fluorene layers.

As a whole, to the best of our knowledge, this is one of the first aromaticity analyses of a system with more than two superimposed molecular layers [27]. Aromaticity criteria show that six-MRs of polyfluorenes are aromatic, whereas five-MRs are not. Further, geometry- and electronic-based criteria consider that aromaticity of fluorene is not affected by increasing the number of fluorene layers. In addition, we have checked that, as expected, aromatic stabilization energy (ASE) values [31] indicate that local aromaticity remains also unchanged when going from F1 (ASE =  $-34.94$  kcal mol $^{-1}$ ) to F2 (ASE =  $-34.66$  kcal mol $^{-1}$ ), with an insignificant change of less than  $0.3$  kcal mol $^{-1}$  [32]. That is, the superposition of fluorene layers does not affect the ASE of a given six-MR and, therefore, its corresponding aromaticity is kept invariant. On the contrary, NICS values yield an increase of local aromaticity that is not real and has to be attributed to magnetic couplings with other rings placed above or below, which influences the chemical shift of the dummy atom where NICS is calculated. Finally, experimental  $^1\text{H}$  NMR chemical shifts also indicate a change of aromaticity from F1 to F4 due to magnetic couplings. Although it is well-known that a simple interpretation of aromaticity based on  $^1\text{H}$  NMR is not applicable in  $\pi$ -stacked systems [34,35], it is worth showing that  $^1\text{H}$  NMR results provide the opposite trend in aromaticity to that given by NICS. As a whole, it is seen how very diverse energetic (ASE), geometric (HOMA) and electronic (PDI and FLU) based aromaticity criteria consider aromaticity constant with the superposition of fluorene layers, whereas only magnetic-based criteria give the opposite trend. Therefore, the present study shows that NICS and  $^1\text{H}$  NMR chemical shifts must be used with caution as descriptors of aromaticity for species having  $\pi$ -stacked aromatic rings.

## Supplementary data

Supporting information available B3LYP/6-31G\* energies and optimized cartesian  $xyz$  coordinates for the F1–F4 species, together with the corresponding values for the species needed to compute the reported ASE values.

## Acknowledgements

Financial help has been furnished by the Spanish MEC Projects No. CTQ2005-08797-C02-01/BQU, CTQ2005-08123-C02-01, and CTQ2005-01117/BQU and by the DURSI Projects No. 2005SGR-00238, 2005SGR-00036, and 2005SGR-00111. P.A. is indebted to the Departament d'Universitats, Recerca i Societat de la Informació (DURSI) of the Generalitat de Catalunya for financial support through the Distinguished University Research Promotion awarded in 2002. J.P. also thanks the DURSI for the post-doctoral fellowship 2005BE00282. We also thank the Centre de Supercomputació de Catalunya (CESCA) for partial funding of computer time. The authors also thank Prof. J.J. Dannenberg for fruitful discussions.

## References

- [1] J.D. Watson, F.H.C. Crick, *Nature* 171 (1953) 737.
- [2] H. Adams, C.A. Hunter, K.R. Lawson, J. Perkins, S.E. Spey, C.J. Urch, J.M. Sanderson, *Chem. Eur. J.* 7 (2001) 4863.
- [3] W. Grimme, H.T. Kaemmerling, J. Lex, R. Gleiter, J. Heinze, M. Dietrich, *Angew. Chem., Int. Ed. Engl.* 30 (1991) 205.
- [4] R. Rathore, S.H. Abdelwahed, I.A. Guzei, *J. Am. Chem. Soc.* 125 (2003) 8712.
- [5] T. Nakano, T. Yade, *J. Am. Chem. Soc.* 125 (2003) 15474.
- [6] R. Rathore, S.H. Abdelwahed, M.K. Kiesewetter, R.C. Reiter, C.D. Stevenson, *J. Phys. Chem. B* 110 (2006) 1536.
- [7] W.S. Kim, J. Kim, J.K. Park, S. Mukamel, S.K. Rhee, Y.K. Choi, J.Y. Lee, *J. Phys. Chem. B* 109 (2005) 2686.
- [8] A. Shurki, P.C. Hiberty, F. Dijkstra, S. Shaik, *J. Phys. Org. Chem.* 16 (2003) 731.
- [9] R.H. Mitchell, *Chem. Rev.* 101 (2001) 1301.
- [10] C.S. Wannere, C. Corminboeuf, W.D. Allen, H.F. Schaeffer III, P.v.R. Schleyer, *Org. Lett.* 7 (2005) 1457.
- [11] F. Faglioni et al., *Org. Lett.* 7 (2005) 3457.
- [12] C. Corminboeuf, T. Heine, G. Seifer, P.v.R. Schleyer, J. Weber, *Phys. Chem. Chem. Phys.* 6 (2004) 273.
- [13] P. Lazzaretti, *Phys. Chem. Chem. Phys.* 6 (2004) 217.
- [14] J. Poater, M. Solà, M. Duran, X. Fradera, *Chem. Eur. J.* 9 (2003) 400.
- [15] J. Poater, M. Duran, M. Solà, B. Silvi, *Chem. Rev.* 105 (2005) 3911.
- [16] Z. Chen, C.S. Wannere, C. Corminboeuf, R. Puchta, P.v.R. Schleyer, *Chem. Rev.* 105 (2005) 3842.
- [17] G. Portella, J. Poater, J.M. Bofill, P. Alemany, M. Solà, *J. Org. Chem.* 70 (2005) 2509, erratum *ibid.*, *J. Org. Chem.* 70 (2005) 4560.
- [18] A.R. Katritzky, K. Jug, D.C. Oniciu, *Chem. Rev.* 101 (2001) 1421.
- [19] M.K. Cyrański, T.M. Krygowski, A.R. Katritzky, P.v.R. Schleyer, *J. Org. Chem.* 67 (2002) 1333.
- [20] J. Kruszewski, T.M. Krygowski, *Tetrahedron Lett.* 13 (1972) 3839.
- [21] P.v.R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N.J.R. van Eikema Hommes, *J. Am. Chem. Soc.* 118 (1996) 6317.
- [22] E. Matito, M. Duran, M. Solà, *J. Chem. Phys.* 122 (2005) 014109.
- [23] T.P. Tauer, C.D. Sherril, *J. Phys. Chem. A* 109 (2005) 10475.
- [24] S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, K. Tanabe, *J. Am. Chem. Soc.* 124 (2002) 104.

- [25] M.J. Frisch et al., GAUSSIAN 03, Revision C.01 ed., Gaussian Inc., Pittsburgh, PA, 2003.
- [26] F.W. Biegler-König, R.F.W. Bader, T.-H. Tang, *J. Comput. Chem.* 3 (1982) 317.
- [27] D. Sebastiani, *ChemPhysChem* 7 (2006) 164.
- [28] C.E. Johnson, F.A. Bovey, *J. Chem. Phys.* 29 (1958) 1012.
- [29] J. Poater, J.M. Bofill, P. Alemany, M. Solà, *J. Org. Chem.* 71 (2006) 1700.
- [30] R.H. Mitchell, *Chem. Rev.* 101 (2001) 1301.
- [31] M.K. Cyrański, *Chem. Rev.* 105 (2005) 3773.
- [32] We have computed the ASE of a six-MR of the polyfluorene from the isodesmic reaction depicted in Chart 2 of Ref. [33], at the B3LYP/6-31G\* level.
- [33] R.W.A. Havenith et al., *J. Am. Chem. Soc.* 124 (2002) 2363.
- [34] P. Gettins, D. Givol, R.A. Dwek, *Biochem. J.* 173 (1978) 713.
- [35] P.R. Ashton, D. Philp, N. Spencer, J.F. Stoddart, D.J. Williams, *J. Chem. Soc., Chem. Commun.* (1994) 181.