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Nonlinear Optical Properties of Retinal Derivatives

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Retinal derivatives with electron donors or acceptors were synthesized and their second order nonlinear optical properties were investigated by electric field induced second harmonic generation(EFISH) method. Retinal derivatives were found to have large second order optical nonlinearities.

The search for better nonlinear optical materials has been carried out in recent years, which will lead to optical signal processing and optical computing in future. The molecules with intramolecular charge transfer (CT) interactions have been found to have large optical nonlinearities.1) The variation of donor-acceptor pairs, however, is limited to conventional substituents, for example, amino, hydroxy, nitro and cyano groups. On the contrary, a long conjugated carbon chain is advantageous in nonlinear optics, since the nearly quadratic dependence of second order hyperpolarizabilities on chain length was predicted by the Equivalent Internal Field (EIF) model2) and was confirmed by the experiments with usual aromatic molecules.3)

In this point of view, long conjugated chain molucules are attractive systems because of their possibilities having very large hyperpolarizabilities. Natural occurring carotenoid compounds are very useful as starting materials, since long conjugated chain molecules are difficult to synthesize from small segments. The nonlinear optical properties of carotenoids themselves have been investigated by several authors, for example second harmonic generation (SHG) in Langmuir-Blodgett film of retinals4) and third harmonic generation (THG) in carotenoids,5) and their advantages to nonlinear optics have been demonstrated.

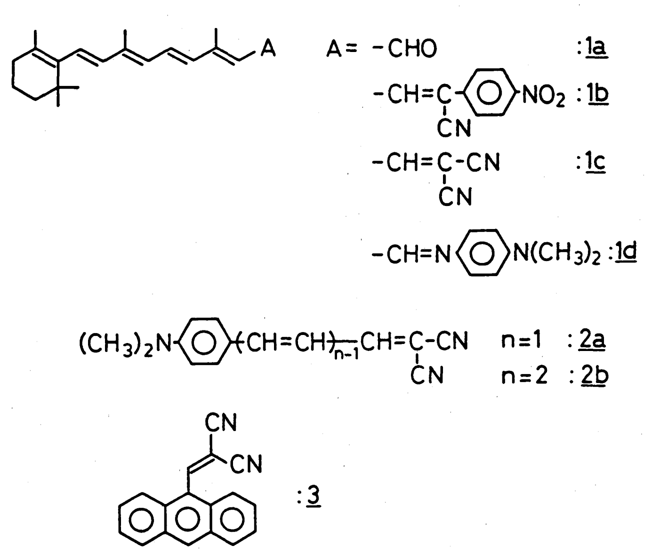

Fig. 1. Molecular structures investigated in the present work.

In the present paper, we have attached electron acceptors to retinal in order to obtain larger optical nonlinearities than carotenoids themselves and investigated the relationship of their nonlinear optical properties with molecular structures.

The molecular structures whose hyperpolarizabilities have been measured are shown in Fig. 1. All the compounds were synthesized in our laboratory from appropriate aldehydes and active methylene compounds such as malononitrile or 4-nitrobenzylcyanide, except for the Schiff base compound (1d), which was synthesized from aldehyde and amine according to the usual method.

The electric field induced second harmonic generation (EFISH) method was used to determine the second order hyperpolarizabilities of molecules. The experimetal setup was similar to that of Garito et al.[6] The fundamental wave (1.06 μm, 1.17 eV) of Nd:YAG laser (Quanta-Ray, DCR-3D, 8ns, 100 kW) was used as a light source. The samples were dissolved in dimethylsulfoxide (DMSO) at the concentrations of 10^{-6} to 10^{-2} mol/l. The product of dipole moment and second order hyperpolarizability ($\mu_0\beta$) was obtained from the concentration dependence of SH intensity and Maker fringe, where re-absorption of SH by molecules and imaginary part of β were taken into account.

The EFISH results are listed in Table 1. There are some compounds with imaginary parts of β, which suggest the effect of two photon resonance,[7] and make β increased. The absorption maximum of 3 (430 nm, 2.88 eV), which is below SH by 0.55 eV, brought small imaginary part of β. The two photon resonance seems to begin at about 0.55 eV below SH.

The introduction of acceptors to retinal unit (1b, 1c) has led to 6 times or more larger $\mu_0\beta$ in real part than retinal itself (1a). This result is

Table1. Second order hyperpolarizabilities and absorption maxima of molecules

Molecule	λmax/nm	Re($\mu_o\beta$)	Im($\mu_o\beta$)
1a	380	230	0
1b	480	1400	3500
1c	470	1300	1500
1d	440	1500	1700
2a	440	620	0
2b	500	3400	3600
3	430	100	80

Hyperpolarizabilities are given in units in 10^{-48}esu.

All samples were dissolved in dimethylsulfoxide.

Re and Im stand for real and imaginary part, respectively.

consistent with EIF model²⁾ and the previous results with usual compounds such as 4-nitroaniline.¹⁾

Since $\mu_o\beta$'s of 4-dimethylamino-4'-cyanostilbene and 4-dimethylamino-4'-nitrostilbene in DMSO solutions were reported to be 820 x 10^{-48}esu and 4200 x 10^{-48}esu respectively³⁾, nitro group is a stronger acceptor than cyano group in nonlinear optics. Therefore 4-nitrophenyl group is expected to be a much stronger acceptor than cyano group. Nevertheless, 4-nitrophenyl derivative 1b had slightly larger $\mu_o\beta$ value than cyano derivative 1c. It suggests that 4-nitrophenyl group is not a suitable acceptor for retinal unit in nonlinear optics, though it is suitable for usual donor groups such as 4-dimethylaminophenyl group.

One should be careful for solvent while comparing $\mu_o\beta$ values, because $\mu_o\beta$ values are reported to change several times by solvent effect.⁷⁾

The Schiff base compound 1d was found to have several times larger $\mu_o\beta$ value than that of retinal itself (1a), which is comparable to that of 1b. However, 1d has electron donating dimethylamino group as well as electron accepting azomethine group, therefore it is difficult to tell which have contributed to the optical nonlinearity.

The anthracene derivative 3 was found to have smaller $\mu_o\beta$ value than the corresponding retinal derivative 1c. Consequently, it leads to reduction of hyperpolarizability in one order of magnitude to involve conjugated carbon chain into an aromatic ring. The reason of smaller $\mu_0\beta$ in 3 is explained by the reduction in charge transfer interaction due to the isolation of π-electrons by a 14-π aromatic ring formation.

Since 2a and 1c have dicyanovinyl group as a common acceptor, 5 double bonds brought a larger $\mu_0\beta$ than dimethylaminophenyl group. Similarly, 1c and 2b have dicyanobutadienyl group as a common acceptor, therefore 4 double bonds brought a smaller $\mu_0\beta$ than dimethylaminophenyl group. Consequently, it suggests that 4.5 double bonds in retinal derivatives have similar effect to 4-dimethylaminophenyl group on nolinear optics.

Since there seems to be no electron donor stronger than dimethylamino group, longer conjugated carbon chains are promising system than that of retinal in order to obtain the molecules with large hyperpolarizabilities, where long conjugated chains should not form aromatic rings but form aliphatic polyene structures.

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