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Indeed, the attacked carbon (C_1) carries a larger electron density in methacrylic acid than in acrylic acid, and this difference is directly responsible for the more negative electrostatic potential generated by MAA along the path of approach of the nucleophile. The difference in charge distribution is thus responsible for different recognition properties at relatively long distances from these molecules. This difference in electron density distribution is also responsible for the difference in the energies required to distort the two molecules upon close-contact interaction with the nucleophile. The distortion of the C_1 carbon with the higher charge density in MAA requires more energy than that in AA. This difference in energy is mainly responsible for the difference in stabilization energies of the stable carbanions produced when the molecules interact with the nucleophile F^-.

The discriminating properties discussed above for the acrylic and methacrylic acids can thus become the basis for structure-reactivity correlations in substituted double bonds with respect to a nucleophilic addition. Furthermore, this type of discriminant reactivity criterion can be correlated with experimental measurements of toxicity.[25] The observed correlation, indicating lower reactivity of MAA derivatives as compared to AA derivatives in nucleophilic addition as well as in the bioassays, supports the hypothesis that Michael addition is a likely molecular mechanism for the biological activity of activated double bonds and reaffirms the discriminating power of the molecular properties. Such discriminant reactivity criteria that are anchored in the properties of the molecules and are based on clear mechanistic hypotheses should provide useful tools for predicting the ability of untested compounds in this series to exhibit similar biological activities.

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Molecular and Macromolecular Nonlinear Optical Materials. Probing Architecture/Electronic Structure/Frequency Doubling Relationships via an SCF-LCAO MECI π Electron Formalism

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Abstract: This contribution explores the use of perturbation theory and the computationally efficient PPP π electron model Hamiltonian to relate quadratic molecular optical nonlinearities to architecture and electronic structure. A detailed study of aniline, nitrobenzene, and *p*-nitroaniline, using all monoexcited configurations, yields β (hyperpolarizability) tensors in good agreement with all-valence-electron CNDO calculations. Moreover, PPP-derived vector (observable) components for frequency doubling ($\beta_{vec}(-2\omega;\omega,\omega)$) are in excellent agreement with experiment over a wide frequency range. For a series of para-disubstituted benzenes, there is a linear relationship between calculated β_{vec} values and Hammett σ parameter differences for the substituents. For a series of α,ω-$N(CH_3)_2,NO_2$-disubstituted trans polyenes, there is a linear relationship over a broad frequency range between calculated ln β_{vec} and the number of double bonds between the substituents. Multiple $N(CH_3)_2,NO_2$ substitution at the polyene ends has little additional effect on β_{vec} beyond that of single substitution. Examination of a simple two-level perturbation model reveals that this insensitivity of β_{vec} to multiple donor/acceptor substitution reflects the corresponding insensitivity of the dipole moment as well as of the energy and oscillator strength of the first optical transition. The utility of the PPP model Hamiltonian in designing new, elaborate nonlinear chromophores is illustrated by an examination of several hypothetical molecules of sequentially varied substitution.

Substances which exhibit highly nonlinear optical (NLO) responses are currently of great scientific and technological interest.[1] While such materials have traditionally been inorganic in nature (e.g., $LiNbO_3$, KH_2PO_4, $KTiOPO_4$, etc.), recent results suggest that organic conjugated π-electron molecular and polymeric NLO materials offer great promise.[2] The attraction vis-à-vis more conventional materials lies in the inherent tunability of organic molecular structures, greatly enhanced NLO responses over a wide frequency range, ultrafast response times, the possibility of better processing/film-forming characteristics, lower dielectric constants, and the possibility of higher laser damage thresholds.[2]

The fundamental relationship describing the change in molecular dipole moment (polarization) upon interaction with an oscillating external electric field can be expressed in a power series (eq 1).[1,2] Here P_i is the polarization induced along the *i*th

$$P_i = \sum_j \alpha_{ij}E_j + \sum_{jk} \beta_{ijk}E_jE_k + \sum_{jkl} \gamma_{ijkl}E_jE_kE_l + ... \qquad (1)$$

molecular axis, E_j is the *j*th component of the applied electric field, α is the linear polarizability, β the quadratic hyperpolarizability, and γ the cubic hyperpolarizability. The even order tensor, β, which is responsible for second harmonic generation (SHG) and frequency mixing, vanishes in a centrosymmetric environment. There are no environmental parity restrictions on the odd order

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(1) (a) Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley: New York, NY, 1984. (b) Zernike, F.; Midwinter, J. E. *Applied Nonlinear Optics*; Wiley: New York, NY, 1973. (c) Abraham, E.; Seaton, C. F.; Smith, S. D. *Sci. Am.* **1984**, 85-93. (d) Giordmaine, J. A. *Sci. Am.* **1964**, 38-49.

(2) (a) *Nonlinear Optical Properties of Organic Molecules and Crystals*: Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, NY, 1987; Vols. 1 and 2. (b) Kowel, S. T.; Ye, L.; Zhang, Y.; Hayden, L. M. *Optical Eng.* **1987**, *26*, 107-112. (c) *SPIE*, "Molecular and Polymeric Optoelectronic Materials: Fundamentals and Applications; Khanarian, G., Ed.; 1986; p 682. (d) Zyss, J. *J. Mol. Electronics* **1985**, *1*, 25-56. (e) *Nonlinear Optical Properties of Organic and Polymeric Materials*; Williams, D. J., ed.; American Chemical Society: Washington, D.C., 1983; ACS Symposium Series 233. (f) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690-703.

0002-7863/88/1510-1707$01.50/0

tensors. The analogous macroscopic polarization arising from an array of molecules is given by eq 2 where the χ's are macroscopic

$$P_I = \sum_J \chi_{IJ}^{\omega} E_J + \sum_{JK} \chi_{IJK}^{2\omega} E_J E_K + \sum_{JKL} \chi_{IJKL}^{3\omega} E_J E_K E_L + \ldots \quad (2)$$

susceptibilities and the indices refer to crystallographic directions. The macroscopic susceptibilities are related to the corresponding molecular terms α, β, γ, etc. by local field corrections (intermolecular interactions) and the density of chromophores as in eq 3 for frequency doubling. Here N is the number of molecules per

$$\chi_{IJK}^{2\omega}(-2\omega;\omega,\omega) = N f_{Ii} f_{Jj} f_{Kk} \beta_{ijk}(-2\omega;\omega,\omega) \quad (3)$$

unit volume, and the f's are local field corrections. Importantly, it can be seen that the nonlinear response of a material is ultimately limited by the optical characteristics of the constituent molecular chromophores.

The design and synthesis of new chromophores having optimized NLO characteristics currently represents a major scientific challenge and one that would benefit from reliable, computationally efficient, and chemically oriented quantum chemical descriptions of NLO phenomena. Several theoretical approaches to calculating molecular NLO properties have been described. Most rigorous are coupled-Hartree–Fock,[3a,b] derivative-Hartree–Fock,[3c] and correlated wave function[4] ab initio procedures which are presently only applicable to small molecules. At the other end of the spectrum are highly simplified/phenomenological two-level[5] and bond additivity[6] models. However, the accuracy with which semiempirical SCF LCAO methods can describe the linear optical properties (transition energies, oscillator strengths) of relatively elaborate molecules suggests application, within a perturbation theoretical framework, to NLO properties. Indeed, all-electron CNDO methods have recently been employed, with success, to calculate first-order molecular NLO properties (β).[7]

We recently communicated[8,9] an alternative approach which capitalizes upon the fundamentally π-electron character of most organic NLO phenomena:[2] the π-electron Pariser, Parr, Pople (PPP) formalism.[10–12] The attraction of this model lies in the far greater computational efficiency of a calculation which deals only with π electrons. Thus, a greater number of π electron configurations can be included in the perturbation theoretic sums over states (affording greater accuracy), more elaborate chromophores and chromophore assemblies can be studied in detail, and a greater number of chromophore conformations and polarization frequencies can be examined. Our initial study[8] of β for 12 diverse types of conjugated organic chromophores revealed excellent agreement with experiment. In the present contribution, we extend this work in three related directions. First, we examine the accuracy of the PPP model in describing the linear and first-order nonlinear optical properties of three experimentally well-characterized model chromophores, with particular attention to the symmetry and frequency dependence of the β tensor. A comparison with CNDO results is also made. Second, we inquire whether there are connections between molecular NLO characteristics and standard physical organic descriptors of substituent electronic effects. Finally, we show how the PPP model can be used to evaluate the NLO characteristics of hypothetical molecular chromophores. We investigate the influence on β of conjugation length, unusual substituents, and multiple substituents.

Theoretical Methods

The individual symmetrized components of the second-order susceptibility tensor can be expressed as in eq 4 by using perturbation theory.[5c,13]

$$\begin{aligned}\beta_{ijk} + \beta_{ikj} = -\frac{e^3}{4\hbar 2}\Bigg[\sum_{\substack{n\neq n'\\ n\neq g\\ n'\neq g}} (r^j_{gn} r^i_{n'n} r^k_{gn'} + {} & r^k_{gn} r^i_{n'n} r^j_{gn'}) \left(\frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}+\omega)} + \frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}-\omega)} \right) + \\ & (r^i_{gn} r^j_{n'n} r^k_{gn'} + r^i_{gn} r^k_{n'n} r^j_{gn'}) \left(\frac{1}{(\omega_{n'g}+2\omega)(\omega_{ng}+\omega)} + \frac{1}{(\omega_{n'g}-2\omega)(\omega_{ng}-\omega)} \right) + \\ & (r^j_{gn'} r^k_{n'n} r^i_{gn} + r^k_{gn'} r^j_{n'n} r^i_{gn}) \left(\frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}-2\omega)} + \frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}+2\omega)} \right) + 4\sum_n [r^j_{gn} r^k_{gn} \Delta r^i_n (\omega_{ng}^2 - 4\omega^2) + \\ & r^i_{gn}(r^k_{gn}\Delta r^j_n + r^j_{gn}\Delta r^k_n)(\omega_{ng}^2 + 2\omega^2)] \frac{1}{(\omega_{ng}^2-\omega^2)(\omega_{ng}^2-4\omega^2)} \Bigg] \end{aligned} \quad (4)$$

Here $r^i_{mn} = \langle \Psi_m | \hat{r}^{(i)} | \Psi_n \rangle$ is the matrix element of the displacement operator $r^{(i)}$ along the ith molecular axis between electronic states Ψ_m and Ψ_n, the energies of which, e_m and e_n, are related to the excitation frequency ω_{mn} by eq 5

$$e_m - e_n \equiv \hbar\omega_{mn} \quad (5)$$

and $\Delta r^i_n \equiv r^i_{nn} - r^i_{gg}$, the difference in dipole moment between the nth state and the ground state (denoted by g) associated with the charge transfer when the nth excitation occurs. Therefore, calculation of β_{vec} requires computation of energies e_m and of matrix elements r_{mn}. The same quantities are employed in the calculation of linear optical properties.

The nature of the PPP Hamiltonian has been extensively discussed elsewhere.[10,11] It is an SCF-LCAO model which employs a π-type atomic orbital basis set. It includes all one-electron terms (nuclear attraction, kinetic energy) and restricts two-electron terms to one-center and two-center Coulomb repulsion. In the present case, as with most semiempirical studies of linear and nonlinear optical properties, the monoexcited configuration interaction (MECI, Tamm–Dancoff) approximation is employed in describing the excited state wave functions ψ_n.[10a,11f] All monoexcited configurations are included in the present calculations.[14] Standard PPP parameters are employed (Table I) and molecules are assumed to be planar in the present work. Of course, deviations from planarity can be accommodated within the framework of the PPP model[16] and will be discussed elsewhere.[17] The Pariser

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(3) (a) Zyss, J.; Berthier, G. *J. Chem. Phys.* **1982**, *77*, 3635–3653. (b) Subbaswamy, K. R.; Mahan, G. D. *J. Chem. Phys.* **1986**, *84*, 3317–3319. (c) Dykstra, C. E.; Jasien, P. J. *Chem. Phys. Lett.* **1984**, *109*, 388–393.

(4) (a) Sekino, H.; Bartlett, R. J. *J. Chem. Phys.* **1986**, *85*, 976–89; **1986**, *84*, 2726. (b) Oddershede, J.; Svendsen, E. N. *Chem. Phys.* **1982**, *64*, 359.

(5) (a) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446–457. (b) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664–2668. (c) Orr, B. J.; Ward, J. F. *Mol. Phys.* **1971**, *20*, 513–526.

(6) Chemla, D. S.; Oudar, J. L.; Jerphagnon, J. *Phys. Rev. B* **1975**, *12*, 4534–4546.

(7) (a) Lalama, S. L.; Garito, A. F. *Phys. Rev. A* **1979**, *20*, 1179–1194. (b) Garito, A. F.; Teng, C. C.; Wong, K. Y.; Enmmankhamiri, O. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 219–258. (c) Docherty, V. J.; Pugh, D.; Morley, J. O. *J. Chem. Soc., Faraday Trans 2* **1985**, *81*, 1179–1192. (d) Allen, S.; Morley, J. O.; Pugh, D.; Docherty, V. J. in ref 2c, pp 20–26. (e) Morrell, J. A.; Albrecht, A. C. *Chem. Phys. Lett.* **1979**, *64*, 46–50.

(8) Li, D.; Marks, T. J.; Ratner, M. A. *Chem. Phys. Lett.* **1986**, *131*, 370–375.

(9) (a) Li, D.; Yang, J.; Ye, C.; Ratner, M. A.; Wong, G.; Marks, T. J. In *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N., Ulrich, D. R., Eds.; Plenum Press: New York, NY, in press. (b) Reported in part at the 193rd ACS National Meeting, Denver, CO, April 5–10, 1987; Abstract PHYS 181. (c) Li, D.; Marks, T. J.; Ratner, M. A. *Mater. Res. Soc. Symp. Ser.*, in press.

(10) (a) Linderberg, J.; Öhrn, Y. *Propagators in Quantum Chemistry*; Academic Press: London, 1974. (b) Murrell, J. N.; Harget, A. J. *Semi-Empirical Self-Consistent-Field Molecular Orbital Theory of Molecules*; Wiley: London, 1972.

(11) (a) Pople, J. A. *Trans. Faraday Soc.* **1953**, *49*, 1375–1385. (b) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 466–471. (c) Pariser, R. *Ibid.* **1953**, *21*, 568–569. (d) Linderberg, J.; Öhrn, Y. *J. Chem. Phys.* **1967**, *49*, 716–727. (e) Koutecky, J. *J. Chem. Phys.* **1967**, *47*, 1501–1511. (f) Jørgensen, P.; Linderberg, J. *Int. J. Quantum Chem.* **1970**, *4*, 587–602.

(12) For another recent application of the PPP model to NLO phenomena, see: Dirk, C. W.; Twieg, R. J.; Wagniere, G. *J. Am. Chem. Soc.* **1986**, *108*, 5387–5395.

(13) (a) Ward, J. F. *Rev. Mod. Phys.* **1965**, *37*, 1–18. (b) Bloembergen, N.; Lotem, H.; Lynch, R. T. *Indian J. Pure Appl. Phys.* **1978**, *16*, 151–158.

Table I. Parameter Summary for PPP Calculations

atom	I (eV)	A (eV)	$\gamma_x x$ (eV)	bond	β_{c-x} (eV)	n_π	r_{c-x} (Å)
C(sp^2)	11.16	0.03		C(sp^2)–C(sp^2)	−2.318	1	1.397[a]
C(sp)	11.19	0.10		C(sp^2)–C(sp)	−2.086	1	1.46[a]
C(sp^3)	11.42	0.58		C(sp^2)–C(sp^3)	−1.182	1	1.52[a]
H_3≡(C)	9.50	0.0		H_3–C	−2.900	1	1.10[a]
CH_3O	33.00	11.47		CH_3O–C(sp^2)	−1.808	2	1.37[a]
O=(N)	17.70	2.47		O(sp^2)–N(sp^2)	−3.000	1	1.21[b]
NH_2	21.47		12.50	H_2N–C(sp^2)	−1.753	2	1.40[c]
NH_2	26.40		16.76	H_2N–C(sp^2)	−2.300	2	1.40[d]
NMe_2	24.30	7.50		Me_2N–C(sp^2)	−1.753	2	1.40[d]
N=(O)	25.73	8.97		O_2N–C(sp^2)	−2.10	2	1.40[b]
N≡(C)	14.12	1.78		N≡C(sp)	−3.00	1	1.20[c]
CH_3S	22.20		13.05	CH_3S–C(sp^2)	−1.00	2	1.70[a]
N(sp)	14.18	1.66		C(sp)–N(sp)	−3.346	1	1.16[a]
CH_3Se	19.17	9.88		CH_3Se–C(sp^2)	−1.390	2	1.92[e]
N(aza)	16.55		14.77	C(sp^3)=N	−2.318	1	1.40[f]
N(pyrrole)	24.00		16.00	C(sp^2)–N	−2.318	1	1.40[f]

[a] Ilavsky, J.; Kuthan *Coll. Czech. Chem. Commun.* **1981**, *46*, 2687–2695. [b] Kiss, A. I.; Szoke, J. *Acta Chim. Acad. Scient. Hung.* **1976**, *89*, 337–346. [c] Reference 11f. [d] Billingsley, F. P., II; Bloor, J. E. *Theor. Chim. Acta (Berlin)* **1968**, *11*, 325–343. [e] Castellan, A.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6824–6827. [f] Downing, J. W.; Michl, J.; Jørgensen, P.; Thulstrup, E. W. *Theor. Chim. Acta (Berlin)* **1974**, *32*, 203–216.

Table II. Comparison of Calculated and Experimental Excitation Energies and Oscillator Strengths

	experimental			PPP			CNDO[d]		
molecule	E (eV)	f	symmetry	E (eV)	f	composition	E (eV)	f	composition
$C_6H_5NH_2$[a]	4.40	0.028	B_2	4.49	0.050	$0.87\chi_{4\to5} - 0.49\chi_{3\to6}$	4.38	0.049	$0.87\chi_{18\to19} - 0.49\chi_{17\to20}$
	5.39	0.144	A_1	5.45	0.369	$0.95\chi_{4\to6} + 0.28\chi_{3\to5}$	5.35	0.175	$0.94\chi_{18\to19} + 0.35\chi_{17\to19}$
	6.40	0.510	B_2	6.45	0.526	$0.79\chi_{3\to6} + 0.48\chi_{4\to5}$	6.47	0.845	$-0.87\chi_{17\to29} - 0.49\chi_{18\to19}$
	6.88	0.570	A_1	6.67	0.871	$0.93\chi_{3\to5} - 0.24\chi_{4\to6}$	6.51	0.919	$-0.94\chi_{17\to19} + 0.35\chi_{18\to29}$
$C_6H_5NO_2$[b]	4.38	0.01	B_2	4.56	0.029	$0.84\chi_{5\to6} + 0.50\chi_{4\to7}$	4.49	0.042	$0.83\chi_{23\to24} - 0.52\chi_{22\to25}$
	5.11	0.17	A_1	5.08	0.418	$-0.96\chi_{1\to6} - 0.15\chi_{4\to8}$	5.28	0.344	$0.98\chi_{22\to24} + 0.27\chi_{23\to25}$
	6.42	0.38	B_2	6.45	0.329	$0.87\chi_{5\to7} + 0.46\chi_{4\to8}$	6.17	0.351	$0.68\chi_{22\to25} + 0.54\chi_{23\to24} + 0.49\chi_{23\to26}$
	7.56	0.87	B_2	7.48	1.25	$0.80\chi_{3\to8} + 0.38\chi_{5\to8} + 0.37\chi_{4\to7}$	7.07	0.683	$0.85\chi_{23\to26} - 0.51\chi_{22\to25} - 0.12\chi_{23\to24}$
p-NO_2-$C_6H_4NH_2$[c]	3.85 (4.3)	0.64	B_2	4.04	0.57	$-0.97\chi_{6\to7} + 0.13\chi_{3\to9} + 0.10\chi_{5\to8}$	4.37	0.493	$-0.98\chi_{26\to27} - 0.17\chi_{25\to28}$
	5.27 (5.6)		A_1	6.06	0.27	$0.97\chi_{4\to7} + 0.16\chi_{3\to8}$	6.18	0.089	$-0.87\chi_{26\to29} + 0.48\chi_{25\to28} - 0.13\chi_{26\to27}$

[a] Experimental data from ref 18. [b] Experimental data from ref 19. [c] Experimental solution phase data from ref 20b. Numbers in parentheses are vapor-phase data from ref 20a. f is from ref 20c. [d] From ref 7a. CNDO with partial MECI.

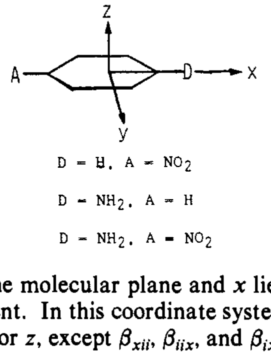
approximation[11] along with the LCAO MO coefficients is employed to calculate the displacement operator matrix elements (eq 6). Here, R^i_λ is the ith (i.e., x, y, or z) Cartesian (geometric) coordinate at atom λ.

$$r^i_{\kappa\lambda} = \delta_{\kappa\lambda} R^i_\lambda \tag{6}$$

The use of a semiempirical model Hamiltonian and of a simple SCF-level ground state clearly limits the accuracy of the present calculations. More extensive studies of small molecules, involving ab initio theory with extensive basis sets and correlations introduced into the ground-state wave functions by using MC-SCF or CI or coupled-cluster procedures and into the excited states in various ways, have been presented.[3,4] For studies of large π-type species, however, use of semiempirical model Hamiltonians, with SCF ground states and MECI excited levels, seems appropriate. The situation is exactly analogous to optical absorption of π species, for which just such a level of theory is quite accurate and appropriate.[10,11]

Comparison with Experiment and CNDO Results. In this section, we consider the linear and NLO properties of three well-studied aromatic chromophores: aniline, nitrobenzene, and p-nitroaniline. In Table II are compared PPP-derived and experimental[18-20] optical excitation energies and oscillator strengths for these molecules. It can be seen that the agreement is excellent. Furthermore, the agreement with published[7a] CNDO results is also excellent. The smaller number of excited states involved in the PPP calculation can be readily appreciated by considering the indices of the configurational wave functions (χ's) in Table II.

For the molecules under consideration, we assume planar (C_{2v}) structures and the coordinate system shown in I, where z is



perpendicular to the molecular plane and x lies in the direction of the dipole moment. In this coordinate system all β_{ijk} are zero when i, j, or $k = y$ or z, except β_{xii}, β_{iix}, and β_{ixi} ($i = y, z$) which are rigorously nonzero by symmetry. However, the Pariser approximation (eq 6)[11] requires that β_{izz}, β_{zzi}, and β_{ziz} are also zero. This is generally an excellent approximation[7d] for molecules with a large dipole moment since the components of β along the dipole

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(14) The advantage of the PPP model can be readily seen in the case of benzene where an MECI π electron calculation would involve nine singlet states, whereas an all valence electron MECI calculation would involve 225 singlet states.

(15) *Tables of Interatomic Distances and Configurations in Molecules and Ions*; Chemical Society: London, 1965; spec. pub. no. 18.

(16) (a) Suzuki, H. *Electronic Absorption Spectra and Geometry of Organic Molecules*; Academic Press: New York, NY, 1967; Chapter 9. (b) Marks, T. J.; Stojakovic, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 1695–1705.

(17) Li, D.; Ratner, M. A.; Marks, T. J., manuscript in preparation.

(18) Aniline data: Kimura, K.; Nagakura, S. *Mol. Phys.* **1965**, *9(2)*, 117–135.

(19) Nitrobenzene data: Nagakura, S.; Kojima, M.; Maruyama, Y. *J. Mol. Spectrosc.* **1964**, *13*, 174–192.

(20) p-Nitroaniline data: (a) Bertinelli, F.; Palmieri, P.; Brilliante, A.; Taliani, C. *Chem. Phys.* **1977**, *25*, 333–341. (b) Corbett, J. F. *Spectrochim. Acta* **1967**, *23A*, 2315–2332. (c) Danilova, V. I.; Morozova, Yu. P. *Opt. Spectrosc.* **1962**, *12*, 5–7.

Table III. Nonzero components of β_{ijk} in Units of 10^{-30} cm^5 esu^{-1} Calculated at 1.17 eV (1.06 μm)

	component	PPP[a]	CNDO[b]
$C_6H_5NH_2$	β_{xxx}	1.71	1.21
	β_{xyy}	−0.32	0.25
	$\beta_{yyx(yxy)}$	−0.27	
	β_{vec}	1.42	1.59
	expt	0.9[c] or 1.1[d]	
$C_6H_5NO_2$	β_{xxx}	−3.37	−2.54
	β_{xyy}	1.86	0.31
	β_{yyx}	1.92	
	β_{vec}	−1.47	−2.30
	expt	−1.97,[f] −2.0,[c] or −2.2[d]	
p-$NO_2C_6H_5NH_2$	β_{xxx}	18.5	8.64
	β_{xyy}	−3.26	−1.33
	β_{yyx}	−2.81	
	β_{vec}	15.5 (15.9)[e]	6.53
	expt	16.9 ± 0.4[e]	

[a] Signs of tensors have been changed where appropriate to adjust from the coordinate system in I to that in ref 7a. [b] Refrence 7a. [c] Levine, B. F.; Bethea, C. G. *J. Chem. Phys.* **1975**, *63*, 2666–2671. [d] Reference 5b. [e] Teng, C. G.; Garito, A. F. *Phys. Rev. Lett.* **1983**, *50*, 350–352. [f] Levine, B. E. *Chem. Phys. Lett.* **1976**, *37*, 516–520.

direction are usually about an order of magnitude or even larger than the other components. Furthermore, because all components of β_{ijk} transform as the Cartesian coordinates, components containing an odd number of y and z indices will vanish in the C_{2v} point group if we assume that the dipole direction is along the x axis.[1a,21] The nonzero tensor components of β_{ijk} are therefore β_{xxx}, β_{xyy}, β_{yxy}, and β_{yyx}. For second harmonic generation, $\beta_{ijk} = \beta_{ikj}$, the independent tensors are therefore β_{xxx}, β_{xyy}, and β_{yyx} (or β_{yxy}). In low-frequency regions, Kleinman symmetry[22] can be used to simplify further the relationship of the tensor components: β_{ijk} does not depend on the interchange of indices. Therefore, it is expected that $\beta_{xyy} = \beta_{yxy} = \beta_{yyx}$, and the only independent tensor components will be β_{xxx} and β_{xyy}.

In Table III, the present full MECI PPP-derived tensors for SHG are compared to published[7a] all valence electron CNDO results (partial MECI) and experimental β_{vec} values. The latter are the β quantities (quantized along the molecular dipole moment) determined by solution phase dc electric field induced SHG experiments[2] and can be expressed as in eq 7 and 8. It can be

$$\beta_i = \beta_{iii} + \tfrac{1}{3}\sum_{i \neq j} (\beta_{jji} + 2\beta_{iij}) \tag{7}$$

$$\beta_{vec}(-2\omega;\omega,\omega) = \beta_i \tag{8}$$

i = direction along molecular dipole axis

seen that there is excellent agreement between the PPP-derived and CNDO-derived tensor components. Furthermore, the accuracy with which the PPP method predicts β_{vec}[23] is comparable to or better than that of the CNDO approach (see also ref 8). In all cases, β_{xxx} is found to be the major component of β_{vec}, as expected for such planar, conjugated molecules with large dipole moments. That β_{vec} and β_{xxx} are largest for the chromophore having both electron-donating and -accepting substituents (in a para orientation) is in accord with numerous empirical observations[2] and the proposed importance of charge-transfer states in determining β.[2e,5b,7a]

For each nonzero β_{ijk} component, the frequency dependence is easily obtained from the PPP calculation, and results are shown in Figures 1, 2, and 3 for aniline, nitrobenzene, and p-nitroaniline, respectively. It is obvious from these results that at low frequencies (i.e., $\hbar\omega < 1.0$ eV), the curves show little dispersion, and Kleinman symmetry is satisfied very well for components corresponding to the same constant of the sum of i, j, k (i.e., $\beta_{yyx} = \beta_{xyy}$). Near resonance, the Kleinman symmetry begins to break down for all components of β_{ijk} ($\beta_{yyx} \neq \beta_{xyy}$), showing that Kleinman symmetry may not rigorously hold at the Nd:YAG laser frequency of 1.17 eV (1.06 μm). Indeed, there is presently no applicable theory for describing the resonance behavior when 2ω approaches the first excitation energy.[2] Figure 4 shows PPP-derived β_{vec} values for aniline, nitrobenzene, and p-nitroaniline as a function of frequency. The agreement with the CNDO-derived[7a] frequency dependences (not shown on these plots) is excellent. In Figure 5, the experimental and PPP-derived frequency dependences of β_{vec} are compared for p-nitroaniline. It can be seen that the PPP-derived β_{vec} values compare favorably with experiment over a wide frequency range prior to the first resonance.

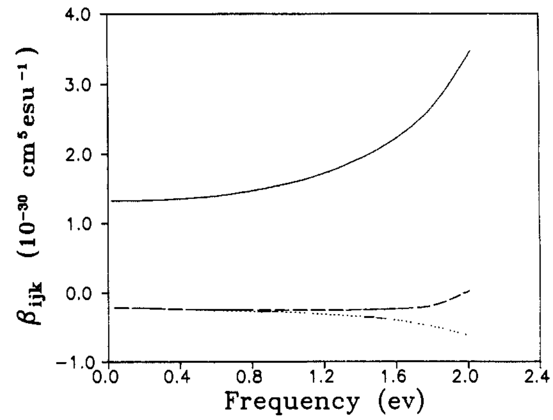

Figure 1. PPP-derived frequency dependence of β_{xxx} (solid line), β_{xyy} (dotted line), and β_{yyx} (dashed line) for aniline.

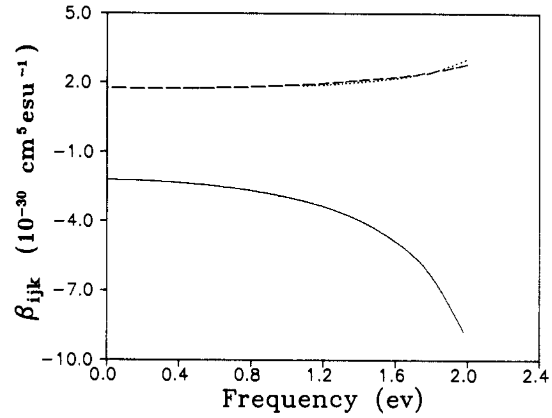

Figure 2. PPP-derived frequency dependence of β_{xxx} (solid line), β_{xyy} (dotted line), and β_{yyx} (dashed line) for nitrobenzene.

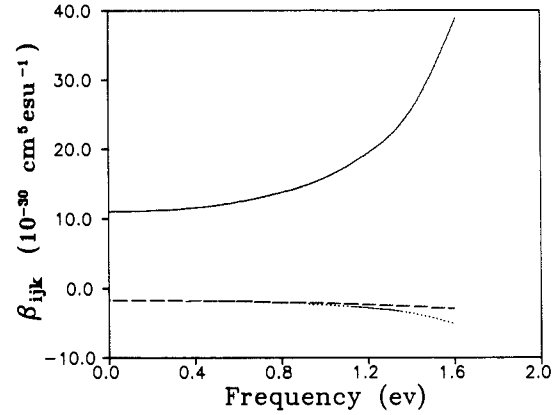

Figure 3. Frequency dependence of β_{xxx} (solid line), β_{xyy} (dotted line), and β_{yyx} (dashed line) for para-nitroaniline.

Connections between NLO Parameters and Classical Substituent Effects. The importance of electron-donating and -accepting conjugated substituents in the construction of high-β chromophores

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(21) (a) Schubert, M.; Wilhelmi, B. *Nonlinear Optics and Quantum Electronics*; Wiley: New York, NY, 1986. (b) Reference 1a.

(22) (a) Kleinman, D. A. *Phys. Rev.* **1952**, *126*, 1977–1979. (b) Wagniere, G. *Appl. Phys. B* **1986**, *41*, 169–172.

(23) Variations in experimental β_{vec} values for the same molecule appear to reflect spatial and temporal fluctuations in measuring laser output. Such artifacts should be most pronounced in early data.

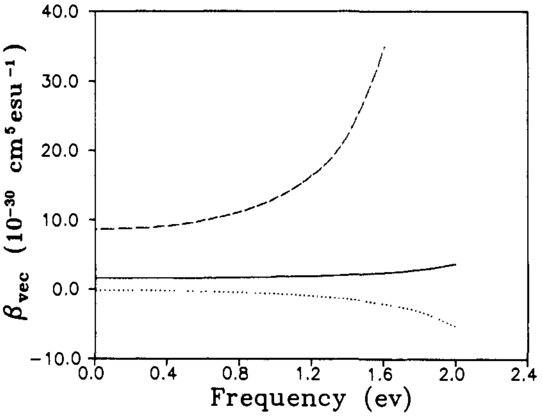

Figure 4. Frequency dependence of β_{vec} for aniline (solid line), nitrobenzene (dotted line), and *p*-nitroaniline (dashed line).

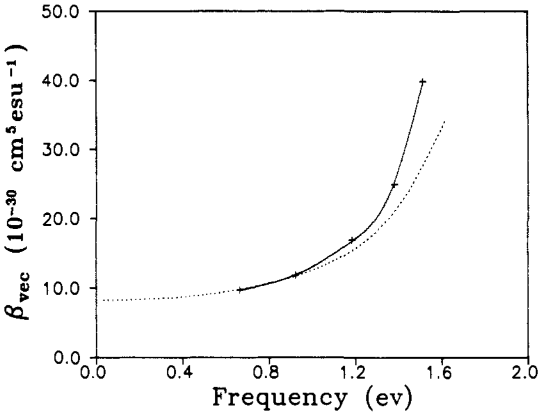

Figure 5. Frequency dependence of β_{vec} for *p*-nitroaniline: experimental β_{vec}^{exp} (solid line) and theoretical β_{vec}^{PPP} (dotted line).

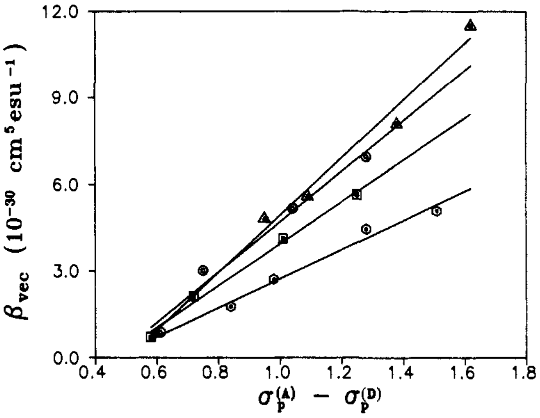

Figure 6. Plot of PPP-derived β_{vec} as a function of $\sigma_p^A - \sigma_p^D$ for a given acceptor at $\hbar\omega$ = 0.0 eV: (▲) NO_2, (○) CHO, (□) COOMe, (○) CN.

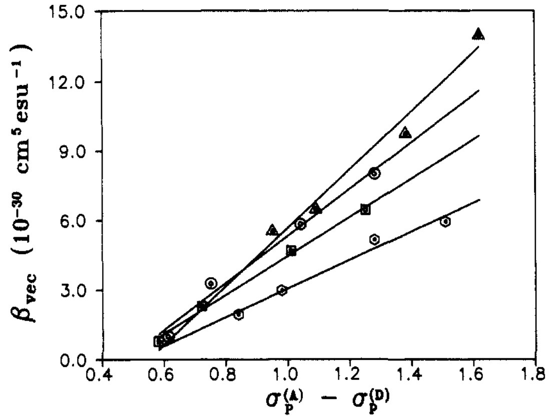

Figure 7. Plot of PPP-derived β_{vec} as a function of $\sigma_p^A - \sigma_p^D$ for a given acceptor at $\hbar\omega$ = 0.656 eV: (▲) NO_2, (○) CHO, (□) COOMe, (○) CN.

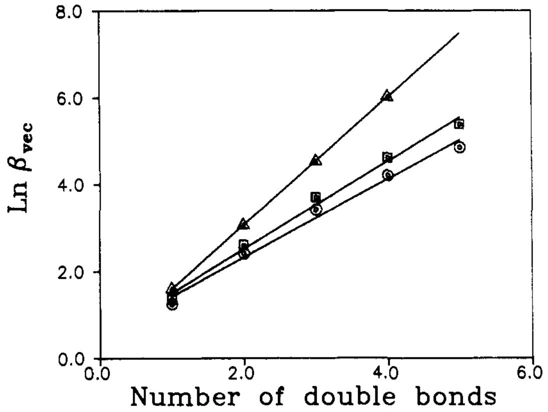

Figure 8. Graph of PPP-derived ln $\beta_{vec}(\omega)$ versus the number of intervening double bonds at various frequencies for the transoid conjugated polyenes $O_2N(HC{=}CH)NMe_2$ (IV): (○) $\hbar\omega$ = 0.0 eV, (□) $\hbar\omega$ = 0.656 eV, (▲) $\hbar\omega$ = 1.17 eV.

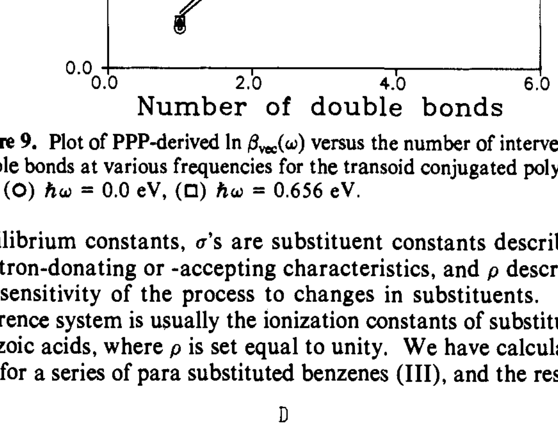

Figure 9. Plot of PPP-derived ln $\beta_{vec}(\omega)$ versus the number of intervening double bonds at various frequencies for the transoid conjugated polyenes VI: (○) $\hbar\omega$ = 0.0 eV, (□) $\hbar\omega$ = 0.656 eV.

is well-established.[2] Given the accuracy with which first-order molecular nonlinearities can be calculated with the PPP formalism, it would be of interest to determine whether useful correlations exist between NLO phenomena and more conventional descriptors (and data bases) of π-electronic structure. The Hammett free-energy relationship provides what is probably the most broadly applicable description of how substituents alter electronic structure in simple aromatic systems (eq 9).[24] Here the *K* values are

$$\log \frac{K}{K_0} = \sigma\rho \qquad (9)$$

equilibrium constants, σ's are substituent constants describing electron-donating or -accepting characteristics, and ρ describes the sensitivity of the process to changes in substituents. The reference system is usually the ionization constants of substituted benzoic acids, where ρ is set equal to unity. We have calculated β_{vec} for a series of para substituted benzenes (III), and the results

III

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[24] (a) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 2nd ed.; Plenum Press: New York, NY, 1984; Part A, pp 179–190. (b) Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119–251. (c) Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 1–84. (d) Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 85–124.

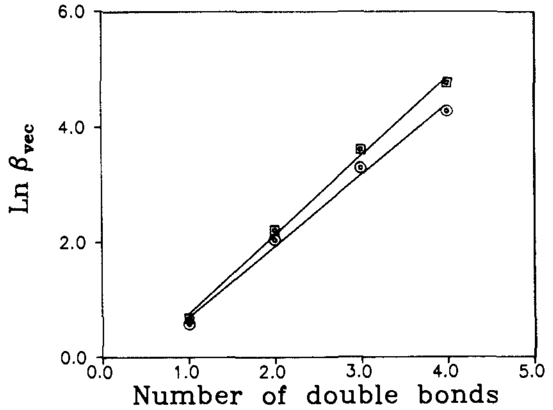


Figure 10. Graph of PPP-derived ln $\beta_{vec}(\omega)$ versus the number of intervening double bonds at various frequencies for the transoid conjugated polyenes VII: (○) $\hbar\omega = 0.0$ eV, (□) $\hbar\omega = 0.656$ eV.

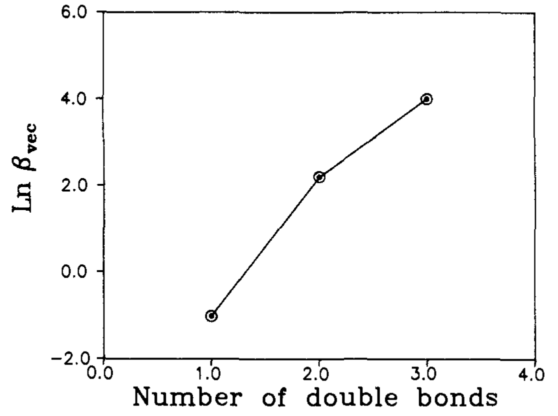
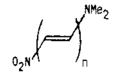
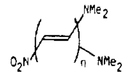
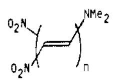
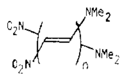


Figure 11. Graph of PPP-derived ln $\beta_{vec}(\omega)$ versus the number of intervening double bonds at the Nd:YAG frequency, $\hbar\omega = 1.17$ eV, for the transoid conjugated polyenes VIII.

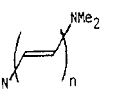
Table IV. Calculated Optical Spectroscopic, Dipole Moment, and β_{vec} (10^{-30} cm^5 esu^{-1}) Parameters for Transoid Linear Polyenes as a Function of the Intervening Double Bonds

n	1	2	3	4	5
 IV					
β_{vec} (0.0 eV)	3.446	11.12	30.28	66.95	127.5
β_{vec} (0.656 eV)	3.823	13.33	40.17	110.4	218.4
β_{vec} (1.17 eV)	4.94	21.63	92.75	406.9	291.7
λ_{max} (eV)	4.68	3.77	3.17	2.75	2.45
f	0.62	1.17	1.65	2.07	2.46
μ (D)	6.09	8.32	10.2	11.8	13.2
 VI					
β_{vec} (0.0 eV)	1.99	7.67	22.42	60.68	131.2
β_{vec} (0.656 eV)	2.23	9.24	30.89	97.23	25.03
λ_{max} (eV)	4.51	3.52	2.92	2.53	2.25
λ_{max} (eV)	4.51	3.52	2.92	2.53	2.25
f	0.38	1.01	1.51	1.95	2.35
μ (D)	6.96	10.3	13.1	15.5	17.6
 VII					
β_{vec} (0.0 eV)	1.79	7.69	26.65	71.84	
β_{vec} (0.656 eV)	1.95	9.09	36.71	116.6	
λ_{max} (eV)	4.24	3.46	2.91	2.51	
f	0.43	1.00	1.53	1.97	
μ (D)	6.51	9.77	12.5	14.8	
 VIII					
β_{vec} (1.17 eV)	0.36	11.05	54.33		
λ_{max} (eV)	4.39	3.19	2.73		
f	0.36	0.66	1.40		
μ (D)	7.98	12.6	16.3		

are correlated at two different frequencies with σ values for para substituents (σ_p) in Figures 6 and 7. It can be seen that for the electron-acceptor substituent A held constant there is a remarkably linear relationship between β_{vec} and σ_p for the electron-donor substituent.

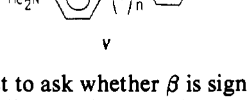
Hypothetical Chromophores. Influence of Molecular Architecture on NLO Characteristics. The PPP method offers an attractive theoretical procedure for investigating diverse molecular characteristics which may or may not lead to enhanced NLO response. Beyond the simple substituent effects discussed in the previous section, it is of interest to examine here how the expanse of the intervening π system, the introduction of multiple donor and/or acceptor substituents, and the introduction of unusual (not commonly employed) substituents affects β parameters.

We have addressed the first two issues via a study of planar, linear trans polyenes. The effect on β_{vec} of the number of trans double bonds in planar polyene IV is shown in Figure 8 for several excitation frequencies. Data are compiled in Table IV. In each case, it can be seen that there is a linear relationship between ln(β_{vec}) and the number of double bonds, i.e., eq 10 obtains, where

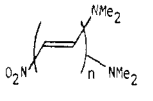

IV

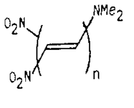
$$\beta_{vec} = Ke^{\alpha n} \qquad n = 1\text{–}5 \tag{10}$$

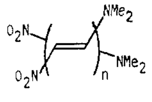
K and α are constants.[25] In the only available experimental data, Dulcic et al.[26] reported that for chromophores V (n = 1–3), $\beta \sim n^2$ based upon three data points.


V

It is next of interest to ask whether β is significantly enhanced by introducing an additional donor and/or acceptor substituent at the terminus of the polyene chain (VI–VIII). Results are summarized in Figures 9–11 and in Table IV, assuming that the substituents remain entirely coplanar with the π system.[27] Two conclusions can be immediately drawn. First, eq 10 again holds. Secondly, the presence of additional donor or acceptor groups effects only a minor enhancement in β_{vec}. This latter result is not intuitively obvious; however, some insight can be gained by considering a model[5] in which eq 4 is reduced to only two states, the


VI


VII


VIII

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[25] A similar CNDO study on such a polyene was recently reported.[7d] Although the results appear qualitatively similar to those from PPP, the data were reported in terms of a "hyperpolarizability density," rendering direct comparison difficult.

[26] (a) Dulcic, A.; Sauteret, C. *J. Chem. Phys.* **1978**, *69*, 3453–3457. (b) Dulcic, A.; Flytzanis, C.; Tang, C. L.; Pepin, D.; Fitzion, M.; Hoppilliard, Y. *J. Chem. Phys.* **1981**, *74*, 1559–1563.

[27] The depression in the n = 1 point of Figure 10 arises from the high symmetry of tetrasubstituted ethylene. The C_2 axis along the dipole moment direction causes several β_{ijk} components (especially β_{yyy}) which are major contributors to β_{vec} to vanish.

ground (g) and the nth excited state (n) eq 11. Here m is the

$$\beta_{iii} = \frac{-3e^2\hbar^2}{2m}\frac{\omega_{gn} f \Delta\mu_{gn}}{[\omega_{gn}^2 - (2\hbar\omega)^2][\omega_{gn}^2 - (\hbar\omega)^2]} \qquad (11)$$

electron mass, ω_{gn} and f the frequency and oscillator strength, respectively, of the nth electronic transition, and $\Delta\mu_{gn}$, the change in dipole moment between the ground and nth excited state, which should scale approximately as μ_g, the dipole moment in the ground state.[28a,b] Consideration of eq 10 with reference to the data in Table IV reveals that the trend in eq 10 reflects increasing f and μ_g as well as falling ω_{gn} (cf., λ_{max}) with increasing conjugation length. Interestingly, however, additional donor and acceptor substituents have, for fixed chain length, only a minor effect on f, μ_g, and λ_{max}. Clearly there is a saturation effect in substitution. This can be understood, qualitatively, by using a simple one-electron, two-site model. Suppose that a given inductive substituent or substituents modify the effective site energy at site b to differ by an energy Δ from that at site a. Then the secular equation becomes

$$\begin{pmatrix} -E & \beta \\ \beta & \Delta - E \end{pmatrix}\begin{pmatrix} C_a \\ C_b \end{pmatrix} = 0 \qquad (12)$$

This can be easily solved in two limits. If the inductive effects are relatively small, $\beta^2 \gg \Delta^2$, and then, to lowest order, we have

$$\frac{\partial(C_b/C_a)}{\partial(\Delta/\beta)} \cong {}^1\!/_2 \qquad (13)$$

which means that the relative contribution of the polarized state scales linearly with the extent Δ of the inductive effect. Under these conditions, we expect that added inductive groups will be just as effective as the first inductive group. On the other hand, if the first group or groups exert a strong inductive effect, the limit $\beta^2 < \Delta^2$ should hold, and in this case the solution to eq 12 yields

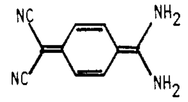
$$\frac{\partial(C_b/C_a)}{\partial(\Delta/\beta)} \cong \beta^2/\Delta^2 \qquad (14)$$

Since $\beta^2 < \Delta^2$, this rate is clearly smaller than linear: for large Δ^2/β^2, it is small indeed. Thus the effect on the wave function due to adding further inductive groups is much diminished once the wave function has already been effectively polarized. Qualitatively, once the wave function has been fairly strongly polarized, it more effectively resists further polarization. Substituent–substituent interaction and saturation effects have been identified in both theoretical and photoelectron spectroscopic studies of substituted benzenes.[29]

Comparable behavior, involving decreasing effectiveness of multiple substitution, is seen in other situations. For example, fluorobenzene will not react with methoxide ion under ordinary conditions, but p-nitrofluorobenzene will, exchanging the fluorine to produce p-nitroanisole. Further substitution, to produce 2,4-dinitrofluorobenzene, produces only a relatively small further rate enhancement.

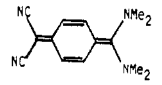
The demonstrated accuracy of the PPP formalism in predicting molecular β parameters also suggests the value in examining trends in hypothetical chromophores prior to undertaking laborious syntheses. An example is the series of substituted quinodimethanes shown below (IX–XV) along with the PPP-derived β_{vec} values at $\hbar\omega$ = 0.0 eV (in units of 10^{-30} cm^5 esu^{-1}). The superiority of NO$_2$ over CN as a β-enhancing acceptor is readily evident. The efficacy of the thio ether functionality as a donor is also evident, and the calculated β_{vec} for XIV is one of the largest known for a small molecule.[2] Substitution of selenium for sulfur effects little change in β_{vec}. The trends in the IX/XI or X/XII pairs versus XIII/XIV indicate that simple additive substituent effects are not operative. Full data for compounds IX–XV are compiled in Table V. In the same vein, the results for substituted stilbenes XVI–XX illustrate further effects of multiple donor–acceptor combinations. While multiple substituent contributions to β may be slightly larger than in the α,ω-substituted polyenes (vide supra), strict additivity relationships do not obtain. Data for these molecules are also compiled in Table V.

IX



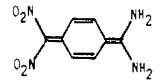
β_{vec} = 60.6

X



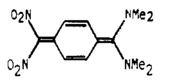
β_{vec} = 81.3

XI



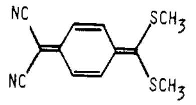
β_{vec} = 253

XII



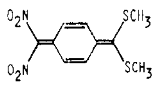
β_{vec} = 181

XIII



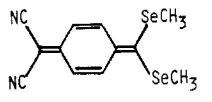
β_{vec} = 6.7

XIV



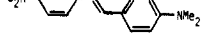
β_{vec} = 308

XV



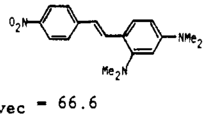
β_{vec} = 295

XVI



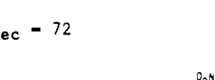
β_{vec} = 57.2

XVII



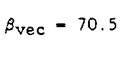
β_{vec} = 66.6

XVIII



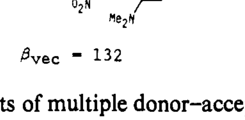
β_{vec} = 72

XIX



β_{vec} = 70.5

XX



β_{vec} = 132

Molecule XXI[9,17] illustrates a fairly large chromophore structure

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[28] (a) A crude estimate of the dipole difference $\Delta\mu_{gn}$ can be made by using a simple two-site picture similar to that originally used by Mulliken in discussing donor–acceptor bonding and by Hush[28b] in considering the transition matrix element in mixed-valence systems. For systems with a large β a two-site approximation (donor-type and acceptor-type states) yields for the HOMO (g orbital)

$$\psi_g = a\phi_D + b\phi_A \qquad |b| \gg |a| \qquad a^2 + b^2 = 1$$

and for the optically accessed orbital (n) most strongly coupled to ψ_g

$$\psi_n = b\phi_D - a\phi_A$$

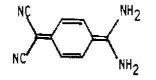
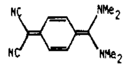
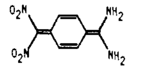
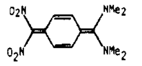
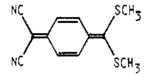
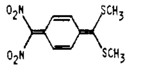
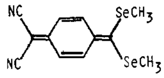
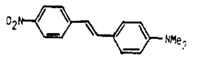
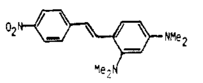
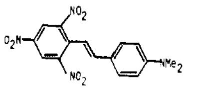
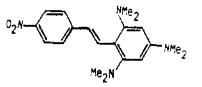
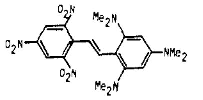
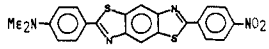
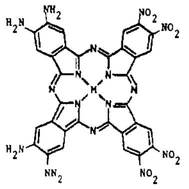
Then, the dipole moment difference is just

$$\Delta\mu_{ng} = \mu_n - \mu_g \propto (b^2 - a^2) - (a^2 - b^2) = 2(b^2 - a^2)$$

Therefore the *difference* in dipole moment is, in this rough estimate, proportional to (simply twice) the ground-state dipole moment. (b) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391–453.

[29] (a) Pross, A.; Radom, L. *Prog. Phys. Org. Chem.* **1981**, *13*, 1–61. (b) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. *Molecular Photoelectron Spectroscopy*; Wiley: New York, 1970; Chapter 11.

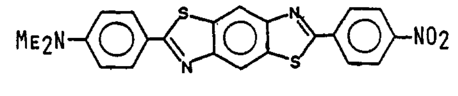
Table V. Calculated Optical Spectroscopic, Dipole Moment, and β_{vec} (10^{-30} cm^5 esu^{-1}) Parameters for Quinodimethane, Stilbene, and Diphenylbenzobisthiazole Chromophores[a]

molecule		$\hbar\omega$ (eV)	β_{vec}	μ (D)	λ_{max} (eV)
IX		0.0	60.6	13.9	2.46
X		0.0	81.3	17.5	2.50
XI		0.0	252.9	16.8	1.21
XII		0.0	181.4	19.9	1.39
XIII		0.0	6.61	8.12	2.60
XIV		0.0	307.9	11.8	0.99
XV		0.0	294.9	12.9	1.02
XVI		0.0 0.656	57.2 73.3	8.93	3.19
XVII		0.0 0.656	66.6 92.1	9.44	2.81
XVIII		0.0 0.656	71.9 104	7.45	2.49
XIX		0.0 0.656	70.5 97.8	8.87	2.76
XX		0.0 0.656	90.4 132	8.37	2.23
XXI		0.0 1.17	142.1 431	8.91	2.96
XXII		0.0	165.1	19.62	2.22

[a] The minus sign of β_{vec} for some chromophores is omitted for simplicity, i.e., $\beta_{vec} = |\beta_I|$.

which is a functionalized fragment of the ultrahigh modulus rigid-rod polymer poly(p-phenylenebenzobisthiazole).[30] The

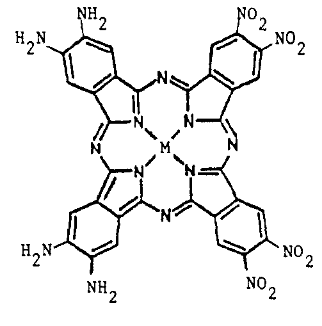
XXI



$\beta_{vec} = 142$

chromophore has recently been synthesized in our laboratory,[9] and the experimental λ_{max} is in good agreement with that predicted in the PPP calculations. Finally, phthalocyanine XXII exemplifies

XXII



M = H_2

$\beta_{vec} = 165$

the type of very elaborate chromophore that can be studied with the present method. Although the molecule is unknown, the

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(30) (a) Feldman, L.; Farris, R. J.; Thomas, E. L. *J. Mater. Sci.* **1985**, *20*, 2719–2726. (b) Allen, S. R.; Farris, R. J.; Thomas, E. L. *J. Mater. Sci.* **1985**, *20*, 2727–2734. (c) Helminiak, T. E. *Org. Coat. Plast. Chem.* **1979**, *4*, 475–479. (d) Choe, E. W.; Kim, S. N. *Macromolecules* **1981**, *14*, 920–924. (e) Wolf, J. F.; Arnold, F. E. *Macromolecules* **1981**, *14*, 909–915. (f) Wolf, J. F.; Lov, G.; Arnold, F. E. *Macromolecules* **1981**, *14*, 915–920. (g) Allen, S. R.; Filippov, A. G.; Farris, R. J.; Thomas, E. L.; Wong, C.-P.; Berry, G. C.; Chenevey, E. C. *Macromolecules* **1981**, *14*, 1135–1138, and references therein.

calculated λ_{max} is in good agreement with existing phthalocyanine optical data.[16b,31]

Conclusions

The results of this investigation demonstrate the wealth of information about quadratic molecular optical nonlinearities which is readily accessible via perturbation theory and the PPP model Hamiltonian. The information includes β tensor components and the frequency dependence thereof, chromophore substituent effects on β, and molecular architecture effects on β. Of course, considerations such as chromophore-laser compatibility (transparency criteria) and the actual number of chromophores that can be packed in a given volume of material ("hyperpolarizability density"[7d]) are also crucial in the design of a frequency-doubling material. The former linear optical information (λ, f) is derived directly from the PPP calculation (or any easily implemented semiempirical calculation), while the latter requires only estimated molecular volumes as additional input. Another advantage of quantum chemical calculation as a prelude to chromophore design and synthesis is realized in the construction of polymeric materials for second harmonic generation. Such materials have been prepared by dispersing an NLO chromophore in a glassy polymer matrix[32] or, more recently, by covalently linking an NLO chromophore to the backbone of a glassy polymer.[9,33] In both cases the requisite noncentrosymmetry of the chromophore arrays is induced by poling above the glass transition temperature in an electric field and then cooling in the electric field. The effectiveness of the poling, in the limit of isolated chromophore molecules, will be directly proportional to the molecular dipole moment.[28a] Hence, being able to evaluate μ_g in advance for a hypothetical chromophore is of obvious benefit in predicting the outcome of the poling experiments.

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(31) Hale, P. D.; Pietro, W. J.; Ratner, M. A.; Ellis, D. E.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 5943–5947.

(32) (a) Singer, K. D.; Sohn, J. E.; Lalama, S. J. *Appl. Phys. Lett.* **1986**, *49*, 248–250. (b) Small, K. D.; Singer, K. D.; Sohn, J. E.; Kuzyk, M. G.; Lalama, S. J. in ref 1d, pp 150–169. (c) Meredith, G. A.; Van Dusen, J. G.; Williams, D. J. *Macromolecules* **1982**, *15*, 1385–1389. (d) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Macromolecules*, in press.

(33) (a) Ye, C.; Marks, T. J.; Yang, J.; Wong, G. K. *Macromolecules* **1987**, *20*, 2322–2324. (b) Ye, C.; Marks, T. J.; Minami, N.; Yang, J.; Wong, G. K. *Mater. Res. Soc. Symp. Series*, in press.

Methyl Radical Formation over Li-Doped MgO. Molecular Orbital Theory

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Abstract: Methane adsorption is known to be activated by the presence of chemically formed O$^-$ at the surface of MgO. In the present theoretical study the activation is shown to be the result of the electron accepting ability of O$^-$. The adsorption of $^\bullet CH_3$ formed by H$^\bullet$ abstraction is weak and is sensitive to the presence of Mg^{2+} surface, edge, and corner dangling orbitals. The methyl radicals easily desorb, which should allow them to dimerize in the gas phase to form ethane, the main observed reaction product. If there are few O$^-$ in the surface planes, further oxidation via a methoxy intermediate is unlikely, which would be the explanation for the absence of CH$_3$OH product. We find that adsorbed methyl species can be reoriented at steps because of an attractive σ donation interaction involving a CH σ bond and Mg^{2+} band-gap surface-state orbitals.

It is well established that O$^-$ centers on oxide surfaces possess the ability to cleave CH bonds.[1-10] Active O$^-$ centers have been prepared by a variety of methods, including chemical, γ-irradiation defect formation, cation doping, and charge-transfer excitation from O^{2-} to the empty cation band. The theoretical explanation for this activity lies in the ease with which an electron from a CH bond can reduce the O$^-$ during hydrogen atom abstraction.[11-14] The interaction between O^{2-} and a CH bond is a closed-shell repulsion with a relatively high H$^\bullet$ abstraction energy barrier.

Recently Lunsford and co-workers have found that the oxidative dimerization of CH$_4$ to yield C$_2$H$_4$ and C$_2$H$_6$ can be achieved in high yield and with good selectivity over Li-promoted MgO catalysts.[8,9] Methyl radicals were produced when CH$_4$ was passed over MgO at ~500 °C in the presence of O$_2$.[9,10] Two pathways are believed to be responsible for the radical formation.[9] Over pure MgO, intrinsic cation vacancies react with O$_2$ to give O$^-$ centers which can abstract H$^\bullet$ from CH$_4$ to produce $^\bullet$CH$_3$(g). For the Li-doped MgO, substitutional Li$^+$ react with O$_2$ to form [Li$^+$O$^-$] centers which can also bring about H$^\bullet$ abstraction from CH$_4$.

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(1) Shvets, V. A.; Vorotyntsev, V. M.; Kazansky, V. B. *Kinet. Katal.* **1969**, *10*, 356.

(2) Kazansky, V. B. *Kinet. Katal.* **1977**, *18*, 43.

(3) Lipatkina, N. I.; Shvets, V. A.; Kazansky, V. B. *Kinet. Katal.* **1978**, *19*, 979.

(4) Kaliaguine, S. L.; Shelimov, B. N.; Kazansky, V. B. *J. Catal.* **1978**, *55*, 384.

(5) Liu, R.-S.; Iwamoto, M.; Lunsford, J. H. *J. Chem. Soc., Chem. Commun.* **1982**, 78.

(6) Liu, H.-F.; Liu, R.-S.; Liew, K. Y.; Johnson, R. E.; Lunsford, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 4117.

(7) Ito, T.; Wang, J.-X.; Lin, C.-H.; Lunsford, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 5062.

(8) Ito, T.; Lunsford, J. H. *Nature (London)* **1985**, *314*, 721.

(9) Driscoll, D. J.; Martir, W.; Wang, J.-X.; Lunsford, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 58.

(10) Driscoll, D. J.; Lunsford, J. H. *J. Phys. Chem.* **1985**, *89*, 4415.

(11) Anderson, A. B.; Ray, N. K. *J. Am. Chem. Soc.* **1985**, *107*, 253.

(12) Mehandru, S. P.; Anderson, A. B.; Brazdil, J. F. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 463.

(13) Mehandru, S. P.; Anderson, A. B.; Brazdil, J. F.; Grasselli, R. K. *J. Phys. Chem.* **1987**, *91*, 2930.

0002-7863/88/1510-1715$01.50/0