Molecular Orbital Study of Flouroaryl Substituted Amino-Borane Dimers: Geometry, Energetics and Reactivity

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The electronic properties in terms of HOMO-LUMO energy, electronegativity, hardness and electrophilicity index have been calculated and discussed in the framework of Unrestricted Hartee-Fock (UHF), semi-emperical parametric method (PM3) for six fluoro-substituted aminoborane dimers, *viz.* [Me$_2$B-µ-N(H)ArF]$_2$ (Ar: 4-C$_6$H$_4$F (**1**), 2-C$_6$F$_5$F (**2**); 3,5-C$_6$H$_3$F$_2$ (**3**); 2,3,4,5-C$_6$HF$_4$ (**4**); 2,3,5,6-C$_6$HF$_4$ (**5**) and C$_6$F$_5$ (**6**)). The calculated parameters mentioned above have been compared with the available experimental and other theoretical estimates. The results are in excellent agreement with the reported estimates. The geometrical parameters calculated are also in good agreement with available experimental and theoretical values. The chemical reactivity is also discussed in terms of electrophilicity index (ω) values.

Keywords: Frontier orbitals, Semi-emperical method, Electronegativity, Electrophilicity index, Hartee-Fock.

INTRODUCTION

In material science, a large number of aluminium-nitrogen compounds, with great importance, obtained from the reactions of organoaluminium complexes with amines as precursors, for the deposition of thin film of aluminium nitride [1-4]. The fluoroaryl aminoalane dimers are used as potential reagents for preparing α-amine, β-diamine and β-ketoimine ligands [5]. These ligand classes are assuming increasing importance in various catalytic processes [6] as well as for the stabilization of unusual oxidative states and bonding situations [7,8]. It has become increasing desirable to employ highly electron withdrawing substituents at the nitrogen atoms of such ligands [9]. In order to develop catalytic systems with enhanced activities at the metal centres. The established method to the synthesis of α-amine, β-diamine ligands involves the reaction of an α- or β-diketones with the appropriate primary amine in the presence of an acid catalyst [10]. In view of this, the fluoro-substituted arylamines being poor nucleophiles, may play significant role as excellent reagents for effecting the desired transformation (due to weaker Al-N and N-H bonds as compared to Al-O and O-H). This idea was further supported from

the report that lithium-aluminium amides will convert aldehydes and cyclic ketones into corresponding imines [11]. A decade ago, Shukla *et al.* [12] synthesized the six fluoroaryl-substituted aminoalane dimers and characterized them by single crystal X-ray crystallography. Tandon and Tandon [13] carried out the quantum calculations on all the six fluoroaryl-substituted aminoalane dimers by using semi-empirical methods parametric method (PM3), for their geometrical and electronic parameters. These workers predicted that the chemical reactivity depends on the dipole moment, apart from other properties such as Frontier orbital energy values (HOMO and LUMO). This prompted us to study theoretically on new ligands with boron as the central atom in place of aluminium. The chemistry of boron element is quite interesting as it can give or take electron easily. Numerous papers and reviews related to boron chemistry have already been there in the literature. In the present work, we have applied the semi-empirical methods parametric method (PM3) to all the six fluoroaryl-substituted primary aminoborane of the type [Me$_2$B-µ-N(H)Ar^F]$_2$ (Ar^F = 4-C$_6$H$_4$F (**1**), 2-C$_6$H$_4$F (**2**), 3,5- C$_6$H$_3$F$_2$ (**3**), 2,3,4,5-C$_6$H$_4$F (**4**), 2,3,5,6-C$_6$H$_4$F (**5**) and C$_6$F$_5$ (**6**) for their geometrical and electronic parameter calculations.

EXPERIMENTAL

In the present study, structures **1-6** have been treated quantum chemically by using PM3 method [14-16] at the level of Unrestricted Hartee-Fock (UHF) approach. The geometry optimization of the structures was performed by using MM+ (molecular mechanics method) and PM3 (UHF). The optimizations were done successively and iteratively till the desired precision and consistency was achieved. This was obtained by the application of the Steepest Decent method followed by Polak-Ribiere conjugate gradient method (convergence limit of 0.001 Kcal mol^{-1} and RMS gradient of 0.001 Kcal/Å/mol). All the computations were performed by using Hyperchem 7.5 program [17].

RESULTS AND DISCUSSION

Each of the six compounds exist in dimer form and are divided into four groups on the basis of energy and electronic structure using (i) 1 and 2 (ii) 3 (iii) 4 and 5 (iv) 6. The optimized geometrical parameters of these compounds are given in Table-1. It can be seen from the table that the predicted value is in excellent agreement with the experimental result taken by microwave spectroscopy [18]. The angles N-B-N which ranges from 85.0° to 87.5° in all six compounds are more acute than B-N-B angles (92.0° to 96.2°). In cubic BN crystals, the angles of B-N-B or N-B-N are found to be 109° and in hexagonal form it is 120° similar to graphite. In the present work, the square planar BN crystals, the angles B-N-B is higher than N-B-N angles. The torsion angle N-B-N-B is highest in compound **2** and almost planar in compound **6** (-3.8°).

It shows that in compound **2**, the aryl groups in dimer are distorted and make this compound very reactive and predicted to be used as a catalyst. The optimized geometries of these compounds are shown in Fig. 1. Further, it has been found that compound **2** and **5** are found to have *trans*-orientation with arene substituents arranged in parallel fashion (see figures).

The average B-N bond length is 1.590 Å for all the six compounds consistent with the other experimental estimates [17]. Both the aryl groups in compound **1** and **4** are planar whereas compounds **2** and **5** are *trans*-oriented with respect to B_2N_2 plane. This may be due to interaction of F-atom at *ortho* position with methyl groups on B-atoms.

Energy and electronic parameters: The calculated energy parameters are given in Table-2. It can be seen from the results that compounds **1-6** are exothermic with **2**, the least and **6**, the most. The theoretical knowledge seem to provide a simple

TABLE-1
SELECTED BOND LENGTHS (Å) AND ANGLE (°) FOR STRUCTURES 1-6

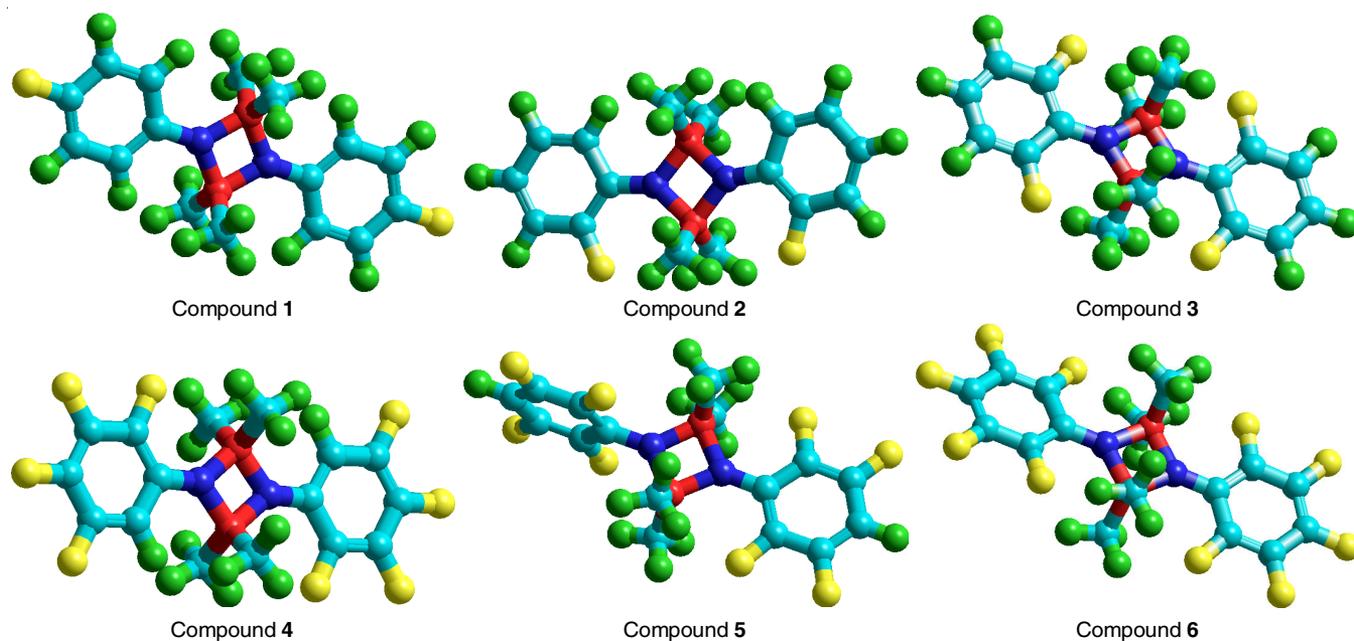| System	Compound **1**	Compound **2**	Compound **3**	Compound **4**	Compound **5**	Compound **6**
r_{BN}	1.591 (1.590)	1.590	1.601	1.587	1.579	1.603
r_{BC}	1.364	1.614	1.615	1.609	1.610	1.607
r_{CF}	1.362	1.363	1.361	1.359	1.417	1.360
r_{BB}	2.346	2.332	2.318	2.338	2.350	2.321
r_{NN}	2.151	2.177	2.209	2.168	2.162	2.215
<NBN	85.0 (86.2)	86.4	87.2	85.7	85.2	87.3
<BNB	95.0 (95.7)	93.9	92.8	94.3	96.2	92.8
<CBC	114.5 (118.0)	113.7	116.9	114.0	116.0	116.8
Torsion angle NBNB	0.03	-3.8	-0.35	0.12	2.7	-0.49

The values in parentheses have been taken from [Ref. 18].

Compound **1**

Compound **2**

Compound **3**

Compound **4**

Compound **5**

Compound **6**

Fig. 1. Optimized geometry of compounds **1-6**

Parameters	Parent molecule	Compound 1	Compound 2	Compound 3	Compound 4	Compound 5	Compound 6
TABLE-2 ENERGETICS AND ELECTRONIC PARAMETERS FOR STRUCTURES **1-6**							
Binding energy (-E) (Kcal mol^{-1})	4421.2	4441.8	4433.4	4438.5	4486.9	4470.7	4489.7
Heat of formation (-H_f) (Kcal mol^{-1})	43.4	130.3	121.9	193.4	374.7	358.5	443.8
-HOMO (eV)	9.199	9.355	9.311	9.421	10.117	10.152	10.210
-LUMO (eV)	0.987	1.285	1.187	1.344	2.037	1.159	2.164
ΔE (eV)	8.212	8.070	8.124	8.077	8.080	8.993	8.046
Dipole moment (μ) (Debye)	0.097	0.0	2.476	0.134	0.0	0.0	0.0
Number of valence electrons	102	114	114	126	150	150	162

principle in chemistry for understanding the structure and chemical reactivity of molecules and alteration in the electron population density distribution. The change of symmetry of highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO), on distribution of molecular structure largely determine the equilibrium geometries of the molecules. In this regard, Fukui [19] established that frontier orbitals govern chemical reactions under the average core potential, solely determine the reaction path. By implementing this principle further investigations have revealed that the energy gap between HOMO and LUMO is an important stability index for molecules and the most stable structure has the largest HOMO-LUMO energy gap [20,21]. Hence, it follows that during molecular transformation, the equilibrium geometry shifts to non-equilibrium position, its corresponding HOMO-LUMO energy gap decreases and the molecule become unstable and chemically more reactive. On the other hand, when it shifts from non-equilibrium to equilibrium position, the HOMO-LUMO energy gap increases and become maximum, making the molecule to attain stability. In the light of this view, we focused on the internal stability among the compounds mentioned here. From isoelectronic perspective, we have divided them in four categories (i) 1,2 (ii) 3 (iii) 4,5 (iv) 6. By looking at the DE (LUMO-HOMO) energy gap, compound **1** seems to be more reactive than compound **2** on the basis of ease of electron flow. Similarly, compound **5** is more stable than compound **4**. The compounds **3** and **6** are found to have least ΔE in comparison to mentioned compounds (Table-2). It depicts to be chemically reactive and can be seen from the electrostatic potential maps also (Fig. 2). But ESP is localized at F-atoms not on B or N atoms. Hence, compound **3** predicted not to be taken as catalyst. On the other hand, the compounds **2** and **5** have high w values (Table-3) as compared to their isoelectronic partners compounds **1** and **4**. So, compounds **2** and **5** are chemically very reactive and predicted to act as catalysts.

Electrophilicity index: Many of the organic reactions can be described in terms of the electro(nucleo)philic addition and substitution. These reactions have got large synthetic potentials and are most widely studied [22-25]. Traditionally, the electrophilicity is treated as kinetic quantity, which explains the rate of reaction through its correlation with activation energy supplemented by thermodynamic stabilities of various species involved. On the other hand, the nucleophilicity and the basicity are often analyzed at par, since both involve the amount of electron density present in it and its potential to donate that. Based on the work of Maynard *et al.* [26] a theoretical definition of electrophilicity has been introduced by Parr *et al.* [27]. It may be noted that both groups have prescribed the definition of electrophilicity through kinetics (reaction rates) and thermodynamic (charge transfer ability) respectively.

The quantum chemical theory has been quite successful in providing theoretical background of popular qualitative chemical concepts. In this regard, several reactivity descriptors have been proposed and used to analyse chemical reactivity and site selectivity. Hardness, electronegativity and polarizability are the global reactivity parameters widely used to understand the global nature of molecules in terms of their stability [28,29].

Theoretical studies: The hardness of two chemical species *viz.* A the acceptor and D the donor is calculated [30] by:

$$\eta = (I_D - A_A)/2$$

where I_D is the ionization potential of the donor and A_A is the electron affinity of the acceptor. In terms of frontier orbital theory, the negative of HOMO is ionization potential (I) and negative of LUMO is electron affinity of the molecular species.

Hence, $\eta = (I–A)/2$

And χ (electronegativity) $= (I+A)/2$

The electrophilicity index (w) has been defined by Parr *et al.* [27,30] as:

$$\omega = \mu^2/2\eta$$

where μ is the chemical potential (negative of χ).

In our present work, these values have been calculated and shown in Table-3. It can be seen from the results that on the isoelectric perspective 'ω' value of compound **1** is less

Parameters	Parent compound	Compound 1	Compound 2	Compound 3	Compound 4	Compound 5	Compound 6
TABLE-3 ELECTRONIC PARAMETERS FOR STRUCTURES **1-6**							
Electronegativity (χ)	4.106	4.035	4.062	4.039	4.040	4.497	4.023
Hardness (η) (eV)	10.186	10.64	10.498	10.765	12.154	11.311	12.374
Chemical potential (μ) (eV)	-4.106	-4.035	-4.062	-4.039	-4.040	-4.497	-4.023
Electrophilicity index (ω) (eV)	0.828	0.765	0.786	0.757	0.671	0.894	0.654
Charge transfer (Δn_{max})	0.403	0.379	0.387	0.375	0.332	0.395	0.325

Compound **1**

Compound **2**

Compound **3**

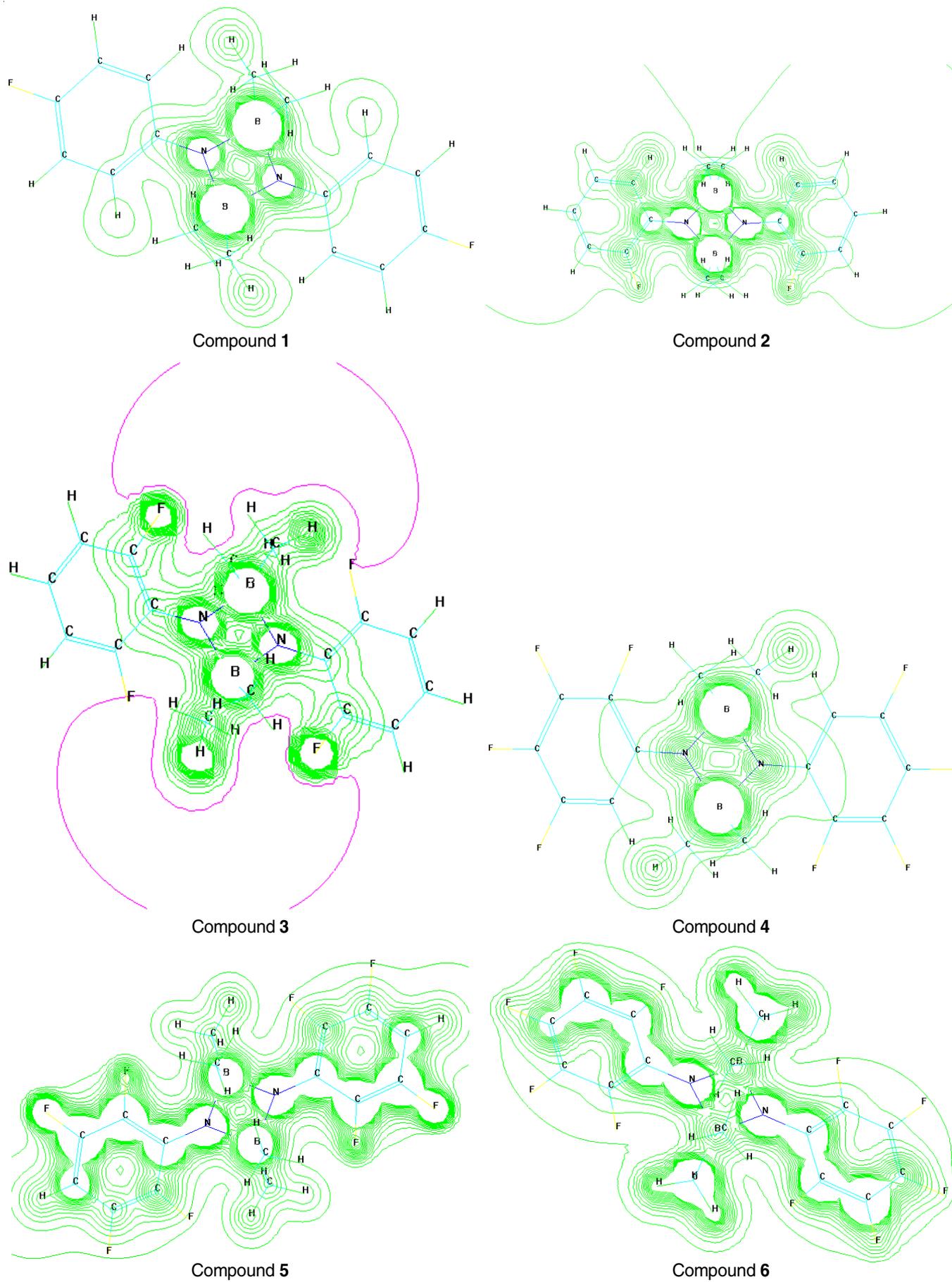Compound **4**

Compound **5**

Compound **6**

Fig. 2. Electrostatic potential map of compounds **1-6**

than compound **2**, which shows the reactivity in terms of flow of electrons. Similar argument is valid for compound **4** being more chemically reactive than compound **5**. When we look at the net atomic charges on selected atoms of all the six compounds shown in Fig. 3, one can see that net electron density on F-atom in compound **1** is more than F-atom in compound **2**. Similarly in compound **4**, the charge on F-atom is more than F-atom in compound **5**. In other compounds, it is distributed equally on F-atoms.

Compounds **2** and **5** are much softer (less η values) in comparison to other compounds. Hence, these two compounds are quite reactive and able to transfer the net charge (Δn) from its potential energy surface (Table-3).

Conclusion

The chemical reactivity depends on several factors, apart from heat of formation, on the role of values of frontier orbitals (HOMO, LUMO), the chemical potential and hardness (softness). A new concept electrophilicity index (ω) quantitatively quite useful to explain the chemical reactivities of compounds acting as catalyst, which are said to be environment friendly, for many organic conversions. The present work was devoted to predict newer catalysts on the basis of the electronic descriptors and have been quite satisfied with findings of fluoroaryl dimers with boron atoms. These compounds, in future, may be crystallized and experimentally studied by other workers. The new compounds with gallium atom are in progress and will be reported elsewhere.
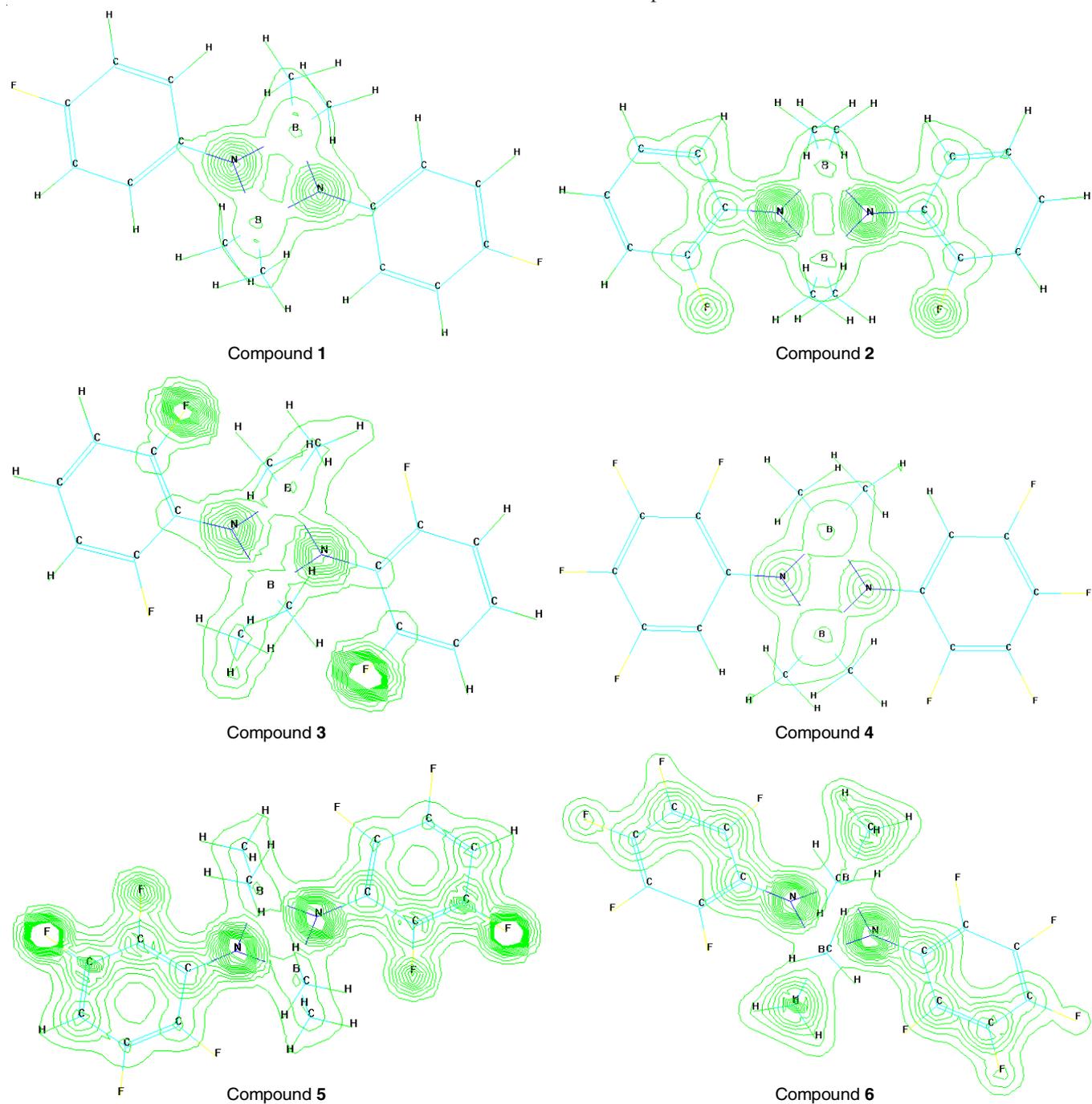

Compound **1**

Compound **2**

Compound **3**

Compound **4**

Compound **5**

Compound **6**

Fig. 3. Total charge density on compounds **1-6**

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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