

Ab initio predictions of large hyperpolarizability push–pull polymers. Julolidinyl-*n*-isoxazolone and julolidinyl-*n*-*N,N'*-diethylthiobarbituric acid

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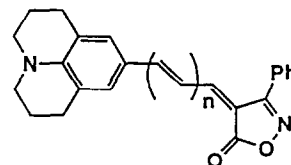
Abstract

Recently significant advances have been made in engineering push–pull organic chromophores to have very large hyperpolarizabilities (β), leading to materials with $\mu\beta$ as high as 15000×10^{-48} esu. Such developments have been slow and costly because of difficulties in synthesis, purification, and measurement. As an alternative we have developed a new quantum mechanical program (PS-GVB/NLO) which provides predictions of β for such molecules far faster than previously possible. We have applied PS-GVB/NLO to predicting α , β , and γ for the high β push–pull organics and find excellent agreement with experiment. This suggests that theory can be used as an effective tool for developing new nonlinear optical materials.

1. Introduction

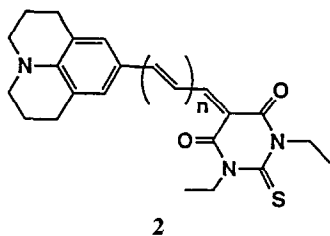
For telecommunications (electrooptic switches), optical information processing, and sensor applications, it is useful to develop organic chromophores with very large first hyperpolarizabilities, β . A major step forward in developing such materials was made recently by Marder et al. [1] who succeeded in developing the highest β organics currently known, julolidinyl-6-isoxazolone (**1** with $n = 6$) and julo-

lidinyl-6-*N,N'*-diethylthiobarbituric acid (**2** with $n = 6$). These push–pull organic materials lead to $\mu\beta(0) = 13600 \times 10^{-48}$ esu and 14920×10^{-48} esu, respectively.



1

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Although semiempirical and ab initio level calculations of hyperpolarizabilities of various molecules have been reported recently [2–6], ab initio level calculations have not been previously reported for molecules of the size of **1** and **2** with $n = 6$. We have developed a new ab initio quantum mechanical program (PS-GVB/NLO) [7,8] which provides predictions of hyperpolarizabilities for such molecules far faster than previously possible and have applied it to predicting the hyperpolarizabilities for **1** with $n = 0, 1, 2, 3$, and 6 , for **2** with $n = 6$.

2. Results

Hartree–Fock (HF) calculations using the 6-31G basis leads to the results in Table 1 and Fig. 1. Here we see that the comparison between theory (in vacuum) and experiment (in chloroform) is good, in particular, the trend with n and the comparison of molecules **1** with **2** is excellent.

The excellent agreement between theory and experiment suggests that theory can be used as an effective tool in developing new nonlinear optical materials. For julolidinyl-6-isoxazolone the total CPU time to obtain μ , α , β , $\mu\beta$, γ is 10 h (on an HP 735 workstation). This is much faster than the pro-

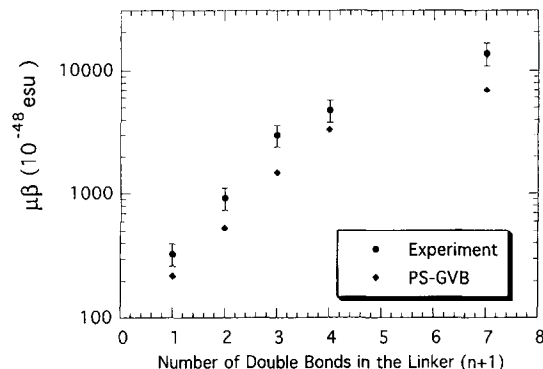


Fig. 1. The hyperpolarizability, $\mu\beta(0)$, for julolidinyl- n -isoxazolone as a function of $N = n + 1$, the number of double bonds in the linker.

cesses of synthesizing and purifying the compounds and then running the experiments to measure the moments and hyperpolarizabilities.

Taking x as the direction of the linker and xz as the plane of the linker leads to the components in Table 2. As expected, the major contribution to β is from β_x . For example, for **1** with $n = 6$, we calculate $\beta_x/\beta_y = 146$ and $\beta_x/\beta_z = 7.2$.

Table 1 shows that the theoretical dipole moment μ for **1** changes smoothly with n (as expected). However, experiment [1] does not. The experimental values of μ are obtained from the changes of the capacitance of the vessel with molecules **1** in chloroform solvent. We believe that this discrepancy is mainly experimental.

The EFISH experiment [1] measures $\mu\beta$ rather than β . Since there is no data on the relation between the μ and β vectors, the experimental value

Table 1

Hyperpolarizabilities for the julolidinyl- n -isoxazolone class (**1**) and julolidinyl- n , N' -diethylthiobarbituric acid class (**2**). Here μ is the dipole moment, $\beta(0)$ is the static hyperpolarizability, and θ is the angle between μ and β . The experiments (Ref. [1]) used chloroform as solvent whereas theory considered molecules in the gas phase

Class	n	$\mu\beta(0)$ (10^{-48} esu)		μ (10^{-18} esu)		$\beta(0)$ (10^{-30} esu)		θ (deg)	
		exp.	PS-GVB	exp.	PS-GVB	exp.	PS-GVB	exp. ^b	PS-GVB
1	0	328 ± 65	218	9.5	10.71	34 ± 7	31	0	49
1	1	919 ± 180	529	9.1	12.47	100 ± 20	60	0	45
1	2	3000 ± 600	1466	9.0	15.49	339 ± 70	117	0	36
1	3	4753 ± 950	3311	9.8	16.65	485 ± 100	232	0	31
1	6 ^a	$13\,600 \pm 2720$	6960	16	17.67	849 ± 100	442	0	27
2	6 ^a	$14\,920 \pm 3000$	6877	—	15.25	—	456	—	9

^a Based on 5-Me, 10-Me substituents. ^b Assumed.

Table 2

Dipole moment μ , polarizability α , first hyperpolarizability β , and second hyper-polarizability γ for molecules **1** and **2**. The units are 10^{-18} esu for μ , 10^{-24} esu for α , 10^{-30} esu for β , and 10^{-36} esu for γ

	n					
	0	1	2	3	6 ^a	6 ^b
μ_x	9.66	11.12	14.29	15.35	16.71	15.20
μ_y	-1.04	-0.35	0.14	-0.73	-0.42	0.09
μ_z	-4.50	-5.65	-5.97	-6.42	-5.72	1.12
α_{xx}	59.40	82.87	113.4	141.02	228.9	242.6
α_{yy}	23.40	19.38	18.91	20.71	24.2	28.0
α_{zz}	36.43	41.53	45.06	40.16	51.4	56.7
α_{xy}	-0.59	-1.69	-2.63	2.92	-1.8	0.8
α_{xz}	10.65	8.66	5.86	3.16	4.0	13.4
α_{yz}	0.27	-3.44	-0.02	7.37	2.9	-1.5
β_{xxx}	27.38	52.78	108.75	206.44	400.48	406.4
β_{yyy}	-1.17	0.74	2.44	14.26	16.39	20.9
β_{zzz}	2.24	3.86	2.69	14.97	20.91	27.5
β_x	28.45	57.38	113.88	229.24	437.77	454.8
β_{yxx}	-0.35	0.44	0.08	13.18	2.78	1.0
β_{yyy}	0.01	0.09	0.12	0.51	-1.11	-0.07
β_{zzz}	0.14	0.23	0.14	0.26	1.41	-0.07
β_y	-0.20	0.76	0.34	13.94	3.07	0.9
β_{zxx}	12.17	18.04	27.24	31.69	59.23	-26.7
β_{zyy}	-0.32	0.03	0.28	-0.22	0.19	-2.9
β_{zzz}	0.74	0.89	-0.71	-1.63	2.02	-4.4
β_z	12.59	18.96	26.81	29.84	61.44	-34.0
γ_{xxx}	21.31	99.84	290.37	640.70	3736.7	4269.9
γ_{yyy}	0.51	0.418	-0.80	-0.08	15.5	4.0
γ_{zzz}	3.09	2.203	7.22	6.81	38.3	45.6

^a Molecule **1**. ^b Molecule **2**.

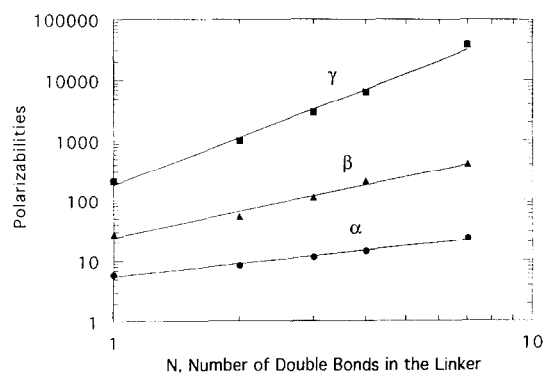


Fig. 2. The dependence of α_{xx} , β_{xxx} , and γ_{xxx} on $N = n + 1$, the number of double bonds in the linker. The solid lines are the least squares fit to the calculated values. The units are 10^{-23} esu for α_{xx} , 10^{-30} esu for β_{xxx} , and 10^{-37} esu for γ_{xxx} .

of $\beta(0)$ is extracted from $\mu\beta$, assuming that μ and β are parallel. However the calculations (Table 1) show that the angle between μ and β of **1** ranges from 27° to 49° , and the angle for **2** is 9° for $n = 6$. Thus the theory is useful in extracting the experimental value of β from $\mu\beta$.

Experimental values were not reported for α (polarizability) and γ (second hyperpolarizability). We show in Fig. 2 the calculated α , β , γ as a function of number of double bonds (N) in the linker for **1**. The lines in the log-log plots of Fig. 2 lead to $\alpha = \alpha_0 N^{0.70}$, $\beta = \beta_0 N^{1.44}$, and $\gamma = \gamma_0 N^{2.65}$. The components of α , β and γ are listed in Table 2¹.

The experiments were carried out for molecules in chloroform whereas the results reported above were for gas phase molecules. In order to determine the effects of solvent, we used PSGVB/solvent [9–11] program which uses DelPhi [12] to evaluate the reaction field using a continuous Poisson–Boltzmann description of the solvent self-consistently with using PS-GVB to calculate the wavefunctions in the reaction field. Table 3 shows the calculated hyperpolarizabilities of **1** with $n = 0, 1, 2$ in chloroform ($\epsilon = 4.806$). Here we see that α is the same in the gas

Table 3

Hyperpolarizabilities of **1** with $n = 0, 1$ and 2 , no solvent indicates a standard gas phase calculation using PS-GVB, solvent indicates PS-GVB/solvate calculation using chloroform, the solvent used in the experiments. The units are 10^{-24} esu for α , 10^{-30} esu for β , and 10^{-36} esu for γ

	$n = 0$		$n = 1$		$n = 2$	
	no solvent	solvent	no solvent	solvent	no solvent	solvent
α_{xx}	59.40	60.88	82.87	82.85	113.4	111.0
α_{zz}	36.43	36.54	41.53	41.35	45.06	44.93
β_x	28.45	33.18	57.38	60.28	113.88	110.09
β_z	12.59	15.04	18.96	18.79	26.81	23.91
γ_{xxx}	21.31	13.06	99.8	76.7	290.37	242.14

¹ We did not calculate the γ_{xyy} , γ_{xzz} and γ_{yzz} components because the electric fields were applied only along the chain direction. Since the dominant contribution to γ is from γ_{xxx} , the other components can be neglected.

Table 4

Hyperpolarizabilities of **1** with $n=1$ with different basis sets, 6-31G and 6-31G** (including polarization functions). The units are 10^{-24} esu for α , 10^{-30} esu for β , and 10^{-36} esu for γ

Basis sets	6-31G	6-31G**
α_{xx}	82.87	83.73
α_{zz}	41.53	42.19
β_x	57.38	57.35
β_z	18.96	17.95
γ_{xxx}	99.8	108.5

phase and in solvent, β changes less than 10%, and γ decreases less than 40% in solvent.

3. Computational details

3.1. Basis sets

All calculations in Table 1 and Fig. 1 were at the Hartree–Fock level using the 6-31G basis set with PS-GVB(v2.01) program [8]. The results in Table 4 show that adding polarization functions to the basis (6-31G**) affects the results by 1% to 8%.

3.2. Geometry

Crystal structures have been reported [1] for **1** with $n=2$ and 3. In estimating the structure for the other molecules, we used the geometries of the donor and acceptor from the crystal structure of $n=3$. The bond lengths for the linker polyene were estimated from the structural data of $n=2, 3$. We assumed that the polymer linker involves a resonance of the two valence bond (VB) configurations with an average bond length of 1.385 Å and an average alternation of δr_n . The experiments lead to $\delta r_2 = 0.037$ Å and $\delta r_3 = 0.049$ Å, respectively, and we use [13] $\delta r = 0.11$ Å for $n = +\infty$. Fitting these results leads to $\delta r_1 = 0.023$ Å and $\delta r_6 = 0.071$ Å; we assumed $\delta r_0 = 0.0$ Å.

For **2**, we assumed that the donor and linker have the same geometry as for **1**. The geometry of the acceptor of **2** was obtained by geometry optimization at the HF/3-21G level.

We assumed that molecules in the gas phase and in the solid state have the same bond length. This is reasonable since the environment in a molecular

crystal is far less polarized than in a polar solvent. For the solvation calculations, we also used the same geometry as for the gas phase. For a polar solvent, this could cause increased errors because of changes in the bond lengths of the linker. To estimate this effect, we used the VB-CT-S model [12,14] coupled with the experimental data. For molecule **1** with $n=3$, VB-CT-S estimates that δr_3 changes from 0.049 to 0.040 Å and β decreases by 7% (the parameters used were: $t = 0.88$ eV, $V = 0.79$ eV, $Q = 0.43$, $r_D = 3$ Å, $r_A = 3$ Å, $r_{DA} = 16$ Å).

3.3. Hyperpolarizabilities

The polarizabilities were obtained by solving for the HF wavefunction in finite fields, \mathcal{E} , and calculating the dipole moments, μ . Considering only the x components, this leads to

$$\mu(\mathcal{E}) = \mu(0) + \alpha\mathcal{E} + \beta\mathcal{E}^2 + \gamma\mathcal{E}^3 + \delta\mathcal{E}^4 + \dots$$

The 5 point calculation uses the values $\mathcal{E} = 0, \pm\mathcal{E}_1, \pm\mathcal{E}_2$ with $\mathcal{E}_2 = 2\mathcal{E}_1$. This leads to

$$\begin{aligned} \alpha &= \frac{2}{3\mathcal{E}_1} [\mu(\mathcal{E}_1) - \mu(-\mathcal{E}_1)] \\ &\quad - \frac{1}{12\mathcal{E}_1} [\mu(\mathcal{E}_2) - \mu(-\mathcal{E}_2)] + \mathcal{O}(\mathcal{E}_1^4), \\ \beta &= \frac{2}{3\mathcal{E}_1^2} [\mu(\mathcal{E}_1) + \mu(-\mathcal{E}_1)] \\ &\quad - \frac{1}{24\mathcal{E}_1^2} [\mu(\mathcal{E}_2) + \mu(-\mathcal{E}_2)] - \frac{5}{4} \frac{\mu(0)}{\mathcal{E}_1^2} \\ &\quad + \mathcal{O}(\mathcal{E}_1^4), \\ \gamma &= -\frac{1}{6\mathcal{E}_1^3} [\mu(\mathcal{E}_1) - \mu(-\mathcal{E}_1)] \\ &\quad + \frac{1}{12\mathcal{E}_1^3} [\mu(\mathcal{E}_2) - \mu(-\mathcal{E}_2)] + \mathcal{O}(\mathcal{E}_1^2). \end{aligned}$$

The magnitudes of the finite field were chosen to minimize the error in β . We used $\mathcal{E}_1 = 0.0024$ au for $n=6$, $\mathcal{E}_1 = 0.0048$ au for $n=1, 2, 3$, and $\mathcal{E}_1 = 0.0098$ au for $n=0$. To test the accuracy, we did two extra point $\pm\mathcal{E}_3$ with $\mathcal{E}_3 = 0.0192$ au for **1** with $n=1$. The β_{xxx} values for calculations with three

points, five points, and seven points are 52.99×10^{-30} , 52.78×10^{-30} , and 52.58×10^{-30} esu, respectively. This indicates that the numerical error in β is less than 1%.

We also tested the accuracy by calculating the hyperpolarizabilities of various molecules and comparing with the results using GAUSSIAN 92 [15] (which uses analytic methods). The agreement between these two methods is excellent. Examples include: *p*-nitrobenzene, $\beta_{zzz} = -111$ au (GAUSSIAN 92) and $\beta_{zzz} = -111$ au (PSGVB); and orthonitroaniline, $\beta_{zzz} = 189$ au (GAUSSIAN 92) and $\beta_{zzz} = 192$ au (PSGVB). Additional details of the hyperpolarizability calculations will be published elsewhere [7].

We also tested the accuracy by calculating the γ of benzene. The EFISH experiment [16] yields $\gamma = 1.5 \times 10^{-36}$ esu. PSGVB calculations at the HF/6-31G level lead to $\gamma = 1.1 \times 10^{-36}$ esu, in reasonable agreement with experiment.

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