the use of vanadium to alter the cofactor specificity of 2′-NADP dependent dehydrogenases is simple, rapid, and convenient and demonstrates the power of simple chemical reactions in modifying enzyme specificity.

Supplementary Material Available: Description of aqueous vanadate reactions, kinetic derivations, and experimental data (12 pages). Ordering information is given on any current masthead page.

On the Second-Order Polarizability of Conjugated π-Electron Molecules with Octupolar Symmetry: The Case of Triaminotrinitrobenzene

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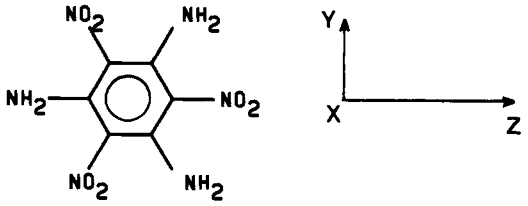
Interest in the quadratic nonlinear optical (NLO) properties of organic molecules and materials keeps steadily growing. Experimental data are now starting to provide a better understanding of the relationship between molecular structure and NLO properties,[1-4] which is of major importance to guide synthesis and materials processing toward novel systems with enhanced characteristics. Compounds with a quadratic NLO response have traditionally been developed according to the general recipe of having an electron-donating group and an electron-accepting group linked by a conjugated segment. *p*-Nitroaniline (pNA) and its derivatives constitute prototypical examples of such an approach. In this case, the second-order polarizability β is often described within the dipolar approximation on the basis of the so-called two-state model:[5]

$$\beta_{\mu}(0) = \frac{3}{2}\,\frac{(\mu_{ge})^2\Delta\mu}{(\hbar\omega_{ge})^2}$$

where $\Delta\mu = \mu_e - \mu_g$ is the difference between the dipole moments in the main excited state and the ground state; $\hbar\omega_{ge}$, the transition energy; and μ_{ge}, the transition dipole moment.

One of the implications of this model is that it is most favorable to have as large as possible a change in dipole moment upon excitation in order to maximize charge separation, and therefore β. However, the expansion of the β tensor in irreducible components can be shown to contain, in addition to a dipolar contribution, an *octupolar contribution*. It has recently been proposed[6] to address specifically the optimization of the octupolar contribution at the microscopic and macroscopic levels. Initial second-harmonic-generation (SHG) powder measurements[7] have helped in identifying 1,3,5-triamino-2,4,6-trinitrobenzene (TATB),



as a prototype candidate molecule and crystal exhibiting a significant β value despite the fact that by symmetry the dipole moment is 0 in all electronic states (in the absence of structural relaxations). Systematic utilization of the two-state model in the dominant context of dipolar systems may have obscured possible significant contributions[6] to β coming from more than a single excited state.

In TATB, the donor and acceptor groups are located at alternate positions on the benzene ring. X-ray diffraction studies indicate that the molecule is planar in the solid state because of strong intra- and intermolecular hydrogen bonding.[8] TATB thus adopts D_{3h} symmetry and is noncentrosymmetric. The crossed character of the intramolecular charge transfers between the amino and nitro groups (for each of them, there are one para and two ortho interactions) leads to a complete cancellation of the vector (dipolar) part of the β tensor. Therefore, β cannot be measured by use of the EFISHG (electric field induced second harmonic generation) technique,[5,9] which is based on the alignment of the molecules along their dipole moment axis.

The components of the β tensor have been evaluated for TATB and pNA, using three different and complementary theoretical methods.[10] The results are given in Table I. It is remarkable to note that the three independent theoretical approaches consistently lead to similar conclusions. Our results thus demonstrate that the intrinsic quadratic nonlinear response of TATB (modulus of the β tensor) is about 1.6–1.8 times larger than that of pNA. This establishes that *octupolar contributions to β are significant.*

The main difference between the pNA and TATB β tensors lies in the strongly different "off-diagonal" β_{zyy} values, while the "diagonal" β_{zzz} values are comparable. In TATB, D_{3h} symmetry imposes $\beta_{zyy} = \beta_{zzz}$,[6] thus making β_{zyy} substantially higher than for C_{2v} molecules such as pNA. It is the additional contribution from the β_{zyy} component which strongly increases the modulus of β, by almost a factor of 2, from pNA to TATB.

The sum-over-states approach allows us to identify the π-electron excited states that contribute most significantly to the off-resonant quadratic nonlinear response. We find, *in marked contrast to the two-state model*, that in addition to the ground state S_0, a set of three doubly degenerate π-electron excited states

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(10) The following theoretical approaches have been considered: (i) finite-field (numerical derivatives) β calculations at the semiempirical Hartree–Fock Austin model 1 (AM1) level;[11] (ii) the ab initio coupled perturbed Hartree–Fock (CPHF) technique whereby β is obtained via analytical derivatives of the total energy as a function of electric field;[12] and (iii) the perturbative sum-over-states (SOS) method based on an intermediate neglect of differential overlap (INDO) Hamiltonian with configuration interaction among singly- and doubly-excited (SDCI) π-states.[13] The geometry of TATB has been optimized at the ab initio 3-21G and AM1 levels under D_{3h} symmetry; the results are very similar. The 3-21G optimized geometry is used for both ab initio CPHF and INDO/SDCI/SOS calculations while the finite-field AM1 calculations are carried out on the basis of the AM1 optimized geometry.

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Table I. Finite-Field AM1, CPHF 3-21G, and INDO/SDCI results on pNA and TATB[a]

	AM1		3-21G		INDO/SDCI	
	pNA	TATB	pNA	TATB	pNA	TATB
μ_z (D)	−7.64	0.0	−7.79	0.0	−8.34	0.0
$\langle\alpha\rangle$ (Å^3)	11.60	18.90	10.50	16.62	–	–
β_{zzz} (10^{-30} esu)	−11.67	−11.08	−9.55	−8.01	−8.53	−7.68
β_{zyy} (10^{-30} esu)	1.93	11.08	1.66	8.01	0.06	7.68
β_{zxx} (10^{-30} esu)	0.0	0.0	0.0	0.0	0.0	0.0
β_z (10^{-30} esu)	−9.74	0.0	−7.89	0.0	−8.47	0.0
$\|\beta\|$ (10^{-30} esu)	12.14	22.16	9.97	16.02	8.53	15.36

[a] Ground-state dipole moment, μ; average first-order polarizability, $\langle\alpha\rangle$; components of the second-order polarizability tensor; *z*-component of the vectorial part of the β tensor, β_z; modulus of the β tensor, $\|\beta\|$. Note that β_z is equal to $\sum_i \beta_{zii}$ and $\|\beta\|^2 = \sum_{i,j,k} \beta_{ijk}^2$. The *y* and *z* axes define the molecular plane with *z* corresponding to the para axis (see sketch of the TATB molecule).

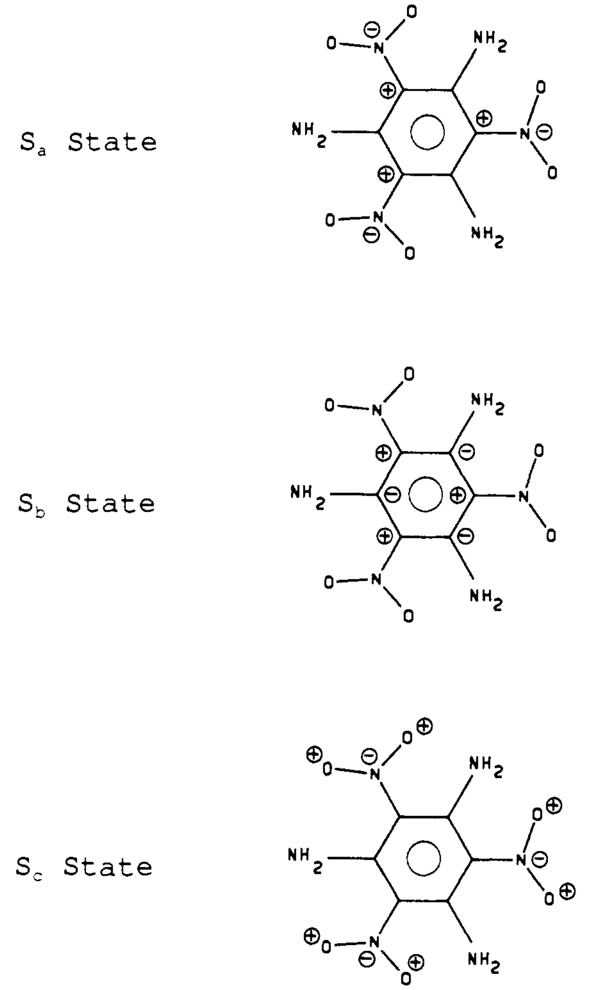

Figure 1. Pictorial representation of the charge transfers in the three excited states which provide the most significant contributions to TATB second-order polarizability. The plus signs (minus signs) represent a decrease (increase) in π-electron charge.

(hereafter denoted S$_a$, S$_b$, and S$_c$ states) play an essential role. These states are located 4.64, 5.26, and 6.64 eV above the ground state, respectively.

Relative to the ground state, the charge density evolutions when going to these excited states are illustrated in Figure 1 and correspond to the following: (i) for the S$_a$ state, there occurs a strong polarization of the carbon–nitro nitrogen bonds, with π-electron density transferred from the carbon atom to the nitrogen atom; (ii) for the S$_b$ state, the polarization mostly involves the ring carbon atoms, with π-electron density being transferred from the carbons attached to the nitro groups to those attached to the amino groups; and (iii) in the case of the S$_c$ state, the polarization occurs mainly within the nitro groups with π-electron density moving from the oxygens to the nitrogens. The calculations indicate that the *contributions to β from π-electron transfers between ortho and para pairs of amino and nitro groups are totally mixed and cannot be separated.* Furthermore, as can be seen from the π-electron density evolutions in the essential excited states of TATB, the π-electron densities on the amino groups are found to be less directly involved in the quadratic nonlinear response than is the case in pNA.

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Poly(germanium enolate): A New Class of Polymer Having a Germanium Enolate Structure in the Main Chain

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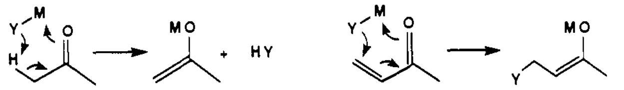
Polymeric enolates are of great interest from the viewpoints of both basic organic chemistry and material science. The fundamental principle for the generation of a metal enolate from the corresponding carbonyl compound requires an appropriate combination of an electrophilic metallic component M and a nucleophilic component Y.[1] All of the known enolates generated by these methods have monomeric structures because the M–Y bond is cleaved; the production of polymeric enolates cannot be achieved.



Divalent germanium compounds (germylenes)[2] are interesting chemical species since they have both a nucleophilic center due to the lone pair of electrons and an electrophilic center due to the 4p vacant orbital on the same germanium atom, which enables us to construct a polymeric form of enolate structure. This communication describes the synthesis of novel germanium-containing polymers **3** having a germanium enolate unit in the main chain (*poly(germanium enolate)*) by alternating copolymerization

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(1) Typical examples include the preparation of lithium enolates from ketones using lithium amides (M^+ = lithium cation, Y^- = amido anion)[13] and silyl enolate formation from silyl hydrides and α,β-unsaturated carbonyl compounds (M^+ = silyl cation, Y^- = hydride ion).[14]

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