

Torsional effects on the molecular polarizabilities of the benzothiazole (A)–benzobisthiazole (B) oligomer A–B₁₃–A

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We outline a method for the calculation of multipole moments and molecular dipole–dipole ($\bar{\alpha}$), dipole–quadrupole ($\bar{\bar{A}}$), and quadrupole–quadrupole ($\bar{\bar{C}}$) polarizabilities, which we have successfully applied to benzothiazole (A)–benzobisthiazole (B) oligomer A–B₁₃–A. Three model rotational isomers have been characterized: (1) the fully planar (000) rotational isomer; (2) a conformation with each unit rotated 10° in the alternate direction (+–+), and (3) a rotational isomer with each unit rotated 10° in the same direction (+++). The dipole moment, $\bar{\mu}$, is smaller for isomers 000 and +–+ than for isomer +++. The calculation of $\bar{\alpha}$, $\bar{\bar{A}}$, and $\bar{\bar{C}}$ has been performed by use of the interacting induced dipoles polarization model, which calculates tensor effective anisotropic point polarizabilities (method of Applequist). The values of $\bar{\alpha}$, $\bar{\bar{A}}$, and $\bar{\bar{C}}$ are in the same order of magnitude as reference calculations (PAPID program).

The values of $\bar{\bar{A}}$ are rather sensitive to $\bar{\mu}$, which varies under rotation, explaining the greatest value of $|A_{xx}|$ for polar isomer +++. This rotational isomer has the maximum hydrophilic accessible surface, which would improve solubility in water. It is found that small torsional changes can enhance solubility by increasing the hydrophilic accessible surface without too much affecting the values of $\bar{\alpha}$ and $\bar{\bar{C}}$. However, the torsion of the oligomer can vary the value of $\bar{\mu}$ and so modify $\bar{\bar{A}}$. © 1996 by Elsevier Science Inc.

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INTRODUCTION

An important goal of computational chemistry research is the design of molecules for specific applications. Factors that must be taken into account include shape, size, electronic properties, and reactivity. For any physical and chemical properties, the molecular shape largely determines the final function, and this is the rationale for conformational studies.

The search for materials with large values of polarizabilities and other optical properties has attracted much interest from the experimental and the theoretical points of view.^{1,2} Until recently most interest has focused on materials belonging to the group of π -conjugated polymers.³ The properties of these polymers still present a challenge to theoreticians and experimentalists because of a variety of new properties brought about by their quasi-one-dimensional structure and the complications due to intermolecular interactions when in the solid state (ordering of chains, inter-chain charge and energy transfer, local field effects, etc.).

An important consequence of various chemical processes involving charge redistribution is the changes in intermolecular interactions of the molecules involved.^{4–7} Monitoring such changes is essential for understanding the molecular mechanism of catalytic activity, the process of vision, photosynthesis, the propagation of signals in biomolecules, etc. Most of these phenomena involve long-range interactions dominated by an electrostatic term.

Knowledge of electronic polarizabilities that characterize the distortion of a molecular electron cloud by an external field is important in describing intermolecular energies (induction term).^{8–12} In addition, the intramolecular force fields used in molecular mechanics are usually based on the assumption that the interaction between nonbonded atoms can be analyzed in the same way as intermolecular interactions.^{13–15} Therefore, a possible improvement of modern force fields is expected from the introduction of an induction term.¹⁶ Unfortunately, accurate experimental data on

the electronic polarizabilities of molecules are rare, especially if one is interested in the whole tensor quantity instead of the usual mean value. Fortunately, modern theoretical chemistry, with the help of powerful computers, can attempt to become a substitute for difficult experimental determinations.¹⁷

For the implementation of the induction term in the interaction potential between small molecules, one assumes that the molecular polarizabilities are known. Molecular polarizabilities are the tensors that allow the computation of several moments induced in a molecule when it is placed in a nonhomogeneous electric field, which can be expanded in a point using the field at this point and its several derivatives. Molecular dipole-dipole polarizability also determines the refractive index of a system. On going from small molecules to macromolecules and to intramolecular interactions, one can assume that atomic or bond increments (i.e., atomic or bond polarizabilities) are available. These increments allow us to divide the global effect into a sum of local effects. We have chosen the simplest way of using atomic increments, with regard to the most easily handled calculation of large molecules.

The theory of higher order polarizabilities has gained importance for the understanding of a variety of phenomena, including nonlinear dielectric and scattering effects, electrooptical phenomena, collisional effects in infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy, and circular intensity differentials in Rayleigh and Raman scattering. When the external electric field is nonuniform the Hamiltonian $\hat{H}(E_a, E_{ab} \dots)$, and the energy $W(E_a, E_{ab} \dots)$ may be expressed as a power series in the electric field, E_a , its gradient, E_{ab} , its Hessian, E_{abc} , etc.¹⁸:

$$W(E_a, E_{ab} \dots) = W - \mu_a E_a - \frac{1}{3} \Theta_{ab} E_{ab} - \frac{1}{2} \alpha_{ab} E_a E_b - \frac{1}{3} A_{a, bc} E_a E_{bc} - \frac{1}{6} C_{ab, cd} E_{ab} E_{cd} - \dots$$

where $a, b, c, d \dots$ denote Cartesian components and the Einstein notation for summation of repeated indexes has been assumed. The electric multiple expansion is formed by the dipole, $\bar{\mu}$, and quadrupole, $\bar{\Theta}$, moments; the polarizability expansion is formed by the dipole-dipole, $\bar{\alpha}$, dipole-quadrupole, \bar{A} , and quadrupole-quadrupole, \bar{C} , polarizabilities.

In the following equations, a partial derivative with respect to $E_{abc} \dots$ is the mathematical operation of taking the derivative with respect to $E_{abc} \dots$ while keeping all other components of the field and its derivatives constant.

The total electric multipole moments of the molecule are

$$\begin{aligned} \mu_a(E_a, E_{ab} \dots) &= - \frac{\partial W(E_a, E_{ab} \dots)}{\partial E_a} \\ &= \mu_a + \alpha_{ab} E_b + \frac{1}{3} A_{a, bc} E_{bc} + \dots \\ \Theta_{ab}(E_a, E_{ab} \dots) &= -3 \frac{\partial W(E_a, E_{ab} \dots)}{\partial E_{ab}} \\ &= \Theta_{ab} + A_{c, ab} E_c + C_{ab, cd} E_{cd} + \dots \end{aligned}$$

In a previous paper¹⁹ we have calculated the multipole moments and molecular polarizabilities of benzothiazole (A)-benzobisthiazole (B) fully planar linear oligomers in

the series A-B₁-A to A-B₁₃-A and the results have been extrapolated to give predictions for polybenzobisthiazole (PBBT). The longitudinal components are largest in $\bar{\alpha}$, \bar{A} , and \bar{C} , reflecting the strong response of the delocalized π electrons to electric fields.

It should be noted that polymers do not usually have well-defined molecular structures.¹⁷ A sample of a polymer will contain molecules having possibly a variety of structures. Rational polymer design technologies rely on a detailed structural knowledge of oligomers at the atomic level. Although the strong C-C, C-N, and C-S bonds maintain the integrity of the polymer, PBBT has a high degree of flexibility because rotation can occur about the intercycle bonds in the polymer chain. Thus the polymer chain can adopt a large number of configurations in three-dimensional space. The torsion angles of the intercycle bonds play a crucial part in determining properties, for these determine the overall polarity of the macromolecule.

We present here a study of $\bar{\alpha}$, \bar{A} , and \bar{C} polarizabilities for the benzothiazole (A)-benzobisthiazole (B) linear oligomer A-B₁₃-A and the torsional effects on these properties. This choice was prompted by the importance of this heteroaromatic structure in rodlike polymeric chains that possess interesting mechanical and optical properties. Apart from the concern for the optimization of the structure to obtain the highest values of $\bar{\alpha}$, \bar{A} , and \bar{C} , we are also interested in processibility of the obtained materials. Therefore, it is advantageous to build molecules with proper attached groups that can improve the solubility of oligomers and polymers in organic solvents and facilitate processing by spin coating or Langmuir-Blodgett deposition.

In this article, we consider a method for the calculation of $\bar{\alpha}$, \bar{A} , and \bar{C} and the torsional effects on these properties. Application of the method for the study of polarizabilities of the benzothiazole (A)-benzobisthiazole (B) linear oligomer A-B₁₃-A are presented and analyzed. We deal with small torsion angles because the molecular polarizabilities are due to π - π overlap between successive monomeric units in the one-dimensional chain and this overlap falls sharply for big rotations. The main scope of this article is to select a convenient method that can be applied to large molecules.

ELECTROSTATIC PROPERTIES

We have written a program called POLAR for the theoretical simulation of molecular electrostatic properties and polarizabilities.¹⁹⁻²² Atomic net charges and polarizabilities are calculated from their σ and π contributions. The σ net charges and polarizabilities are estimated by the principle of electronegativity equalization^{23,24} but applied bond by bond in the molecule.¹⁹⁻²² The π net charges and polarizabilities are evaluated by the method of Hückel. Dipole, $\bar{\mu}$, and tensor quadrupole, $\bar{\Theta}$, moments are calculated from the point (atomic) distribution of net charges. The molecule is brought into its principal inertial coordinate system.

In describing the partial charge method developed for the Mulliken scale,²⁵ Huheey²⁶ has mentioned that most elements approximately double their (Mulliken) electronegativities as the partial charge approaches +1 whereas their

electronegativities essentially disappear (approach zero) as the partial charge approaches -1. The Mulliken and Pauling scales are roughly proportional, so Huheey's observation may be expressed in Pauling units as²⁴

$$X_{eq} = X_A + \Delta_A X_A$$

or

$$\Delta_A = \frac{X_{eq} - X_A}{X_A}$$

Here, X_{eq} is the electronegativity as equalized through Sanderson's principle, X_A is the initial, prebonded electronegativity of a particular atom A and Δ_A is the σ partial charge on A. Charge conservation leads to a general expression for X_{eq} :

$$X_{eq} = \frac{N + q}{\sum_{atoms} v_A / X_A}$$

where $N = \sum v$ equals the total number of atoms in the species formula and q is the σ molecular charge.

The σ partial charge Δ_A on atom A can be generalized as

$$\Delta_A = \sum_{bonds} \frac{X_{eq, b} - X_A}{X_A}$$

and the electronegativity equalized for bonds is given as

$$X_{eq, b} = \frac{2 + (q/m)}{(1/X_A) + (1/X_B)}$$

where m is the number of bonds in the molecule.

Sanderson's principle allows the calculation of the σ atomic polarizabilities (equalized bond by bond) as:

$$\alpha_A = \frac{\partial \Delta_A}{\partial X_A} = \sum_{bonds} \frac{(1 + L_A - \Delta_A) \left(2 - \frac{q}{m} \right) X_B}{(2 + L_A + L_B - \Delta_A - \Delta_B)(X_A + X_B)^2}$$

where the coefficients $(1 - \Delta_A)$ and $(2 - \Delta_A - \Delta_B)$ have been corrected to take into account the number of lone pairs on atoms A and B, L_A and L_B , respectively.

The σ tensor atomic polarizabilities are calculated as

$$\begin{aligned} \bar{\alpha}_\sigma &= \sum_{bonds} \frac{\alpha_\sigma}{\alpha^\parallel + 2\alpha^\perp} \begin{bmatrix} \alpha^\perp & 0 & 0 \\ 0 & \alpha^\perp & 0 \\ 0 & 0 & \alpha^\parallel \end{bmatrix} \\ &= \sum_{bonds} \frac{\alpha_\sigma}{3.676} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1.676 \end{bmatrix} \end{aligned}$$

using a series of internal coordinate systems for each bond, where the z axis is defined as the bond direction. The diagonal form of $\bar{\alpha}_\sigma$ has two distinct components α^\parallel and α^\perp , parallel and perpendicular, respectively, to the bond axis. The parameter $\alpha^\parallel/\alpha^\perp = 1.676$ has been obtained by fitting the additive isotropic bonding polarizabilities without dipolar interactions (parameters of Vogel²⁷). These bonding polarizabilities have been implemented in the database of the SIBFA program for the evaluation of the intra- and inter-

molecular interaction energies of biological macromolecules making use of a partition scheme.²⁸

The π atomic net charges and polarizabilities are calculated with the Hückel molecular orbital (HMO) theory and added to the σ component parts: $\Delta = \Delta_\sigma + \Delta_\pi$ and $\alpha = \alpha_\sigma + \alpha_\pi$. The calculation of dipole and quadrupole moments from the point (atomic) distribution of net charges has been reported elsewhere.¹⁹⁻²²

The π tensor atomic polarizabilities are calculated as

$$\begin{aligned} \bar{\alpha}_\pi &= \sum_{bonds} \frac{\alpha_\pi}{\alpha^\parallel + 2\alpha^\perp} \begin{bmatrix} \alpha^\perp & 0 & 0 \\ 0 & \alpha^\perp & 0 \\ 0 & 0 & \alpha^\parallel \end{bmatrix} \\ &= \sum_{bonds} \frac{\alpha_\pi}{5} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 3 \end{bmatrix} \end{aligned}$$

using a series of internal coordinate systems for each bond where the z axis is defined as the bond direction. The parameter $\alpha^\parallel/\alpha^\perp = 3$ has been obtained from the experimental polarizability component parts of benzene.

VARIATION OF THE HÜCKEL β PARAMETER WITH THE TORSION ANGLE

It is well known that the intercycle π conjugation vanishes for perpendicular cycles. So, the Hückel β parameter should decrease for out-of-plane conformations, tending to zero for perpendicular polycyclic structures. Therefore, if the functional relation of the π conjugation parameters with respect to the dihedral angles is known, improvements can be made in the simple Hückel calculations.²⁹ Mulliken^{30,31} has proposed that the Hückel β parameter be proportional to the overlap integral S and has shown that in diatomic systems the proportionality holds rather well at bond distances of interest. For Slater overlap integrals³² β as a function of distance has been calculated.³³

Although there is no convincing evidence as to which β -distance curve to use, Mulliken's success with diatomic molecules^{30,31,34} is suggestive, as is a successful application to calculation of ionization potentials.³⁵ Thus, in first approximation, β is proportional to the overlap integral S between two fragments. This is certainly a crude approximation but often used to deduce the tendency in the variation of β . It should be noted that the overlap integral S between two parallel orbitals with no spherical symmetry varies as the cosine of their relative torsion angle θ . Acceptance of the assumption further implies that β can be evaluated, in first approximation, between p_z orbitals twisted from coplanarity by an angle θ as³⁶⁻³⁹

$$\beta = \beta_0 \cos \theta$$

Thus, it is convenient to define a standard β_0 (being equal to the β parameter for benzene) for the planar dihedral angles θ and to modify other β parameters (in units of the standard β_0) with the use of this dimensionless function.

Of course, this method is not exact. It should be stressed that the rotation of a torsion angle can generate conformational changes. For example, the bond distance can vary and the overlap between two atomic orbitals decreases exponen-

tially when the distance between them increases. So, the overlap integral S not only depends on the relative orientation of the p_z orbitals directly involved in the fragment-fragment bonding but also on second-neighbor overlaps between p_z orbitals belonging each to a different fragment. The proper β function in this case is considerably different from the cosine function being used. An improved estimate of the β function can be expected from some kind of empirical information. Joachim et al.⁴⁰ have evaluated the electronic coupling, V_{ab} , of the binuclear mixed valence $M^{II}-L-M^{III}$ complex $[(NH_3)_5Ru\text{-bipyridyl-Ru}(NH_3)_5]^{5+}$ in the valence bond electronic states $M^{II}-L-M^{III}$ (a) and $M^{III}-L-M^{II}$ (b). When a pyridine ring rotates around the ligand axis, $\pi-\pi$ $V_{ab}(\theta)$ can be best fitted by a $\cos^{1.15}\theta$ function. From this observation we assume that the β function is universal and has the same form as the electronic coupling function, V_{ab} , of complex $[(NH_3)_5Ru\text{-bipyridyl-Ru}(NH_3)_5]^{5+}$:

$$\beta = \beta_0 \cos^{1.15}\theta$$

INTERACTING INDUCED DIPOLES POLARIZATION MODEL FOR MOLECULAR POLARIZABILITIES

The calculation of molecular polarizabilities has been carried out by the interacting induced dipoles polarization model^{13-15,19,20} that calculates tensor effective anisotropic point polarizabilities by the method of Applequist et al.⁴¹⁻⁴⁴

One considers the molecule as being made up of N atoms (represented by $i, j, k \dots$), each of which acts as a point particle located at the nucleus and responds to an electric field only by the induction of a dipole moment, which is a linear function of the local field.^{15,19,20,44} If a Cartesian component of the field owing to the permanent multipole moments is E_a^i , then the induced moment μ_a^i in atom i is

$$\mu_a^i = \alpha^i \left(E_a^i + \sum_{j(\neq i)} T_{ab}^{ij} \mu_b^j \right) \quad (1)$$

where α^i is the polarizability of atom i and T_{ab}^{ij} is the symmetrical field gradient tensor, $T_{ab}^{ij} = (1/e)\nabla_a^i E_b^j$, e is the charge of the proton, and the subscripts $a, b, c \dots$ stand for the Cartesian components x, y, z . The expression in parenthesis is the total electric field at atom i , consisting of the external field plus the fields of all the other induced dipoles in the molecule.

The set of coupled linear Eqs. (1) for the induced dipole moments can conveniently be expressed, in compact matrix equation form, if one introduces the $3N \times 3N$ matrices \bar{T} and $\bar{\alpha}$, with elements T_{ab}^{ij} and $\alpha_{ab}^i \delta^{ij}$ (δ^{ij} being the Kronecker δ), respectively.^{15,19,20,44} To suppress the restriction in the sum, the elements T_{ab}^{ij} are defined as zero. Similarly \bar{E} and $\bar{\mu}$ are $3N \times 1$ column vectors with elements E_a^i and μ_a^i . Equation (1) is thus written in matrix form,

$$\bar{\mu} = \bar{\alpha} (\bar{I} \bar{E} + \bar{T} \bar{\mu}) = \bar{\alpha} \bar{I} \bar{E} + \bar{\alpha} \bar{T} \bar{\mu}$$

where \bar{I} is the $3N \times 3N$ -dimensional unit matrix. This matrix equation can be solved for the induced dipoles as

$$\bar{\mu} = (\bar{I} - \bar{\alpha} \bar{T})^{-1} \bar{\alpha} \bar{E} = \bar{A} \bar{E}$$

Here the symmetrical many-body polarizability matrix, A , has been introduced:

$$\bar{A} = (\bar{I} - \bar{\alpha} \bar{T})^{-1} \bar{\alpha}$$

It is important to emphasize that the many-body polarizability matrix describes a nonlocal polarizability response of the system.^{15,19,20,44} In effect, an electrostatic field at the point j gives rise not only to an induced moment at j (proportional to the diagonal block element A_{ab}^{jj}), but it contributes (*nonlocally*) to the induced moments of all the other sites as well.

The compact matrix equation $\bar{\mu} = \bar{A} \bar{E}$ is equivalent to the N matrix equations^{19,44}:

$$\bar{\mu}^i = \sum_{j=1}^N \bar{A}^{ij} \bar{E}^j$$

Let the molecule be in a uniform applied field, so that $\bar{E}^j = \bar{E}$ for all j . Then this equation becomes

$$\bar{\mu}^i = \left[\sum_{j=1}^N \bar{A}^{ij} \right] \bar{E} = \bar{\alpha}^{\text{eff}, i} \bar{E}$$

The coefficient of \bar{E} in this equation is seen to be an effective (i.e., additive) polarizability of unit i , $\bar{\alpha}^{\text{eff}, i}$. The total moment induced in the molecule $\bar{\mu}^{\text{mol}}$ is

$$\bar{\mu}^{\text{mol}} = \sum_{i=1}^N \bar{\mu}^i = \left[\sum_{i=1}^N \sum_{j=1}^N \bar{A}^{ij} \right] \bar{E} = \left[\sum_{i=1}^N \bar{\alpha}^{\text{eff}, i} \right] \bar{E}$$

from which it is seen that the molecular polarizability tensor $\bar{\alpha}^{\text{mol}}$ is

$$\bar{\alpha}^{\text{mol}} = \sum_{i=1}^N \sum_{j=1}^N \bar{A}^{ij} = \sum_{i=1}^N \bar{\alpha}^{\text{eff}, i} \quad (2)$$

which is exact for the model described. From energetic considerations it is known that $\bar{\alpha}$ is a Hermitian matrix⁴⁵ and must therefore be symmetric if all elements are real. It can be readily verified that this symmetry condition holds for $\bar{\alpha}^{\text{mol}}$ calculated by Eq. (2), starting with the observation that \bar{A}^{-1} and hence \bar{A} are symmetric for real, symmetric $\bar{\alpha}^i$. This is true regardless of the symmetry of the molecule.

Equation (2) is suitable for numerical calculations of $\bar{\alpha}^{\text{mol}}$.^{19,44} In the case of a diatomic molecule AB whose atoms have isotropic polarizabilities α^A and α^B the results can be placed in a simple and more explicit form. The diagonal form of $\bar{\alpha}^{\text{mol}}$ has two distinct components α^{\parallel} and α^{\perp} , parallel and perpendicular, respectively, to the bond axis. Silberstein's equations^{41-43,46} for this case are the following, which may also be derived from the above.

$$\alpha^{\parallel} = \frac{\alpha^A + \alpha^B + \frac{4\alpha^A \alpha^B}{r^3}}{1 - \frac{4\alpha^A \alpha^B}{r^6}} \quad (3)$$

$$\alpha^{\perp} = \frac{\alpha^A + \alpha^B - \frac{2\alpha^A \alpha^B}{r^3}}{1 - \frac{\alpha^A \alpha^B}{r^6}} \quad (4)$$

where r is the distance between atoms.

These relations illustrate certain essential features of the atom dipole interaction model: (1) the molecule becomes anisotropic even though the atoms are isotropic; (2) the predicted polarizability of a molecule parallel to its long axis is generally greater than that perpendicular to the long axis; and (3) deviations from additivity of polarizabilities become large as the atom polarizabilities approach r^3 .^{19,44}

The most notable feature of molecular polarizability surfaces is a curve of discontinuity along which the polarizability approaches $\pm\infty$.^{19,44} Its origin for diatomic molecules can be seen in Eqs. (3) and (4), where the denominators vanish when $\alpha^A \alpha^B$ approaches $r^6/4$ or r^6 , respectively. Thus α^A and α^B are inversely related along the curve of discontinuity for this case. (The general condition for infinite polarizability is $\det \bar{A}^{-1} = 0$; infinite polarizability means that $\bar{\mu}$ is nonvanishing when $\bar{E} = 0$, and this is possible only if $\det \bar{A}^{-1} = 0$).

The significance of a polarizability of $\pm\infty$ is that the molecule is in a state of resonance and absorbs energy from the applied field.^{19,44} This occurs in spite of the fact that we have not introduced any absorption properties of the atoms. This behavior of the model can be understood from its close relation to the classic system of N coupled oscillators, which likewise shows resonance under conditions other than the resonance conditions of the isolated oscillators.⁴⁷ There is evidence that the absorption properties⁴⁸⁻⁵⁰ of some types of systems can be predicted from the point dipole interaction approach used here, but it seems doubtful that this could be done reliably for molecules with our model; among other things,⁴⁹ the neglect of electron exchange between atoms is probably serious. In the immediate vicinity of the resonance condition the polarizability is bound to be in error because the model does not take into account damping effects, which would prevent the polarizability from going to infinity. Therefore, for the present we regard the resonance conditions wherever they appear simply as indications that the coupling between atoms has far exceeded the extent that can be treated by the model.

IMPROVEMENTS IN THE INTERACTING INDUCED DIPOLES POLARIZATION MODEL

We have implemented the following improvements in the model¹⁹: (1) We have used a damping function in the calculation of the symmetrical field gradient tensor

$$\bar{T}^{ij} = -\frac{3}{r^5} \begin{bmatrix} x^2 - 1/3 r^2 & xy & xz \\ xy & y^2 - 1/3 r^2 & yz \\ xz & yz & z^2 - 1/3 r^2 \end{bmatrix}$$

in order to prevent the polarizability from going to infinity.¹⁶ Thus, if r is lesser than the cutoff value,

$$s = 1.662(\alpha^i \alpha^j)^{1/6}$$

the field gradient tensor is now evaluated as

$$\bar{T}^{ij} = -\frac{3v^4}{r^5} \begin{bmatrix} x^2 - \frac{4v^3 - 3v^4}{3v^4} r^2 & xy & xz \\ xy & y^2 - \frac{4v^3 - 3v^4}{3v^4} r^2 & yz \\ xz & yz & z^2 - \frac{4v^3 - 3v^4}{3v^4} r^2 \end{bmatrix}$$

where $v = r/s$. (2) We have neglected the interaction between bonded atoms and for atoms with distance lying in an interval defined by $[r^{inf}, r^{sup}]$.¹⁶ Furthermore, we have improved this using the following algorithm¹⁹:

- Step 1: Set r^{inf} to zero.
- Step 2: Neglect interaction for atoms with distance lying in the interval $[r^{inf}, r^{sup}]$.
- Step 3: If a test indicates resonance conditions then increment r^{inf} by 1 au and continue from step 2.
- Step 4: Stop.

(3) To build up the many-body polarizability matrix, $\bar{\bar{A}}$, we have used the tensor atomic polarizabilities, $\bar{\alpha} = \bar{\alpha}_\sigma + \bar{\alpha}_\pi$, instead of scalar polarizabilities, α .¹⁹

We have implemented the following tests indicating a resonance condition¹⁹: (1) Test if the $\bar{\bar{A}}^{-1}$ matrix is singular¹⁶: $\det \bar{\bar{A}}^{-1} = 0$; (2) test if the $\bar{\bar{A}}^{-1}$ matrix is not defined positive: some $\bar{\bar{A}}^{-1}$ eigenvalue is less than or equal to zero¹⁶; (3) test of the $\bar{\bar{A}}$ matrix is not defined positive: some $\bar{\bar{A}}$ eigenvalue is less than or equal to zero¹⁹; (4) test if some effective $\bar{\alpha}^{eff,i}$ matrix is not defined positive: some $\bar{\alpha}^{eff,i}$ eigenvalue is less than or equal to zero.¹⁹

The values of $\bar{\alpha}$, $\bar{\bar{A}}$, and $\bar{\bar{C}}$ are calculated with this model. The anisotropy of $\bar{\alpha}$ is evaluated as¹⁶

$$\gamma = \left[\frac{\sum_{a, b(a \neq a)}^{3,3} (\alpha_{aa} - \alpha_{bb})^2}{2} \right]^{1/2}$$

The vector components of $\bar{\bar{A}}$ are defined as

$$A_a = A_{a,aa} + \frac{\sum_{b(a \neq a)}^3 (A_{a,bb} + 2A_{b,ba})}{3}$$

and are related to experimental quantities.¹⁹

A fully operative version of the POLAR program including the whole interacting induced dipoles polarization model^{21,22,41-44} has been implemented into the MM2 program for molecular mechanics.^{51,52} A description of the implementation has been reported elsewhere.¹⁹ We have called the new version MMID.¹³⁻¹⁵ The polarization energy can now be calculated by three options: (1) no polarization (this option has been introduced for compatibility), (2) non-interacting induced dipoles polarization model (a simplified version in which the induced dipoles do not produce further

induced dipoles, and (3) interacting induced dipoles polarization model (method of Applequist et al.⁴¹⁻⁴⁴).

GEOMETRIC DESCRIPTORS AND TOPOLOGICAL INDICES

The TOPO program for the theoretical simulation of the molecular shape has been described elsewhere.¹⁹⁻²² The surface of molecules can be represented by the external surface of a set of overlapping spheres with appropriate radii, centered on the nuclei of the atoms.⁵³⁻⁵⁷ If the radii are those of van der Waals,⁵⁸ the bare (solvent free) molecular surface is obtained^{53,54}; if the radii are those of van der Waals plus the effective radius of a solvent molecule, the solvent-accessible molecular surface is now obtained.⁵⁵

The theoretical simulation of the molecular shape is helped by the calculation of geometric descriptors and topological indices of the molecules.^{53,54} The molecule is treated as a solid in space defined by tracing spheres about the atomic nuclei. It is computationally enclosed in a graduated rectangular box and the geometric descriptors evaluated by counting points within the solid or close to chosen surfaces. The molecular volume, V , is concurrently approximated as $V = P \cdot \text{GRID}^3$, where P is the number of points within the molecular volume (within distance R_x of any atomic nucleus, X) and GRID is the size of the mesh grid.

As a first approximation, the bare molecular surface area could be calculated as $S = Q \cdot \text{GRID}^2$, where Q is the number of points close to the bare surface area (within distance between R_x and $R_x + \text{GRID}$ of any atomic nucleus, X). However, the estimate has been improved⁵⁴: If the point falls exactly on the surface of one of the atomic spheres, it accounts indeed for GRID^2 units of area on the bare molecular surface. This is because the total surface of atom X can accommodate $4\pi R_x^2/\text{GRID}^2$ points. When a point falls beyond the surface, it represents GRID^2 units of area on the surface of a sphere of radius $R > R_x$, not on the surface of atom X . On the surface of X it accounts only for a fraction of this quantity, namely, $\text{GRID}^2(R_x/R)^2$. The total bare surface area is, therefore, calculated as $S = F \cdot \text{GRID}^2$, where F is the sum of elements AF defined as $AF = R_x^2/R^2(I)$ for those points close enough to the surface of any atom X . R_x^2 is the squared radius of atom X and $R^2(I)$ is the squared distance of point I from the atomic nucleus X . Meyer⁵⁴ has written a program including the OEPP (one element per point) subprogram that allows the calculation of the molecular volume and bare surface area. We have written a version of this subprogram (we have called it ATOEPP) that allows the atom-to-atom partition analysis of these geometric descriptors into their atomic component parts.¹⁹⁻²²

Two topological indices of molecular shape can be now calculated: G and G' .⁵⁴ The ratio $G = S_e/S$ has been interpreted as a descriptor of molecular globularity; S_e is the surface area of a sphere of volume equal to the molecular volume, V . The ratio $G' = S/V$ has been interpreted as a descriptor of molecular rugosity.

The importance of the solvent validates the assumption that the properties of the systems solvated in water are strongly related to the contact surface between solute and water molecules.^{55,57} We can propose a new molecular geometric descriptor that is the solvent-accessible surface AS .⁵⁵

This surface is denoted when a spherical probe is allowed to roll on the outside while maintaining contact with the bare molecular surface. The continuous sheet defined by the locus of the center of the probe is the accessible surface. Alternately, the accessible surface is calculated as the bare molecular surface by using pseudo-atoms, whose van der Waals radii were increased by the radius, R , of the probe. The accessibility is a dimensionless quantity varying between 0 and 1 and represents the ratio of the accessible surface area in a particular structure to the accessible surface area of the same atom when isolated from the molecule.⁵⁵

Fractal surfaces⁵⁹ provide a means for characterizing the irregularity of molecular surfaces.⁶⁰ The area of the accessible surface, AS , depends on the value of the probe radius, R . The fractal dimension, D , of the molecules may be obtained according to Lewis and Rees⁶⁰ as

$$D = 2 - \frac{d(\log AS)}{d(\log R)}$$

The fractal dimension, D , provides a quantitative indication of the degree of surface accessibility toward different solvents. The larger the D value the faster the accessible surface area drops with an increase in solvent molecular size.

An almost fully operative version of the TOPO program has been implemented into the AMYR program for the theoretical simulation of molecular associations and chemical reactions.⁸⁻¹² The algorithm allows the characterization of molecular units and aggregates. All the geometric descriptors and topological indices but fractal dimension can now be calculated.

SOLUBILITIES AND PARTITION COEFFICIENTS

It has been said that the solubility of oligomers and polymers is advantageous to facilitate processing. Although the solubility of oligomers and polymers in water is generally small, it can be improved by changing this liquid by a less polar (organic) solvent. Lipophilic parameters are a measure of the preference of a solute between two solvents.⁶¹ These parameters are quite numerous and have different characters: the parameter of Hansch,⁶²⁻⁶⁸ the π -SCAP parameter,^{61,69} the PARACHOR parameter,^{70,71} the CSA (cavity surface area) parameter,⁵⁶ etc.

The lipophilic parameter of Hansch,⁶² π_x , can be calculated from the partition coefficients of the molecules between two solvents (generally 1-octanol and water). The parameter π_x compares a reference molecule with a substitution derivative and can be defined as

$$\pi_x = \log \frac{P_x}{P_H}$$

where P_x is the partition coefficient of the molecule substituted by X and P_H is the partition coefficient of the reference molecule, measured under the same experimental conditions. The 1-octanol–water couple is the most used solvent system and the parameters π_x are relative to this system. Hansch and Leo⁶² have tabulated the π_x values for a large number of substituents.

Additional attempts have been carried out to divide the

partition coefficient in order to obtain a system of increments by atoms or by groups.⁶³⁻⁶⁵ A new method has been proposed by Hopfinger^{66,67} to calculate $\log P$ and π_x . The method is called π -SCAP (solvent-dependent conformational analysis program) and has been initially used to evaluate the Gibbs free energy of solvation of macromolecules. From these data and with the equation $-RT \ln (\ln = \text{Neperian logarithm}) P = \Delta(\Delta G_{\text{solv}}) = \Delta G_{\text{solv,o}} - \Delta G_{\text{solv,w}}$ one can calculate $\log P = 0.17567(\Delta G_{\text{solv,w}} - \Delta G_{\text{solv,o}})$ where T has been taken as 298 K and $\Delta G_{\text{solv,w}}$ and $\Delta G_{\text{solv,o}}$ (in $\text{kJ} \cdot \text{mol}^{-1}$) are the Gibbs free energies of solvation of the molecule, considered in water and in 1-octanol, respectively.

The model^{66,67} is based on the concept of a solvation sphere.⁶⁸ The molecule is divided into groups of atoms. The starting hypothesis is that one can center, independently on each group of the solute molecule, a solvation sphere. The size of this sphere depends on the solvent and on the considered group. This sphere is occupied by a certain number of solvent molecules. A variation of free energy, due to the extraction of a solvent molecule, is associated with each solvation sphere.

The intersecting volume, V° , among the solvation sphere and the van der Waals spheres of the remaining atoms (not bonded to the group under consideration) in the molecule is calculated. This volume allows the evaluation of the group solvation effective volume for a given conformation of the studied molecule. The model therefore has four parameters per solvent: (1) n , maximum number of solvent molecules allowed to fill the solvation sphere; (2) Δg , variation of Gibbs free energy associated with the extraction of one solvent molecule out of the solvation sphere; (3) R_v , radius of the solvation sphere; and (4) V_f , free volume available for a solvent molecule in the solvation sphere. One also has V_s : volume of the solvent molecule.

The values of n , R_v , and Δg can be obtained from the minimization of the configuration energy in a force model.⁶⁶ Alternately, we use the Δg empirical values calculated by Gibson and Scheraga.⁶⁸

The calculation of V_f is described as follows. In the solvation sphere, part of the volume excludes solvent molecules. This volume consists of the van der Waals volume of the group at which the sphere is centered and of a volume representing the groups bonded to the central group. The latter volume is represented by a number of cylinders equal to the number of atoms bonded to the central group and where the axes pass by the center of the sphere. The radius of these cylinders is taken as three-quarters of the van der Waals radius of the central group and these cylinders are disposed in such a way as to respect the valence geometry of the group (sp^2 , sp^3 , etc.).

The difference between the total volume of the solvation sphere and the excluded volume, represents the volume, V' , that is actually available for the solvent molecules. Therefore, V_f can be calculated as

$$V_f = \frac{V'}{n} - V_s$$

The variation of Gibbs free energy associated with the extraction of all the solvent molecules out of the solvation spheres of a group is

$$\Delta G_R = n \Delta g \left(1 - \frac{V^\circ}{V'} \right)$$

and the variation of the Gibbs free energy associated with the extraction of all the solvent molecules out of the solvent spheres of the molecule is the sum of the Gibbs free energies, ΔG_R , of each group making up the molecule:

$$\Delta G_{\text{extr}} = \sum_{R=1}^N \Delta G_R$$

The solvation free energy of the molecule is simply:

$$\Delta G_{\text{solv}} = -\Delta G_{\text{extr}}$$

Although this is a simple method we have found important difficulties in working out the volume V' . The ascertained values are different from those given by Hopfinger.^{66,67} For example, the value of V_f for the (CH) aromatic group solvated in water is 3.3 \AA^3 (fitted parameter of Hopfinger) and 48.14 \AA^3 (calculated using the geometric procedure indicated by Hopfinger). The parametric value of V_f given by Hopfinger underestimates the calculated value, being the mean relative error -46% .^{19,20} Under these conditions for the coherence of the calculations, we suggest evaluating the values of V_f by making use of a computer program. Pascal⁶¹ has written a program, called SCAP, that makes use of the subprogram KOROBO⁶⁹ (that allows the calculation of the surfaces and volumes by the method of Korobov) in order to recalculate the volume V' and evaluate the Gibbs free energies of solvation in water and in 1-octanol as well as the partition coefficient.^{72,73}

CALCULATION RESULTS AND DISCUSSION

Three model rotational isomers of the benzothiazole (A)–benzobisthiazole (B) linear oligomer A–B₁₃–A have been characterized: (1) The fully planar (000) rotational isomer; (2) a conformation in which each unit is rotated 10° , rotations being performed in the alternate directions (+--+), and (3) a rotational isomer in which each unit is rotated 10° , all rotations being performed in the same direction (+++) (see Color Plate 1). The dipole, μ , and tensor quadrupole, Θ , moments for the rotational isomers are reported in Table 1. The geometry of the oligomer has been taken from the optimization of the monomeric units with MMID (Molecular Mechanics with Interacting Dipoles polarization), a molecular mechanics computer program¹³⁻¹⁵ operating with the MM2 parameterization.^{51,52} The linear oligomer is arranged in an all-*trans* configuration (defined from both $\text{N}=\text{C}$ double bonds in consecutive units). Each rotational isomer is brought into its principal inertial coordinate system. The length x of the oligomer is defined as the maximum length (corresponding to the translation axis in polybenzobisthiazole), the height z as its minimum thickness, and its width y is measured at right angles to the axes indicated by the length and height. The origin is the center of mass for each conformation.

The value of the dipole moment, μ , is smaller for the 000 and +--+ rotational isomers (in the range 1.455–1.456D) than for the +++ conformation ($\mu = 7.760\text{D}$). Although the high dipole moment of the latter conformation slightly modifies the mean value of the quadrupole moment, Θ , [in the range

Table 1. Electrostatic properties for the benzothiazole (A)–benzobisthiazole (B) A–B₁₃–A linear oligomer

Conformation	μ^a	Θ^b	Θ_1^c	Θ_2	Θ_3
000 ^d	1.456	–77.149	–481.042	0.000	249.596
+–+ ^e	1.455	–77.179	–487.949	1.118	255.293
+++ ^f	7.760	–76.502	–870.542	15.135	625.901

^aDipole moment (debyes).^bMean quadrupole moment (debyes · ångström).^cQuadrupole moment tensor eigenvalues Θ_1 , Θ_2 , and Θ_3 (debyes · ångström).^dFully planar rotational isomer.^eEach unit is rotated 10°. Rotations are performed in the alternate directions.^fEach unit is rotated 10°. All rotations are performed in the same direction.

–77.2 – (–76.5)D Å], the dipole moment forces a charge redistribution in the oligomer that rather modifies the quadrupole moment tensor, $\bar{\Theta}$. Thus, the eigenvector analysis shows that $\bar{\Theta}$ becomes more anisotropic on going from the 000 and +–+ rotational isomers [Θ_1 in the range –488 – (–481)D Å, Θ_3 in the range 250–255 D Å] to the +++ conformation ($\Theta_1 = -870.542$ D Å, $\Theta_3 = 625.901$ D Å).

The molecular $\bar{\alpha}$, \bar{A} , and \bar{C} tensors for the rotational isomers of the A–B₁₃–A linear oligomer are summarized in Tables 2 to 4. The value of $\bar{\alpha}$ is slightly varied on going from one conformation to other (in the range 681–699 Å³). The values are on the same order of magnitude as reference calculations carried out with the PAPID program (in the range 369–788 Å³), which uses a database of atomic polarizabilities built up from coupled Hartree–Fock calculations of the polarizability tensors of a series of molecules containing the main functional groups that are present in peptides.¹⁶ In particular, these reference calculations show a smaller value of $\bar{\alpha}$ for the 000 and +–+ rotational isomers (in the range 369.0–369.1 Å³) than for the +++ conformation ($\alpha = 788.493$ Å³). The eigenvector analysis shows that this discrepancy is due to the α_3 eigenvalue (see the ninth column of Table 2), which approximately corresponds to the α_{xx} Cartesian component (in the eleventh column of Table 2).

The results show that, for the 000 and +–+ rotational isomers, the calculated anisotropies, γ , of the $\bar{\alpha}$ tensors (in the range 975–983 Å³) are greater than for the +++ conformation ($\gamma = 905.699$ Å³), with the oligomers being more polarizable along the chain direction than across the bonds ($\alpha_{xx} > \alpha_{zz}$). However, for the 000 and +–+ rotational isomers, the PAPID results (γ in the range 501–502 Å³) are less anisotropic than for the +++ conformation ($\gamma = 1512.906$ Å³). The values of \bar{A} and \bar{C} are also anisotropic, with the oligomers being more polarizable along the chain direction than across the bonds ($|A_x| > |A_z|$, $|A_{xx}| > |A_{zz}|$ and $C_{xx,xx} > C_{zz,zz}$).

It can be seen from Table 4 that the values of \bar{C} are slightly varied for the three rotational isomers. However, the PAPID reference calculations are smaller for the 000 and +–+ rotational isomers than for the +++ conformation. We have pointed out elsewhere that $\bar{\alpha}$ and \bar{C} are sensitive to the length of the oligomer while \bar{A} is also sensitive to the molecular dipole moment.¹⁹ This explains why the 000 and +–+ rotational isomers with smaller dipole moments (in the range

1.455–1.456D in Table 1) show smaller values of $|\bar{A}|$ (e.g. $|A_{x,xx}|$ in the range 67–99 Å⁴) while the polar +++ conformation (with a dipole moment of 7.760D) presents the greatest values of $|\bar{A}|$ (e.g. $|A_{x,xx}| = 279.517$ Å⁴). The results are on the same order of magnitude as the PAPID reference calculations. Note, however, that the PAPID program is based on a similar but different method and the reference results for A_x and $A_{x,xx}$ show the reverse sign of the POLAR values. This indicates the high sensitivity of the results to the approaches included in both programs.

The calculations of the geometric descriptors and topological indices in Tables 5 and 6 are compared with reference calculations carried out with the GEPOL (GEometry of POLYhedron) program.^{74–77} This program has been developed in this laboratory by E. Silla and colleagues. The algorithm calculates three kinds of envelope surfaces: (1) The van der Waals molecular surface, which is the external surface resulting from a set of spheres centered on the atoms or groups forming the molecule, (2) the solvent-accessible surface, which is the surface generated by the center of the solvent, considered as a rigid sphere, when it rolls around the van der Waals surface,⁵⁵ and (3) the solvent-excluding surface, which is composed of two parts: the contact surface and the reentrant surface. The contact surface is the part of the van der Waals surface of each atom that is accessible to a probe sphere of a given radius. The reentrant surface is defined as the inward-facing part of the probe sphere when this is simultaneously in contact with more than one atom. The GEPOL program is fast and efficient.

The geometric descriptors for the rotational isomers of the A–B₁₃–A linear oligomer are listed in Table 5. The value of the molecular volume, V , is slightly varied (in the range 1962–1963 Å³) on going from one conformation to other. The values compare well with reference calculations carried out with the GEPOL program^{74–77} (in the range 2063–2066 Å³). The molecular surface area, S , is smaller for the 000 and +–+ rotational isomers (in the range 1990–1991 Å²) than for the +++ conformation ($S = 1994.11$ Å²). The behavior of the water-accessible surface area, AS , its hydrophilic (HLAS) contribution, and the side chain-accessible surface area, AS' , is the same as has been noticed for the molecular surface area. However, the hydrophobic (HBAS) component of AS is greater for the 000 and +–+ rotational isomers (in the range 2526–2534 Å²) than for the +++ conformation (HBAS = 2475.35 Å²). The largest value of HLAS (and lowest value of HBAS) for the +++ rotational isomer favors solubility in water, which is fundamental for the processability of the material.

Table 2. Molecular dipole-dipole polarizabilities for the benzothiazole (A)–benzobisthiazole (B) A–B₁₃–Alinear oligomer

Conformation	α (Å ³) ^a	α ref. ^b	α_1 (Å ³) ^c	α_1 ref. ^b	α_2 (Å ³)	α_2 ref. ^b	α_3 (Å ³)	α_3 ref. ^b	α_{xx} ^d	α_{xx} ref. ^b
000 ^e	698.920	369.071	337.801	134.312	406.049	279.597	1 352.910	693.304	1 352.894	693.279
+-+ ^f	696.756	368.959	339.058	136.054	405.879	278.129	1 345.330	692.694	1 345.317	692.670
+++ ^g	680.958	788.493	372.504	265.305	385.661	303.315	1 284.710	1 796.858	1 284.709	1 796.849
	α_{xy}	α_{xy} ref. ^b	α_{xz}	α_{xz} ref. ^b	α_{yy}	α_{yy} ref. ^b	α_{yz}	α_{yz} ref. ^b	α_{zz}	α_{zz} ref. ^b
000 ^e	3.967	3.254	0.000	0.000	337.816	279.623	0.000	0.000	406.049	134.312
+-+ ^f	3.608	3.142	-0.019	0.030	339.071	278.151	0.131	-0.479	405.879	136.055
+++ ^g	0.662	-0.204	-0.041	3.721	372.528	303.065	0.553	-3.073	385.637	265.564

^aMean molecular dipole-dipole polarizability (Å³).

^bReference: calculations carried out with the PAPID program.

^cMolecular dipole-dipole polarizability tensor eigenvalues α_1 , α_2 , and α_3 (Å³).

^dMolecular dipole-dipole polarizability tensor Cartesian components (Å³).

^eFully planar rotational isomer.

^fEach unit is rotated 10°. Rotations are performed in the alternate directions.

^gEach unit is rotated 10°. All rotations are performed in the same direction.

Table 3. Molecular dipole-quadrupole polarizabilities for the benzothiazole (A)–benzobisthiazole (B) A–B₁₃–A linear oligomer

Conformation	A_x^a	A_x ref. ^b	A_y	A_y ref. ^b	A_z	A_z ref. ^b	A_{xx}^c	A_{xx} ref. ^b	A_{xy}	A_{xy} ref. ^b	A_{xz}	A_{xz} ref. ^b
000 ^d	39.560	-74.771	3.669	-18.616	0.000	0.000	67.188	-162.785	43.131	-54.616	0.000	0.000
+-+ ^e	58.381	81.496	-2.592	19.046	0.921	-0.415	99.435	177.905	-38.411	56.520	7.622	0.344
+++ ^f	-17.239	5 349.979	-21.759	-9.987	4.660	-43.104	-279.517	8 002.807	-139.378	-82.109	-5.274	-188.778
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$A_{x,yy}$	$A_{x,yy}$ ref. ^b	$A_{x,yz}$	$A_{x,yz}$ ref. ^b	$A_{x,zz}$	$A_{x,zz}$ ref. ^b	$A_{y,zz}$	$A_{y,zz}$ ref. ^b	$A_{y,xx}$	$A_{y,xx}$ ref. ^b	$A_{y,xy}$	$A_{y,xy}$ ref. ^b	$A_{y,xz}$
000 ^d	-33.600	81.297	0.000	-33.588	0.000	61.888	81.488	-63.352	-63.352	4.728	44.250	-14.542
+-+ ^e	-49.572	-88.796	0.338	-49.863	-0.077	-55.805	-89.109	65.849	65.849	-29.038	-14.542	-14.542
+++ ^f	114.056	-4 051.394	-2.151	165.461	-14.778	-190.518	-3 951.413	-118.983	-118.983	670.933	-1 807.497	-1 807.497
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$A_{y,xz}$	$A_{y,xz}$ ref. ^b	$A_{y,yy}$	$A_{y,yy}$ ref. ^b	$A_{y,yz}$	$A_{y,yz}$ ref. ^b	$A_{y,zz}$	$A_{y,zz}$ ref. ^b	$A_{y,zz}$	$A_{y,zz}$ ref. ^b	$A_{z,xx}$	$A_{z,xx}$ ref. ^b	$A_{z,xx}$
000 ^d	0.000	0.000	-33.788	28.086	0.000	0.000	0.000	-28.100	35.266	0.000	0.000	0.000
+-+ ^e	-45.983	100.693	30.708	-29.372	-0.370	-0.492	-0.492	25.097	-36.477	10.787	1.103	1.103
+++ ^f	228.939	-630.843	101.965	68.925	4.100	-1.865	-1.865	88.553	50.058	-10.954	-246.688	-246.688
<hr/>												
$A_{z,xy}$	$A_{z,xy}$ ref. ^b	$A_{z,xz}$	$A_{z,xz}$ ref. ^b	$A_{z,yy}$	$A_{z,yy}$ ref. ^b	$A_{z,yz}$	$A_{z,yz}$ ref. ^b	$A_{z,yz}$	$A_{z,yz}$ ref. ^b	$A_{z,zz}$	$A_{z,zz}$ ref. ^b	$A_{z,zz}$
000 ^d	0.000	0.000	-12.575	6.378	0.000	0.000	0.000	-3.840	-1.394	0.000	0.000	0.000
+-+ ^e	-45.960	100.787	17.174	-41.120	-4.916	-0.628	-0.628	3.816	1.421	-5.871	-0.475	-0.475
+++ ^f	228.572	-628.211	-417.274	1 829.657	2.790	120.700	120.700	4.775	-1.797	8.164	125.988	125.988

^aMolecular dipole-quadrupole polarizability \times vector component (\AA^4).^bReference: calculations carried out with the PAPID program.^cMolecular dipole-quadrupole polarizability tensor Cartesian components (\AA^4).^dFully planar rotational isomer.^eEach unit is rotated 10° . Rotations are performed in the alternate directions.^fEach unit is rotated 10° . All rotations are performed in the same direction.

Table 4. Molecular quadrupole-quadrupole polarizabilities for the benzothiazole (A)–benzobisthiazole (B) A–B₁₃–A linear oligomer

Conformation	$C_{xx,xx}^a$	$C_{xx,xx}^{ref.b}$	$C_{xx,yy}^a$	$C_{xx,yy}^{ref.b}$	$C_{xx,xz}^a$	$C_{xx,xz}^{ref.b}$	$C_{xx,yz}^a$	$C_{xx,yz}^{ref.b}$	$C_{xy,xy}^a$	$C_{xy,xy}^{ref.b}$	$C_{xy,xz}^a$	$C_{xy,xz}^{ref.b}$	$C_{xy,yz}^a$	$C_{xy,yz}^{ref.b}$	$C_{yy,yy}^a$	$C_{yy,yy}^{ref.b}$
000 ^c	1 863 537.781	1 037 571.163	5 209.654	2 207.727	0.000	0.000					−932 174.783	−519 279.956				
++ ^d	1 852 839.475	1 036 606.649	4 835.452	2 071.781	−123.577	46.423					−926 798.981	−518 776.491				
+++ ^e	1 835 496.642	2 522 996.982	616.387	−3 027.337	−856.284	4 609.896					−917 858.623	−1 261 881.595				
000 ^c			−931 362.998	−518 291.207	316 036.674	268 760.783					0.000	0.000				
++ ^d	−119.667	−94.311	−926 040.494	−517 830.158	317 315.653	267 212.337					1 036.418	−2 741.679				
+++ ^e	−604.761	−1 136.391	−917 638.019	−1 261 115.387	340 858.151	304 561.848					5 441.561	−19 586.170				
000 ^c																
++ ^d	−2 777.073	−1 230.190	0.000	0.000	−2 432.581	−977.538					380 764.479	126 584.612				
+++ ^e	−2 589.345	−1 160.524	20.650	16.468	−2 246.107	−911.257					380 555.557	128 394.296				
	−479.137	1 389.841	176.835	126.098	−137.250	1 637.496					363 316.491	240 047.676				
000 ^c																
++ ^d	0.000	0.000	−249.660	−26.117	0.000	0.000					466 573.361	260 222.636				
+++ ^e	24.578	−14.015	−248.421	−26.706	98.999	−32.408					463 892.066	259 961.101				
	213.400	−2 327.430	−294.855	−152.063	642.884	−2 282.466					459 479.416	631 561.063				
000 ^c																
++ ^d	0.000	0.000	465 601.422	259 057.321	708.235	347.106					0.000	0.000				
+++ ^e	59.171	47.087	462 906.915	258 815.390	691.586	350.327					60.496	47.224				
	322.297	561.336	458 379.207	630 320.532	512.075	439.987					282.464	575.055				
000 ^c																
++ ^d																
+++ ^e																

^aMolecular quadrupole-quadrupole polarizability tensor Cartesian components (\AA^5).

^bReference: calculations carried out with the PAPID program.

^cFully planar rotational isomer.

^dEach unit is rotated 10°. Rotations are performed in the alternate directions.

^eEach unit is rotated 10°. All rotations are performed in the same direction.

Table 5. Geometrical descriptors for the benzothiazole (A)–benzobisthiazole (B) A–B₁₃–A linear oligomer

Conformation	<i>V</i> (Å ³) ^a	<i>V</i> ref. ^b	<i>S</i> (Å ²) ^c	<i>S</i> ref. ^b	AS (Å ²) ^d	AS ref. ^b	HBAS ^e	HLAS ^f	AS' (Å ²) ^g	AS' ref. ^b
000 ^h	1 961.6	2 065.5	1 990.29	2 175.68	3 032.06	3 190.15	2 534.48	497.58	4 990.88	5 176.78
+–+ ⁱ	1 963.0	2 065.9	1 990.86	2 176.02	3 029.03	3 194.47	2 526.39	502.65	5 000.54	5 187.87
+++ ^j	1 962.7	2 062.5	1 994.11	2 177.48	3 055.78	3 227.36	2 475.35	580.44	5 047.17	5 244.73

^aMolecular volume (Å³).^bReference: calculations carried out with the GEPOL program.^cMolecular surface area (Å²).^dWater accessible surface area (Å²).^eHydrophobic accessible surface area (Å²).^fHydrophilic accessible surface area (Å²).^gSide-chain accessible surface area (Å²).^hFully planar rotational isomer.ⁱEach unit is rotated 10°. Rotations are performed in the alternate directions.^jEach unit is rotated 10°. All rotations are performed in the same direction.

The topological indices for the rotational isomers of the A–B₁₃–A linear oligomer are reported in Table 6. The globularity index, *G*, is slightly varied (in the range 0.380–0.381) on going from one rotational isomer to other. The values compare well with reference calculations carried out with the GEPOL program^{74–77} (*G* = 0.360). The behavior of the rugosity index, *G'* (in the range 1.014–1.016 Å^{–1}), the fractal dimension of the solvent-accessible surface, *D* (in the range 1.51–1.52), and the fractal dimension averaged for nonburied atoms (with nonzero accessible surface area), *D'* (in the range 1.56–1.57), is the same as has been noticed for the globularity index.

The comparison between the TOPO and GEPOL programs is of special interest because the latter does not allow an atom-to-atom partition analysis of the geometric descriptors and topological indices.^{19–22}

The atom-to-atom partition for each thiazolic nitrogen atom in the central unit of the oligomer is reported in Table 7. The contribution of this nitrogen atom to the molecular volume is slightly smaller for the 000 and +–+ rotational isomers (*V* = 9.2 Å³) than for the +++ conformation (*V* = 9.3 Å³). This torsional effect has a steric cause and is due to the partial opening of the oligomer structure occurring under rotation. The trend of the contribution of the nitrogen atom to the molecular surface area, *S*, is the same as has been pointed out for the molecular volume. It should be noted that the polar thiazolic nitrogens are the only atoms that contribute to the hydrophilic accessible surface area, HLAS. This therefore explains why the +++ rotational iso-

mer shows the greatest value of HLAS in Table 5. The molecular globularity at the surface of the nitrogen atom, *G*, is minimum and the molecular rugosity at this atom, *G'*, is maximum for this conformation. The contribution of the nitrogen atom to the water-accessible surface area, AS, is rather smaller for the 000 and +–+ rotational isomers than for the +++ conformation. Thus, the accessibility of the nitrogen atom surface in the 000 and +–+ rotational isomers is about 18% and increases to about 21% for the +++ conformation. The fractal dimension for the nitrogen atom solvent-accessible surface, *D'*, for the 000 and +–+ rotational isomers takes a rather high value (in the range 1.80–1.81) when compared with the molecular value averaged for nonburied atoms (*D'* = 1.56) in the last column of Table 6. This means that the irregularity of the molecular surface near the nitrogen atom is maximum for these conformers.

The solvation descriptors for the rotational isomers of the A–B₁₃–A linear oligomer are reported in Table 8. The negative Gibbs free energy of solvation in water is smaller for the 000 and +–+ rotational isomers (in the range 122–123 kJ · mol^{–1}) than for the +++ conformation (–Δ*G*_{solv,w} = 126.07 kJ · mol^{–1}). This is due to the greater accessibility of the polar thiazolic nitrogen atoms (see the seventh column of Table 7). However, the negative Gibbs free energy of solvation in 1-octanol is slightly varied on going from one conformation to other (in the range 336–337 kJ · mol^{–1}), so the 1-octanol–water partition coefficient, *P*, is greater for the 000 and +–+ rotational isomers (log *P* in the range 37.5–37.7) than for the +++ conformation (log *P* = 36.91). The cavity

Table 6. Topological indices for the benzothiazole (A)–benzobisthiazole (B) A–B₁₃–A linear oligomer

Conformation	<i>G</i> ^a	<i>G</i> ref. ^b	<i>G'</i> ^c	<i>G'</i> ref. ^b	<i>D</i> ^d	<i>D</i> ref. ^b	<i>D'</i> ^e
000 ^f	0.381	0.360	1.015	1.053	1.52	1.53	1.56
+–+ ^g	0.381	0.360	1.014	1.053	1.51	1.53	1.56
+++ ^h	0.380	0.360	1.016	1.056	1.51	1.53	1.57

^aMolecular globularity.^bReference: calculations carried out with the GEPOL program.^cMolecular rugosity (Å^{–1}).^dFractal dimension of the solvent-accessible surface.^eFractal dimension of the solvent-accessible surface averaged for nonburied atoms.^fFully planar rotational isomer.^gEach unit is rotated 10°. Rotations are performed in the alternate directions.^hEach unit is rotated 10°. All rotations are performed in the same direction.

Table 7. Geometric descriptors and topological indices for the benzothiazole (A)–benzobisthiazole (B) A–B₁₃–A linear oligomer: Atom–atom partition for each thiazolic nitrogen atom in the central unit

Conformation	V (Å ³) ^a	S (Å ²) ^b	G^c	G' (Å ⁻¹) ^d	AS (Å ²) ^e	Accessibility ^f	D'^g
000 ^h	9.2	12.13	1.752	1.317	18.11	0.180	1.81
+-+ ⁱ	9.2	12.01	1.769	1.304	18.22	0.181	1.80
+++ ^j	9.3	12.39	1.720	1.339	21.32	0.212	1.62

^aMolecular volume (Å³).

^bMolecular surface area (Å²).

^cMolecular globularity.

^dMolecular rugosity (Å⁻¹).

^eWater-accessible surface area (Å²).

^fAccessibility of the accessible surface.

^gFractal dimension of the solvent-accessible surface.

^hFully planar rotational isomer.

ⁱEach unit is rotated 10°. Rotations are performed in the alternate directions.

^jEach unit is rotated 10°. All rotations are performed in the same direction.

volume, $V_{\text{cav, w}}$, and surface area, $S_{\text{cav, w}}$, in water are greater for the 000 and +-+ rotational isomers than for the +++ conformation. However, the cavity volume in 1-octanol, $V_{\text{cav, o}}$, is maximum for the +++ rotational isomer and the cavity surface area in 1-octanol, $S_{\text{cav, o}}$, is maximum for the 000 conformation.

CONCLUSIONS

In this article we have outlined a method for the calculation of multipole moments and molecular $\bar{\alpha}$, \bar{A} , and \bar{C} polarizabilities that we have successfully applied to three model rotational isomers of the A–B₁₃–A linear oligomer.

From the results of our work, the following conclusions can be drawn:

1. The $\bar{\alpha}$, \bar{A} , and \bar{C} polarizabilities increase rapidly with the length of the conjugated π -electron system. The components in the chain direction are largest in $\bar{\alpha}$, \bar{A} , and \bar{C} , reflecting the strong response of the delocalized π electrons to electric fields.
2. Inclusion of heteroatoms in the π -electron system can be beneficial for the $\bar{\alpha}$, \bar{A} , and \bar{C} polarizabilities, owing to either the role of additional p and/or d or-

bitals provided by the heteroatoms or to the role of steric factors in the π -electron conjugation.

3. Small torsional changes in the A–B₁₃–A linear oligomer can enhance solubility by increasing the hydrophilic accessible surface without too much affecting $\bar{\alpha}$ and \bar{C} .
4. The torsion of the A–B₁₃–A linear oligomer can vary the dipole moment and so modify the \bar{A} polarizability.

A last but not least conclusion would be that the difference between the PAPID and POLAR methods introduces important numerical effects in the resulting polarizabilities. The main difference in the theory is that while the former performs the coupling of isotropic atomic polarizabilities, the latter starts from anisotropic ones. We think that the main conclusion of this work is the extreme sensitivity of the numerical results (which for large oligomers can reach up to 100%) to the above assumption relative to starting polarizabilities.

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Table 8. Solvation descriptors for the benzothiazole (A)–benzobisthiazole (B) A–B₁₃–A linear oligomer

Conformation	$\Delta G_{\text{sol, w}}$ ^a	$\Delta G_{\text{sol, o}}$ ^b	$\log P^c$	$V_{\text{cav, w}}$ ^d	$S_{\text{cav, w}}$ ^e	$V_{\text{cav, o}}$ ^f	$S_{\text{cav, o}}$ ^g
000 ^h	–122.52	–335.80	37.50	15 967.9	5 421.03	25 516.7	6 920.04
+-+ ⁱ	–121.94	–336.56	37.70	15 839.2	5 408.46	25 721.3	6 890.83
+++ ^j	–126.07	–336.20	36.91	15 261.9	5 320.97	25 798.6	6 893.58

^aGibbs free energy of solvation in water (kJ · mol⁻¹).

^bGibbs free energy of solvation in 1-octanol (kJ · mol⁻¹).

^c P is the 1-octanol/water partition coefficient.

^dCavity volume in water (Å³).

^eCavity surface area in water (Å²).

^fCavity volume in 1-octanol (Å³).

^gCavity surface area in 1-octanol (Å²).

^hFully planar rotational isomer.

ⁱEach unit is rotated 10°. Rotations are performed in the alternate directions.

^jEach unit is rotated 10°. All rotations are performed in the same direction.

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