RESEARCH PAPER

Application of Superhalogens in the Design of Organic Superconductors

Ambrish K. Srivastava,*[a] Abhishek Kumar,[b] Sugriva N. Tiwari,[a] and Neeraj Misra[b]

Dedicated to Prof. K. Bechgaard, who passed away on March 7, 2017

Abstract: Bechgaard salts, (TMTSF)ₓX (TMTSF = tetramethyl tetraselenafulvalene and X = complex anion), form the most popular series of organic superconductors. In these salts, TMTSF molecules act as super-electron donor and X as acceptor. We computationally examine the electronic structure and properties of X in commonly used (TMTSF)ₓX (X = NO₃, BF₄, ClO₄, PF₆) superconductors and notice that they belong to the class of superhalogens due to their higher vertical detachment energy than halogen anions. This prompted us to choose other superhalogens such as X = BO₂, BH₄, B₂F₆, AuF₆ and study their (TMTSF)ₓX complexes. Our findings suggest that these complexes behave more or less similar to those of established (TMTSF)ₓX superconductors, particularly for X = BO₂ and B₂F₆. We, therefore, believe that the concept of superhalogen can be successfully applied in the design of novel organic superconductors.

Organic superconductors (OSCs) are of particular interest due to their high anisotropy and other intriguing properties. W. A. Little [1] proposed for the first time in 1964 the possibility of synthesis of organic polymers, which might exhibit superconductivity. K. Bechgaard [2] discovered the first organic superconductor, (TMTSF)₂PF₆ in 1980 (TMTSF = tetramethyl tetraselenafulvalene), which led to the synthesis of a series of related organic compounds, known as Bechgaard salts [3]. In this series, (TMTSF)₂ClO₄ is particularly interesting due to its superconducting property at ambient pressure [4]. These materials are considered quasi-one-dimensional due to the fact that superconduction can only occur along a single axis. The Fabre salts form another series of compounds belonging to this class, which are composed of tetramethyl tetrathiafulvalene (TMTTF). The quasi two-dimensional materials such as bisethylenedithio tetrathiafulvalene (BEDT-TTF) series and three-dimensional alkali metal doped fullerenes based organic superconductors are also well studied [5, 6]. The alkali-doped fullerene RbCs₂C₆₀ is known to possess the highest critical temperature of 33 K at ambient pressure [7]. Despite these facts, Bechgaard salts have many other properties that make them particularly interesting. For instance, these salts can easily undergo any phase by varying both temperature and pressure. In (TMTSF)ₓX (where X = complex anion), TMTSF serves as electron donor and X behaves as electron acceptor, thus forming a charge transfer complex with metal like characteristics.

Although much attention has been paid to electron donors for OSCs [8], the studies on the role of X are relatively scarce. Here, we focus on the electronic structure and properties of complex anions (X⁻) and notice that they all belong to a special class of species, known as superhalogen. Superhalogen, proposed by Gutsev and Boldyrev [9] in 1981 and experimentally confirmed by Wang et al. [10] in 1999, are the species with higher electron affinity (EA) or vertical detachment energy (VDE) than those of halogen. Superhalogens have been continuously studied [11] due to their possible applications in a variety of fields [12]. This provides us an opportunity to analyze other superhalogens for their possible role in the design of new materials for organic superconductors.

We first analyze the molecular structure and superhalogen nature of complex anions (X⁻) commonly employed in (TMTSF)ₓX series of organic superconductors such as NO₃⁻, BF₄⁻, ClO₄⁻, PF₆⁻, etc. as displayed in Fig. 1. The structures of NO₃⁻ and PF₆⁻ are trigonal planar and octahedral with the bond lengths of 1.26 Å and 1.65Å, respectively, whereas both BF₄⁻ and ClO₄⁻ are tetrahedral with the bond lengths of 1.42 Å and 1.50 Å, respectively.

The VDE of anions is calculated as the difference of total electronic energy of neutral system and corresponding anion both at anionic equilibrium structure.

[a] Dr. A. K. Srivastava, Prof. S. N. Tiwari
Department of Physics
DDU Gorakhpur University
Civil Lines, Gorakhpur, 273009, Uttar Pradesh, India
E-mail: ambrishphysics@gmail.com
[b] Mr. A. Kumar, Prof. N. Misra
Department of Physics
University of Lucknow
University Road, Lucknow, 226007, Uttar Pradesh, India

Figure 1. Equilibrium structures of superhalogen anions considered in this study (a) and TMTSF molecule (b).
ituated by BF$_4^-$. In TMTSF, these interactions are shown by dashed lines. Furthermore, TMTSF molecule a is tetrahedral like BF$_4^-$. BH$_4^-$, B$_2$F$_7^-$, and AuF$_6^-$ also displayed in Fig. 1. The VDEs of these superhalogen anions lie in the range 4.35 eV – 8.53 eV as listed in Table 1. BO$_7^-$ is linear with bond lengths of 1.26 Å, same as those of NO$_3^-$. BH$_4^-$ is tetrahedral like BF$_4^-$, in which H atoms are employed instead of F as ligands. In B$_2$F$_7^-$, one of F ligands in BF$_4^-$ is substituted by BF$_2$ moiety itself. Like PF$_5^-$, AuF$_6^-$ is octahedral with the bond lengths of 1.96 Å. Therefore, these anions also possess some structural similarity with those of complex anions used in OSCs. We have also optimized the structure of TMTSF molecule as shown in Fig. 1. In TMTSF, there exist two pentagon rings containing two Se atoms each, which are connected head to head via C=C bond and substituted with two –CH$_2$ groups at other C positions. The ring systems are not coplanar, but possessing boat conformation having dihedral angle between rings (δ) of 105° as marked in Fig. 1.

The equilibrium structures of (TMTSF)$_2$X complexes for aforementioned superhalogens (X) are displayed in Fig. 2. One can note that the geometrical structures of (TMTSF)$_2$X are significantly affected by the geometry of X. For trigonal planar NO$_3^-$, both TMTSF molecules possess stacked configuration. For tetrahedral BF$_4^-$ and ClO$_4^-$, both TMTSF units are almost parallel to each other. In case of octahedral PF$_5^-$, two TMTSF units become perpendicular to each other. Furthermore, TMTSF molecules arrange themselves parallel for tetrahedral BH$_4^-$ (like BF$_4^-$ and ClO$_4^-$) and perpendicular for octahedral AuF$_6^-$ (like PF$_5^-$). Moreover, these two units become collinear for linear NO$_3^-$ and stacked for B$_2$F$_7^-$ as clearly seen in Fig. 2.

Table 1 lists the interaction lengths ($d_{int}$) between TMTSF units and X along with their interaction energy ($\Delta E_{int}$), calculated as below:

$$\Delta E_{int} = E[X] + E[(TMTSF)X] - E[(TMTSF)_2]$$

where $E[X]$ represents total electronic energy of respective species. The interaction energy is an important parameter for measuring the strength of charge-transfer interaction in (TMTSF)$_2$X complexes. For typical OSCs, our calculated $\Delta E_{int}$ ranges from 1.34 eV for X = NO$_3^-$ to 5.11 eV for X = PF$_5^-$ in case of proposed (TMTSF)$_2$X complexes, this $\Delta E_{int}$ value varies between 0.52 eV for X = BH$_4^-$ and 6.31 eV for X = AuF$_6^-$ This may suggest that the stability of proposed complexes is comparable to or even greater than traditional OSCs, excluding the case of BH$_4^-$. Note that all these complexes are stabilized by hydrogen-bonding interactions expect (TMTSF)$_2$BH$_4^-$, which is stabilized by dihydrogen bonding.

Table 1. Vertical detachment energy (VDE) of X, interaction bond-length ($d_{int}$) and energy ($\Delta E_{int}$), net charge on X ($Q_X$), frontier orbital energy ($E_{int}$), dihedral angle between rings of TMTSF (δ) and deformation energy ($\Delta E_{def}$) for various (TMTSF)$_2$X complexes.

| X       | VDE (eV) | $d_{int}$ (Å) | $\Delta E_{int}$ (eV) | $Q_X$ (e) | $E_{int}$ (eV) | δ (°) | $\Delta E_{def}$ (eV) |
|---------|----------|---------------|-----------------------|-----------|----------------|-------|------------------------|
| NO$_3^-$ | 4.10     | 2.21-2.40     | 1.34                  | -0.64     | 0.61           | 173°  | 0.18                   |
| BO$_2^-$ | 4.35     | 2.05          | 1.79                  | -0.79     | 0.18           | 180°  | 0.10                   |
| BH$_4^-$ | 4.42     | 2.26-2.56     | 0.52                  | -0.72     | 0.71           | 160°  | 0.17                   |
| ClO$_4^-$| 5.65     | 2.34-2.44     | 2.57                  | -0.86     | 0.68           | 158°  | 0.15                   |
| BF$_4^-$ | 7.39     | 2.31-2.36     | 4.62                  | -0.71     | 0.71           | 159°  | 0.17                   |
| PF$_5^-$ | 8.22     | 2.33-2.74     | 5.11                  | -0.87     | 0.23           | 173°  | 0.12                   |
| AuF$_6^-$| 8.51     | 2.05-2.82     | 6.31                  | -1.59     | 1.35           | 176°  | 0.31                   |
| B$_2$F$_7^-$| 8.53 | 2.40-2.65     | 4.94                  | -0.85     | 0.33           | 161°  | 0.08                   |

As already known [13], the OSCs tend to have about half the donor (D) oxidized to D$^{+}$, with an average charge of +1/2 per D. In (TMTSF)$_2$X complexes, the electron transfer takes place from both TMTSF molecules to X moiety such that X becomes negatively charged leaving positive charge on TMTSF molecules. We have calculated atomic charge on X ($Q_X$) in these complexes.
and listed in Table 1. For traditional OSCs, the Q₂ value lies between -0.64e for X = NO₂ and -0.87e for X = PF₆. For other (TMTSF)ₓX complexes studied, the Q₂ takes values between 0.10e for X = CS₂ and 0.85e for X = BF₄, excluding AuF₆.

Therefore, in the light of electron transfer and interaction energy, BO₂, BH₄ and B₂F₇ superhalogen complexes are analogous to those of NO₂, BF₄, ClO₄ and PF₆. For AuF₆, however, the electron transfer increases to -1.59e leading to significant increase in the interaction energy of (TMTSF)₂AuF₆ complexes (see Table 1). In order to compare the reactivity (conductivity) of (TMTSF)ₓX complexes, we refer to their frontier orbital energy gap (E_{gap}) listed in Table 1. This energy gap corresponds to the band gap in solids. The E_{gap} value of (TMTSF)₂X complexes varies between 0.23 eV for X = PF₆ and 0.71 for X = BF₄. For X = BO₂, BH₄ and B₂F₇, this E_{gap} value lies between 0.18 eV–0.71 eV. Evidently, E_{gap} values of all (TMTSF)ₓX complexes studied are less than 1 eV, except that of (TMTSF)₂AuF₆ (1.35 eV). This may further suggest the applicability of BO₂, BH₄ and B₂F₇ superhalogen complexes in the design of new OSCs.

As mentioned earlier, neutral TMTSF molecules possess boat like configurations (see Fig. 1). Due to electron-transfer from TMTSF molecules to X, their structures tend to be distorted and become planar. It has been suggested [14] that the conduction in OSCs leads to a coupling between electron-transfer and the boat deformation phonon modes and this electron-phonon coupling is responsible for the superconductivity. Therefore, we have analyzed the deformation of TMTSF boat structure towards planarity. In Table 1, we have also listed the dihedral angle between rings (δ) of TMTSF molecules in (TMTSF)ₓX complexes and deformation energy (∆E_{def}) calculated as below:

\[ \Delta E_{def} = E_{deformed} - E_{boat} \]

where E_{boat} is total electronic energy of (TMTSF)₂ in their equilibrium boat configuration and E_{deformed} is that of deformed (TMTSF)ₓ configuration in (TMTSF)ₓX complex. This deformation creates destabilization in the TMTSF molecules, which can be quantified by ∆E_{def}. Lower the ∆E_{def} value, higher the stabilization of neutral TMTSF in boat configuration. It has been established that the better OSCs possess larger stabilization of the boat deformation for neutral donor [13], hence smaller ∆E_{def} value. For OSCs considered here, the ∆E_{def} ranges 0.12–0.18 eV (2.8–4.2 kcal/mol). Note that (TMTSF)₂PF₆ is better OSC than (TMTSF)₂NOₓ in terms of critical temperature [3], which is in accordance with their smaller ∆E_{def} values. Therefore, considering ∆E_{def} as the most relevant parameter for OSCs, (TMTSF)₂BO₂ and (TMTSF)₂BF₄ may perform better than those of (TMTSF)₂PF₆ and (TMTSF)₂ClO₄. Although (TMTSF)₂AuF₆ possesses significantly larger ∆E_{def} value (0.31 eV) like E_{gap} and Q₂ values, the ∆E_{def} of (TMTSF)₂BH₄ is also equal to that of (TMTSF)₂BF₄, consequently it should also possess desired properties for superconductivity.

In summary, the concept of superhalogen is indeed useful in designing potential candidates for OSCs. Having established that all acceptors of super-electrons in OSCs belong to the class of superhalogen, a new series of Bechgaard salts, (TMTSF)ₓX can be realized where X is a superhalogen. Similar conclusion also applies to Fabre salts as well as two-dimensional salts such as (BETS)₃GaCl₄ (BETS = bisethylenedithio tetraselenafuvalene) [15]. Our computed VDE of GaCl₄ is 6.25 eV, which clearly suggest its superhalogen nature. Our proposed (TMTSF)₂BO₂ and (TMTSF)₂BF₄ complexes are found to be suitable candidates for OSCs. These findings should motivate experimentalists for further exploration of their properties.

**Methods**

We have used density functional theory (DFT) with B3LYP hybrid exchange-correlation functional [16] and triple-ζ basis set 6-311++G(d,p) including diffuse and polarization functions for all atoms (except Au, for which SDD pseudopotential has been employed) as implemented in Gaussian 09 program [17]. Considering the size of systems as well as popularity of the functional, the present computational scheme seems appropriate. The geometry of the structures were fully optimized without any symmetry constraint and followed by frequency calculations in order to ensure that the optimized structures belong to true minima in the potential energy surface.

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