



# Dipole (hyper)polarizabilities of fluorinated benzenes: An ab initio investigation

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## ABSTRACT

Relative stabilities, dipole moments and response electric properties of fluorinated benzenes have been studied using Hartree–Fock (HF) and correlated second-order Møller–Plesset perturbation theory (MP2) with the Sadlej's POL basis set. At the highest MP2/POL level, on passing from benzene to hexafluorobenzene the electronic mean polarizability value increases by only 3%, whereas the difference on the polarizability anisotropy is comparatively larger (+19%). The polarizability anisotropy of fluorobenzenes depends on the fluorination, increasing progressively with the increases of the number of fluorine atoms, following a near-additive atomic contribution law. Dipole moments and first-order hyperpolarizabilities among the investigated isomers differ up to a factor of two, these properties being potentially useful to discriminate the fluorobenzene isomers. Hyperpolarizability differences between the fluorinated isomers have been elucidated using hyperpolarizability density analyses. Electron correlation effects evaluated at the MP2 level are especially important for the first-order hyperpolarizabilities, increasing the HF values by 20–30%.

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## 1. Introduction

Fluorine-based organic compounds are widely used in industries to produce precursors for medicinal and agricultural applications [1–3]. Owing to the noticeable electronegativity difference between carbon and fluorine atoms, C–Fs are generally strong polar bonds. It is especially evident for fluoroaromatics, where H/F exchanges drastically perturb electrostatic distributions [4,5]. Addition of fluorine atoms is expected to decrease the partial negative charge above the aromatic ring, thus reducing the attractive electrostatic force between aromatic molecules and diminishing the binding energy with cationic partners. However, there are indications showing that fluorine atoms are actively involved in the binding of fluoroaromatic drugs to proteins and drug receptors, with promising properties for pharmaceutical applications [6,7].

Fluorobenzenes, are the smallest fluorinated aromatic compounds, being of great interest in the research of anesthetic substances [8]. Aromaticity of the series of fluorinated benzenes was explored by means of nucleus independent chemical shift calculations [5,9], extra cyclic resonance energy [5] and homostructural reactions [10]. Aromatic–aromatic and cation–aromatic noncovalent interactions are of fundamental importance for aromatic and cationic amino acids in determining functionality and stability of proteins [11,12]. The role of molecular polarizability and other electric properties, especially dipole and quadrupole moments of

fluoroaromatics, can be crucial in binding of drugs to active sites [13]. Dipole moments and polarizabilities of fluorobenzenes were the subject of many experimental and theoretical studies [13–23].

In the present work dipole moments and electronic dipole (hyper)polarizabilities of benzene (**B**), fluorobenzene (**FB**), 1,2-difluorobenzene (**1,2-DFB**), 1,3-difluorobenzene (**1,3-DFB**), 1,4-difluorobenzene (**1,4-DFB**), 1,2,3-trifluorobenzene (**1,2,3-TrFB**), 1,2,4-trifluorobenzene (**1,2,4-TrFB**), 1,3,5-trifluorobenzene (**1,3,5-TrFB**), 1,2,3,4-tetrafluorobenzene (**1,2,3,4-TeFB**), 1,2,3,5-tetrafluorobenzene (**1,2,3,5-TeFB**), 1,2,4,5-tetrafluorobenzene (**1,2,4,5-TeFB**), pentafluorobenzene (**PFB**) and hexafluorobenzene (**HFB**) are determined theoretically by using ab initio methods. The main aim is to characterize and analyze the electric properties in relation to the number and position of the fluorine atoms in the benzene ring. Very little is known about the hyperpolarizabilities of fluorobenzenes. To the best of our knowledge, experimental and computational studies on first-order hyperpolarizabilities are available only for **FB** and **PFB** [16,18,20,23,24]. The electronic hyperpolarizabilities are used as molecular descriptors in QSPR studies beside to the commonly employed electric properties such as polarizabilities, dipole, quadrupole and octupole moments [25–27]. Recently, Jameh-Bozorgi and Beigi theoretically investigated dipole moments and polarizabilities of fluorothiophenes as promising materials to build conducting polymers [28]. The rest of the paper is organized as follows: the computational methodologies are described in Section 2. The relative stabilities, basis set effects on the electric properties, dipole moments and electronic (hyper)polarizabilities are presented and discussed in Section 3. Finally our conclusions are summarized in Section 4.

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## 2. Computational details

The geometries of the investigated compounds (Fig. 1) were optimized in gas phase at DFT level using the B97-1 functional [29] with the 6-311G\*\* basis set [30]. The B97-1 method in combination with basis sets of triplet-zeta quality was previously employed with success for geometry optimization of cyclic compounds [31–33]. Dipole moment components ( $\mu_i$ ), static electronic polarizability ( $\alpha_{ij}$ ) and first-order hyperpolarizability tensor components ( $\beta_{ijk}$ ) were computed analytically at the Hartree–Fock (HF) level within the time-dependent HF (TD-HF) theory, respectively, as first, second and third derivatives of energy ( $E$ ) with respect to the Cartesian components of electric field ( $F$ ) [34,35]:

$$E(F) = E(0) - \sum_i \mu_i F_i - \frac{1}{2} \sum_{ij} \alpha_{ij} F_i F_j - \frac{1}{6} \sum_{ijk} \beta_{ijk} F_i F_j F_k \dots \quad (1)$$

$$\mu_i = - \left[ \frac{\partial E(F)}{\partial F_i} \right]_{F \rightarrow 0}, \quad \alpha_{ij} = - \left[ \frac{\partial^2 E(F)}{\partial F_i \partial F_j} \right]_{F \rightarrow 0}, \quad (2)$$

$$\beta_{ijk} = - \left[ \frac{\partial^3 E(F)}{\partial F_i \partial F_j \partial F_k} \right]_{F \rightarrow 0}$$

It is well-known that the electronic (hyper)polarizabilities are significantly affected by electron correlation effects [36–43]. Thus in the present work we also performed calculations at the correlated second-order Møller–Plesset perturbation theory (MP2) within the frozen-core approximation [30]. The MP2 dipole moment and (hyper)polarizability values were computed numerically by means of the finite field (FF) procedure described by Kurtz et al. [44], using an  $F$  value of 0.005 a.u. The accuracy of the FF approach was checked at the HF level, by comparing the properties obtained by the analytical and numerical computations. It is widely recognized in literature that, for an accurate (hyper)polarizability prediction it is necessary the use of flexible basis sets, including polarized and diffuse functions [42,43,45,46]. All the calculations presented here were carried out using the Sadlej's POL basis set [47]. It consists of a [10s5p2d/5s3p2d] contraction for the first-row atoms (carbon and fluorine) and a [5s2p/3s2p] contraction for hydrogen. This basis set was specifically designed to accurately determine response electric properties. The POL basis set is available from the EMLS basis set library [48,49] and was previously employed for (hyper)polarizability calculations of the  $\text{CH}_{4-n}\text{F}_n$  ( $n = 0-4$ ) series of compounds [50] and  $\pi$ -conjugated molecules [51–55].

In the present work we report dipole moments ( $\mu$ ), mean polarizabilities ( $\langle \alpha \rangle$ ), polarizability anisotropies ( $\Delta_1 \alpha$ ,  $\Delta_2 \alpha$ ,  $\Delta_3 \alpha$ ), mean first-order hyperpolarizabilities ( $\beta_{vec}$ ), which are rotationally invariant quantities [56–60]:

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \quad (3)$$

$$\langle \alpha \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (4)$$

$$\Delta \alpha_1 = \frac{1}{2} (\alpha_{xx} + \alpha_{yy}) - \alpha_{zz} \quad (5)$$

$$\Delta \alpha_2 = \left\{ \frac{1}{2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2)] \right\}^{1/2} \quad (6)$$

$$\Delta \alpha_3 = [(\Delta \alpha_2)^2 - (\Delta \alpha_1)^2]^{1/2} \quad (7)$$

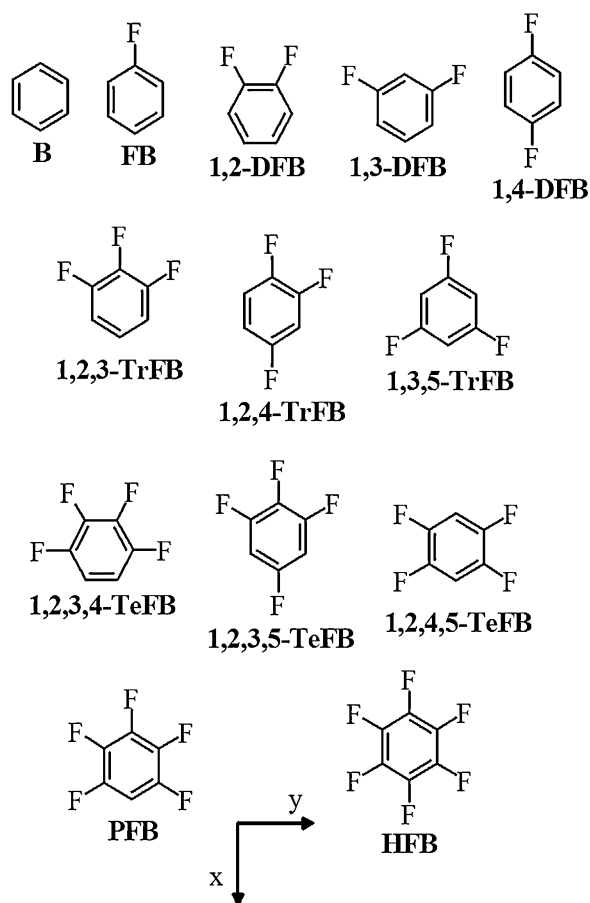


Fig. 1. Molecular structures and Cartesian coordinate system.

$$\beta_{vec} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \quad (8)$$

where  $\beta_i$  ( $i = x, y, z$ ) is given by

$$\beta_i = \frac{1}{3} \sum_{j=x,y,z} (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \quad (9)$$

Atomic units are used throughout the work. Conversion factor to the SI are: 1 a.u. of  $\mu(ea_0) = 8.478358 \times 10^{-30}$  Cm; 1 a.u. of  $\alpha(e^2 a_0^2 E_h^{-1}) = 1.648778 \times 10^{-41}$  C<sup>2</sup>m<sup>2</sup> J<sup>-2</sup>; 1 a.u. of  $\beta(e^3 a_0^3 E_h^{-2}) = 3.206361 \times 10^{-53}$  C<sup>3</sup> m<sup>3</sup> J<sup>-2</sup>.

All calculations were performed with Gaussian 03 program [61] and Firefly QC package [62], which is partially based on the GAMESS (US) [63] source code.

## 3. Results and discussion

The geometry of benzene and fluorobenzenes were optimized at the B97-1/6-311G\*\* level and the Cartesian coordinates are given in Tables S1–S10 of the Supplementary data. The agreement between the calculated and available experimental structures of **B**,

**FB**, **1,3-DFB**, **1,3,5-TrFB** and **HFB** [64–70] is satisfactorily, the largest deviation being obtained for the C–F bond length of **1,3,5-TrFB** (0.02 Å).

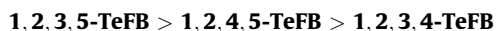
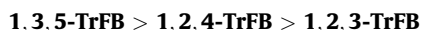
**Table 1**Relative energies ( $E_R$ ) and molecular hardness ( $\eta$ ) of di-, tri- and tetra-fluorobenzenes.<sup>a</sup>

Compound	HF/POL		MP2/POL
	$E_R$	$\eta$	$E_R$
<b>1,2-DFB</b>	4.09	120.15	4.12
<b>1,3-DFB</b>	0.00	120.85	0.00
<b>1,4-DFB</b>	1.00	120.07	0.92
<b>1,2,3-TrFB</b>	7.91	124.07	7.61
<b>1,2,4-TrFB</b>	4.86	122.46	4.43
<b>1,3,5-TrFB</b>	0.00	127.30	0.00
<b>1,2,3,4-TeFB</b>	3.87	125.46	3.71
<b>1,2,3,5-TeFB</b>	0.00	127.07	0.00
<b>1,2,4,5-TeFB</b>	0.94	125.69	0.76

<sup>a</sup> Calculations are carried out on the B97-1/6-311G\*\* geometries. Values in kcal/mol.

### 3.1. Relative stability and hardness of di-, tri- and tetra-fluorobenzenes

The relative energies for the di-, tri- and tetra-fluorobenzene isomers calculated at the HF/POL and MP2/POL on the B97-1/6-311G\*\* geometries are reported in Table 1. At the HF/POL level of computation the order of stability is:



This order is influenced by electrostatic repulsion interactions of the negatively charged fluorine atoms. The effect of the electron correlation (HF/POL  $\rightarrow$  MP2/POL) is modest (within 8%) and does not alter the above order obtained at the HF/POL level. Additionally, we investigated the relative stability of the isomers by using hardness [71]. Hardness ( $\eta$ ) is a molecular property commonly employed to characterize the relative stability and



reactivity of series of compounds [71]. An operative expression of  $\eta$  is given in terms of ionization energy (IE) and electron affinity (EA), which can be approximated by highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)

energies ( $\epsilon$ ), respectively:

$$\eta = \frac{1}{2}(\text{IE} - \text{EA}) \approx \frac{1}{2}(\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}) \quad (10)$$

The calculated HF/POL  $\eta$  values are included in Table 1. In agreement with the relative energies, the most stable isomer is predicted to be the hardest one. However, for the di-fluorobenzene isomers the  $\eta$  values are very close to each other.

### 3.2. Basis set effects on the electric properties

As a case test we investigated the basis set effects on the calculated  $\mu$ ,  $\alpha$  and  $\beta$  values of **FB**. Comparisons were performed at the HF and MP2 levels using the POL [47] and Dunning's correlation-consistent triple-zeta aug-cc-pVTZ [72] basis sets. The results are presented in Tables 2–4. The aug-cc-pVTZ basis set consists of [4s3p2d] functions for hydrogen and of [5s4p3d2f] functions for carbon and fluorine atoms. For **FB** this basis set gives a total of 437 basis functions, which are more than double the functions for the POL basis set. The results show that, when passing from the MP2/POL to MP2/aug-cc-pVTZ level, only marginal effects are observed on the computed properties. In fact, the  $\mu$ ,  $\langle\alpha\rangle$ ,  $\Delta_2\alpha$  and  $\beta_{\text{vec}}$  values vary by 0.8, 0.2, 0.0 and 7.5%, respectively. The corresponding percentages obtained at the HF level are almost similar being 1.0, 0.4, 0.1, and 6.0%, respectively. The above findings are in consistency with the results previously published on electronic (hyper)polarizabilities using the two basis sets [73–77]. However it is important to note that, for **FB** the MP2/aug-cc-pVTZ hyperpolarizability calculations require a CPU time ca. five times greater than that with the POL basis set. Thus, the POL basis set can be regarded as a good compromise between accuracy and computational cost and will be thoroughly used for the subsequent computations.

### 3.3. Dipole moments

Benzene, **1,4-DFB**, **1,3,5-TrFB**, **1,2,4,5-TeFB** and **HFB**, owing to their symmetrical arrangement of atoms are non-polar molecules. The calculated  $\mu$  values of the remaining fluorobenzenes obtained at the HF/POL and MP2/POL levels on the B97-1/6-311G\*\* geometries are collected in Table 2. Both the employed theoretical levels concordantly predict the following order of  $\mu$  values:

As should be expected, the  $\mu$  values are roughly determined by the mutual disposition of the vectorial contributions from the C–H and C–F bond moments. From present computations, the  $\mu$  value of **1,2,3-TrFB** is calculated to be ca. the double of the value for **PFB**.

**Table 2**Dipole moments ( $\mu$ ) and static electronic first-order hyperpolarizabilities ( $\beta_{\text{vec}}$ ) of fluorinated benzenes.<sup>a</sup>

Compound	Symm.	$\mu$			$\beta_{\text{vec}}$	
		HF	MP2	Exp.	HF	MP2
<b>FB</b> <sup>b</sup>	C <sub>2v</sub>	0.700 (0.693)	0.588 (0.593)	0.629 <sup>c</sup> ; 0.563 <sup>d</sup>	189.4 (178.6)	233.1 (216.9)
<b>1,2-DFB</b>	C <sub>2v</sub>	1.188	0.986	0.968 <sup>c</sup>	306.3	381.7
<b>1,3-DFB</b>	C <sub>2v</sub>	0.697	0.580	0.594 <sup>c</sup>	175.8	217.1
<b>1,2,3-TrFB</b>	C <sub>2v</sub>	1.359	1.117		333.5	418.9
<b>1,2,4-TrFB</b>	C <sub>s</sub>	0.676	0.555	0.552	163.8	204.8
<b>1,2,3,4-TeFB</b>	C <sub>2v</sub>	1.165	0.949	0.952	271.8	342.9
<b>1,2,3,5-TeFB</b>	C <sub>2v</sub>	0.663	0.538	0.574	152.0	192.2
<b>PFB</b>	C <sub>2v</sub>	0.662	0.534	0.566 <sup>e</sup>	147.2	187.1

<sup>a</sup> Basis set POL. Calculations are carried out on the B97-1/6-311G\*\* geometries. Values in a.u.<sup>b</sup> Value in parentheses refers to the aug-cc-pVTZ basis set.<sup>c</sup> Ref. [78].<sup>d</sup> Ref. [79].<sup>e</sup> Ref. [80].

**Table 3**Static electronic mean polarizabilities ( $\langle\alpha\rangle$ ),  $\alpha_{xx} - \alpha_{zz}$  polarizability differences and polarizability exaltation index values ( $\Gamma$ ) of benzene and fluorinated benzenes.<sup>a</sup>

Compound	Symm.	$\langle\alpha\rangle$			$\alpha_{xx} - \alpha_{zz}$			$\Gamma$	
		HF <sup>b</sup>	MP2 <sup>c</sup>	Exp.	HF	MP2	Exp.	HF	MP2
<b>B</b>	D <sub>6h</sub>	68.28	69.66	67.48 <sup>d</sup> ; 74.22 <sup>e</sup>	34.40	36.57	37.79 <sup>f</sup>	-22.26	-14.46
<b>FB</b> <sup>g</sup>	C <sub>2v</sub>	67.38 (67.63)	69.56 (69.42)	74.22 <sup>e</sup> ; 75.4 <sup>h</sup>	35.25 (35.29)	38.56 (38.58)	38.88 <sup>i</sup>	-21.74	-13.48
<b>1,2-DFB</b>	C <sub>2v</sub>	66.97	69.84		36.08	39.86		-20.73	-12.12
<b>1,3-DFB</b>	C <sub>2v</sub>	66.74	69.68		35.00	37.53		-20.96	-12.28
<b>1,4-DFB</b>	D <sub>2h</sub>	66.57	69.37		36.01	40.15		-21.13	-12.59
<b>1,2,3-TrFB</b>	C <sub>2v</sub>	66.75	70.28		36.25	39.83		-19.53	-10.60
<b>1,2,4-TrFB</b>	C <sub>s</sub>	66.40	69.91		36.02	39.47		-19.88	-10.97
<b>1,3,5-TrFB</b>	D <sub>3h</sub>	66.35	70.02		36.20	39.95	39.48 <sup>f</sup>	-19.93	-10.86
<b>1,2,3,4-TeFB</b>	C <sub>2v</sub>	66.58	70.67		36.75	40.18		-18.28	-9.13
<b>1,2,3,5-TeFB</b>	C <sub>2v</sub>	66.41	70.58		37.33	41.91		-18.45	-9.22
<b>1,2,4,5-TeFB</b>	D <sub>2h</sub>	66.28	70.38		35.88	38.60		-18.58	-9.42
<b>PFB</b>	C <sub>2v</sub>	66.63	71.28	69.7 <sup>h</sup>	37.44	41.30	41.48 <sup>i</sup>	-16.81	-7.44
<b>HFB</b>	D <sub>6h</sub>	66.99	72.12	79.15 <sup>j</sup>	38.90	43.66	42.82 <sup>f</sup>	-15.03	-5.52

<sup>a</sup> Basis set POL. Calculations are carried out on the B97-1/6-311G\*\* geometries. Values in a.u.<sup>b</sup> Atomic  $\langle\alpha\rangle$  values: 4.49 a.u. (H), 10.60 a.u. (C), 3.07 a.u. (F).<sup>c</sup> Atomic  $\langle\alpha\rangle$  values: 4.49 a.u. (H), 9.53 a.u. (C), 3.41 a.u. (F).<sup>d</sup> Experimental gas phase value extrapolated at  $h\omega = 0$  a.u. [81].<sup>e</sup> Experimental liquid phase value extrapolated at  $h\omega = 0$  a.u. [20].<sup>f</sup> Experimental gas phase value at  $h\omega = 0.072$  a.u. [18].<sup>g</sup> Value in parentheses refers to the aug-cc-pVTZ basis set.<sup>h</sup> Experimental gas phase value extrapolated at  $h\omega = 0$  a.u. [17].<sup>i</sup> Experimental gas phase value at  $h\omega = 0.072$  a.u. [17].<sup>j</sup> Experimental gas phase value extrapolated at  $h\omega = 0$  a.u. [19].

The electron correlation effect at the MP2/POL level decreases the HF/POL  $\mu$  values by 0.1–0.2 a.u. (ca. 20%). The MP2/POL  $\mu$  values reproduce the experimental figures [78–80] within 0.01–0.04 a.u. (2–7%). Additionally, our calculated values agree reasonably well with previous theoretical estimates [13–15].

### 3.4. Electronic polarizabilities

The calculated static electronic  $\alpha$  values of the investigated compounds are reported in Tables 3 and 4. Frequency-dependent experimental polarizabilities are available for **B** [17–20,81–87], **FB** [17,20], **1,3,5-TrFB** [18], **PFB** [17] and **HFB** [18,19]. However it is important to mention that, there are significant discrepancies among the observed  $\langle\alpha\rangle$  values obtained using various techniques, which in the case of **B** can reach up to 10%. Our calculated  $\langle\alpha\rangle$  data of **B** agree reasonable well (within 1–3%) with the gas-phase zero-frequency extrapolated value of Alms et al. [81]. The calculated  $\langle\alpha\rangle$  values are little affected by the F  $\rightarrow$  H substitution. In fact, as can be appreciated from the data reported in Table 3, the present  $\langle\alpha\rangle$  values vary in rather narrow range (0–3 a.u.). Among the di-, tri- and tetra-fluorobenzene isomers the differences are much small (within

0.4 a.u.). However, our calculations predict  $\langle\alpha\rangle(\mathbf{B}) \sim \langle\alpha\rangle(\mathbf{FB})$  in agreement with the most recent experimental values reported by Cheng et al. [20]. On the whole, the introduction of electron correlation contributions (HF  $\rightarrow$  MP2) increases the  $\langle\alpha\rangle$  values, in line with the usual literature data [32,33,36–43,52,54,55,57–60]. This effect increases with the increase of the number of fluorine atoms, ranging from 1.4 a.u. (+2%) for **B** to 5.1 a.u. (+7%) for **HFB**. Thus, at the MP2/POL level,  $\langle\alpha\rangle(\mathbf{HFB}) > \langle\alpha\rangle(\mathbf{B})$ , whereas at the HF/POL level the contrary occurs. In a previous study, Trudell determined the  $\langle\alpha\rangle$  values of **B** and fluorinated benzenes at the HF/6-31G\*\* level [13], which due to the lacking of diffuse functions underestimate the HF/POL data by 8–20 a.u. (10–30%). Present MP2/POL  $\langle\alpha\rangle$  values correctly reproduce the data formerly reported by Perez and Sadlej for **B** (within 0.2 a.u.) [88] and by Soteras et al. [21] for **B**, **FB**, **1,4-DFB** and **1,3,5-TrFB** (within 0.2 a.u.), using the same level of calculation but different geometries. Our correlated  $\langle\alpha\rangle(\mathbf{B})$  value of 69.66 a.u. agrees satisfactorily with the available high-level theoretical data previously obtained at the MP2/[5s3p2d/3s2p] (69.28 a.u.) [60], MP2/6-31G(+sd + sp) (69.79 a.u.) [89], MP2/HUZ-SV(+sd + sp) (68.50 a.u.) [90], CCSD/POL (68.30 a.u.) [91], TD-DFT-PW91/[8s6p4d4f, 4s3p3d] (69.56 a.u.) [92], B3LYP/aug-cc-pVDZ

**Table 4**Static electronic polarizability anisotropies ( $\Delta_1\alpha$ ,  $\Delta_2\alpha$ ,  $\Delta_3\alpha$ ) of benzene and fluorinated benzenes.<sup>a</sup>

Compound	Symm.	$\Delta_1\alpha$		$\Delta_2\alpha$		$\Delta_3\alpha$	
		HF	MP2	HF	MP2	HF	MP2
<b>B</b>	D <sub>6h</sub>	34.40	36.57	34.40	36.57	0.00	0.00
<b>FB</b> <sup>b</sup>	C <sub>2v</sub>	34.94 (34.99)	37.60 (37.70)	34.94 (34.99)	37.63 (37.63)	0.55 (0.53)	1.67 (1.71)
<b>1,2-DFB</b>	C <sub>2v</sub>	35.62	38.73	35.63	38.78	0.80	1.96
<b>1,3-DFB</b>	C <sub>2v</sub>	35.53	38.72	35.54	38.77	0.91	2.05
<b>1,4-DFB</b>	D <sub>2h</sub>	35.56	38.55	35.56	38.66	0.79	2.77
<b>1,2,3-TrFB</b>	C <sub>2v</sub>	36.32	39.90	36.32	39.90	0.13	0.12
<b>1,2,4-TrFB</b>	C <sub>s</sub>	36.30	39.83	36.30	39.83	0.48	0.61
<b>1,3,5-TrFB</b>	D <sub>3h</sub>	36.20	39.95	36.20	39.95	0.00	0.00
<b>1,2,3,4-TeFB</b>	C <sub>2v</sub>	37.12	41.08	37.13	41.11	0.64	1.55
<b>1,2,3,5-TeFB</b>	C <sub>2v</sub>	37.06	41.12	37.06	41.14	0.48	1.38
<b>1,2,4,5-TeFB</b>	D <sub>2h</sub>	37.12	41.09	37.18	41.31	2.15	4.30
<b>PFB</b>	C <sub>2v</sub>	37.96	42.37	37.97	42.41	0.90	1.85
<b>HFB</b>	D <sub>6h</sub>	38.90	43.66	38.90	43.66	0.00	0.00

<sup>a</sup> Basis set POL. Calculations are carried out on the B97-1/6-311G\*\* geometries. Values in a.u.<sup>b</sup> Value in parentheses refers to the aug-cc-pVTZ basis set.

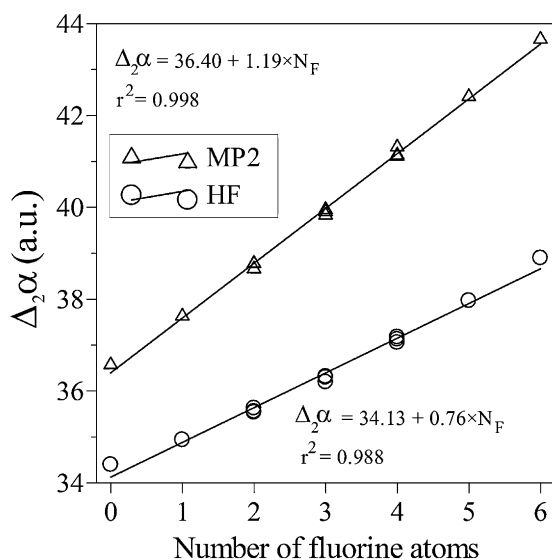
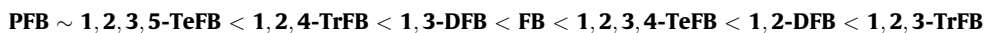


Fig. 2. Calculated  $\Delta_2\alpha$  values as a function of the number of fluorine atoms of fluorinated benzenes. Basis set POL.

(70.23 a.u.) [90], BLYP/DNP + 2 (70.78 a.u.) [16]. Additionally, the MP2/POL ( $\alpha$ ) data of **FB** (69.56 a.u.) and **HFB** (72.12 a.u.) are in good agreement, respectively, with those obtained at the BLYP/DNP + 2 (71.26 a.u.) [16] and LB94-LDA/POL (72.50 a.u.) [22] levels.

As can be appreciated from the data collected in Table 4,  $\Delta_1\alpha$  and  $\Delta_2\alpha$  values are almost equivalent each other (within 0.11 a.u., 0.3%), consistently with the results previously obtained by Thakkar and co-workers on series of ring-like compounds [57–60]. On the other hand, the  $\Delta_3\alpha$  data are much smaller than the corresponding  $\Delta_1\alpha$  and  $\Delta_2\alpha$  values, the largest datum in the series being predicted for **1,2,4,5-TeFB** (4.30 a.u. at the MP2/POL level). In comparison to the  $\langle\alpha\rangle$  values, the effects of the hydrogen-fluorine substitutions are much more substantial for the calculated polarizability anisotropy values. In fact, at both the employed theoretical levels, the  $\Delta_2\alpha$  value increases steadily with the number of fluorine atoms ( $N_F$ ), an excellent linear relationship between  $\Delta_2\alpha$  and  $N_F$  being obtained (Fig. 2,  $r^2 = 1.00$  and  $0.99$ ). In particular, at the MP2/POL level on passing from **B** to **HFB** the  $\Delta_2\alpha$  value increases by 7.1 a.u. (+19%). These results indicate that, for the series of fluorobenzenes the  $\Delta_2\alpha$  value is ruled by an additive law. Additive models for electronic polarizabilities using number and type of atoms and bonds were previously explored on some series of heterocyclic compounds [58–60]. As expected, the effects of the electron correlation on the  $\Delta_2\alpha$  values are positive and as for  $\langle\alpha\rangle$  increase with the fluorination, ranging from 2.2 a.u. (+6%) for **B** to 4.8 a.u. (+12%) for **HFB**. Similarly to the  $\langle\alpha\rangle$  data, the  $\Delta_2\alpha$  values do not change significantly among the investigated isomers



(within 0.2 a.u.). For **B**, **FB**, **1,3,5-TrFB**, **PFB** and **HFB** uniform experimental data are available for the  $\alpha_{xx} - \alpha_{zz}$  difference obtained at the He/Ne laser wavelength of 632.8 nm ( $\hbar\omega = 0.072$  a.u.) [17,18]. Thus, we carried out a comparison between the calculated static and experimental dynamic  $\alpha_{xx} - \alpha_{zz}$  values (Table 3). The relationships are illustrated in Fig. 3, showing a very good agreement in both cases ( $r^2 = 0.96$  and  $0.99$ ).

Besides to the  $\langle\alpha\rangle$ , polarizability anisotropies and  $\alpha_{xx} - \alpha_{zz}$  values, we also evaluated the polarizability exaltation index, which is determined as  $\Gamma = \langle\alpha\rangle(\text{mol}) - \sum_i \langle\alpha\rangle_i$ , where  $\langle\alpha\rangle(\text{mol})$  is the

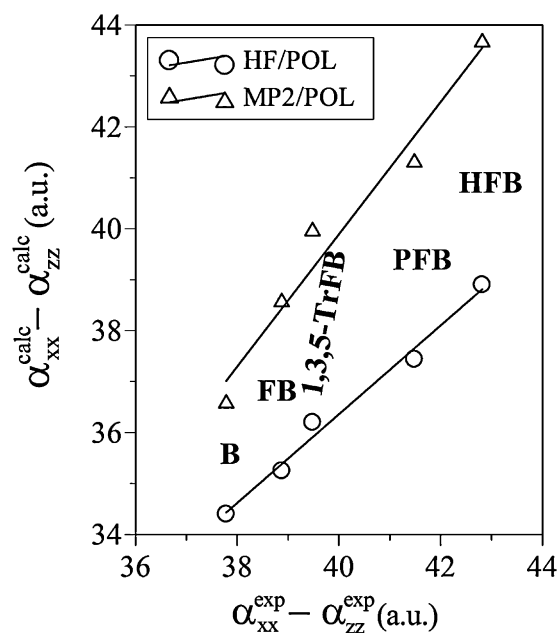


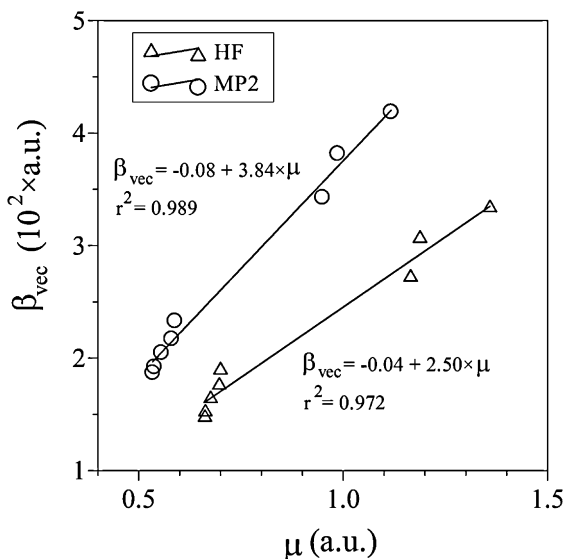
Fig. 3. Relationship between calculated static and experimental dynamic [17,18]  $\alpha_{xx} - \alpha_{zz}$  values of benzene and fluorinated benzenes. HF/POL:  $\alpha_{xx}^{\text{calc}} - \alpha_{zz}^{\text{calc}} = 0.87 \times (\alpha_{xx}^{\text{exp}} - \alpha_{zz}^{\text{exp}}) + 1.55$  ( $r^2 = 0.988$ ); MP2/POL:  $\alpha_{xx}^{\text{calc}} - \alpha_{zz}^{\text{calc}} = 1.30 \times (\alpha_{xx}^{\text{exp}} - \alpha_{zz}^{\text{exp}}) - 12.05$  ( $r^2 = 0.964$ ).

mean polarizability of a molecule and  $\sum_i \langle\alpha\rangle_i$  is the summation of the atomic polarizability of the atoms which constitute the molecule. Calculated  $\Gamma$  values were previously employed to estimate relative aromaticity of furan homologues [51] and stabilities of atomic clusters [77,93,94]. A large negative  $\Gamma$  value denotes a very stable structure. The results reported in Table 3 show that, for all the investigated compounds the  $\Gamma$  value is negative and steadily increases (less negative) as the number of fluorine atoms increases. Specifically, at the MP2/POL (HF/POL) level the absolute  $|\Gamma|$  value of **B** is higher than that of **HFB** by a factor of 2.6 (1.5).

### 3.5. Electronic hyperpolarizabilities

Table 2 collects the static electronic  $\beta_{\text{vec}}$  values of the fluorinated benzenes. As for the  $\mu$  values, the symmetric **B**, **1,4-DFB**, **1,3,5-TrFB**, **1,2,4,5-TeFB** and **HFB** molecules do not exhibit  $\beta_{\text{vec}}$  values. We are aware of experimental frequency-dependent first-order hyperpolarizabilities of **FB** from electric-field induced second harmonic generation (EFISHG) at  $\lambda = 1910$  nm [20] and from electrooptical Kerr effect (EOKE) at  $\lambda = 632.8$  nm [17] and for **PFB** from EOKE experiment at  $\lambda = 632.8$  nm [17]. The order of the calculated  $\beta_{\text{vec}}$  values is analogous to that obtained for  $\mu$ :

In particular,  $\beta_{\text{vec}}(\mathbf{1,2,3}\text{-TrFB})$  is calculated to be ca. twice the value obtained for **PFB**. However, with respect to the  $\mu$  values, the electron correlation effects on the  $\beta_{\text{vec}}$  data are positive and more significant, increasing the HF/POL values by 40–85 a.u. (20–30%). It is worth noting that, the present MP2/POL  $\beta_{\text{vec}}$  datum of **FB** (233.1 a.u.) agrees reasonably well with the estimate of Matsuzawa and Dixon [16], previously obtained at the BLYP/DNP + 2 level (249.1 a.u.). In agreement with experiment [17], the calculated static hyperpolarizability value of **FB** is higher than the corresponding value for **PFB**, the MP2/POL  $\beta_{\text{vec}}(\mathbf{FB})/\beta_{\text{vec}}(\mathbf{PFB})$



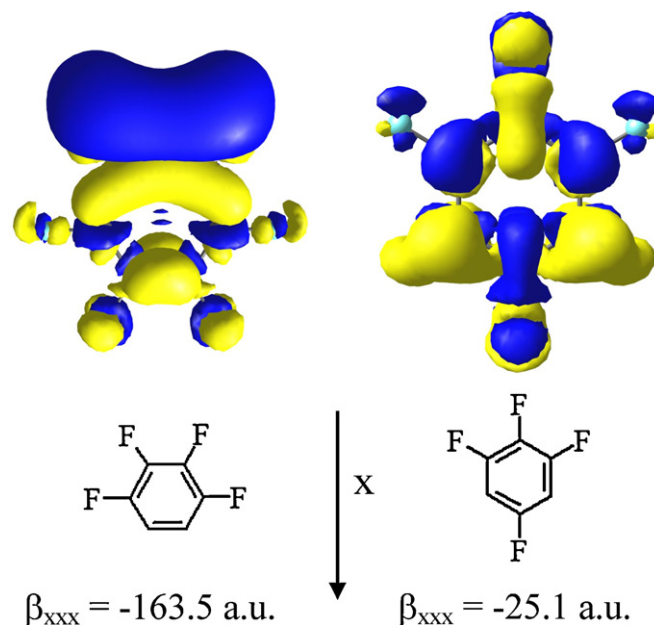
**Fig. 4.** Relationship between calculated  $\beta_{vec}$  and  $\mu$  values of fluorinated benzenes. Basis set POL.

ratio of 1.25 being slightly higher than the experimental ratio (1.12). This discrepancy is mainly due to neglecting of frequency-dependent dispersion effects and vibrational contributions by the present calculations. Interestingly, a linear relationship between  $\beta_{vec}$  and  $\mu$  values ( $r^2 = 0.97$  and  $0.99$ ) is obtained (Fig. 4). This result suggests that, as for the  $\mu$  data, the  $\beta_{vec}$  values of the fluorobenzenes are affected by the mutual disposition among the C–H and C–F bonds, mesomeric effects being expected to be negligible for  $\beta$ . Additionally, by analogy to the  $\mu$  data, the  $\beta_{vec}$  values are rather different among the fluorobenzene isomers. Indeed, on passing from **1,2,3-TrFB** to **1,2,4-TrFB**, the  $\beta_{vec}$  value decreases by about a factor of two, whereas  $\beta_{vec}$  of **1,3,5-TrFB** is zero. A similar situation occurs for di- and tetra-fluorobenzenes, where the  $\beta_{vec}(\mathbf{1,2-DFB})/\beta_{vec}(\mathbf{1,3-DFB})$  and  $\beta_{vec}(\mathbf{1,2,3,4-TeFB})/\beta_{vec}(\mathbf{1,2,3,5-TeFB})$  ratios are predicted to be 1.75 and 1.78, respectively. Thus, anticipating future NLO applications, fluorobenzene isomers might be identified through EFISHG and EOKE studies. As a test case, we analyzed the hyperpolarizability differences between **1,2,3,4-TeFB** and **1,2,3,5-TeFB**. For **1,2,3,4-TeFB**,  $\beta_{xxx}$  is the largest hyperpolarizability component, which is calculated to be  $-163.5$  and  $-206.8$  a.u. at the HF/POL and MP2/POL level, respectively, contributing to ca. 60% of the total hyperpolarizability. The corresponding  $\beta_{xxx}$  values for **1,2,3,5-TeFB** are significantly less negative, being computed to be  $-25.1$  and  $-46.7$  a.u., respectively, almost determining the predicted  $\beta_{vec}$  differences between the isomers. The above results can be elucidated on the basis of the spatial contributions of electrons to the first-order hyperpolarizability, through a density analysis as described in details in Refs. [95–97]. The  $\beta$  density,  $\rho^{(2)}(r)$ , is defined as follows ( $r$  denotes the position vector):

$$\rho(r, F) = \rho^{(0)}(r) + \sum_j \rho_j^{(1)}(r) F_j + \frac{1}{2!} \sum_j \rho_{jk}^{(2)}(r) F_j F_k + \frac{1}{3!} \sum_j \rho_{jkl}^{(3)}(r) F_j F_k F_l + \dots \quad (11)$$

$$\beta_{ijk} = -\frac{1}{2!} \int r \rho_{ijk}^{(2)}(r) dr \quad (12)$$

$$\rho_{jk}^{(2)}(r) = \left. \frac{\partial^2 \rho(r, F)}{\partial F_j \partial F_k} \right|_{F_j=0, F_k=0} \quad (13)$$



**Fig. 5.** Hyperpolarizability density distributions for **1,2,3,4-TeFB** and **1,2,3,5-TeFB**. The yellow and blue surfaces (color figure online) refer to positive and negative  $\rho_{xx}^{(2)}(r)$  densities, respectively, computed at the iso-surface of 1 a.u. HF/POL results. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The  $\rho^{(2)}(r)$  values were here evaluated at the HF/POL level for the  $xx$  component through a numerical procedure [96]. When considering a pair of localized positive and negative  $\rho^{(2)}(r)$  densities, the magnitude of their contribution to  $\beta$  is proportional to the distance between them, while the sign is positive if the positive-to-negative  $\rho^{(2)}(r)$  direction coincides with the positive direction of the coordinate system. Fig. 5 illustrates the  $\rho_{xx}^{(2)}(r)$  distribution for **1,2,3,4-TeFB** and **1,2,3,5-TeFB** isomers. As can be appreciated from the figure, for **1,2,3,4-TeFB** the most relevant negative and positive  $\rho_{xx}^{(2)}(r)$  contributions are well-separated, determining the relatively great and negative  $\beta_{xxx}$  value. By contrast, **1,2,3,5-TeFB** exhibits some negative–positive localized  $\rho_{xx}^{(2)}(r)$  pairs which are in mutual opposition to each other. As a result, the  $\rho_{xx}^{(2)}(r)$  pairs contributions tend to cancel to each other, giving a comparatively smaller  $\beta_{xxx}$  value than that obtained for **1,2,3,4-TeFB**.

#### 4. Conclusions

In this study, we reported the relative stabilities, dipole moments and static electronic (hyper)polarizabilities of benzene and fluorinated benzenes using HF and MP2 levels with the Sadlej's POL basis set. The relevant conclusions are as follows:

- The mean electronic polarizability little changes along the series of the investigated compounds. On the other hand, the electronic polarizability anisotropy  $\Delta_2\alpha$  steadily increases with the fluorination, being linearly related to the number of fluorine atoms with good statistics. For this series of molecules the polarizability anisotropy  $\Delta_2\alpha$  is nearly controlled by an additive law.
- The dipole moments and electronic first-order hyperpolarizabilities are linearly related to each other, suggesting that they are essentially determined by the mutual disposition of the C–H and C–F bonds, the C–F mesomeric effects on these properties being marginal.

- (c) The isomers of di-, tri- and tetra-fluorobenzenes could be discriminated on the basis of their dipole moments and electronic first-order hyperpolarizability values, which differ from each other up to a factor of two. The hyperpolarizability differences among the investigated isomers are clarified using hyperpolarizability density analyses.
- (d) The electron correlation effects evaluated at the MP2/POL level are significant for dipole moments and especially first-order hyperpolarizabilities, while they are little or moderate for the relative energies and electronic polarizabilities.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jfluchem.2012.07.016>.

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