Table II. Parameters Used in the Extended Hückel Calculations

orbital		H_{ii} (eV)	ζ_1	ζ_2	C_1[a]	C_2[a]
Mo	4d	−12.30	4.54	1.90	0.5899	0.5899
	5s	−9.66	1.956			
	5p	−6.36	1.90			
W	5d	−10.40	4.98	2.07	0.6683	0.5422
	6s	−8.62	2.34			
	6p	−5.17	2.31			
P	3d	−7	1.4			
	3s	−18.6	1.60			
	3p	−14.0	1.60			
N	2s	−26.0	1.95			
	2p	−13.4	1.95			
Cl	3s	−30.0	2.033			
	3p	−15.0	2.033			
F	2s	−40.0	2.425			
	2p	−18.1	2.425			

[a] Coefficients used in the double-ζ expansion of the d orbitals.

In the case at hand of cyclic P containing compounds some interactions (**15b**) can be played out equally well by PX_2 σ^* as by 3d on P. But others (**15a**, **18**) have no PX_2 σ^* symmetry equivalent. So P 3d orbitals could play a role, especially if the in-plane π system were important, as we concluded it is in $(L_nMoN)_4$. We repeated our calculations on $(F_2PN)_4$ with 3d orbitals on P, placed at various energies. In each case a localized, bond-alternating structure is computed. But the degree of alternation is much smaller than in the transition-metal nitride case. We do not want to say that this is an argument against the involvement of 3d orbitals. More likely it is a failure of the extended Hückel method, or insufficient geometry optimization. The many known molecules may pucker to varying degrees, but they retain (with some exceptions) equal P–N bond lengths. We would nevertheless keep an eye out for small bond alternation.

To summarize: (1) There is an obvious analogy between d–p π orbitals of linear and cyclic early transition-metal nitrides and the p π orbitals of polyenes. This leads to predicted stability for some as yet unsynthesized MoN oligomers such as the cyclic trimer. (2) There should be a continuum of delocalization and tendency to localize or alternate bonds in cyclic heteromorphic systems. The 4*n* systems will localize by a second-order Jahn–Teller mechanism when the energy splitting between the (nondegenerate) nonbonding orbital combinations is relatively small. It is so in the $(L_nMoN)_4$ system but not in $(X_2PN)_4$.

Acknowledgment. Funding for this work was provided by the Cornell University Materials Science Center through the National Science Foundation (Grant No. DMR821722A02). We thank Christine Gray for the typing and Jane Jorgensen and Elisabeth Fields for the drawings.

Appendix

The Extended Hückel method was used for all calculations.[33] Parameters[34] are listed in Table II. Mo–N and Mo–Cl bond lengths were taken from the $[MoNCl_3 \cdot O(C_4H_9)_2]_4$ X-ray structure.[35] Experimental bond lengths were also used for $[W_3N_2Cl_{14}]^{2-}$[1c] and $(F_2PN)_4$.[36]

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The Contribution of π Electrons to Second Harmonic Generation in Organic Molecules

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Abstract: The frequency-dependent hyperpolarizability for sum frequency generation is calculated within a π electron approximation for a series of unsaturated organic compounds and compared to experimental data measured in polar and nonpolar liquid media. A procedure is also suggested to investigate the influence of electrostatic intermolecular interaction on the hyperpolarizability of small clusters of molecules in relative positions corresponding to the crystal structure.

I. Introduction

For about a decade an active and systematic search has been conducted for materials exhibiting large optical nonlinear responses. Much attention has been given to organic compounds, in view of their application to second harmonic generation (SHG) from the near infrared to the visible. It has been observed that particular, noncentrosymmetric polar unsaturated molecules may exhibit unusually large hyperpolarizabilities.[1-26] Molecules in which intramolecular charge-transfer transitions occur and in which the dipole moments of the excited states are large appear to be particularly suited for this purpose. Efficient SHG furthermore requires the doubled frequency still to lie in the region where the molecule is transparent; it should however not be too far removed from the lowest frequency transitions. There is every

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indication that the lower excited states, which in the molecules of interest are mainly of π–π^* symmetry, make an important, if not the major, contribution to SHG in the wavelength range of interest.[1,7,9,15,16,19-26]

In the first part of this paper we calculate the contribution of the π electrons to the SHG tensor in a series of selected molecules by the PPP method. Our aim is to find an inexpensive computational procedure which gives correct orders of magnitude for the frequency-dependent hyperpolarizability and which reproduces correctly relative trends, such as substituent effects, within classes of similar compounds. This then should enable one to scan a variety of relatively large molecules and to provide a guidance in planning the synthesis of new chromophores with particular nonlinear optical properties. A number of computational investigations of SHG in organic compounds have been published by using the CNDO/S method[14-16,24,26] and the INDO method.[20,21,35] The explicit inclusion of the σ electrons makes these latter methods potentially more accurate than PPP, but the description of the π–π^* states is not necessarily always better, and the computational labor is significantly larger. The PPP method has already been used to assess the second-[1] and third-order[1,27,28] polarizability in various unsaturated hydrocarbons in a static electric field. To exhibit sum frequency generation in the liquid state, where there is random orientation, the molecules must be optically active. If both frequencies are the same, i.e., in the case of SHG, the effect altogether vanishes.[29] DC electric field induced second harmonic generation (EFISH) due to anisotropic averaging may be observed in the liquid state for molecules with a permanent dipole moment. This method has been widely applied to obtain an averaged value for the molecular hyperpolarizability.[6,9,10,23,24,30-32] The experimental values so obtained will serve as a comparison for our calculations on single molecules.

To be SHG active, crystals must belong to noncentrosymmetric space groups,[29] and evidently for all practical purposes the individual molecules in the crystal must also be noncentrosymmetric. However, it often occurs that noncentrosymmetric molecules crystallize in centrosymmetric space groups, making them useless, for our aims. In the preparation of new organic materials for SHG, the hyperpolarizability of the individual molecules is therefore not the sole criterion, but the relative spatial arrangement of the molecules within the crystal lattice is also of decisive importance. In an attempt to deduce the bulk hyperpolarizability, a first approximation consists in an additive superposition of the contributions of the individual molecules.[33,34] This approach neglects the mutual influence of the molecules on each other, which undoubtedly may be important. A recent application of INDO and ab initio SCF methods to urea in the isolated and hydrogen-bonded crystalline state requires extensive computations.[35] In the second part of this paper we try to assess the importance of intermolecular interaction in the frame of the PPP model. By examining small clusters of molecules in the relative spatial positions dictated by the crystal structure and by including in the calculation electron repulsion terms also between atomic centers on different molecules, we study the changes induced in the tensor elements of the hyperpolarizability by electrostatic effects.

II. Method of Calculation

The calculation of the sum frequency generation tensor

$$\chi^{(2)}_{ijk}\,(\omega_1 + \omega_2;-\omega_1,-\omega_2) \equiv \beta_{ijk}$$

is based on the addition of six terms, as given by Ward[36] (Appendix 1). These expressions entail double summations over all eigenstates of the unperturbed molecular system considered. For practical reasons the infinite sums have to be truncated, and it has already been shown that a limited number of terms may lead to reasonable results.[14,15] If the frequencies of incident radiation ω_1 and ω_2 are set equal to zero, our adopted expressions do not automatically go into the correctly normalized formula for the static second-order hyperpolarizability. Strictly speaking, some normalization terms should be added,[37] which for simplicity are here neglected. Furthermore, the formula deduced in ref 36 are adequate as long as the radiation frequencies ω_1 and ω_2 are far removed from molecular resonances. Otherwise, if damping effects are to be included, one has to deal with eight terms[38] instead of the six terms mentioned above. Our routine computes the 27 tensor elements of β_{ijk} for eight pairs of frequencies ω_1, ω_2, which may be arbitrarily chosen but should not coincide with molecular resonances. This, nevertheless, allows one to investigate the dispersion of the hyperpolarizability tensor.

The basic quantities needed for the calculation of β_{ijk} are obtained through SCF-MO, single-CI calculations in the frame of the PPP approximation.[39,40] The molecular dipole moments are calculated within the ZDO approximation. On the other hand, the transition moments are computed in the dipole velocity form by an ab initio routine working in a Slater orbital basis.[41] Although this may seem inconsistent, it has been observed that in semiempirical calculations of the kind used here, transition moments computed in the dipole vector form tend to be too large.

For our calculations we have essentially used standard parameters, and we have not calibrated them on measured hyperpolarizabilities, except for small adjustments described in Section III.

Parametrization 1 (P1): Valence state ionization potentials I_p, one-center electron repulsion integrals γ_{pp}, and resonance integrals β_{pq} are given in ref 42 and 43. The electron repulsion integrals γ_{pq} are computed by the charged sphere approximation.[39] These parameters have been quite successful in predicting electronic spectral properties and dipole moments of benzene derivatives with highly polar substituents[42] and of bile pigments.[43]

Parametrization 2 (P2): Valence state ionization potentials and one-center electron repulsion integrals are listed in ref 44, as deduced by Hinze and Jaffe. The resonance integrals are computed by the Wolfsberg–Helmholz formula[45] with a pro-

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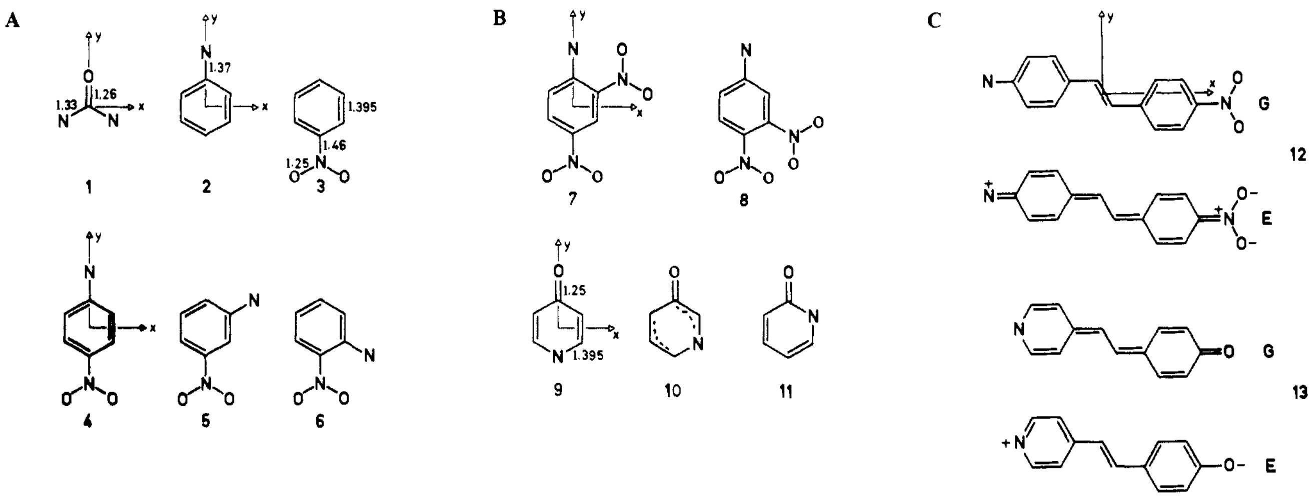

Figure 1. Molecules considered in this investigation and molecular coordinate systems adopted. Averaged bond lengths are indicated in Å units. For the stilbene derivative and the merocyanine, "G" refers to the ground-state structure, "E" to the excited-state structure.

portionality constant $k = 0.86$, the quantities γ_{pq} by the Mataga–Nishimoto procedure.[46]

The calculated averaged molecular hyperpolarizabilities $\bar{\beta}$ (Appendix 2) for single molecules are compared to results from EFISH measurements in liquids. It is seen that the measured data are very much dependent on the polarity of the medium.[47] Ideally, all measurements should be performed in the same nonpolar solvent and the results extrapolated to infinite dilution.[23,24] In the absence of such uniform experimental data for a large number of compounds of different structure, it is indeed difficult to search for an optimal parametrization. Rather, it seems preferable to use more than one standard parametrization in a consistent fashion and to compare different computed results with experiment.

III. Calculations on Single Molecules

The computed data shown in Table Ia–e have been obtained with parametrization 1. For most of these calculations we have used averaged, or idealized, bond lengths, as indicated in Figure 1a,b, setting the C–C resonance integrals inside the benzene rings uniformly equal to −2.46 eV. In the pyridones **9**, **10**, and **11** and in stilbazolium betaine (**13**), molecules with a ground-state quinoid structure, the C–C resonance integrals were however scaled to "single" and "double" bonds with the values −2.40 and −2.50 eV, respectively. Furthermore, subsequent calculations showed some quantitative improvement of the calculated hyperpolarizabilities if crystallographically determined bond lengths were considered and all the resonance integrals adjusted accordingly.[54] The values so obtained are designated as such in Table Ia and b. Unless otherwise specified, all calculated hyperpolarizabilities are at a photon energy of $\hbar\omega_1 = \hbar\omega_2 = 1.17$ eV, corresponding to the 1.06 μ line of the Nd-YAG laser.

Figure 2 represents the different types of terms entering the hyperpolarizability tensor components for a hypothetical three-level system of C_{2v} symmetry, such as the π electron system of urea. We see how the molecular selection rules influence the different hyperpolarizability components. For instance, the dipole moment of one excited state enters YYY (b1) and that of the other excited state XXY and YXX (b2). The transition moment between the two excited states, being x-polarized (case c), only enters XXY and YXX but not YYY.

A comment should be made concerning the calculation of transition moments between near-degenerate excited states in the dipole velocity form. The expression

$$\langle k|\vec{r}|l\rangle = \frac{\hbar^2}{m(E_l - E_k)}\langle k|\vec{\nabla}|l\rangle$$

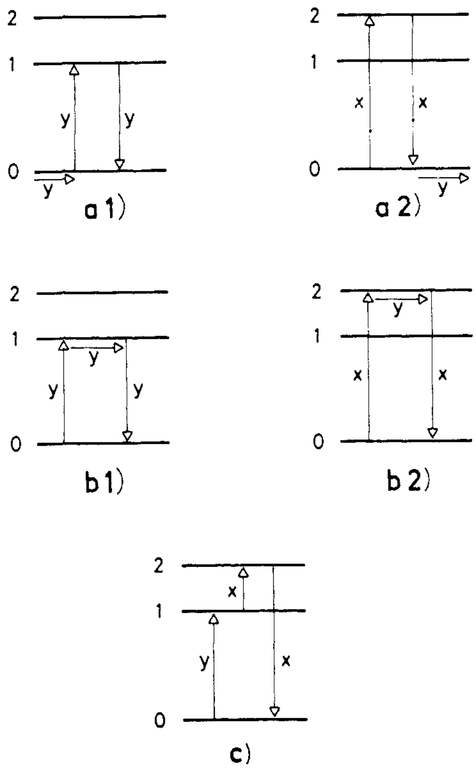

Figure 2. Simplified energy level scheme showing different kinds of contributions to the expression for the hyperpolarizability. Every arrow represents an electric dipole moment or an electric dipole transiton moment. The molecular dipole moment is assumed to lie in the y-direction, and the transitions to be either x- or y-polarized.

gives the relation between transition moments in the dipole vector and in the dipole velocity form. If the state l is equal to the state k, then the expression at left represents the dipole moment and is finite. At right, both the energy denominator as well as $\langle k|\vec{\nabla}|l\rangle$ are zero, thereby leading to an indefinite expression which must also be finite. If $l \neq k$, and $E_l - E_k$ goes to zero, as may be the case in an accidental degeneracy, then $\langle k|\vec{\nabla}|l\rangle$ must also go to zero, otherwise the right-hand side blows up. If the wave functions with which we describe our system are approximate, and we have a near-degeneracy, then it may occur that $E_l - E_k$ goes to zero more quickly than $\langle k|\vec{\nabla}|l\rangle$ does, and the resulting numerical value of the quotient may increase inappropriately. In such cases it may become necessary to calculate transition moments in the dipole vector form.

The relative importance of the contributions of the lower excited states to the hyperpolarizability does not justify the neglect of

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Table I. Computed (P1) and Experimental Data for Molecules **1**–**13**[a]

(a) **1**–**3**

molecule	**1**	**2**	**3**	molecule	**1**	**2**	**3**
E_1	$6.11/5.99^{b}$	4.32	4.58	β **XXY**	$5.632/2.928^{b}$	−3.833	−1.155
E_1 exp	5.9^{c}	4.13^{d}	4.43^{d}	β **YXX**	$6.515/3.063^{b}$	−4.295	−1.240
μ_0 Y	$-4.98/-5.32^{b}$	2.607	4.583	β **YYY**	$1.112/-1.538^{b}$	3.034	6.546
$\vert\mu_0\vert$ exp	4.56^{e}	1.58^{d}	4.2^{d}	$\bar{\beta}$	$-7.04/1.44^{b}$	−0.95	5.36
μ_1 Y	$-8.87/-3.03^{b}$	6.701	9.685	$\vert\bar{\beta}\vert$ exp	2.3^{e}	0.89^{e}	2.0^{e}
μ_2 Y	$-3.42/-8.99^{b}$						

(b) Nitroanilines **4**–**6**

molecule	**4**	**5**	6	molecule	**4**	**5**	6
E_1	3.81	3.24	3.07	β **XXY**	−1.535	2.490	5.458
E_1 exp	$3.85^{i}/3.35^{d}$	3.57^{i}	3.29^{i}	β **YXX**	−2.111	1.742	6.121
μ_0 **X**		2.412	2.928	β **XYY**		2.175	9.666
μ_0 **Y**	8.247	6.043	3.998	β **YXY**		3.522	10.326
$\vert\mu_0\vert$ exp	$6.3^{j}/6.8^{d}$	4.9^{j}	4.3^{j}	β **YYY**	37.018	9.471	18.831
μ_1 **X**		6.519	7.667	$\bar{\beta}$	$35.3/26.8^{f}$	$12.9/8.1^{g}$	$26.4/8.6,^{h}$ 9.9^{h}
μ_1 **Y**	18.117	16.551	10.146	$\bar{\beta}$ exp	34.5^{k}	6^{k}	10.2^{k}
β **XXX**		2.324	1.031				

(c) Dinitroanilines **7** and **8**

molecule	**7**	**8**	molecule	**7**	**8**
E_1	3.24	3.42	β **XXY**	−6.543	−3.091
E_1 exp	$3.92^{m}/3.44^{n}$		β **YXX**	−8.426	−4.321
μ_0 **X**	−4.417	−3.406	β **XYY**	3.549	−4.081
μ_0 **Y**	5.860	9.604	β **YXY**	1.966	−6.258
μ_0 exp	6.53^{o}	8.96^{o}	β **YYY**	26.170	18.370
μ_1 **X**	−11.667	−8.333	$\bar{\beta}$	22.55	16.42
μ_1 **Y**	6.981	17.223	$\bar{\beta}$ exp	$21.^{l}$	
β **XXX**	−14.759	−1.655			

(d) Pyridones **9**–**11**

molecule	**9**	**10**	**11**	molecule	**9**	**10**	**11**
E_1	3.67	3.13	3.77	β **XXX**		−1.923	1.562
E_1 exp	$4.86^{p,q}$		4.20p	β **XXY**	3.584	1.724	−0.602
μ_0 **X**		3.272	2.653	β **YXX**	3.770	0.755	−1.135
μ_0 **Y**	−6.345	−5.386	−2.326	β **XYY**		0.270	1.661
μ_0 exp	$\sim 6.^{r}$			β **YXY**		−0.460	1.643
μ_1 **X**		1.827	3.175	β **YYY**	5.473	8.333	7.423
μ_1 **Y**	−4.816	−2.011	0.811	$\bar{\beta}$	−9.12	−9.43	−1.97

(e) **12** and **13**

molecule	**12**	**13**	molecule	**12**	**13**
E_1	3.23	2.52	β **XXY**	29.949	−151.303
E_1 exp	3.06^{s}	2.05^{t}	β **YXX**	37.483	−38.619
μ_0 **X**	−10.005	−15.172	β **XYY**	−1.647	−25.076
μ_0 **Y**	0.708	1.145	β **YXY**	−4.578	−13.395
μ_0 exp	$7.54^{s}/6.83^{o}$		β **YYY**	0.984	16.259
μ_1 **X**	−19.272	−3.618	$\bar{\beta}$	248.4	−230.6
μ_1 **Y**	1.528	−0.067	$\bar{\beta}$ exp	260^{s}	-210^{t}
β **XXX**	−243.008	241.198			

[a] See Figure 1. E_1: transition energy from the ground state to the first excited state in eV. μ_0 and μ_1: dipole moment of the ground state and first excited state, respectively, in Debye units. $\bar{\beta}$: SHG hyperpolarizability in units of 10^{-30} cm^4/statvolt. [b] Values are based on adjusted resonance integrals (see text). [c] Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: 1974. [d] Reference 42. [e] References 48 and 49. [f] Quantities are computed with adjusted resonance integrals. Coordinates from Trueblood, K. N.; Goldish, E.; Donohue, J. Acta Cryst **1961**, *14*, 1009. [g] Coordinates from Delugeard, Y.; Messager, J. C. *Acta Crystallogr.* **1975**, *B31*, 2809. [h] Two unique molecules in unit cell; coordinates from Dhaneshwar, N. N.; Tavale, S. S.; Pant, L. M. *Acta Crystallogr.* **1978**, *B34*, 2507. [i] Godfrey, M.; Murrell, J. N. *Proc. Roy. Soc.* **1964**, *A278*, 71. Corbett, J. F. *Spectrochim. Acta* **1967**, *23A*, 2315; hexane. [j] Reference 7. [k] Reference 9. [l] Reference 9. [m] Balasubramanian, A.; Capindale, J. B.; Forbes, W. F. *Can. J. Chem.* **1964**, *42*, 2674 in CCl_4. [n] Milliaresi, E. E.; Ruchkin, V. E.; Orlova, T. I.; Efremov, V. V. *Dokl. Akad. Nauk. S.S.S.R.* **1972**, 202; in hexane. [o] McClellan, A. L. *Tables of Experimental Dipole Moments*; W. H. Freeman: San Francisco, 1963; Vol. 1. [p] Cyclohexane; ref 55. [q] 2,6-di-*tert*-butyl-4-pyridone. [r] Exner, O. *Dipole Moments in Organic Chemistry*; Georg Thieme: 1975. Batts, B. D.; Madeley, A. J. *Austr J. Chem.* **1972**, *25*, 2605. [s] Reference 10. [t] *N*-octadecylmerocyanine in pyridine, ref 52; see also reference 53.

higher excited states without closer examination. In smaller π electron systems the number of excited states is limited by the magnitude of the CI matrix. In larger molecules we have somewhat arbitrarily set the limit at 30 states. This already entails the calculation of 31 dipole moments and 465 transition moments, 435 of which are between excited states. In a large, long wavelength absorbing molecule, such as 4-amino-4′-nitrostilbene (**12**), the 20th excited state already lies at about 7.5 eV, in the vacuum UV. This is a region where σ–σ^* transitions start to become important which however we neglect anyhow in the frame of our π electron model. We believe that their contribution to SHG in the molecules considered, going from the near-IR into the visible region, is not of primary importance. Figure 3 shows the dependence of the YYY hyperpolarizability component of *p*-nitroaniline (**4**) on the number of excited states, up to a maximum of 24 (determined by the number of singly excited configurations). This data clearly shows the relative importance of the lower excited states. Similar observations concerning the limited influence of higher excited states were also independently made by other workers for that same molecule in the frame of CNDO calculations.[15,16]

The smallest molecule which we consider is urea (**1**), the nonlinear optical properties of which have been extensively investigated.[35,49] In the frame of our PPP model only two excited

Table II. Comparison of Computed and Measured Values for $\bar{\beta}$ in Units of 10^{-30} cm^4/statvolt[o]

	$\omega_1 = \omega_2 = 1.17$ eV (1.06 μ)				$\omega_1 = \omega_2 = 0.94$ eV (1.318 μ)			
	$\bar{\beta}$ calculated		$\bar{\beta}$ measured		$\bar{\beta}$ calculated		$\bar{\beta}$ measured	
	P1	P2	polar	nonpolar	P1	P2	polar	nonpolar
aniline	−0.95	2.49	1.48[b]		−1.09	2.22	0.79[c]	
nitrobenzene	5.36	2.35	2.27[b]	2.0[d]	4.47	2.16	1.97[c]	
o-nitroaniline	26.4	2.23[a]	10.2[e]		17.8	1.61[a]	6.4[c]	
m-nitroaniline	12.9	6.44[a]	6.0[e]		10.6	5.68[a]	4.2[c]	
p-nitroaniline	35.3	12.3[a]	34.5[n]	16.9[f]	27.2	10.5[a]	21.1[c]	6.4[g]
4-amino-		303.9	260[h]					
4′-nitrostilbene	248.4	456.6[a]	450[i]		165.4	265.6[a]		390.[k]
							100[l]	
merocyanine	−230.6	−124.5			−82.1	−38.8	−210[m]	

[a] Valence state ionization potentials of nitrogen atoms adjusted (see text). [b] Neat; ref 48. [c] Neat or melt; ref 7. [d] Benzene; ref 50. [e] Acetone; ref 9. [f] Dioxane; ref 24. [g] Stilbene; ref 51. [h] Acetone: ref 10. [i] 4-*N*,*N*-Dimethylamino-4′-nitrostilbene (DANS), acetone; ref 10. [k] DANS, stilbene, ref 51. [l] *N*-Octadecylmerocyanine, methanol; ref 52. [m] *N*-Octadecylmerocyanine, ref 52. [n] Methanol; ref 9. [o] Computations with parametrization P1 and P2. Data from measurements in polar and nonpolar media.

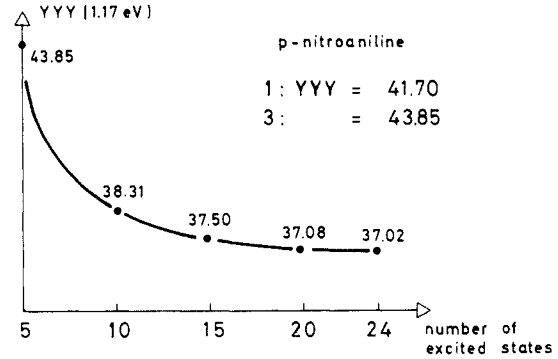

Figure 3. Value of the **YYY** tensor component of the hyperpolarizability of *p*-nitroaniline and its dependence upon the number of excited states considered in the calculation.

π–π^* states are taken into account, predicted to lie around 6 eV, which admittedly is an oversimplification. Accordingly, the computed hyperpolarizability is also strongly parameter-dependent. We nonetheless list these results to show the orders of magnitude involved. The crucial test for the PPP method are the benzene derivatives and larger unsaturated systems. Table II shows the experimental data to be strongly dependent on solvent (medium) polarity. In summary, results for $\bar{\beta}$ based on P1 tend to agree better with data measured in polar media, whereas calculations with P2 in general give smaller absolute values, as do also measurements in nonpolar media. In the nitroanilines **4**, **5**, and **6**, P1 predicts for the relative value of $\bar{\beta}$ the sequence $p > o > m$, in agreement with the experimental data available, both in solution and neat. However, with P2 one finds $p > m > o$, the result for the ortho compound being surprisingly small. It would indeed be interesting to obtain experimental data on *o*- and *m*-nitroaniline in nonpolar solvents, comparable to that available for *p*-nitroaniline[24,51] and nitrobenzene.[50] In deviation from standard practice for P2,[44] the valence state ionization potential of $\ddot{N}$ in the nitroamino compounds was set equal to −23.73 eV for N(amino) and −26.73 eV for N(nitro). If in both cases the usual value of −25.73 eV is adopted, the charge-transfer properties of the excited states are described inadequately.

Calculations with both parametrizations P1 and P2 are in agreement with each other and with experiment in predicting $\bar{\beta}$ for the merocyanine stilbazolium betaine (**13**; Table Ie, Table II) to be negative. A negative hyperpolarizability seems to be a common feature of compounds with a quinoid ground state.[1,16,52]

Figure 1c shows that in the chemical bond description the ground-state structure of 4-amino-4′-nitrostilbene (**12**) is benzenoid (G), while the excited state structure (E) is quinoid. In the merocyanine **13** it is the opposite. One furthermore notices that in **12** the computed excited state dipole moments tend to be larger than the ground state dipole moment, in **13**, on the other hand, smaller.

Negative hyperpolarizabilities are also predicted for the pyridones **9**, **10** and **11** (Table Id), but no experimental data seem to exist on their nonlinear optical properties. In aqueous solution 2- and 4-pyridone exist predominantly in the oxo form, and in nonpolar solvents they tautomerize partly to the corresponding hydroxypyridines.[55]

IV. Calculations on Molecular Dimers and Clusters

The idea of considering the hyperpolarizability, or SHG susceptibility, of a cluster of molecules as the sum of individual molecular contributions (N) has been explored in detail.[33,34] It

$$P_i^{(2)} = \sum_N \sum_{jk} \chi^{(2)}_{N,ijk} \, {}^1\vec{E}_j \, {}^2\vec{E}_k$$

presupposes that intermolecular interactions are negligible. In particular cases this assumption may be justified. However, where large transition moments occur or (and) molecules are closely packed, the energy splitting between otherwise degenerate molecular transitions may become substantial as well as the concomitant shift in transition intensity. One cannot a priori exclude that the hyperpolarizability is thereby not affected in a significant manner. Furthermore, the charge distribution within the molecules in the cluster will be influenced by the surroundings. Even small shifts in the molecular dipole moments may add up to measurable contributions.

This part of our investigation is an exploratory one. As a first step we consider a molecular dimer, or small cluster of molecules within the crystal lattice, as a "supermolecule". The electrostatic interactions between individual molecules in the cluster are taken into account. However, intermolecular exchange effects are neglected. We remain within the (local) π electron approximation and the general approach of the PPP method. As is illustrated in Figure 5, the resonance integrals between atomic centers belonging to the π electron system of different individual molecules are set equal to zero. The electron repulsion integrals between all relevant atomic centers within the cluster are however included in our calculation. This approach has already been applied to interpret the long wavelength electronic spectrum of coupled chromophores in dimers[43] and in small polymers.[56] The parametrization is, of course, the same as that adopted for single

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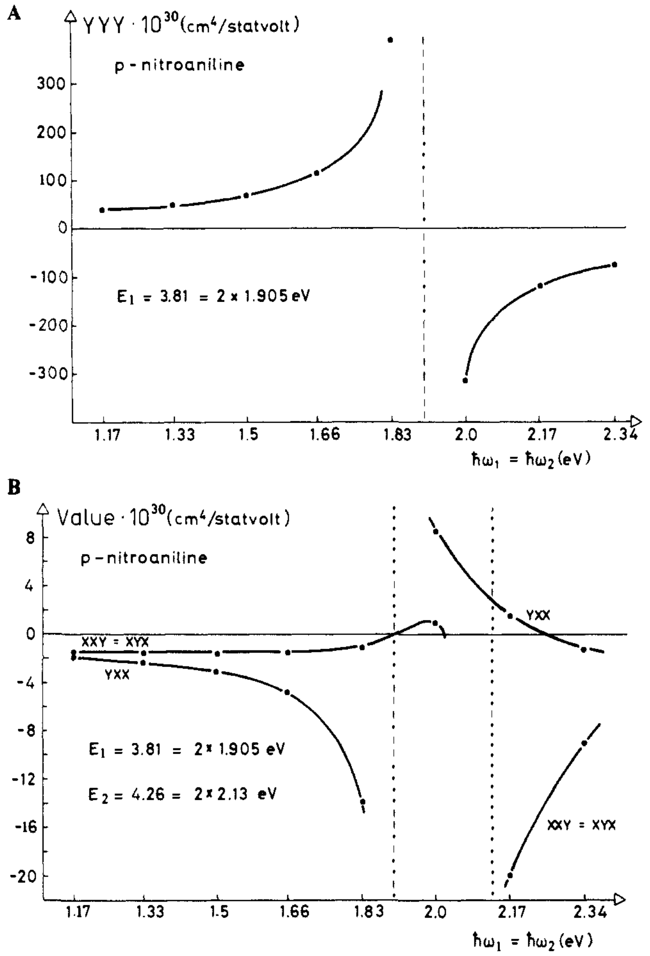

Figure 4. (a) Radiation frequency dependence of the **YYY** tensor component of the hyperpolarizability of *p*-nitroaniline. Notice the anomalous dispersion at the two-photon resonance with the first excited state. (b) Radiation frequency dependence of the **XXY** = **XYX** and of the **YXX** tensor components of the hyperpolarizability of *p*-nitroaniline. At 1.17 eV, the value of **YXX** is close to that of **XXY** = **XYX**, reflecting approximate fulfilment of Kleinman symmetry.[63] As the energy region is approached where two-photon resonances occur, the two curves show markedly different behavior.

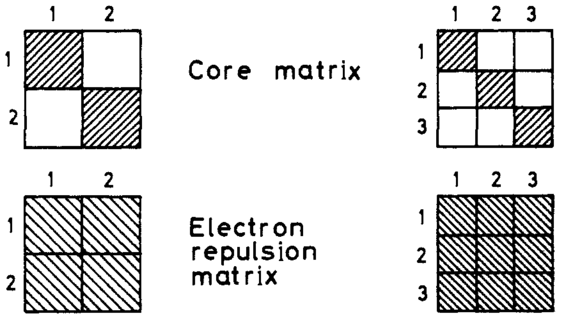

Figure 5. Form of the PPP core matrix and of the electron repulsion matrix for a molecular dimer and trimer. Exchange effects between molecules are neglected. Intermolecular electrostatic effects are taken into account explicitly in the calculation.

molecules, and the SCF-single-CI calculation proceeds analogously. In the course of setting up the CI matrix, the program also generates intermolecular charge-transfer configurations which, however, because of the ZDO approximation, do not mix with the configurations representing intramolecular excitations.

The calculation of the electric dipole transition moments requires some special comment. For reasons spelled out in Section II, we calculate the transition moments in the dipole velocity form with an ab initio routine.[41] Since in a molecular cluster the individual monomers are not necessarily coplanar, care must be taken to correctly transform the atomic p$_\pi$ functions. They must all be expressed in terms of components defined within the overall reference frame of the cluster. A second point concerns the occurrence of accidental degeneracies. The electric dipole transition moment between quasidegenerate states in the dipole velocity form may artificially blow up, for reasons given in Section III. In such cases, calculations should be repeated by using the dipole vector form, eventually in a suitable approximation, such as that of Linderberg.[54]

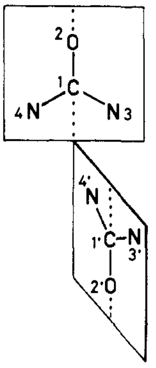

Figure 6. Structure of urea showing the unit cell dimer.

As a first example we consider urea which crystallizes in the tetragonal $P\bar{4}2_1m$—D_{2d}^3 space group and contains two molecules per unit cell.[57,58] As we have seen in Section III, urea is not particularly well suited for the PPP method. Furthermore, in the crystal, hydrogen bonding effects appear to be important which elude calculations within the π electron approximation. Zyss and Berthier[35] have made an extensive study of the urea molecule and crystal in the frame of INDO and ab initio calculations. Their approach is more accurate than ours but should however become very laborious for larger molecules. Here we try to treat electrostatic intermolecular interactions in a manner as simple as possible, and we use urea as a first example to illustrate our procedure.

Table IIIa gives the Cartesian coordinates of the C, N, and O atoms in the unit cell. The computed π electron hyperpolarizability tensor components are found in Table IIIb. The quantity β refers to the unit cell dimer (see also Figure 6), and β(I) and β(II) pertain to the isolated urea monomers in their respective sites. The difference between the results for the unit cell dimer and for the sum of the corresponding monomer contributions is significant and requires some comment. If we consider the dimer as a composite molecule and calculate the averaged hyperpolarizability $\bar{\beta} = 5kT\bar{\gamma}_r/\mu_o$ for it (Appendix 2), we obtain $\bar{\beta}$ = 7.00 in units of 10^{-30} cm^4/statvolt. This corresponds to an average contribution of 3.50 per monomer. For the isolated monomers we find in the same units $\bar{\beta}$(I) = $\bar{\beta}$(II) = 1.46. If the intermolecular interaction is neglected, $\bar{\beta}$ cannot be computed for the unit cell dimer. The dipole moments of the two urea molecules in their crystal sites add to zero: μ_l(I) + μ_l(II) = 0, for all states *l*. Intermolecular interaction, on the other hand, induces a nonvanishing dipole moment in the dimer: μ_0 = 0.138 D, μ_1 = 2.315 D, μ_2 = 2.496 D, and μ_3 = 3.700 D, etc. Whereas in the dimer *without* interaction, all contributions to the hyperpolarizability of the type a1, a2, b1, and b2 (Figure 2) are absent, in the interacting dimer these terms may have a substantial influence on the result. We do not claim however that the unit cell dimer with interaction between monomers gives any fundamentally better indication of the bulk properties than the isolated monomers. The infinite lattice of D_{2d} symmetry has a vanishing overall dipole moment; small finite clusters of molecules within the crystal lattice will always have a resulting dipole moment, either through incomplete cancellation of the isolated monomer dipole moments or due to the asymmetry of the intermolecular polarization.

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Table III

(a) Cartesian Coordinates in Å Units for the Unit Cell Dimer of Urea[57,58]

	I				II		
	x	y	z		x	y	z
1	0.	2.8305	1.5587	1′	2.8305	0.	−1.5587
2	0.	2.8305	2.8211	2′	2.8305	0.	−2.8211
3	0.8090	3.6395	0.8708	3′	3.6395	−0.8090	−0.8708
4	−0.8090	2.0215	0.8708	4′	2.0215	0.8090	−0.8708

(b) Hyperpolarizability Data on the Unit Cell Dimer of Urea[b]

	β	β(I)	β(II)	β(I) + β(II)
XXX	2.561	0.	0.	0.
XXY	1.085	0.	0.	0.
XXZ	0.056	−1.481	1.481	0.
XYY	−0.894	0.	0.	0.
XYZ	−2.439	−1.481	−1.481	−2.962
XZZ	2.931	0.	0.	0.
YXX	0.894	0.	0.	0.
YXY	−1.085	0.	0.	0.
YXZ	−2.439	−1.481	−1.481	−2.962
YYY	−2.561	0.	0.	0.
YYZ	0.056	−1.481	1.481	0.
YZZ	−2.931	0.	0.	0.
ZXX	0.084	−1.550	1.550	0.
ZXY	−2.546	−1.550	−1.550	−3.100
ZXZ	3.703	0.	0.	0.
ZYY	0.084	−1.550	1.550	0.
ZYZ	−3.703	0.	0.	0.
ZZZ	5.173	1.549	−1.549	0.

[a] See Figure 6. [b] Calculations with parametrization P1 and adjusted resonance integrals (see Table Ia and text). β refers to the dimer, β(I) and β(II) to the monomers in their respective unit cell sites.

Our second example (see Figure 7) is the monoclinic $P2_1\text{-}C_2^2$ unit cell of the compound PNP. We consider this system as the dimer of the π electron chromophore of 2-amino-5-nitropyridine and neglect the influence of the atoms not participating in the charge transfer π electron system. In Table IVb we again compare the computed hyperpolarizability data for the interacting dimer, β, with the sum of the contributions of the noninteracting monomers in their respective crystal sites, β(I) + β(II). There is, at best, agreement as to the sign of the contributions and some qualitative trends. For monomeric 2-amino-5-nitropyridine we find $\bar{\beta} = 32.7$ in units of 10^{-30} cm^4/statvolt (compare with the value for p-nitroaniline in Table Ib). In the same units we obtain for the dimer including intermolecular interaction $\bar{\beta} = 15.8$; for the dimer in which intermolecular interaction is neglected $\bar{\beta} = 29.2$. The calculated data presented in Table IVc gives an indication of how the intermolecular interaction manifests itself. The dipole moments of the two monomers add to a resulting moment of 6.006 D in negative $\vec{j}$ direction. The dipole moment of the dimer is mainly in the same direction with a value of 6.222 D. We thus find a difference of about 0.22 D which must correspond to an induced increment of dipole moment. In an attempt to interpret this finding in a simple manner, we assume the dipole moments of the separate monomers to be located at a given point on the respective molecules (for simplicity we choose the carbon atoms 1 and 1′) and compute the electrostatic dipole–dipole interaction energy between them. From the data given in Table

$$\Delta\epsilon = \frac{\vec{\mu}(\mathrm{I})\cdot\vec{\mu}(\mathrm{II})}{R^3} - \frac{3\vec{\mu}(\mathrm{I})\cdot\vec{R}\vec{\mu}(\mathrm{II})\cdot\vec{R}}{R^5}$$

IVa and c, we obtain $\Delta\epsilon = -0.128 \times 10^{-12}$ erg $= -0.08$ eV which corresponds to an effective field, at the site of one molecule due to the dipole moment of the other, of $E_{\mathrm{eff}} = 1.584 \times 10^4$ CGS. This effective field then induces an increment of electric dipole moment $\Delta\mu$ in the molecule on which it acts

$$\Delta\mu = \bar{\alpha}E_{\mathrm{eff}}$$

where for simplicity $\bar{\alpha}$ is taken as an averaged first-order electric polarizability and is assumed, for this kind of molecule, to be of the order of 10^{-23} cm^3.[59,60] We then find

$$\Delta\mu \approx 0.16\ \mathrm{D}$$

which, as an order of magnitude, agrees with our results from Table IVc. For the excited-state dipole moments the differences due to intermolecular interaction are even more pronounced but shall not be interpreted in detail here. The data in Table IVc also show how through exciton-type electrostatic interaction the longest wavelength transition gets split by 0.07 eV, with a concomitant shift in transition intensity. As the reader can easily verify, the dimer transition moments are well approximated by

$$\vec{\mu}_{01} = \frac{1}{2^{1/2}}\{\vec{\mu}_{01}\ (\mathrm{I}) - \vec{\mu}_{01}\ (\mathrm{II})\}$$

$$\vec{\mu}_{02} = \frac{1}{2^{1/2}}\{\vec{\mu}_{01}\ (\mathrm{I}) + \vec{\mu}_{01}\ (\mathrm{II})\}$$

In summary, our calculated results on molecular oligomers show a variety of mechanisms by which intermolecular interactions manifest themselves. In order to estimate bulk hyperpolarizabilities for SHG from molecular hyperpolarizabilities, there is evidence that these interactions cannot be ignored.

V. Conclusions

From our results it appears that in molecules containing systems of conjugated double bonds the π electrons make the dominant contribution to the hyperpolarizability for SHG at the near IR–visible wavelengths. SCF–MO–CI calculations within the frame of the PPP approximation predict correct orders of magnitude and describe trends within classes of analogous molecules in a consistent way. Consequently, the procedure should prove useful in exploring the nonlinear optical properties of possible candidates for SHG which have not yet been synthesized. At shorter wavelengths, where the excitation of σ electrons comes into play, the application of computational procedures which take these electrons into account explicitly undoubtedly becomes necessary. In evaluating the SHG hyperpolarizability of molecular crystals

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Table IV

(a) Cartesian Coordinates for the Atoms of Interest in the Unit Cell Dimer of PNP[a]

	I				II		
	x	y	z		x	y	z
1	-1.0003	-3.0032	-1.3053	1′	1.0003	4.4788	1.3053
2	-0.1423	-3.6946	-2.0966	2′	0.1423	3.7874	2.0966
3	0.7046	-3.0018	-2.8561	3′	-0.7046	4.4802	2.8561
4	0.7469	-1.6356	-2.8689	4′	-0.7469	5.8464	2.8689
5	-0.1176	-0.9068	-2.0494	5′	0.1176	6.5752	2.0494
6	-0.9905	-1.5892	-1.2534	6′	0.9905	5.8928	1.2534
7	-1.8323	-3.7320	-0.5457	7′	1.8323	3.7500	0.5457
8	1.6878	-0.9547	-3.7149	8′	-1.6878	6.5273	3.7149
9	2.3248	-1.6146	-4.5277	9′	-2.3248	5.8674	4.5277
10	1.8531	0.2529	-3.5928	10′	-1.8531	7.7349	3.5928

(b) Hyperpolarizability Data for the PNP Unit Cell Dimer[b]

	β	β(I)	β(II)	β(I) + β(II)
XXX	4.185	-9.332	9.332	0.
XXY	-5.642	-6.527	-6.527	-13.054
XXZ	-3.377	8.756	-8.756	0.
XYY	-0.770	-4.267	4.267	0.
XYZ	6.263	6.368	6.368	12.736
XZZ	2.433	-7.842	7.842	0.
YXX	-3.871	-6.658	-6.658	-13.316
YXY	-1.322	-4.463	4.463	0.
YXZ	4.380	6.403	6.403	12.806
YYY	-5.167	-2.073	-2.073	-4.146
YYZ	3.276	4.564	-4.564	0.
YZZ	-4.096	-5.918	-5.918	-11.836
ZXX	-3.191	8.707	-8.707	0.
ZXY	6.416	6.340	6.340	12.680
ZXZ	2.110	-7.841	7.841	0.
ZYY	2.835	4.441	-4.441	0.
ZYZ	-6.221	-5.981	-5.981	-11.962
ZZZ	-1.520	6.668	-6.668	0.

(c) Computed Data for the Ground and Lowest Excited States of the 2-amino-5-nitropyridine Monomers and the Unit Cell Dimer in PNP[c]

	monomer I			monomer II			unit cell dimer			
	$\vec{i}$	$\vec{j}$	$\vec{k}$	$\vec{i}$	$\vec{j}$	$\vec{k}$	$\vec{i}$	$\vec{j}$	$\vec{k}$	
$\vec{\mu}_0$	-5.616	-3.003	4.991	5.616	-3.003	-4.991	0.009	-6.222	-0.033	$\vec{\mu}_0$
$\vec{\mu}_1$	-11.254	-7.481	10.050	11.254	-7.481	-10.050	-1.886	-10.682	1.681	$\vec{\mu}_1$
							1.931	-10.787	-1.764	$\vec{\mu}_2$
$\vec{\mu}_{01}$	-2.668	-2.130	2.412	-2.668	2.130	2.412	-0.557	-3.096	0.461	$\vec{\mu}_{01}$
							-3.617	0.647	3.315	$\vec{\mu}_{02}$
E_1		3.976			3.976			3.915		E_1
								3.972		E_2

[a] See Figure 7. Data from ref 64. [b] Calculations with parametrization P1. See also legend to Table IIIb. [c] For units see Table Ia and text.

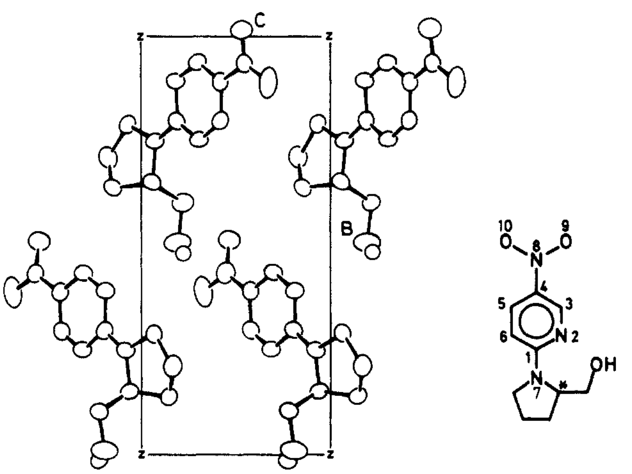

Figure 7. Formula and (monoclinic) crystal structure of optically active PNP (*N*-(5-nitropyridyl)-2-L-prolinol). The asymmetric center is indicated in the formula. A similar structure, NPP (*N*-(4-nitrophenyl)-L-prolinol), is described in ref 65.

it seems dangerous to merely add up the individual molecular contributions. From our calculations it appears that intermolecular interactions play an important and nonnegligible role.

Acknowledgment. We thank Dr. J. D. Swalen for his continued interest in this research and for his advice and suggestions. One of us (G.W.) is grateful to the IBM Corporation and the IBM World Trade Corporation for making a stay at the IBM Research Center in San Jose possible.

Appendix 1

The relevant component of induced polarization responsible for sum frequency generation is written[36]

$$\vec{p}^{(2)}(\omega_1 + \omega_2; -\omega_1, -\omega_2) = \frac{1}{\hbar^2}\{\sum_k\sum_l \frac{\vec{\mu}_{al}(\vec{\mu}_{lk}\cdot{}^2\vec{E}_-)(\vec{\mu}_{ka}\cdot{}^1\vec{E}_-)}{(\omega_{la} - \omega_1 - \omega_2)\ (\omega_{\mathrm{ka}} - \omega_1)} + \sum_k\sum_l \frac{\vec{\mu}_{al}(\vec{\mu}_{lk}\cdot{}^1\vec{E}_-)(\vec{\mu}_{ka}\cdot{}^2\vec{E}_-)}{(\omega_{la} - \omega_1 - \omega_2)(\omega_{ka} - \omega_2)} + \sum_k\sum_l \frac{(\vec{\mu}_{al}\cdot{}^2\vec{E}_-)\vec{\mu}_{lk}(\vec{\mu}_{ka}\cdot{}^1\vec{E}_-)}{(\omega_{la} + \omega_2)(\omega_{ka} - \omega_1)} +$$

$$\sum_k\sum_l \frac{(\vec{\mu}_{al}\cdot{}^1\vec{E}_-)\vec{\mu}_{lk}(\vec{\mu}_{ka}\cdot{}^2\vec{E}_-)}{(\omega_{la} + \omega_1)(\omega_{ka} - \omega_2)} + \sum_k\sum_l \frac{(\vec{\mu}_{al}\cdot{}^2\vec{E}^-)(\vec{\mu}_{lk}\cdot{}^1\vec{E}_-)\vec{\mu}_{ka}}{(\omega_{la} + \omega_2)(\omega_{ka} + \omega_1 + \omega_2)} + \sum_k\sum_l \frac{(\vec{\mu}_{al}\cdot{}^1\vec{E}_-)(\vec{\mu}_{lk}\cdot{}^2\vec{E}_-)\vec{\mu}_{ka}}{(\omega_{la} + \omega_1)(\omega_{ka} + \omega_1 + \omega_2)}\} \quad \text{(A1.1)}$$

where $\vec{\mu}$ is the electric dipole operator.

The tensor components of the susceptibility, or frequency-dependent hyperpolarizability, for sum frequency generation is defined by the relation[29]

$$p_i^{(2)}\ (\omega_1 + \omega_2; -\omega_1, -\omega_2) = \chi^{(2)}_{ijk}\ (\omega_1 + \omega_2; -\omega_1, -\omega_2)\ {}^1E_{j-}{}^2E_{k-} \equiv \beta_{ijk}{}^1E_j{}^2E_k \quad (A1.2)$$

$p_i^{(2)}$ is the component of induced polarization in direction i due to the field components in directions j and k, respectively. In accordance, the tensor expressions appearing in the text are defined in such a manner that the first index always refers to the component of polarization, the second and third index to the field components one and two, respectively. We notice that the first two expressions in (A1.1), in which two-photon resonances may occur, will tend to make the predominant contribution in the wavelength range of interest.

Appendix 2

The susceptibility for the electric field-induced sum frequency generation, in particular second harmonic generation (EFISH), is a fourth rank tensor. The actual third-order electronic effect

$$\chi^{(3)}(\omega_1 + \omega_2; 0, -\omega_1, -\omega_2) \equiv \gamma_e$$

is in general very small. The temperature-dependent effect due to anisotropic averaging

$$\chi^{(3)}(\omega_1 + \omega_2; 0, -\omega_1, -\omega_2; kT) \equiv \gamma_r$$

depends on the molecular dipole moment μ_0 and the second-order hyperpolarizability $\chi^{(2)} \equiv \beta$.[30,31,61] Using the expression A2 of ref 62 allows one to easily deduce the relevant averaged quantity. If the polarization of both incident beams is parallel to the static field, one finds to first order in $(kT)^{-1}$

$$\bar{\gamma}_r = \frac{1}{5kT}[\mu_{0x}\beta_{xxx} + \mu_{0y}\beta_{yyy} + \mu_{0z}\beta_{zzz} + \tfrac{1}{3}\{\mu_{0x}(\beta_{xyy} + \beta_{yxy} + \beta_{yyx} + \beta_{xzz} + \beta_{zxz} + \beta_{zzx}) + \mu_{0y}(\beta_{yxx} + \beta_{xyx} + \beta_{xxy} + \beta_{yzz} + \beta_{zyz} + \beta_{zzy}) + \mu_{0z}(\beta_{zxx} + \beta_{xzx} + \beta_{xxz} + \beta_{zyy} + \beta_{yzy} + \beta_{yyz})\}] \equiv \frac{1}{5kT}\vec{\mu}_0\vec{\beta} = \frac{1}{5kT}\mu_0\bar{\beta}; \qquad \mu_0 = |\vec{\mu}_0| \quad (A2.1)$$

μ_0 is by definition always positive; μ_{0x}, μ_{0y}, and μ_{0z} are the components of the dipole moment of the molecule (unit cell) with respect to the molecule-fixed (unit cell-fixed) axes and may, according to the choice of axes, be positive or negative. If one chooses the y-axis, say, to be parallel to the dipole moment, expression A2.1 reduces to[16]

$$\bar{\gamma}_r = \frac{1}{5kT}\mu_0\{\beta_{yyy} + \tfrac{1}{3}(\beta_{yxx} + 2\beta_{xxy} + \beta_{yzz} + 2\beta_{zzy})\} \quad (A2.2)$$

Use has been made here of the trivial indentity for SHG, that $B_{xyx} = \beta_{xxy}$ and $\beta_{zyz} = \beta_{zzy}$. If Kleinman's symmetry rule[63] is additionally fulfilled (which in general is not, or very approximately, the case), expression A2.2 becomes

$$\bar{\gamma}_r = \frac{1}{5kT}\mu_0(\beta_{yyy} + \beta_{yxx} + \beta_{yzz}) \quad (A2.3)$$

In the absence of z-polarized transitions, such as in many of our examples, the terms β_{yzz}, β_{zzy} evidently vanish.

Registry No. 1, 57-13-6; **2**, 62-53-3; **3**, 98-95-3; **4**, 100-01-6; **5**, 99-09-2; **6**, 88-74-4; **7**, 97-02-9; **8**, 610-41-3; **9**, 108-96-3; **10**, 58064-43-0; **11**, 142-08-5; **12**, 4629-58-7; **13**, 103367-99-3.

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The Stabilization of α-Substituted Methyl Cations by First- and Second-Row Substituents

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Abstract: In this paper we report the results obtained in an ab initio SCF-MO study at an extended computational level on the effects of first- and second-row substituents upon the stabilities of α-substituted carbocations. Accurate stabilization energies have been computed for the various species, and in each case we have decomposed the stabilization energy values into the following component terms: (i) the σ-effects; (ii) the nonbonded interaction effects; (iii) the d-orbital effects; and (iv) the correlation energy effects. We have found that in the comparison along a column the differences between the stabilization energies are small with the only exception of the pair NH_2, PH_2 where additional effects associated with the planarization of the XH_2 group must be considered. Futhermore, it has been found that the differences between the stabilization energies along a row are more pronounced and that the trend is determined by the π-donation effects.

(I) Introduction

The effect of first- and second-row substituents upon the stabilities of α-substituted carbocations is a chemical problem of significant interest. In fact carbocations play an important role in chemical synthesis as well as in physical organic chemistry.[1] First-row substituents (in particular OR) are known to stabilize an adjacent carbocationic center more than the second-row analogue[2] (in particular SR). For instance, chloromethyl ethyl ether hydrolyzes in aqueous dioxane about 1600 times faster than chloromethyl sulfide.[3] The reaction was assumed in both cases

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