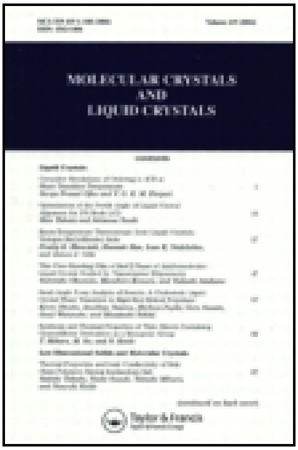

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Exceptional Second-Order Nonlinear Optical Susceptibilities in Organic Compounds

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EXCEPTIONAL SECOND-ORDER NONLINEAR OPTICAL SUSCEPTIBILITIES IN ORGANIC COMPOUNDS

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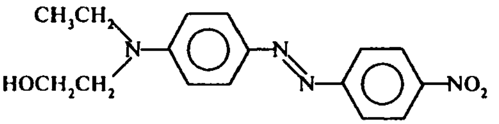
Abstract Molecular second-order nonlinear optical susceptibilities (β) of donor-acceptor substituted organic compounds were measured in dimethyl sulfoxide solution using electric field induced second harmonic generation. The experimental data and theoretical interpretations of the trends led to compounds with values of β useful for imparting high bulk susceptibilities on polymeric materials. Exceptionally high values of β were reached relative to analogues of similar size through the use of tricyanovinyl and dithiolylidenemethyl substituents.

INTRODUCTION

Organic nonlinear optical materials are expected to be of value in the fabrication of guided-wave optical devices.[1] In order to utilize second-order effects, it is necessary to design and prepare stable, highly optically nonlinear materials that can be processed into light-guides of good optical quality. Glassy polymers offer several inherent advantages[2] over other classes of matter in terms of processability and optical transmission. These polymers are transformed into nonlinearly active ones by the incorporation of molecules or subunits possessing high values of the second-order coefficient β and orienting them in an electric field, as demonstrated[3] for solutions of Disperse Red 1 (DR1)



DR1

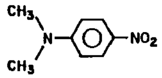
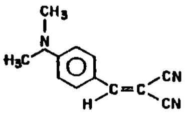
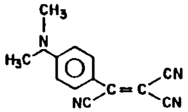
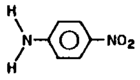
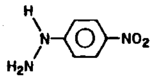
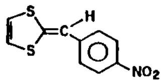
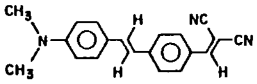
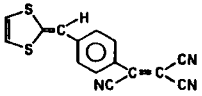
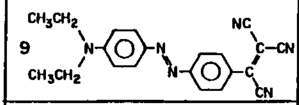
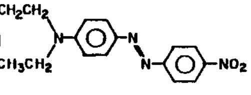
in poly(methyl methacrylate). Although this system exhibited the bulk second-order polarizability $\chi^{(2)}$ that was predicted from the β value of DR1 and a thermodynamic model of the poled solution, significant improvements are necessary to obtain a practical device material. Such improvements would be realized through augmentation of the molecular hyperpolarizabilities and dipole moments, and by increasing the density, net orientation, and directional stability of the active species in the polymer matrix. This presentation focuses on optimization of relevant molecular properties using synthetic and physical organic chemical methodology.

It is well known that the generic organic molecule useful in second-order nonlinear optics consists of a strongly electron donating group linked to an electron acceptor by some conjugated bridge.[4] Many of the compounds evaluated to date have been variations on a theme of nitro acceptors and amino or oxy donors.[5] Also, measurements of β have not generally been performed under consistent conditions for different molecules. Our aim is to study molecules with substituents that are strong electron donors or acceptors, and directly measure their second-order susceptibilities in a manner that permits systematic conclusions to be drawn.

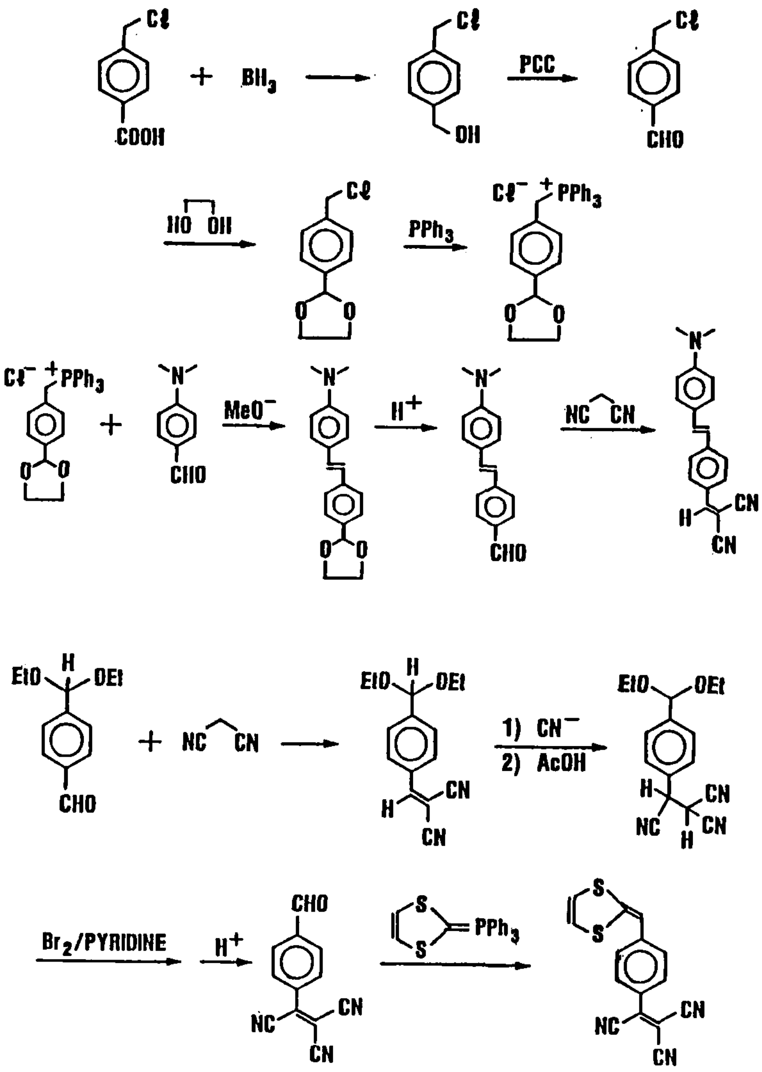
RESULTS

The compounds studied are listed in Table 1. Some of the more interesting compounds required new synthetic sequences; two examples are presented in Scheme 1. Note the extensive use of protecting groups to insure selective reactions and the importance of Wittig condensations in assembling the molecular components. Such cyanovinyl acceptors were suggested by Stamatoff et. al. for their potential use in nonlinear optical materials.[6]

Table 1

	MOLECULE	$\beta\mu$	β	β_0
1		138	21	12
2		271	31	16
3		846	78	26
4		75*	12	9
5		102	15	9.5
6		358	52	25
7		2650	323	133
8		1200*	–	–
9		4110*	390	154
DR1		1090	125	47

$\beta\mu$ in units of $10^{-30}cm^5D/esu$; β, β_0 in units of $10^{-30}cm^5/esu$


Cl
COOH
BH3
OH
PCC
CHO
HO OH
PPh3
Cl− +PPh3
O O
MeO−
H+
NC CN
CN
EtO OEt
H
1) CN−
2) AcOH
NC
Br2/PYRIDINE
S
=PPh3

Scheme 1

Experimental values of $\beta\mu$ were obtained for a series of organic compounds as solutions in dimethyl sulfoxide (DMSO) using electric field induced second harmonic generation (EFISH).[7] This technique directly measures the relevant nonlinear optical properties of the molecule. The use of aprotic solvents, such as DMSO and dioxane, is critical to any measurement of β, since deducing molecular properties from solution measurements requires the use of macroscopic local field models which break down for the short-range interactions and associations present in protic solvents such as methanol. The macroscopic nonlinear optical susceptibility of a poled polymer glass incorporating a nonlinear optical moiety is directly proportional to $\beta\mu$, which is the quantity measured using EFISH techniques.[3] Values of β may be obtained by dividing by dipole moment magnitudes. A comparision of the contributions of molecular moments to β is made through the quantity β_0, in which the dependence of β on the electronic transition energies of the compounds is approximately factored out using a two level model which is given by,[8]

$$\beta_{xxx}(-2\omega;\omega,\omega) = \frac{e^3|\mu_{01}|^2(\mu_{11}-\mu_{00})}{\hbar^2} \text{ x}F(\omega) \qquad (1)$$

where

$$F(\omega) = \frac{3\omega_0^2}{(\omega_0^2 - \omega^2)(\omega_0^2 - 4\omega^2)} \qquad (2)$$

and where e is the electronic charge, and the μ's are molecular moments. The quantity β_0 is calculated by dividing the measured value of β by $F(\omega)$ at the measured fundamental frequency, and multiplying by $F(0)$. The data are obtained at a fundamental wavelength of 1.356 µm, and are summarized in Table 1.

For a series of three molecules (1-3) differing only in the acceptor group, there is a dramatic increase in β and β_0 in the sequence nitro, dicyanovinyl, tricyanovinyl. A correlation is obtained on plotting β_0, a resonance-dominated quantity, vs $\sigma_{\bar{R}}$, a resonance-dominated Hammett constant (Figure 1), suggesting that β

increases with ground state resonance.

A more sophisticated approach is to employ semi-empirical molecular orbital calculations of π-electron configuration[9] in order to theoretically predict the trends in β and μ for this series of compounds. Figure 2 is a dispersion plot of theoretical β as a function of the second harmonic energy of the probe beam. This plot emphasizes differences due to dispersion, since all three curves rise sharply near the transition frequencies of the respective molecules and shows that β increases as the second harmonic of the measurement frequency approaches the first excitation energy. Figure 3 shows the same three curves positioned relative to an arbitrary common transition frequency ω_1. Here the ordering is due to differences in the contribution of molecular moments to the hyperpolarizabilities. The tricyanovinyl group induces greater changes in dipole moment upon excitation, and also leads to a much better projection of the ground state dipole moment on the main hyperpolarizability component relative to the dicyanovinyl substituent.

We also examined a series in which the donor was varied and the acceptor was kept constant (1,4-6). The quantity βμ changes very little when the amino group of p-nitroaniline is modified, but increases substantially when it is replaced by the easily ionized dithiolylidinemethyl group (6). A value for σ_p^+ for this dithiole donor was obtained from ^{13}C NMR, and a Hammett plot of β_0 vs σ_p^+ is shown in Figure 4; no correlation is observed. The main contributor to increased β_0 in the dithiole compound is an excited state-related moment, since the ground state Hammett constants do not predict such an increase, as they did in the case of the acceptor sequence.

By assembling the best electron donor and acceptor in this series (8), the highest value of βμ for a disubstituted benzene is achieved. Additionally, the generally accepted hypothesis that longer conjugated π-electron systems give rise to larger values of β and βμ within series in which both donor and acceptor are constant (for example, 1 and DR1, 2 and 7), is confirmed. By incorporating the tricyanovinyl acceptor in an amino-substituted azo dye (9), an unusually high value of β is obtained that is several times larger than that of the

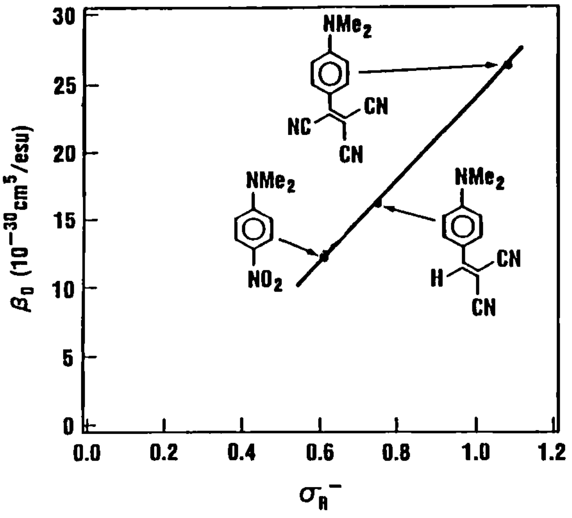


Figure 1

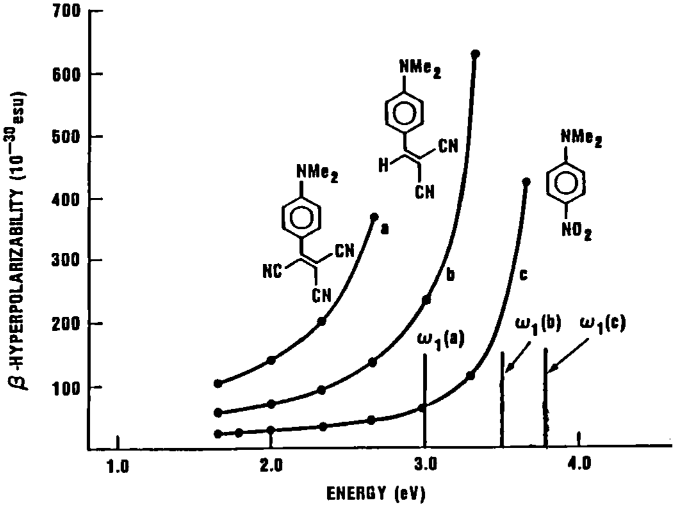


Figure2

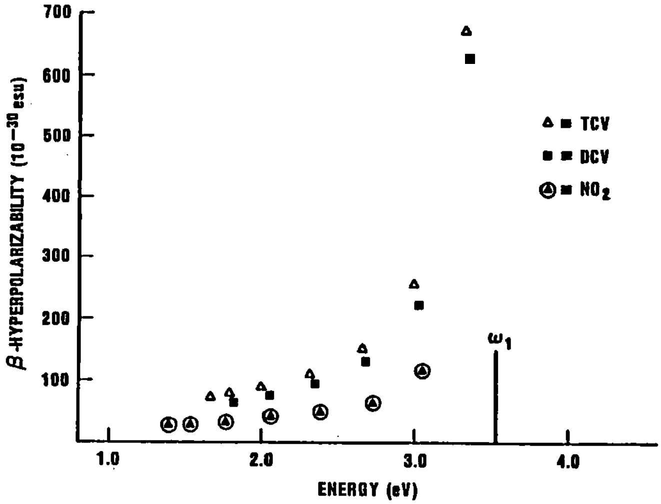


Figure 3

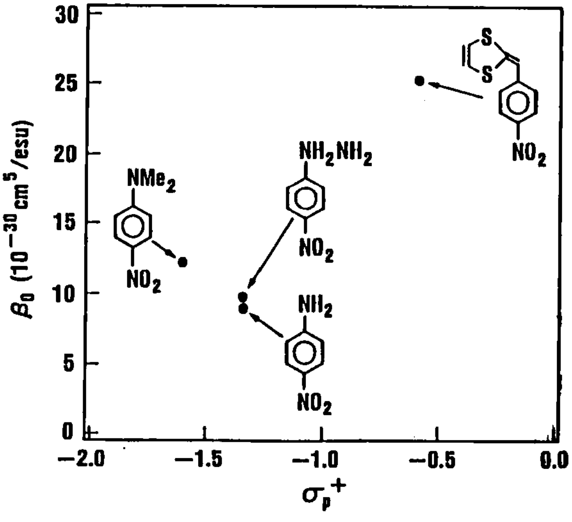


Figure 4

azo dye DR1, without substantially increasing the size of the chromophore.

Conclusion

We have studied several structural variables relevant to hyperpolarizabilities in organic molecules using infinite dilution solution measurements of electric field induced second harmonic generation. Using this systematic and direct measurement of β on a diverse series of compounds, molecular engineering techniques have been extended to produce species possessing exceptional second-order nonlinear optical susceptibilities.

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