Conceptual density functional study on the formation of supermolecules by the chemical interaction of some ligands as electron pair donors and boron trifluoride as electron pair acceptor

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A number of Lewis bases, viz., HCN, HNC, H$_2$C-CN and H$_2$C-NC are allowed to chemically interact with BFs$_3$, a Lewis acid, through the process of charge transfer and bond formation leading to the formation of F$_2$B-NCH, F$_2$B-CN, F$_2$B-NC-CH$_3$, F$_2$B-CN-CH$_3$ supermolecules. The ligands chosen are structural isomers with different donating atomic sites of varying degrees of softness. The density functional descriptors like hardness and chemical potential or electronegativity are involved to study the rationality of formation of such charge transfer complexes. The fundamental theoretical generalizations relied upon in the study are the maximum hardness principle and the electronegativity or chemical potential equalization principle. The present work also attempts to address the stability of the above supermolecules in terms of the recently suggested semimempirical algorithms involving the above stated density functional descriptors. The computed chemical potential induced charge transfer and hardness induced reaction energy of all such supermolecules are perfectly in accordance with their theoretical predictions. The computed values of the hardness, chemical potential and electronegativity of the donors, the acceptor and the supermolecules reveal that the formation of acid-base supermolecules are in accordance with the electronegativity equalization principle and the maximum hardness principle. The variation of heats of formation of the supermolecules with the change of structure of ligands can be correlated in terms of conceptual density functional descriptors like chemical potential and global hardness. The present work is presented as one more validity test of maximum hardness principle, MHP and chemical potential equalization principle of the density functional theory.

Studies on the density functional theory (DFT) basically deal with three aspects, namely, theoretical, conceptual, and computational$^{14}$. The conceptual density functional theory has demonstrated its amazing power to quantify the long time qualitative theoretical principles used for the rationalization and understanding of the relationship between molecular structure and reactivity. Some important density functional reactivity descriptors are chemical potential ($\mu$) and global hardness ($\eta$), and the local softness and Fukui functions. These descriptors are either global or local and have been introduced by Parr and coworkers$^{4,5}$. The exact density functional definitions$^{6,7}$ of the chemical potential, $\mu$ and hardness, $\eta$ are as follows:

$$\mu = \langle \partial E/\partial N \rangle_v \quad \ldots(1)$$

$$\eta = 1/2(\partial \mu/\partial N)_v \quad \ldots(2)$$

where $N$ is the number of electrons and $v$ is the potential due to the nuclei plus any external potential.

Thus, DFT provides a new theoretical quantity called chemical potential ($\mu$) and it was found to be identical with the negative of electronegativity. Sanderson$^8$ postulated that electronegativity tends to equalize during chemical reaction. A number of workers$^{3,9,10,11}$ have critically analyzed the role of chemical potential in chemistry and have concluded that the chemical potential provides a new rationale for explaining chemical reaction through the process of charge transfer. They$^{6,10,11}$ have also justified the electronegativity equalization principle of Sanderson$^8$ in terms of this new DFT parameter, $\mu$. According to this principle, the charge transfer occurs from a system of higher chemical potential (lower electronegativity) to a lower chemical potential (higher electronegativity) until the chemical potential of two interacting systems become equal. The density functional treatment of the qualitative hard-soft acid base, HSAB$^{12,13}$ principle of Mulliken and Pearson put it on a sound theoretical basis. The descriptor hardness, $\eta$, has been identified as a cardinal index of chemical reactivity and stability$^{14}$ and it provides a
Thus the qualitative evolved aggregate stability of chemical scale to decide the relative stability among the molecules. The culmination of the importance of the global hardness was with the enunciation of maximum hardness principle, MHP, by Pearson. Thus the qualitative maximum hardness principle evolved with time and it is now considered as a law of nature. The two density functional descriptors, the chemical potential and the global hardness, have a potential role in relating the charge transfer and stability of chemical systems. If two chemical systems A and B are involved in a reaction, the charge transfer is induced by electronegativity (chemical potential) difference while the hardness (\( \eta \)) tends to resist the charge transfer. The number of electron transfer, \( \Delta N \) between A and B is given by

\[
\Delta N = (\mu_B - \mu_A) / (\eta_B + \eta_A)
\]

where \( \mu \)'s stand for chemical potential and \( \eta \)'s stand for hardness of molecules in the separated state. The formula above shows that the difference in electronegativities drives the electron transfer while the sum of hardness attenuates the charge transfer. Various rationale of formation of the charge transfer complexes have been introduced in terms of the descriptors under consideration.

In the present work, we propose to explore the rationale of the formation and the stability of some donor-acceptor supermolecules in terms of the above conceptual density functional descriptors. We rely upon the various formulae of computing the amount of charge transfer and heat of reaction during chemical combination in terms of density functional descriptors.

We have already applied these descriptors and parameters derived from such descriptors in the study of \( F_2 B - NH_3 \) supermolecule. The necessary formulae of computing the required quantities are presented below:

(i) The Sanderson's expression for chemical potential (\( \mu_a \)) of an aggregate from isolated fragments:

\[
\mu_a = - \left( \frac{1}{n} \prod_i |\mu_i| \right)^{1/n}
\]

where \( \mu_i \) is the chemical potential of the \( i^{th} \) fragment, \( \mu_a \) is the chemical potential of the aggregate and \( n \) is the number of isolated fragments forming the aggregate.

(ii) Ghosh et al. suggested that the hardness of an aggregate molecule is the reciprocal of the aggregate softness computed as the average of the softness of the constituent fragments. The additivity formula of Ghosh et al. is

\[
\frac{1}{\eta_A^n} = \frac{1}{n} \sum \left( \frac{1}{\eta_i} \right)
\]

where \( \eta_A^n \) is the hardness of the aggregate, \( \eta_i \) is the hardness of \( i^{th} \) fragments and \( n \) is the number of fragments.

(iii) Datta on the other hand suggested a geometric mean formula for the same purpose of computing hardness of an adduct from its constituents. Datta's product formula is

\[
\mu_A^n = - \left( \prod_i |\eta_i| \right)^{1/n}
\]

where \( \eta_A^n \) is the hardness of the aggregate, \( \eta_i \) is the hardness of \( i^{th} \) fragments and \( n \) is the number of fragments.

(iv) Gazquez pointed out that the hardness and softness concepts play a fundamental role in the description of chemical events and the energy of the bond between A and B is determined by the hardness difference. The amount of charge transfer \( \Delta N \) from donor (of lower electronegativity) to acceptor (of higher electronegativity) and the reaction energy, \( \Delta E_{	ext{rec}} \) may be evaluated as

\[
\Delta N = \frac{(\mu_B - \mu_A)}{(\eta_B + \eta_A)}
\]

\[
\Delta E_{	ext{rec}} = - \frac{1}{2} (\eta_{AB} - \eta_A - \eta_B)
\]

where \( \eta_{AB} \) represents global hardness of adduct A-B and the other quantities are as stated above.

In the present study, A is BF3, a Lewis acid and B's are HCN, HNC, H2C-CN, H2C-NC, the Lewis bases. We have theoretically allowed the formation of supermolecules like HCN-BF3, HNC-BF3, H2C-CN-BF3, H2C-NC-BF3 and have tested the rationale of the formation of such complexes in terms of the theoretical quantities derived from density functional descriptors stated above. The molecule BF3, is a hard acid in Pearson's HSAB classification. In spite of its hardness, the molecule is found to form stable and well defined adducts with a large number of Lewis bases. The characteristic structural behaviour exhibited by BF3 is that the molecule, in spite of high
energy of activation, sharply reorganizes from its planar \( D_{2d} \) equilibrium geometry to pyramidal shape \( C_{3v} \). In chemical response, the donors as well as acceptors evolve, through a physical process of structural reorganization, from equilibrium conformations toward the non-equilibrium conformations through the transition state with appropriate symmetry. Ghosh and Jana have proved that such structural reorganization is a condition precedent to occur in the event of chemical reaction of charge transfer and bond formation for symmetry reason. It is also theoretically observed that such an evolution in geometry is associated with modification of their reactivity through the change in global hardness, MO parameters and chemical potentials. These ligands are chosen judiciously so that they are structural isomers to each other and it is expected that the study of complexes formed by these ligands will reveal interesting features of donor-acceptor interaction. Gámez analyzed the complex formation in terms of two types of charge rearrangements—transfer and reshuffling and evaluated heat of reaction in terms of the density functional descriptors. These compounds are already experimentally known.

**Methods of Computation**

**Computation of \( \eta \) and \( \mu \)**

Pal et al. have pointed out that although the quantities, \( \eta \) and \( \mu \) are rigorously defined in terms of DFT, these cannot be obtained using \textit{ab initio} wave function formalism. Parr et al. suggested approximate formulae of calculation of hardness and chemical potential in terms of ionization potential and electron affinity. Now, the operational and approximate formulae are

\[
\eta = -(I+A)/2 \quad \mu = (I-A)/2 \quad \ldots (8)
\]

where \( I \) is ionization potential and \( A \) is electron affinity.

On further approximation in terms of Koopmans’ theorem,

\[
I = -\varepsilon_{\text{HOMO}}A = -\varepsilon_{\text{LUMO}} \quad \ldots (9)
\]

\( \varepsilon_{\text{HOMO}} \) and \( \varepsilon_{\text{LUMO}} \) are the energy values of HOMO and LUMO respectively.

Hardness (\( \eta \)) and chemical potential (\( \mu \)) may be operatively defines as follows:

\[
\mu = (\varepsilon_{\text{HOMO}} + \varepsilon_{\text{LUMO}})/2 \quad \ldots (10)
\]

\( \eta = (-\varepsilon_{\text{HOMO}} + \varepsilon_{\text{LUMO}})/2 \quad \ldots (11) \)

N-ends of donors HCN, CH\(_3\)CN, and C-end of HNC and CH\(_3\)NC are approached to the B-end of BF\(_3\) \( (C_3v) \) along \( C_3(Z) \) axis to obtain the supermolecules. The energy is minimized for each supermolecule following geometry optimization technique (GOT). In the present study, we have adopted approximate SCF-MO theory of Pople to calculate the geometry of the supermolecules and the eigen value spectrum of the donors and acceptor in separated states, and that of the supermolecules. From the computed eigen value spectrum, we have calculated the \( I \) and \( A \) invoking Koopmans’ theorem (Eq. 9) and then evaluated the density functional descriptors. Standard parameters and STO basis set have been used. The coulomb and the overlap integrals are computed through the explicit analytical formulae of Roothaan.

The evaluated amount of the charge transferred from the donors to acceptor moiety, and the reaction energies of all the systems are presented in Table 1. The chemical potential (\( \mu \)) and electronegativity (\( \gamma \)) values evaluated through Sanderson’s equation are presented in Table 2. Table 3 contains the evaluated hardness value of supermolecules using empirical formula given by Parr and Pearson, Ghosh’s \( \gamma \) additivity scheme and the formula of Datta. The heats of formation data of all four supermolecules are represented in Table 4.

**Discussion**

**Formation of supermolecule, HCN-BF\(_3\)**

Chemical interaction of donor, HCN, and acceptor BF\(_3\) gives the supermolecule HCN-BF\(_3\). The optimized geometry can be seen from Fig. 1. It is evident from Table 1 that the global hardness and chemical potential of the donor moiety are greater than those of the acceptor moiety. The global hardness of the supermolecule is less than that of the reacting systems. The evaluated amount of charge transferred from the donor to the acceptor moiety is 0.12440 and the reaction energy is 0.27208 (a.u). From Tables 1 and 2 it is evident that the electronegativity of the supermolecule computed through the formulae of Parr and Pearson, and that of Sanderson is in between the electronegativities of the donor and the acceptor systems. Since the electronegativity equalization principle of Sanderson is a cardinal principle in this study, it is pertinent to make a short resume of the concept. It postulates that when two or more atoms which are initially different
Table 1—The global hardness (\(\eta\)), chemical potential (\(\mu\)) of BF\(_3\), donors and supermolecules, charge transfer (\(\Delta N\)) and reaction energy (\(\Delta E\)).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(\eta) (a.u)</th>
<th>(\mu) (a.u)</th>
<th>(\Delta N = \frac{(\mu_B - \mu_A)}{\left(\eta_B + \eta_A\right)}) (a.u.)</th>
<th>(\eta_A - \eta_B - \eta_A) (a.u.)</th>
<th>(\Delta E_{\text{react}} = -\frac{1}{2} \left(\eta_{AB} - \eta_A - \eta_B\right)) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF(_3)</td>
<td>0.40722</td>
<td>-0.32481</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCN</td>
<td>0.45065</td>
<td>-0.21809</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(_3)B–NCH</td>
<td>0.31376</td>
<td>-0.30211</td>
<td>0.12440</td>
<td>-0.54417</td>
<td>0.272085</td>
</tr>
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<tr>
<td>HNC</td>
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<td>-0.17967</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>F(_3)B–CNH</td>
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<td>-0.26926</td>
<td>0.17838</td>
<td>-0.48411</td>
<td>0.24206</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)CN</td>
<td>0.36022</td>
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</tr>
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<td>F(_3)B–NCCH(_3)</td>
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<td>-0.46067</td>
<td>0.23034</td>
</tr>
<tr>
<td>BF(_3)</td>
<td>0.40722</td>
<td>-0.32481</td>
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<tr>
<td>CH(_3)NC</td>
<td>0.39718</td>
<td>-0.18513</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(_3)B–CNCH(_3)</td>
<td>0.30009</td>
<td>-0.29864</td>
<td>0.17364</td>
<td>-0.50431</td>
<td>0.25216</td>
</tr>
</tbody>
</table>

Table 2—Calculation of the chemical potential (\(\eta\)) of the supermolecule according to Sanderson's additivity scheme.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(\mu) (a.u)</th>
<th>(\chi) (a.u)</th>
<th>(\sqrt{(\mu_B \mu_A)}) (a.u.)</th>
<th>(\sqrt{(\chi_B \chi_A)}) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF(_3)</td>
<td>-0.32481</td>
<td>0.32481</td>
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<tr>
<td>HCN</td>
<td>-0.21809</td>
<td>0.21809</td>
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</tr>
<tr>
<td>F(_3)B–NCH</td>
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<td>0.30211</td>
<td>-0.26615</td>
<td>0.26615</td>
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<tr>
<td>BF(_3)</td>
<td>-0.32481</td>
<td>0.32481</td>
<td></td>
<td></td>
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<tr>
<td>HNC</td>
<td>-0.17967</td>
<td>0.17967</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(_3)B–CNH</td>
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<td>0.26926</td>
<td>-0.24158</td>
<td>0.24158</td>
</tr>
<tr>
<td>BF(_3)</td>
<td>-0.32481</td>
<td>0.32481</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)CN</td>
<td>-0.1750</td>
<td>0.1750</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(_3)B–NCCH(_3)</td>
<td>-0.28185</td>
<td>0.28185</td>
<td>-0.23841</td>
<td>0.23841</td>
</tr>
<tr>
<td>BF(_3)</td>
<td>-0.32481</td>
<td>0.32481</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)NC</td>
<td>-0.18513</td>
<td>0.18513</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(_3)B–CNCH(_3)</td>
<td>-0.29864</td>
<td>0.29864</td>
<td>-0.24522</td>
<td>0.24522</td>
</tr>
</tbody>
</table>

Table 3—Calculation of the global hardness (\(\eta\)) of the supermolecule according to additivity schemes of (a) Ghosh and (b) Datta.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(\eta)</th>
<th>(\eta) (a)</th>
<th>(\eta) (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF(_3)</td>
<td>0.40722</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCN</td>
<td>0.45065</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(_3)B–NCH</td>
<td>0.31376</td>
<td>0.42783</td>
<td>0.42838</td>
</tr>
<tr>
<td>BF(_3)</td>
<td>0.40722</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNC</td>
<td>0.40645</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(_3)B–CNH</td>
<td>0.32956</td>
<td>0.40683</td>
<td>0.40683</td>
</tr>
<tr>
<td>BF(_3)</td>
<td>0.40722</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)CN</td>
<td>0.36022</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(_3)B–NCCH(_3)</td>
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<td>0.38299</td>
<td>0.38228</td>
</tr>
<tr>
<td>BF(_3)</td>
<td>0.40422</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)NC</td>
<td>0.39718</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(_3)B–CNCH(_3)</td>
<td>0.30009</td>
<td>0.40214</td>
<td>0.40216</td>
</tr>
</tbody>
</table>

Table 4—Comparison of heats of formation of the different supermolecules (The energy of the acceptor moiety, BF\(_3\) is ~86.73270 a.u.).

<table>
<thead>
<tr>
<th>Donor</th>
<th>Energy (a.u.)</th>
<th>Supermolecule</th>
<th>Heat of formation (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN</td>
<td>-19.05874</td>
<td>HCN-BF(_3)</td>
<td>-68.86538</td>
</tr>
<tr>
<td>HNC</td>
<td>-19.01482</td>
<td>HNC-BF(_3)</td>
<td>-89.722497</td>
</tr>
<tr>
<td>CH(_3)CN</td>
<td>-27.67412</td>
<td>CH(_3)CN-BF(_3)</td>
<td>-121.67051</td>
</tr>
<tr>
<td>CH(_3)NC</td>
<td>-114.40064</td>
<td>CH(_3)NC-BF(_3)</td>
<td>-82.65096</td>
</tr>
</tbody>
</table>

Fig. 1—Different optimized geometric parameters of supermolecules.
in electronegativity unite, their electronegativities become equalized at some intermediate value in the molecule. Thus, the formation of the supermolecule is in accordance with the electronegativity equalization principle of Sanderson. Gazquez$^{23}$ divided the total interaction energy into two contributions: one that corresponds to the charge transfer process between two reactants at constant external potential, and the second one that corresponds to a reshuffling of electron density at constant chemical potential. He further pointed out that the reaction energy is negative when the sum of the hardness of the product is greater than the sum of the hardness of the reactants and it is positive when just the opposite occurs. In the present study, it has been observed that the hardness of the adduct supermolecule is less than the sum of the hardness of the reactants and that the reaction energy is positive. Thus, the formation of the instant supermolecule is in accordance with the theoretical prediction of Gazquez. Table 3 demonstrates that the global hardness evaluated through the additivity formulae of Ghosh$^{24}$ and Datta$^{22}$ are different than those obtained through the formula of Parr and Pearson$^{4}$.

**Formation of supermolecule HNC–BF$_3$**

The above supermolecule is formed by the approach of the C-end of HNC to the B-end of BF$_3$. The optimized geometry is presented in Fig. 1. It is well known that the donor HNC is a structural isomer of HCN. We may correlate the donor ability of the two molecules from their computed chemical potentials. From Table 1 we see that the chemical potential of HNC is greater than that of HCN. This immediately indicates that HNC is a stronger base (donor) than its isomer, HCN. The magnitude of the computed transferred charge in the case of HNC is 0.17838 and in the case of its isomer it is 0.12440. We may further correlate this fact by pointing out the electronegativity or local softness of attaching atoms. The C atom is softer than the N atom and hence the chemical interaction of charge transfer where the attaching atom is C, is expected to be stronger than that in the case of HCN where the attaching atom is N.

Now considering the chemical potential data from Tables 1 and 2 we see that the chemical potential of the supermolecule is in between the chemical potential values of the donor and acceptor. Thus, the formation of the supermolecule HNC–BF$_3$ is in accordance with the electronegativity equalization principle of Sanderson. One important aspect is that the hardness of the supermolecule is less than the sum of the hardness of the reactants. Hence, reaction energy should be positive according to the theoretical prediction of Gazquez. Table 1 reveals that the evaluated reaction energy of the supermolecule is positive. Hence, this result is also a validity of Gazquez empirical formulae of calculating reaction energy.

**Formation of adduct supermolecule, H$_3$C-CN-BF$_3$**

The supermolecule H$_3$C-CN-BF$_3$ is formed by the chemical interaction of the donor H$_3$C-CN and acceptor, BF$_3$. The optimized geometry of the supermolecule is displayed in Fig. 1. From Tables 1 and 2, we see that the chemical potential of the donor is higher than that of acceptor and that of the supermolecule is in between the corresponding values of the donor and acceptor and hence the formation of the supermolecule CH$_3$CN–BF$_3$ is in accordance with the electronegativity equalization principle of Sanderson. The amount of charge transferred from donor to acceptor moiety is 0.19520 and the calculated reaction energy is 0.23034. From Tables 1 and 3, we note that the hardness of the supermolecule is less than the sum of the hardness of the interacting species. The reaction energy is also positive. The formation of the donor-acceptor or charge-transfer complex is, thus, in accordance with the theoretical prediction in terms of density functional descriptors by Gazquez.

**Formation of adduct supermolecule, H$_3$C-NC-BF$_3$**

The supermolecule is formed by chemical interaction of the donor and its optimized geometry is shown in Fig. 1. From Tables 1 and 2, we see that the chemical potential of the donor is higher than that of the acceptor and that of the supermolecule is in between the corresponding values of the donor and acceptor. Hence, the formation of the supermolecule CH$_3$NC–BF$_3$ is in accordance with the electronegativity equalization principle of Sanderson. The amount of charge transferred from donor to acceptor moiety is 0.17364 and the calculated reaction energy is 0.25216. From Tables 1 and 3, we note that the hardness of the supermolecule is less than the sum of the hardness of the interacting species. The reaction energy is positive. The formation of the donor-acceptor or charge-transfer complex is in accordance with the theoretical prediction in terms of density functional descriptors by Gazquez.
The effect of structural isomerism in the ligands

Between the two structural isomers, HCN and HNC, HNC has greater chemical potential than HCN. Hence, HNC should transfer a larger amount of charge when the acceptor unit is the same. Also, the $\Delta N$ depends upon the hardness descriptor, $\eta$. The adduct formed through larger quantity of charge transfer is expected to be more stable. From Table 1, it is evident that the amount of charge transfer is larger in the formation of HNC–BF$_3$ as compared to that of HCN–BF$_3$. Further, it is evident from Table 4 that the magnitude of heat of formation of supermolecule, HNC–BF$_3$ (−89.7250 kcal/mol) is greater than that of HCN–BF$_3$ supermolecule (−68.86538 kcal/mol).

Thus, the stability of the donor-acceptor charge transfer complexes can be justified in terms of the amount of charge transfer evaluated through the density functional descriptors.

The effect of $-\text{CH}_3$ substitution

The substitution of H atom by $-\text{CH}_3$ group generates two distinct situations: Firstly, CH$_3$CN and HCN or CH$_3$NC and HNC type, and, secondly, CH$_3$CN and CH$_3$NC.

Substitution of H by $-\text{CH}_3$ group in HCN and HNC donors generate CH$_3$CN and CH$_3$NC structural isomers respectively. It is expected that the substitution of H atom by $-\text{CH}_3$ group will modify the basicity of such chemical systems. We have already noted above that the amount of charge transfer and magnitudes of heat of formation are greater for the HNC–BF$_3$ adduct than for the HCN–BF$_3$ adduct, i.e., B atom of BF$_3$ attaches to C atom of the donor more strongly than the N atom. Such variation of the stability of adducts can be correlated in terms of softness and/or hardness of attaching centers, and the chemical potential of the ligands. But when the $-\text{CH}_3$ substitution occurs, the amount of charge transfer and the magnitudes of heat of formation are larger for H$_3$C–CN–BF$_3$ than the H$_3$C–NC–BF$_3$, i.e., the situation is just reversed on $-\text{CH}_3$ substitution. The correlation comes from the chemical potential data (Table 1). Effect of $\text{CH}_3$ substitution on HCN increases the chemical potential of product molecule. Now, it can be easily predicted that the amount of charge transfer in case of H$_3$C–CN–BF$_3$ is greater than that of HCN–BF$_3$. Comparing the amount of charge transfer from Table 1, and the magnitudes of heat of formation from Table 4, it is evident that H$_3$C–CN–BF$_3$ is more stable than HCN–BF$_3$. But the effect of $-\text{CH}_3$ substitution is not so prominent in case of HNC. From Table 1, we see that chemical potential of HNC is greater than that of H$_3$C–NC. Probably, inductive effect of $-\text{CH}_3$ group is not so effective when it is attached to more negative N-end of C=N moiety.

In order to justify the difference of basicity of the two ligands, H$_3$C–CN and H$_3$C–NC, we see that chemical potential of H$_3$C–CN is higher as compared to that of H$_3$C–NC (Table 1). Therefore, it is quite possible that H$_3$C–CN is a stronger electron donating ligand than H$_3$C–NC. Now the amounts of charge transfer computed in terms of density functional descriptors are 0.19520 and 0.17364 in forming the supermolecules CH$_3$CN–BF$_3$ and CH$_3$NC–BF$_3$ respectively. Table 4 demonstrates that the magnitude of heats of formation of supermolecule CH$_3$CN–BF$_3$ is greater than that of CH$_3$NC–BF$_3$ supermolecule.

It is to be noted that the global hardness of the 'aggregate', i.e., the supermolecule, calculated in terms of the hardness values of isolated fragments through the additivity formulae of Ghosh and Datta are nearly equal to each other but significantly different from that calculated directly by the formula suggested by Parr and Pearson. In each case, we have seen that the donors have lower electronegativity and higher chemical potential than the acceptor moiety. The electronegativity and chemical potential of the donor-acceptor supermolecules are in between the corresponding values of the donor and acceptor systems in the separated state. Computed density functional descriptors predict that methyl substitution in HCN donor would increase the amount of charge transfer and the stability of the complexes of these ligands.

Conclusions

The BF$_3$, a Lewis acid and a number of Lewis bases, viz., HCN, HNC, H$_3$C–CN and H$_3$C–NC, are allowed to chemically interact through the process of charge transfer leading to the formation of supermolecules like F$_3$B–NCH, F$_3$B–CNH, F$_3$B–NC–CH$_3$, F$_3$B–CN–CH$_3$. The donor ligands are structural isomers with the attaching atoms of different softness. It is demonstrated that the formation of the above charge transfer complexes can be rationalized in terms of density functional descriptors like hardness and chemical potential, and theoretical generalizations like the maximum hardness principle and the electronegativity equalization principle. The computed values of the hardness, chemical potential and electronegativity of the donors, the acceptor and the supermolecules reveal that the formation of acid-
base supermolecules are in accordance with the electronegativity equalization principle and the maximum hardness principle. The variation of heats of formation of the supermolecules and the effect of substitution of H by –CH₃ group in the donor molecules can be correlated in terms of conceptual density functional descriptors like chemical potential and global hardness. The present calculation of heat of reaction and amount of charge transfer through the formulæ derived by Gázquez in as many as four different examples of donor-acceptor interaction is one more validity test of the maximum hardness principle MHP, and chemical potential equalization principle.

References