REGULAR ARTICLE

Electronic structures and nonlinear optical properties of supramolecular associations of benzo-2,1,3-chalcogendiazoles by the elongation method

Anna Pomogaeva · Feng Long Gu · Akira Imamura · Yuriko Aoki

Abstract The investigations of one-dimensional periodic associations of benzo-2,1,3-chalcogendiazoles have been carried out by the elongation method. S, Se and Te chalcogens have been in use. For the polymers, band structures and local densities of states were extracted from ab initio calculations of electronic structure of the 15 units' oligomers. Static electric (hyper)polarizabilities were studied by the elongation finite-field method.

1 Introduction

Supramolecular assemblies, constructed from small building molecular blocks to complex structures, have attracted

A. Pomogaeva
Department of Molecular and Material Sciences,
Interdisciplinary Graduate School of Engineering Sciences,
Kyushu University, Kasuga, Fukuoka 816-8580, Japan

F. L. Gu (✉) · Y. Aoki (✉)
Department of Material Sciences, Faculty of Engineering
Sciences, Kyushu University, Kasuga,
Fukuoka 816-8580, Japan
e-mail: gu@cube.kyushu-u.ac.jp

Y. Aoki
e-mail: aoki@mm.kyushu-u.ac.jp

A. Imamura
Hiroshima Kokusai Gakuin University, Nakano, Aki-ku 6-20-1,
Hiroshima 739-0321, Japan

Y. Aoki
Japan Science and Technology Agency, CREST,
4-1-8 Hon-chou, Kawaguchi, Saitama 332-0012, Japan

much attention in the past few years [1, 2]. Weak interactions among molecules in such associations are currently of great interest in chemistry and crystal engineering. The remarkable feature of the weakly bonded systems is that the noncovalent, intermolecular interactions form the basis of the highly specific recognition, reaction, transport, etc. processes. In association with organized polymolecular assemblies, functional supermolecules capable of displaying processes of highest efficiency and selectivity may lead to the development of molecular and nanoscale electronic devices, such as high-tech sensors, devices for drug delivery, data storage and so on. The forces involved in the supramolecular associations include well-known hydrogen bonding, van der Waals forces, π–π interactions of aromatic rings, metal coordination, secondary bonding interactions and so on [3]. Detailed review of the principles of associations in crystalline molecular complexes has recently been done by Herbstein [4] in his monograph.

The concept, secondary bonding interactions (SBI), firstly introduced by Alcock [5], refers to molecular complexes associated by bonds with lengths that are longer than the sums of covalent radii of the atoms involved, but shorter than the sums of van der Waals radii. Remarkable progress in synthetic chemistry has created many new structural types of weakly interacting systems, many of which involve chalcogen atoms in the SBI [6].

Recently, SBI between organochalcogen–nitrogen heterocycles, such as derivatives of the 1,2,5-chalcogenadiazoles rings, has been under study by Cozzolino et al. [7–9]. The structure of benzo-2,1,3-chalcogendiazole supramolecular synthons is shown in Fig. 1a. For such compounds, a bonding model is based on the donation of a nitrogen's lone pair into a σ^* antibonding orbital. Being an analog of hydrogen bonding, these SBIs have distinctive features that could be used to control the properties of self-

assembled materials [9]. The relativistic density functional theory (DFT) within local density approximation (LDA) has been employed for analyzing SBI in [7–9]. It has been determined that tellurium (Te) derivatives possess the strongest association, where attractive interaction is the product of a combination of electrostatic and orbital contributions. It also has been predicted by building short chain models, and proved by experiment, the formation of ribbon polymer by the SBIs [8] (see Fig. 1b).

It is expected that in contrast with hydrogen bonds, SBIs should enhance conductivity. However, the prediction of conductive properties of extended periodic systems using periodic boundary conditions (PBC) confronts some particular difficulties with treatment of long-range coulomb interactions [10], quasilinear dependencies that occur even for medium-sized basis sets [11–13] and cases of poor self-consistent field convergence behavior [14]. Further complications are related to the treatment of infinite systems in an external field [15–18]. The difficulties are more pronounced in case of complex systems, especially with heavy atoms like Te. On the other hand, whereas the description of an ideal periodic system, as a rule, is easily achieved by plane waves, a more chemically oriented approach is preferable to treat an extended system as built from atoms or molecular units.

Recently, an efficient method for building band structure of polymers, based on finite oligomer calculations, has been proposed [19]. It allows a polymer to be studied on the same quantum-chemical background as the monomer. The elongation method, which has been introduced by Imamura et al. [20] in 1991 and further developed [21] for different kinds of systems and different levels of approximation [22], can provide accurate computations of electronic systems for fairly long oligomers. In our present work, we apply the elongation method along with band structure calculations based on finite cluster approximation to study electronic system of ribbon polymers assembled by SBI (Fig. 1b).
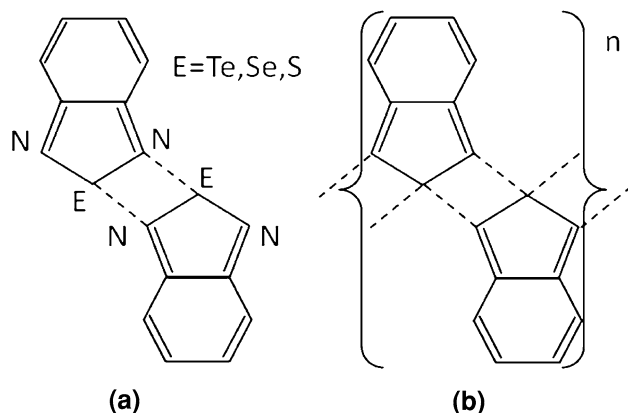

Fig. 1 Dimer (**a**) and ribbon polymer (**b**) structures of benzo-2,1,3-chalcogenadiazole

Since complexes possessing electron donor and acceptor units are promising for the potential nonlinear optical (NLO) properties, supramolecular assemblies with possible charge transfer are attractive for NLO-oriented studies [23]. The presence of atoms with large polarizability like Te, in supramolecular polymeric structures, would possibly improve NLO properties. Recently, optical second-harmonic generation efficiency of selected supramolecular associations of organotelluriums has been reported by Srivastava [24].

To have a common background in all directions of our investigations, we chose Hartee-Fock (HF) level of approximation, because DFT methods confront difficulties in the treatment of NLO properties. It has been noticed that conventional DFT significantly overestimates polarizability (α) and hyperpolarizability (γ) and gives catastrophically divergent values for long chain lengths [25, 26], though some corrections of DFT approximation can achieve success in NLO investigations [27, 28]. Thus, HF level has been used throughout this work and, additionally, we applied DFT/B3LYP approximation for band structure calculations in the case of Te-containing polymer. For supramolecular polymeric complexes (Fig. 1b), α and γ were calculated by the elongation finite-field (FF) method [29].

This paper is organized as follows. In Sect. 2, the geometry analysis is presented and interaction energy of chalcogenadiazoles dimers is discussed. In Sect. 3, band structures and local densities of states (LDOS) of the corresponding polymer systems are obtained by finite oligomer calculations. Section 3.2 is devoted to calculations of nonlinear static (hyper)polarizability. Some concluding remarks are made in Sect. 4.

2 Dimer

In Table 1, the bond lengths for compounds shown in Fig. 1 are presented. The geometry parameters were obtained by optimization with GAMESS software [30] at the HF level. The geometry of polymers was obtained by geometry optimization of short oligomers: odd numbered oligomers (5 moleculs, C_{2v} symmetry) were optimized to get intramolecular geometry parameters and even number oligomers (10 molecules, C_{2h} symmetry) to get intermolecular geometry parameters. The optimization was performed with 6-311G basis for dimers and polymers. To take relativistic effects into account for the case, we chose effective core potential (ECP) [31] for chalcogen atoms with the corresponding valence double zeta (SBKJC-VDZ) basis set [32, 33]. For dimers, a basis set including polarized functions was applied as well. ECP [32, 33] with SBKJC polarized (p,2d) basis set [34, 35] related to

Table 1 E···N (SBI) intermolecular and E–N intramolecular distances (Å) for benzo-2,1,3-chalcogenadiazole supramolecular structures optimized at the RHF level with 6-311G basis set (ECP/SBKJC VDZ for chalcogen atoms) and with 6-311G** basis set (ECP/SBKJC Polarized (p,2d) for chalcogen atoms) (italics)

Chalcogen	Sums of Van der Waals radii [4]	Dimer		Polymer	
		E···N	E–N	E···N	E–N
E = Te	3.61	2.419	2.066	2.678	2.076
		2.760	*2.017*		
E = Se	3.45	2.544	1.747	2.777	1.746
		3.201	*1.809*		
E = S	3.35	3.264	1.764	3.286	1.761
		3.230	*1.708*		

Table 2 The principal energy contributions (kJ/Mol) to the total interaction energy calculated at the RHF level for dimers of benzo-2,1,3-chalcogenadiazole by the RVS method with 6-311G basis set (ECP/SBKJC VDZ for chalcogen atoms) and with 6-311G** basis set (ECP/SBKJC Polarized (p,2d) for chalcogen atoms) (italics)

Energy components	E = Te	E = Se	E = S
Total interaction energy	−27.71	−19.94	−2.30
$E_{dimer} - 2E_{monomer}$	*−12.15*	*−3.53*	*−2.42*
BSSE corrected	−26.37	−14.32	−1.80
Total interaction energy	*−11.26*	*−2.84*	*−0.83*
Electrostatic energy	−70.63	−60.70	−3.31
	−31.89	*−6.78*	*−3.67*
Exchange repulsion energy	100.22	84.21	3.10
	39.52	*6.47*	*4.50*
Polarization energy	−21.73	−11.25	−0.53
	−9.08	*−0.95*	*−0.60*
Charge transfer energy	−29.57	−27.74	−1.04
	−8.39	*−1.51*	*−1.05*

chalcogen atoms and 6-311G** for N, C and H atoms were chosen.

From Table 1, one can see that although the exact numbers for these basis sets are different, all E···N bonds in the complexes are bigger than intramolecular E–N bonds, but significantly less than the sums of Van der Waals radii (for the same dimers, in [7], LDA calculations with all-electron basis set and zero-order regular approximation concerning relativistic effect provide intermediate E···N distances, 2.604 (Te), 2.924 (Se), compared with our data from Table 1).

Extended periodic structures on base with Se and S chalcogen atoms were not obtained in practice but benzo-2,1,3-telluradiazoles can form ribbon polymers in the solid state with 2.682–2.72 Å Te···N SBI [8], which is in correspondence with our calculated value of Te···N 2.678 Å presented in Table 1.

The interaction energy decomposition for dimers obtained by reduced variational space (RVS) method [36] designed for weakly interacted complexes is provided in Table 2. In spite of the fact that interaction energies calculated with basis set including polarized functions are found to be significantly less, the common tendency looks similar. The biggest interaction energy is obtained in the case of Te atom. The order of the interaction energies for benzo-2,1,3-chalcogendiazole dimers is Te > Se > S, which is the same as determined by DFT calculations in [9]. For Te, BSSE is about 4.8% from the total interaction energy for smaller basis set and about 7.4% for basis set with polarized functions. From Table 2, one can see that in both cases charge transfer as well as polarization energy contribution plays a significant role in the binding interaction that could be promising for the prospect of NLO properties. Charge transfer contribution is about 24% from the sum of electrostatic, polarization and charge transfer energies in case of 6-311G/VDZ basis set, and about 17% in the case of bigger basis set. Further, for oligomers

calculations, we use only moderate basis set, without polarized functions.

As discussed in previous studies [7], E···N interaction is the result of combination of electrostatic and covalent contributions that overcome strong repulsion energy. Thus, from the point of view of material design, for SBI systems, the most interesting is specific covalent contribution. For E···N SBI, it is mainly due to the donation of the lone pairs of the nitrogen atom to σ* antibonding orbitals. The importance of this kind of interaction for organization of the molecules by means of SBI into ribbon chain also can be seen from band structure as we will discuss below. We would like to mention about the substantial difference between the system with Te atom and other chalcogens. From Fig. 2, it could be seen that unlike S-contained dimer, in the Te-contained dimer, π system also contributes to stabilization energy. For example, on dimerization, HOMO of monomer (a_2 symmetry) splits into HOMO-1 (a_u) and HOMO-2 (b_g) of dimer. While π states of S-dimers are higher in energy than the ones for the corresponding monomer, in case of Te-dimer, for example, bonding orbital HOMO-2 (b_g) is lower than the monomer' s level on 0.3 eV for the 6-311G/VDZ basis set and on 0.16 eV in case of the 6-311G**/SBKJC (p,2d) basis set. The upmost valence π orbitals are degenerated in pairs in the case of S. However, as seen in Fig. 3, such states split for bonding and antibonding orbitals with the growing interaction in case of Te-contained dimer. Figure 4 shows the change of electron density for stabilized (for Te) π states of monomers and dimers of benzo-2,1,3-chalcogendiazoles. From the mapping changes between monomer and dimer, one can see that for Te-contained dimer the change is the most significant. Nevertheless, while these mapped occupied π
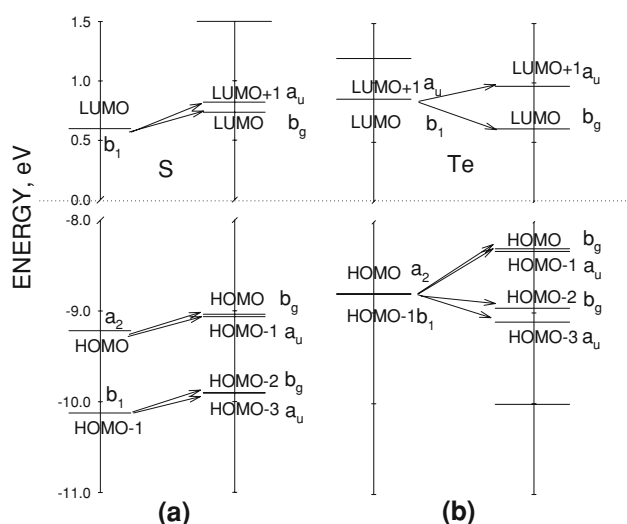
Fig. 2 π-orbital energies of benzo-2,1,3-chalcogenadiazoles on dimerization in the case of E = S (**a**) and E = Te (**b**). *Left-hand panels* are energies of MOs for one molecule (C$_{2v}$); *right-hand panels* are energies of MOs for dimer (C$_{2h}$) form RHF/6-311G with ECP/VDZ applied for chalcogen atoms

Fig. 4 Redistribution of electron density on dimerization of benzo-2,1,3-chalcogendiasoles for stabilizing π-orbitals in the vicinity of HOMO–LUMO gap. b$_1$, a$_2$, and b$_g$, a$_u$ mark symmetry representations of one molecule and the dimer, respectively (compare with Figs. 2, 3)

3 Polymer

3.1 Band structure

Band structures of the polymers have been obtained from finite cluster calculations by means of the elongation method. The elongation method is designed for calculating electronic states of large quasi-one-dimensional periodic and nonperiodic systems. In analogy to polymerization mechanism, the elongation method extends the polymer chain by stepwise adding a monomer unit to a starting cluster. Unlike conventional oligomer calculations, the elongation method works with regionally localized molecular orbitals (MO). It allows reducing variational space of the system and, therefore, can help to achieve a significant saving in computation time almost without loss of accuracy. The elongation method has proved its efficiency in treating systems at HF and DFT levels [37]. The detailed discussion of the elongation method is beyond the purpose of the present paper and can be found in literature [22, 38]. In addition to the advantages, the elongation method can be applied to the building of band structures [39].

The idea of building the band structure from finite oligomer calculations without applying PBC is based on the assumption that most of the MOs of a long oligomer are rendering of Bloch character of crystal orbitals (CO) of the corresponding polymer system. It makes possible to assign k value for every MO of oligomer for projections of the ab initio calculated MOs onto real linear combinations of model COs:
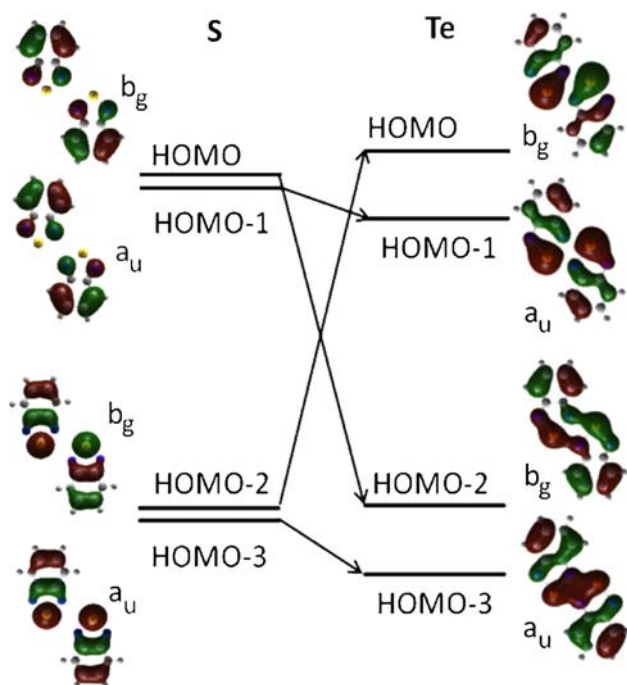

Fig. 3 Scheme of valence π-orbitals of benzo-2,1,3-chalcogen(S, Te)diasole dimers (compare with Fig. 2)

orbitals are antibonding for both S and Se dimers, the LUMO has bonding character also in the case of Se. This analysis is consistent with the range in interaction energies, Te > Se > S, as obtained by our calculations (see Table 2).
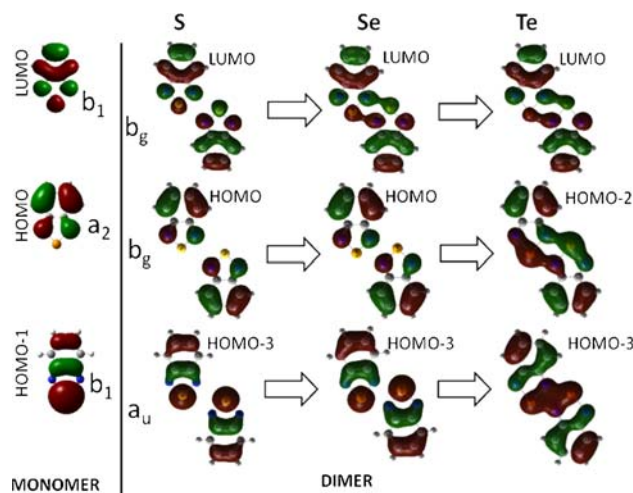
$$X_q^r = \sum_j C_{jr}^{MO} \sum_{j'} \sin\left(\frac{\pi j' q}{M+1}\right) \left\langle \chi_j^r \mid \chi_{j'}^r \right\rangle,$$
$$Y_q^r = \sum_j C_{jr}^{MO} \sum_{j'} \cos\left(\frac{\pi j' q}{M+1}\right) \left\langle \chi_j^r \mid \chi_{j'}^r \right\rangle \qquad (1)$$

Here, C_{jr}^{MO} are the expansion coefficients of MOs over a set of atomic orbitals (AO) χ_j^r, where r is the AO in the jth unit. q refers to the wave vector k within the first Brillouin zone (BZ) as

$$k = \frac{q}{M+1}\frac{\pi}{a}, \quad q = 1, 2, \ldots M, \quad 0 < k < \frac{\pi}{a}, \qquad (2)$$

where a is the translation length and M is the number of unit cells in the oligomer. For every MO, k-value could be assigned by looking for the maximum of the quantity:

$$R_q = \sum_r \sqrt{\left(X_q^r\right)^2 + \left(Y_q^r\right)^2} \qquad (3)$$

The procedure to build the band structure is presented in detail in [19] and the application of the methodology for the elongation method is discussed in [39].

For the present calculations, polymers (Fig. 1b) with $E = $ Te, Se, S) have been elongated up to 15 units of length. In the calculations, ECP with respective VDZ basis set for chalcogen atoms and 6-311G all-electron basis set for others atoms have been applied. In Fig. 5, the band structures of the polymers obtained at the HF level are presented. The lack of exact degeneracy of states in X point ($k = \pi/a$) requested by the symmetry is due to the small numerical error of extrapolation of the bands to the edges of BZ, which is unavoidable for finite cluster calculations.
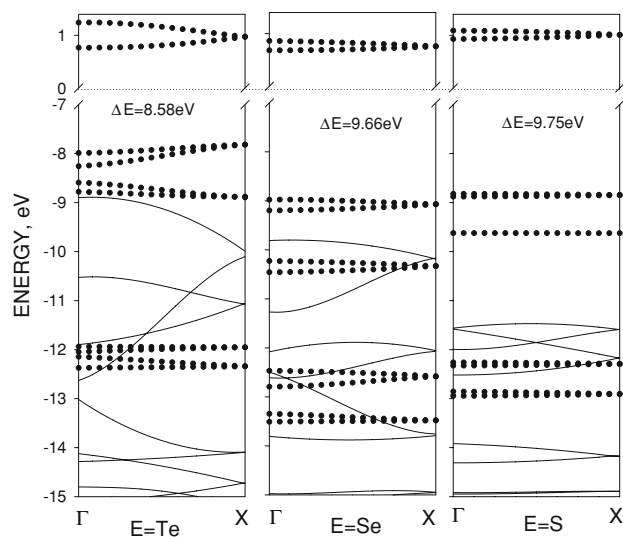
The values of the fundamental gap obtained from our HF calculations are 9.75, 9.66 and 8.58 eV for $E = $ S, Se and Te, respectively. It is easy to see from Fig. 5 that π states are much less interactive for the compounds than σ ones. The π states of telluradiazoles's polymer have some dispersion, while they are almost degenerated in case of chalcogen $E = $ S. The main contribution to the interaction is provided by valence σ states. The difference in the dispersion of the valence σ bands is significant in the case of different chalcogens. Te-polymer was obtained experimentally in the solid state, whereas there was no S or Se polymers existing, expectedly because the interactions S···N and Se···N were not sufficiently strong to synthesize the corresponding SBI-associated polymers [8].

While the comparison between the oligomers and the nature of bands could be explored with the HF method, the question of possible conductivity could not be solved by HF calculations because electron correlation was neglected in the approximation. Thus, for the oligomer assembled with benzo-2,1,3-telluradiazole molecules, we performed elongation DFT calculations with hybrid functional B3LYP [40]. The corresponding band structure is presented in Fig. 6a. The main qualitative features of the band structure
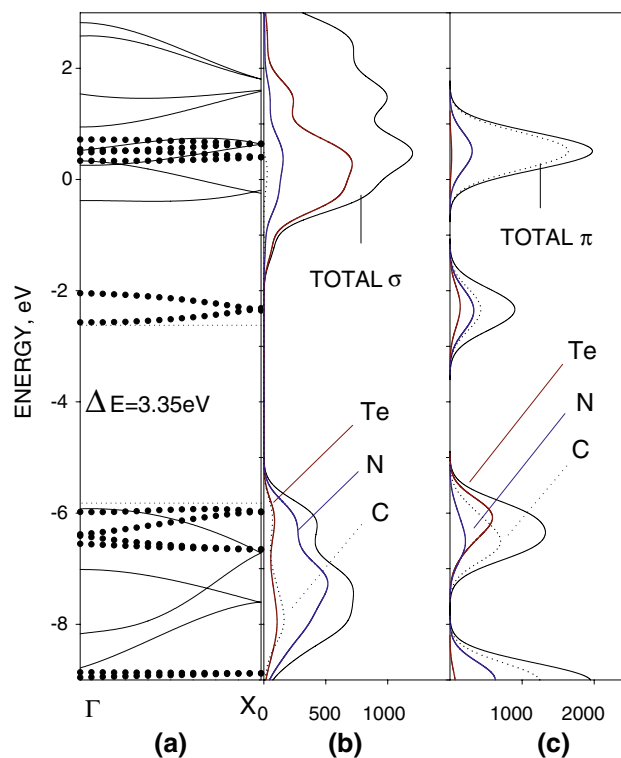

Fig. 6 Band structure (**a**) and LDOS of σ (**b**) and π (**c**) systems of benzo-2,1,3-telluradiasole ribbon polymers extracted from elongation DFT/B3LYP/6-311G (with ECP/VDZ for Te) calculations of 15-unit oligomers. *Black circles* are π bands and *lines* are σ bands for the band structure. For LDOS, *black lines* are total DOS; *red, blue* and *dotted lines* are Te, N and C LDOS contributions, respectively

Fig. 5 Band structures of benzo-2,1,3-chalcogendiasoles ribbon polymers extracted from the elongation RHF/6-311G (with ECP/ VDZ for chalcogen atoms) calculations of 15-unit oligomers. *Circles* are π bands. *Lines* are σ bands

are similar to the HF calculations, but the relative shift of the bands brings σ orbitals to the top of the valence zone. In Fig. 6b, c, LDOSs for σ and π systems with the atomic component contributions are shown. The valence π bands have a big contribution from Te atoms. The most interacted is valence σ band formed mainly by N-centered orbitals with small contribution from Te and C atoms. In the conductivity zone, the lowest σ bands are formed mainly by Te-centered orbitals with some contribution from nitrogens. It supports the idea of the critical impotency of donor–acceptor interaction between the lone pair of nitrogen and σ^* orbital centered on tellurium for E···N SBI. While the main interaction among monomers in the supramolecular association is electrostatic, specific binding interaction is based on the donation of a lone pair into a σ^* antibonding orbital [6, 7].

The energy gap in the DFT–B3LYP band structure calculation is found to be 3.35 eV. Taking into account that DFT calculations tend to underestimate the value, it could be fixed that such molecular construct should have insulator properties. Although, since the valence σ band is rather bent and its holes have some mobility, doping with electron acceptor atoms, probably, could lead to splitting of states from the top of the valence zone and lead to the appearance of defective levels in the energy gap.

3.2 NLO properties

Materials having fast nonlinear optical responses can be used for optical signal processing, optical computers and other optical devices. It has created an immense interest in the search for new materials with enhanced optical nonlinearity [41, 42]. Quantum chemical studies can provide a priori information of the nonlinear properties.

It is known that intermolecular charge transfer between electron donating and accepting moieties marks possible NLO properties of molecular associations [23]. However, to observe bulk NLO effects, it requires that the individual NLO units be oriented with respect to each other. This understanding has led to explorations of bulk composite materials and periodic supramolecular chains.

The nonlinear response to an electric field is given by the hyperpolarizability per unit cell and this quantity slowly saturates with respect to increasing chain length. However, when an electric field is presented in a polymer, the unbound potential destroys the periodicity. This unbound potential problem in PBC calculations has been solved by Kirtman, Gu and Bishop [43, 44]. Nevertheless, since the reliability of the method is extremely sensitive to the number of interacting unit cells, it is still sensible, in case of big unit cell, to use finite oligomer method wherein results for increasingly large oligomers are extrapolated to the infinite chain limit. Finite oligomer approximation has

been widely used in NLO properties of polymer as well as in crystalline systems [45, 46].

The elongation FF method provides the possibility of calculating the static electric (hyper)polarizabilities of long chains [29]. Using field-dependent Fock matrix, the (hyper)polarizabilities are obtained for every elongation step. In the presence of an external field, the total energy of the system is written as a power series of the field magnitudes,

$$W(E) = W(0) - \mu_i^0 E_i - \frac{1}{2}\alpha_{ij}E_iE_j - \frac{1}{6}\beta_{ijk}E_iE_jE_k$$
$$- \frac{1}{24}\gamma_{ijkl}E_iE_jE_kE_l + \ldots \tag{4}$$

where $W(0)$ is the field free total energy. Thus, the (hyper)polarizabilities tensors can be evaluated by numerical differentiation, e. g.

$$\alpha_{ij} = \left(\frac{\partial^2 W(\mathbf{E})}{\partial E_i \partial E_j}\right)_{E=0} \quad \beta_{ijk} = \left(\frac{\partial^3 W(\mathbf{E})}{\partial E_i \partial E_j \partial E_k}\right)_{E=0}$$
$$\gamma_{ijkl} = \left(\frac{\partial^4 W(\mathbf{E})}{\partial E_i \partial E_j \partial E_k \partial E_l}\right)_{E=0} \tag{5}$$

In case of quasi-one-dimensional systems, the most important components are diagonal along the chain's direction.

The elongation FF method has been successfully applied to the treatment of NLO properties of complex quasi-periodic systems [22, 47–50]. In the present work, nonlinear static (hyper)polarizabilities were calculated by the elongation FF method for the series of oligomers where benzo-2,1,3-chalcogendiazoles molecules were associated with each other by means of SBI. Total energy calculations were carried out for electric fields $E = 0$, ± 0.001, ± 0.002 a.u.

Due to the symmetry of the systems, the first hyperpolarizability (β) is zero. In Fig. 7, the dependences of polarizability (α) per unit cell on the oligomer's length are presented for the ribbon chains with different chalcogen atoms. In spite of the relatively small basis set, α does not exhibit unusual behavior [27, 28]. For all chains of interest, 15 units are sufficient for good convergence of polarizabilities with respective values 323 (Te), 265 (Se) and 212 (S) a.u. The analogous dependences for second hyperpolarizability (γ) are provided in Fig. 8. While the character of α dependences is similar for different chalcogens, γ increases more slowly in case of S compared with Te and Se. For the last ones, second-order hyperpolarizability per unit cell grows significantly from 14 to 15 units of the oligomer's length.

For both α and γ dependencies, the quantities are noticeably bigger in the case of Te. However, even in this case, the quantities are much less than for well-known π-conjugated polymer [27, 28]. Thus, even taking into
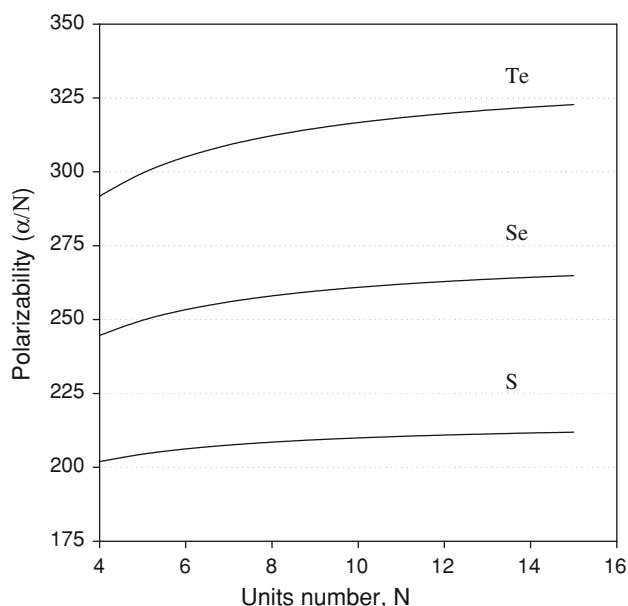
Fig. 7 Static polarizability (per unit cell) for the series of benzo-2,1,3-chalcogen(S,Se,Te)diasoles ribbon oligomers of different lengths calculated by the elongation FF method (RHF/6-311G with ECP/VDZ for chalcogen atoms)
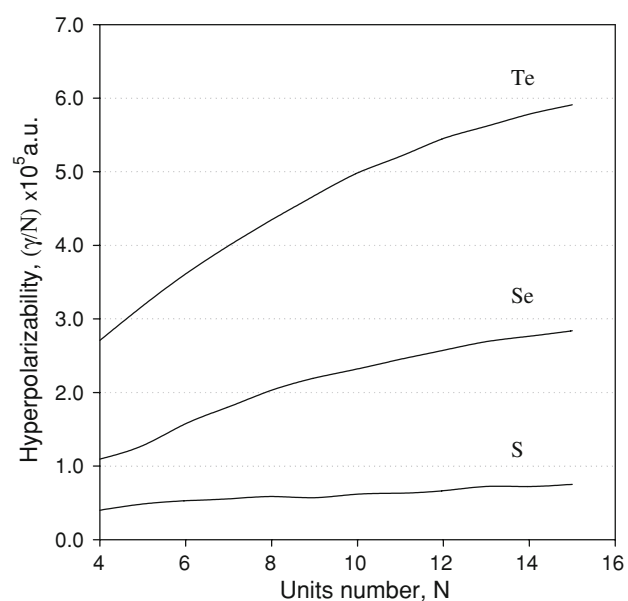

Fig. 8 Static second hyperpolarizability (per unit cell) for the series of benzo-2,1,3-chalcogen(S,Se,Te)diasoles ribbon oligomers of different lengths calculated by the elongation FF method (RHF/6-311G with ECP/VDZ for chalcogen atoms)

account the incompleteness of the basis set in our investigations, these SBI polymers are not well suited for applications in nonlinear optics. To make a last conclusion, it should be noticed that including electron correlation into energy calculations, as a rule, reduces the polarizability and the reduction becomes greater with increasing oligomer

length. The influence of correlation effect on γ is greater, but inverse and strongly depends on the level of approximation [27, 28, 51].

4 Conclusion

Weakly interacted molecules of benzo-2,1,3-chalcogen-diazoles, forming supramolecular synthons by means of chalcogen–nitrogen SBI, have been focused on in this paper. The complexes with Te, Se and S chalcogen atoms have been investigated comparatively. In the case of telluradiazole dimers, the interaction energy has been found to be substantially bigger with significant charge transfer contribution.

Band structures of corresponding ribbon polymer were built from finite oligomer calculations performed by the elongation method at HF as well as DFT levels. Valence σ bands are the most interactive in the polymers and this interaction is much more profound in the case of Te chalcogen atoms. The polymer associated with telluradiazoles has the smallest energy gap, but it was found to be a nonconductor with a band gap of about 3.4 eV from the DFT calculations.

Static polarizability and second hyperpolarizability were calculated for these polymers by the elongation FF method. Both quantities were found to be bigger for Te-associated polymers. In this case, the polarizability is found to be about 323 a.u. per unit cell and second hyperpolarizability does not exceed 7.0×10^5 a.u. per unit cell.

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