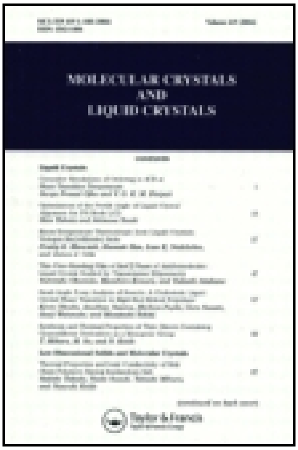

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Design and Evaluation of Organic Nonlinear Optical Materials with a Large Pockels Effect

T. Yoshimura [a]

[a] Fujitsu Laboratories Ltd., 10-1 Morinosato-Wakamiya, Atsugi, Kanagawa-ken, 243-1, Japan

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Design and Evaluation of Organic Nonlinear Optical Materials with a Large Pockels Effect

T. YOSHIMURA

Fujitsu Laboratories Ltd., 10-1 Morinosato-Wakamiya, Atsugi, Kanagawa-ken 243-1, Japan

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This paper reviews a method of examining the Pockels effect in small and thin flakes of organic material, and discusses the possibility of further improving the Pockels effect in organic materials in terms of the molecular orbital method. The electro-optic coefficient r_{33} of the styrylpyridinium cyanine dye (SPCD) crystal was estimated from the AC modulation method to be about 430 pm/V at a wavelength λ of 633 nm, 6 times larger than the r_{11} of 2-methyl-4-nitroaniline (MNA). To improve the Pockels effect further, artificial molecules with a polydiacetylene structure were designed. By adjusting conjugated lengths and donor- and acceptor-substitution sites in the molecules, a large second-order hyperpolarizability was obtained, corresponding to an electro-optic coefficient about 10 times larger than r_{11} of MNA at a detuning energy of 0.2 eV.

Keywords: organic nonlinear optical materials, pockels effect, molecular orbital method, polydiacethylene structure

I. INTRODUCTION

Organic materials with polarized conjugated systems have attracted increasing interest because of their second-order nonlinear optical properties. For second harmonic generation (SHG), many new materials, superior to inorganic materials like lithium niobate $LiNbO_3$ have been found. This suggests that organic materials hold promise for the production of the Pockels effect[1–7] which, as well as SHG, is involved in the second-order nonlinear optical property.

There are two problems in using organic materials for the Pockels effect: the method of examination; and the fact that the Pockels effect, in general, cannot be improved as much as SHG, because this effect is proportional to the second-order nonlinear susceptibility $\chi^{(2)}$ while the SHG efficiency is proportional to $(\chi^{(2)})^2$.

Organic materials are often available in the form of small flakes. In this case, a special technique which is suitable for examining the Pockels effect in the materials is needed. The previously-reported AC modulation method[5] can realize a sensitive detection of the Pockels effect in a thin film of small area. The technique is briefly reviewed in this paper.

Further improvement of the Pockels effect in organic materials requires artificial materials. The second-order hyperpolarizability of new one-dimensional conjugated molecules with donor and acceptor substitution using the molecular orbital method is also described.

II. EXAMINATION OF THE POCKELS EFFECT BY THE AC MODULATION METHOD

The AC modulation method (Figure 1)[5] is based on detecting phase retardation. To apply an electric field to the crystal flakes, a slit-type nickel-chromium electrode with a 5 μm gap was pressed against the crystal. Linearly polarized light at 633 nm passes through the crystal, transmitted through the analyzer, and is detected by a photodetector. When AC voltage is applied to the crystal, detector output is modulated by the electro-optic phase retardation $\Delta\delta$ induced in the crystal. The ratio of the AC component of the detector output V_{AC} to 0 V detector output V_{DC} is

$$\begin{aligned} V_{AC}/V_{DC} &= [E_{0\theta}(\delta_0)^2 - E_{0\theta}(\delta_0 + \Delta\delta)^2] \,/\, E_{0\theta}(\delta_0)^2 \\ E_{0\theta}(\delta)^2 &= E_0{}^2\,[(\cos\phi\cos\theta + \sin\phi\sin\theta\cos\delta)^2 + (\sin\phi\sin\theta\sin\delta)^2], \end{aligned} \tag{1}$$

where, δ_0 is the phase retardation at 0 V, ϕ the angle of polarizer, and θ the angle of the analyzer. Substituting V_{AC}, V_{DC}, δ_0, ϕ, and θ into Equation (1) yields $\Delta\delta$.

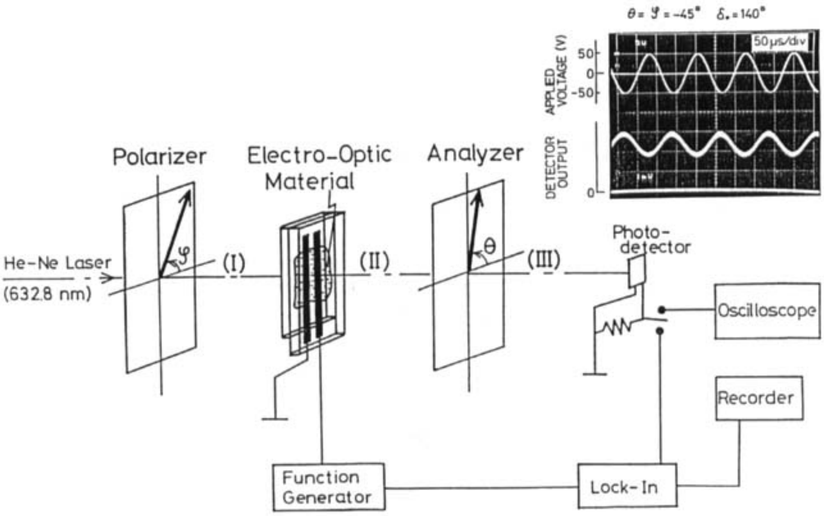

FIGURE 1 Measurement system of AC modulation method.

The figure of merit for the electro-optic phase retardation F can then be determined by

$$F = (\lambda_0 \Delta\delta D) / (2\pi V L), \tag{2}$$

where, λ_0 is the wavelength, D the electrode gap, L the film thickness, and V the applied voltage.

Using the AC modulation method, the electro-optic coefficient r_{33} of SPCD crystal has been estimated as 430 pm/V at a wavelength of 633 nm, 6 times larger than the r_{11} of 2-methyl-4-nitroaniline (MNA). One of the reasons for the large Pockels effect in SPCD is the resonant effect. It is known that the Pockels effect is greatly enhanced as the energy gap becomes close to the incident photon energy. Since the absorption edge of SPCD crystal is about 2 eV and that of the MNA is about 2.5 eV, the resonant enhancement is larger in SPCD than in MNA for the photon energy of 1.95 eV (wavelength of 633 nm).

The SPCD thin-film crystal has considerable absorption loss in the near infrared region, and is susceptible to mechanical, thermal, and chemical attack. The Pockels effect alone is not enough greatly to improve electroptic devices. Further research on the Pockels effect in organic materials is needed.

III. SECOND-ORDER HYPERPOLARIZABILITY OF NEW ONE-DIMENSIONAL CONJUGATED MOLECULES

Further improvement of the Pockels effect in organic materials requires artificial materials. The second-order hyperpolarizability of new one-dimensional conjugated molecules with donor and acceptor substitution has been investigated[8,9] using the molecular orbital method.

The second-order hyperpolarizability β for the Pockels effect corresponding to the chain direction is calculated based on Ward's expression,[10]

$$\beta = -\frac{e^3}{2\hbar^2}\left[\sum_{\substack{g\neq n' \\ n\neq n' \\ n\neq g}} r_{gn'}\, r_{n'n}\, r_{ng}\, \frac{3\omega_{n'g}\omega_{ng} + \omega^2}{(\omega_{n'g}^2 - \omega^2)(\omega_{ng}^2 - \omega^2)} + \sum_{n} r_{gn}^2\, \Delta r_n \frac{3\,\omega_{ng}^2 + \omega^2}{(\omega_{ng}^2 - \omega^2)^2}\right] \tag{3}$$

Here, r_{gn} is the transition dipole moment between the ground and excited states and $r_{n'n}$ is that between two excited states. Δr_n is the difference in the dipole moment between the excited and ground states. $\hbar\omega_{ng}$ is the excitation energy from the ground to excited state. $\hbar\omega$ is the energy of the incident photons. r_{gn}, $r_{n'n}$ and Δr_n were calculated using the Austin Model 1 (AM1) method[11] with a single-excitation configuration interaction (SCI) involving eight unoccupied orbitals above the lowest unoccupied molecular orbital (LUMO) and six occupied orbitals below the highest

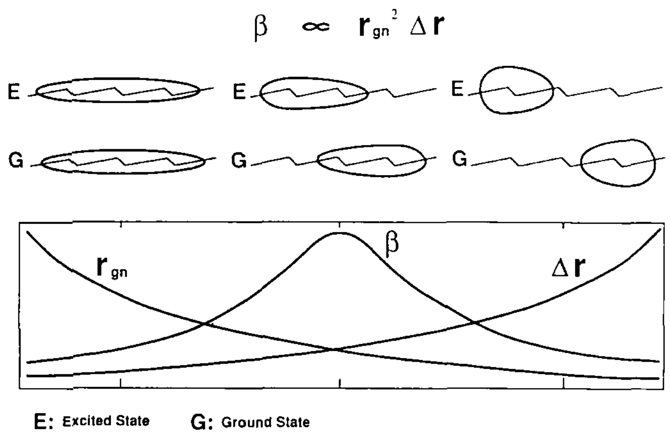

FIGURE 2 Qualitative guidelines for designing second-order nonlinear optical materials for the Pockels effect.

occupied molecular orbital (HOMO). The excited state Ψ_n is expressed by configuration functions $\chi_{i\to j}$ as follows,

$$\Psi_n = \sum_{i,j} C_{n,i\to j}\, \chi_{i\to j} \tag{4}$$

In Figure 2, three cases of the wave function shape are shown schematically. The charge separation between the excited and ground states increases from left to right and the wave function overlap between the two states decreases, i.e., Δr increases and r_{gn} decreases in a trade-off relationship. Since, in the two-level model,[12]

$$\beta \propto r_{gn}^2\, \Delta r, \tag{5}$$

β is at its maximum in the middle of the wave function, and both the charge separation and wave function overlap must be considered to optimize β.

Figure 3 shows the structure of the new molecules and the second-order hyperpolarizabilities. These molecules have a polydiacetylene structure and an acetylenic backbone. NH_2 is the donor (D) and NO_2 the acceptor (A). DA, and DADA are types of donor and acceptor substitution, and the numbers following them indicate the number of carbon sites (N_c) in the conjugated chain. Second-order hyperpolarizability per 10 Å of molecule, ρ_β, (Figure 3) is plotted for a detuning energy of 0.2 eV from the first excited states. The excited state determining the absorption edge of molecules is denoted by the first excited state. Although ρ_β was calculated using Equation (3), a major part of ρ_β comes from the first excited state, implying that overall tendencies in Figure 3 can be explained in terms of the first excited state. ρ_β varies with molecular length and donor- and acceptor-substitution sites. In a DA molecule, ρ_β is at its maximum at $N_c = 18$. Morley reported similar behavior of the β vs N_c curve in polyenes and polyphenyls having one donor and one acceptor at opposite sides.[13] The DADA molecule ρ_β increases monotonically with N_c. DA18

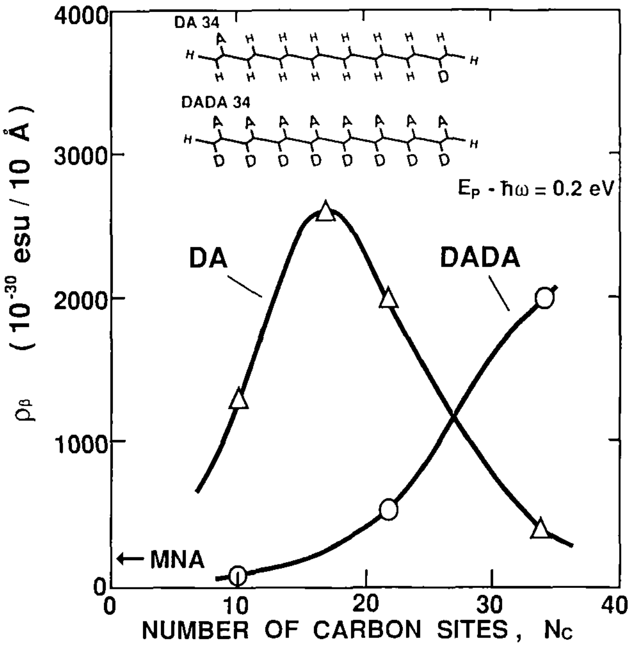

FIGURE 3 Structure and second-order hyperpolarizability as a function of N_c for the new one-dimensional conjugated molecules. The vertical axis is the second-order hyperpolarizability per 10 Å of molecule. E_p is the excitation energy for the first excited state.

has a maximum ρ_β of about 2500×10^{-30} esu/10 Å at $N_c = 18$, which corresponds to an electro-optic coefficient of about $10 \times r_{11}$(MNA). Here, r_{11}(MNA) was also calculated for a detuning energy of 0.2 eV.

The results in Figure 3 can be explained in terms of the dependence of dipole moments r_{gn} and Δr on N_c. It can be seen from Figure 4 that, for the DA molecule, r_{gn} increases and Δr decreases with increasing N_c. Consequently, as Figure 3 show, ρ_β is maximum at the intermediate molecular length of $N_c = 18$. In the DADA

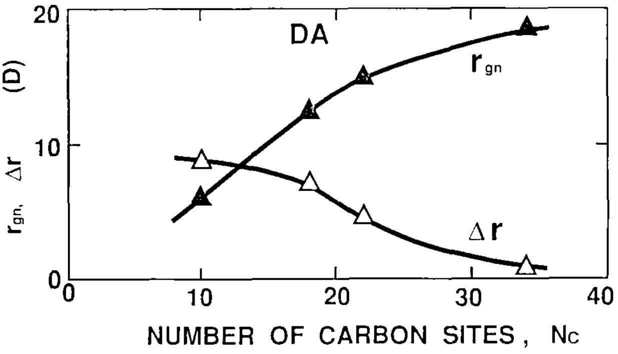

FIGURE 4 N_c dependences of dipole moments r_{gn} and Δr.

molecule, both Δr and r_{gn} increase with N_c, reflected in the monotonic increase in ρ_β with N_c. This parallels the qualitative guideline (Figure 2) that the balance between r_{gn} and Δr is important in improving β.

Figure 5 shows molecular orbitals near the Fermi surface for DA34. The charge separation in the chain direction appears mainly in the HOMO and LUMO. In other molecular orbitals, electrons tend to extend wholely in the molecules. DADA34 has a similar tendency. The contour diagrams in Figure 6 show $C_{n,i\to j}^2$ for the first excited state. $C_{n,i\to j}$ represents the fraction of the configuration function involved in Ψ_n as described in Equation (4). Combining the results from Figure 6 with the shape of the molecular orbitals described above, the relationship between the shape of wave functions and the dipole moments is clarified. In DA10, the G1→E1 component, which corresponds to the LUMO to HOMO transition, is dominant. So, charge separation of this molecule becomes large because the G1→EN and GM→E1 components in Ψ_n mainly contribute to Δr due to the large charge sep-

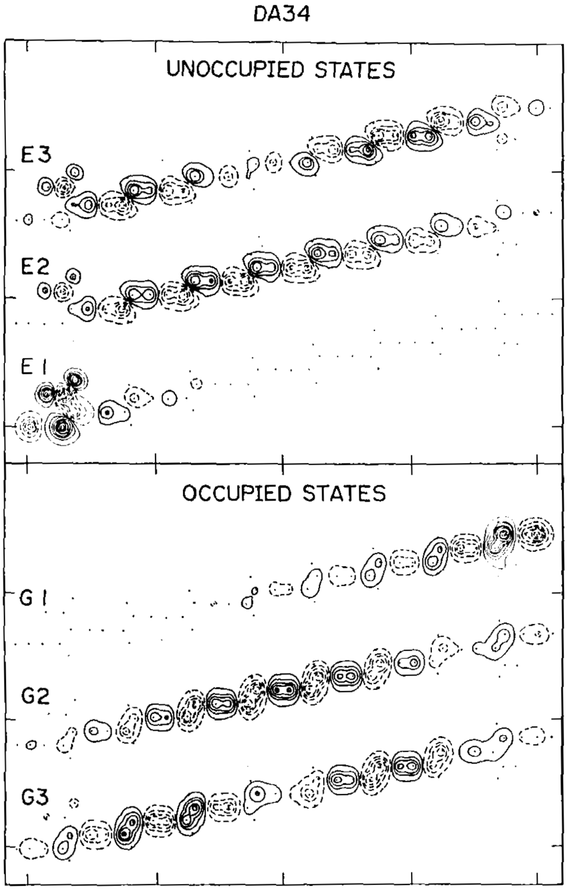

FIGURE 5 Contour diagrams of molecular orbitals near the Fermi surface in the plane z = 0.6 Å for DA34. G1 is HOMO and E1 is LUMO.

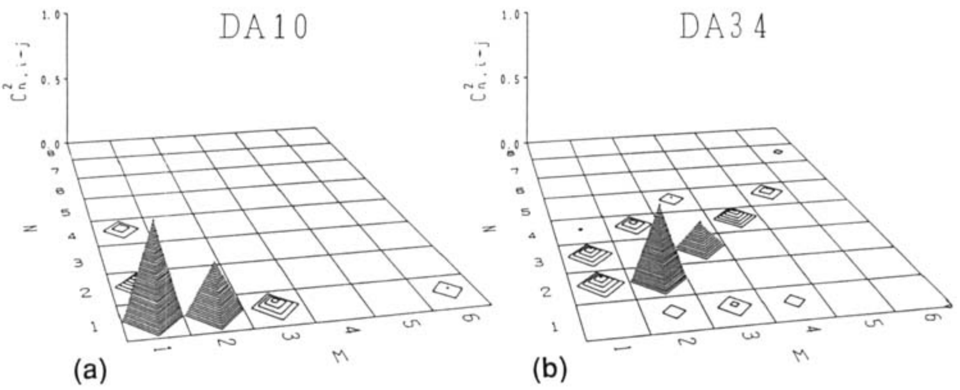

FIGURE 6 $C_{n,i\to j}^2$ for the first excited states of DA molecules. M represents the occupied molecular orbitals GM (M = 1, 2, ... , 6) and N represents the unoccupied molecular orbitals EN (N = 1, 2, ... , 8). The height of the quadrangular pyramid at the area determined by M and N indicates $C_{n,GM\to EN}^2$.

aration in HOMO and LUMO. With increasing N_c, the contribution of G1→E1 component to Ψ_n is drastically reduced. This reduces the charge separations, and Δr. At the same time, the wave function overlap between the ground and excited states increases with N_c. This enhances r_{gn}. These results are consistent with Figure 4. For the DADA molecule, on the other hand, the contribution of G1→EN component to Ψ_n remains large when N_c increases from 10 to 34. This increases Δr with increasing N_c with the aid of the effect of an increase in the molecular length on the dipole moment.

Thus, to attain large second-order optical nonlinearity (Pockels effect), the charge separation of the wave function must be controlled by adjusting donor and acceptor sites and by adjusting the conjugated length, then optimizing r_{gn} and Δr.

In the future, systematic studies of the relationship between optical nonlinearity and the wavefunction must be done by simulating various types of one-dimensional conjugated molecules.

IV. CONCLUSIONS

A method of examining the Pockels effect on small thin flakes of organic material has been discussed, and further improvements in the Pockels effect have been investigated using the molecular orbital method. The electro-optic coefficient r_{33} of SPCD crystal estimated by the AC modulation method is 430 pm/V at a wavelength of 633 nm, 6 times larger than the r_{11} of 2-methyl-4-nitroaniline (MNA). To improve the Pockels effect further, artificial molecules with a polydiacetylene structure were designed. By adjusting conjugated lengths and donor- and acceptor-substitution sites in the molecules, a large second-order hyperpolarizability is expected, corresponding to an electro-optic coefficient about $10\times r_{11}$(MNA) at a detuning energy of 0.2 eV.

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