

Effect of Medium Polarity on the Second-Order Polarizability of an Octupolar Chromophore: An *ab initio* Reaction Field Study of Triaminotrinitrobenzene

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The Self-Consistent Reaction Field theory (extended to include an ellipsoidal cavity for the solute and a multipolar expansion of the field) is used to investigate the influence of medium polarity on the second-order nonlinear optical response of the prototypical octupolar compound 1,3,5-triamino-2,4,6-trinitrobenzene, TATB. Despite the absence of any dipole moment in TATB, the effect of medium polarity is

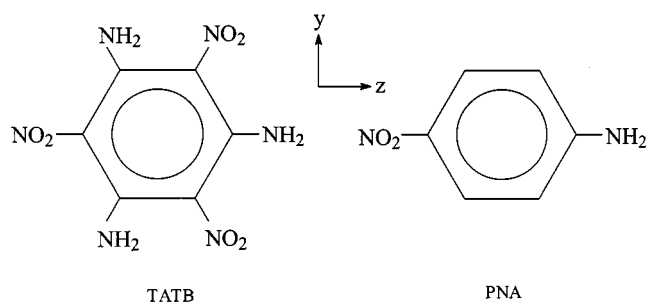
found to be significant; for instance, the β_{zzz} tensor component of TATB is calculated to be twice as large in dichloromethane (electric permittivity $\epsilon = 9.1$) as in the gas phase ($\epsilon = 1$). This enhancement factor is similar to, though somewhat smaller than the one calculated for the dipolar counterpart of TATB, i.e. *p*-nitroaniline.

It is now well established that medium polarity can exert a profound influence on the molecular polarizabilities of donor-acceptor conjugated chromophores; it can even be exploited to fine tune and enhance the second- or third-order nonlinear optical (NLO) response^[1]. Many theoretical studies based on the Self-Consistent Reaction Field (SCRF) theory have characterized the effect of solvent polarity on the geometric and electronic structure as well as the NLO properties of dipolar compounds, such as acetonitrile^{[2][3]} and push-pull derivatives of polyenes, arylenes, or arylenevinyls^{[4][5][6][7]}. In a previous study on *p*-nitroaniline and a push-pull hexatriene^[8], it was demonstrated that it is possible to calculate accurately the solvent dependence of the second-order polarizability, β , at the SCRF level and to obtain excellent agreement with experiment provided: (i) the quasi-one-dimensional chromophores are inserted into an ellipsoidal (rather than spherical) cavity; and (ii) the interactions between the chromophore and the surrounding medium are evaluated using a multipolar expansion going beyond the traditional dipolar approximation.

In the present Communication, we extend our previous work on dipolar chromophores to a prototypical *octupolar* chromophore, 1,3,5-triamino-2,4,6-trinitrobenzene, TATB, see Figure 1. In octupolar nonlinear optical chromophores such as TATB, whose investigation has been pioneered by Zyss and co-workers^{[9][10]}, all the state dipole moments are zero by symmetry and the second-order polarizability tensor has only septor («octupolar») components and no vector («dipolar») components. We stress that a similar theoretical study has been recently reported by Agren and co-

workers^[11]; however, these authors addressed the tricyanomethide ion, $C(CN)_3^-$, which carries a net negative charge and is accompanied by a counter-ion; this is likely to influence the interaction with the solvent molecules, especially at lower permittivities.

Figure 1. Chemical formulas of TATB and PNA and orientation of the axes used in the calculations of the molecular polarizabilities



TATB is nearly insoluble in common solvents; the existence of a significant second-order polarizability in this compound has been experimentally established in the solid state^{[12][13][14]}. However, soluble analogs of TATB^[15], as well as other soluble octupolar chromophores^{[16][17][18][19]}, have been prepared and characterized. Therefore, a theoretical study providing understanding of the environment effect on a prototypical neutral octupolar NLO chromophore such as TATB appears to be fully pertinent.

Our theoretical methodology is taken to be the same as the one used in our previous study on dipolar chromophores^[8]; this will also allow us to make direct comparisons

to the results on *p*-nitroaniline, PNA, the dipolar counterpart of TATB. Briefly, the methodology consists in exploiting an expanded self-consistent reaction field (SCRf) theory, i.e., considering the solute to occupy an ellipsoidal cavity within a dielectric continuum representing the medium and taking into account the self-consistent solute/medium interactions as described by multipolar terms up to 2^6 -poles. For TATB, such an extended multipolar expansion is of course essential since there can exist no solute-medium dipole-dipole interaction with a non-dipolar molecule. As for the cavity shape, an oblate ellipsoidal cavity is expected to be more adequate for the planar TATB molecule than a spherical one (the shape of the cavity is built on the basis of atomic van der Waals spheres). The calculations were carried out at the Hartree-Fock *ab initio* level, with the same 3-21G basis set as in our previous work (where it was shown to be sufficient)^[8], using the Gaussian-92 program^[20] with the SCRf routines^[21]. The components of β are calculated analytically via electric field derivatives of the total energy within a coupled perturbed Hartree-Fock approach^[22]. The geometry optimization indicates that, as is the case in the solid state^[14], an isolated TATB molecule adopts D_{3h} symmetry (with planar amino groups) due to strong hydrogen bonding.

The TATB molecule is strictly non-dipolar; however, it possesses non-vanishing quadrupolar and higher-order moments (as mentioned above, it is referred to as an "octupolar" NLO chromophore^{[9][12]} in the sense that only the $J = 3$ tensor component contributes to β). The major part, over 75%, of the TATB – dielectric medium interaction energy (on the order of several kcal/mol in total) is found for quadrupolar and octupolar interactions, while higher-order terms turn out not to be significant (dipolar interactions strictly vanish). The medium effect on the geometry of TATB is weak; the bond lengths change by less than 0.01 Å. These results for interaction energy and geometry changes are very similar to those found previously for PNA^[8].

The calculated hyperpolarizability values for TATB are listed in Table 1 for dielectric media corresponding to solvents such as 1,4-dioxane, dichloromethane, acetone, acetonitrile, and nitromethane ($\epsilon = 2.2, 9.1, 20.7, 37.5, 37.5$, respectively); the evolution of β is also shown in Figure 2. By symmetry, the only non-zero components of the second-order polarizability tensor are $\beta_{zzz} = -\beta_{zyy} = -\beta_{yzy} = -\beta_{yyz}$; consequently, all the vector components $\beta_i = \sum_j \beta_{ijj}$ and the vector modulus $\beta_v = \sum_i \beta_i^2$ are zero and the modulus of the β tensor, $\beta = (\sum_{i,j,k} \beta_{ijk}^2)^{1/2} = 2\beta_{zzz}$. For the sake of comparison, the calculated β_v values for PNA^[8], which are dominated by the β_{zzz} component are also listed in Table 1. In the gas phase, the calculated β_{zzz} tensor components for TATB, 8.0×10^{-30} esu, is nearly identical to the β_v value of PNA, 7.9×10^{-30} esu. In both cases, the modifications in the second-order polarizability induced by the medium polarity are important. In TATB, the values calculated for high-polarity media are more than twice as large as those in vacuum. The solvent effect on the NLO response of TATB is, however, weaker than that found ex-

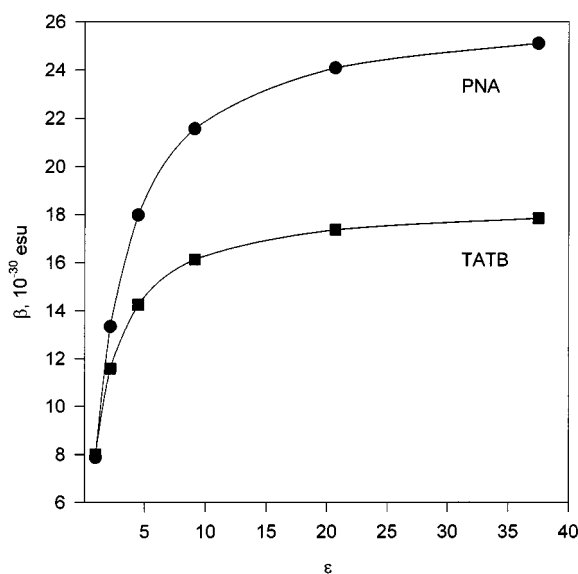
perimentally and theoretically for its dipolar counterpart, PNA.

Table 1. Evolution of the 3-21G-SCRf ($l = 6$, ellipsoidal cavity) theoretical second-order polarizability values (in 10^{-30} esu) for PNA^[a] and TATB, as a function of the solvent dielectric constant ϵ

ϵ	PNA: β_v	TATB: β_{zzz}
1	7.88	8.01
2.2	13.34	11.58
4.48	17.98	14.24
9.1	21.56	16.12
20.7	24.08	17.36
37.5	25.10	17.84

^[a] Values from ref.^[8] and multiplied by 2 in order to conform to the power series expansion of polarization used for TATB.

Figure 2. Evolution of the second-order polarizability as a function of medium permittivity (β_v for PNA, β_{zzz} for TATB)



A rapid saturation of the solvent effect is expected within Onsager theory; it has already been pointed out for PNA^[8]; it is even more pronounced for TATB: the β value is predicted to increase by 77% when the molecule is transferred from the gas phase ($\epsilon = 1$) into a medium with $\epsilon = 4.47$ corresponding to a solvent mixture used in the PNA study^[8], and only by an additional 25% between this solvent and the highly polar nitromethane ($\epsilon = 37.5$). It is interesting to note that this kind of evolution resolves an apparent controversy between the theoretical results from this work and the conclusions from an experimental work on soluble TATB analogs, tri(*iso*-propylamino)trinitrobenzene, TIATB, and trihydroxytrinitrobenzene, THTN^[15]. In the latter work, the comparison between the β_{333} values of TIATB measured in chloroform ($\epsilon = 4.8$) and nitromethane ($\epsilon = 37.5$), 16 ± 4 and $19 \pm 5 \times 10^{-30}$ esu respectively, as well as a similar dependence for THTN, lead the authors to the conclusion that an octupolar NLO chromophore is nearly insensitive to the solvent. As a matter of fact, the measured increase in second-order polarizability of TIATB in going

from chloroform to nitromethane is fully consistent with our theoretical results, given the experimental error bars.

In conclusion, the solvent effect on the first hyperpolarizability of a neutral octupolar NLO chromophore is significant. In the case of TATB, going from the gas phase to media with high dielectric constants leads to a doubling of the β_{zzz} component; in the case of the dipolar counterpart of TATB, *p*-nitroaniline, the β_v value is tripled.

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