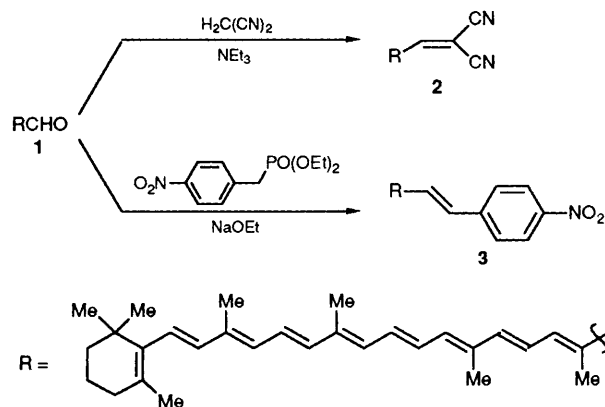


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At present most donor-acceptor nonlinear optical chromophores in their ground-state contain aromatic groups, which from simple resonance structure considerations become quinoidal when the molecule is in its charge-separated state. Investigations on a typical neutral donor-acceptor substituted compound¹ indicate that for a given chain length β is larger when the molecule does not have to lose aromaticity upon charge-transfer polarization. As aromaticity is stabilizing, its

We wished to probe the effects of aromaticity and the introduction of ground- and excited-state dipole moments on both the second- and third-order hyperpolarizabilities of a series of compounds very closely related to the well-studied molecule, β -carotene.¹⁰ Blanchard-Desce and coworkers^{11–13} have investigated the nonlinear optical properties of some



Scheme 1 Synthesis of acceptor-substituted β -apo-8'-carotenoid compounds

Table 1 Selected linear and nonlinear optical properties in chloroform of substituted β -apo-8'-carotenoids in Scheme 1

Compound	λ_{\max}/nm	$\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	$\mu/10^{-18} \text{ esu}$	$\beta/10^{-30} \text{ esu}$	$\beta(0)/10^{-30} \text{ esu}$	$\mu\text{-}\beta/10^{-48} \text{ esu}$
1	476	89 000	6.5	147	104	956
2	566	98 200	7.7	570	337	4389
3	502	95 700	7.0	220	148	1540

related compounds with chain lengths shorter than and equal to β -apo-8'-carotenal, **1** (Scheme 1), substituted with a series of donors and an aldehyde acceptor, and Ikeda and co-workers¹⁴ have examined a series of retinal-derived compounds. In this contribution we report on the synthesis and second-order nonlinear optical properties of β -apo-8'-carotenal derivatives with terminal acceptor substituents, whose structures are more closely related to β -carotene than those in the previous studies.^{11–14}

The new compounds were readily synthesized (Scheme 1) using standard Knoevenagel¹⁵ conditions for the synthesis of **2** and Wadsworth–Emmons¹⁶ conditions for **3**. The compounds were purified by chromatography on silica, recrystallized and then characterized by UV–VIS, ¹H and ¹H COSY NMR and mass spectroscopy, as well as elemental analysis.† β values were measured in chloroform solution by EFISH using 1.907 μm fundamental radiation.^{6,7}

Table 1 shows values of the optical absorption maximum (λ_{\max}), the extinction coefficient (ϵ), the dipole moment (μ), first hyperpolarizability (β), the zero frequency form of β [$\beta(0)$] corrected for dispersion using a two-state model¹⁷ and the dot product of β and μ ($\mu\text{-}\beta$), which of interest in poled polymer applications. Although these chromophores have no heteroatom donor, their hyperpolarizabilities are reasonably large, with each having a $\beta(0)$ significantly larger than that of the prototypical stilbene compound 4-*N,N*-dimethylamino-4'-nitrostilbene (DANS) [$\beta(0) = 55 \times 10^{-30} \text{ esu}$]. These rather large nonlinearities can be explained by the large intrinsic polarizability of the extended π -electron system. For polyenes, the HOMO–LUMO gap decreases with increasing conjugation length resulting from the energy of the LUMO being lowered and that of the HOMO being raised. In molecular orbital terms, a donor is a high lying occupied orbital, and thus, in long polyenes, the HOMO itself can act as a donor. As the length of the conjugated chain is increased, the HOMO becomes a more effective donor.

Dicyanovinyl groups are stronger acceptors than aldehydes, and this is reaffirmed by compound **2** having a $\beta(0)$ value of over three times greater than for compound **1**. Nitro groups are also stronger acceptors than aldehydes, but on looking at the $\beta(0)$ value for **3** it is not substantially greater than for **1**,

even although it is 6 atoms longer. This low value can be explained by the nitrophenyl acceptor containing a stabilizing aromatic group which hinders the formation of the charge-separated form of the molecule and hence reduces the polarizability and therefore $\beta(0)$.¹⁸

In summary, $\beta(0)$ values of aldehyde **1**, dicyanovinyl **2** and nitrophenyl **3** acceptor-substituted β -apo-8'-carotenal chromophores measured by EFISH, are all large in view of the fact that no conventional donor is present, with **2** giving the largest value. The aromatic ring in compound **3** may hinder the formation of the charge-separated state, causing $\beta(0)$ to be greatly reduced.

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† Characterizing data for **2**: Yield, 15%. M.p., 184–186 °C. ¹H and ¹H COSY NMR (CD₂Cl₂) δ 1.03 (s, 6H), 1.47 (m, 2H), 1.62 (m, 2H), 1.72 (s, 3H), 1.99 (s, 3H), 2.00 (s, 3H), 2.02 (s, 3H), 2.03 (m, 2H), 2.27 (s, 3H), 6.15 (d, 1H, *J* 15.86 Hz), 6.18 (d, 1H, *J* 10.40 Hz), 6.24 (d, 1H, *J* 16.04 Hz), 6.31 (d, 1H, *J* 11.93 Hz), 6.39 (d, 1H, *J* 14.96 Hz), 6.54 (d, 1H, *J* 11.63 Hz), 6.64 (dd, 1H, *J* 14.76, 11.54 Hz), 6.68 (dd, 1H, *J* 13.91, 12.18 Hz), 6.78 (dd, 1H, *J* 14.93, 11.43 Hz), 6.86 (dd, 1H, *J* 13.75, 12.12 Hz), 6.80 (d, 1H, *J* 11.56 Hz), 6.81 (d, 1H, *J* 14.86 Hz), 7.26 (s, 1H). Satisfactory elemental analyses were obtained. High-resolution EIMS, *m/z* calc. for C₃₃H₄₀N₂: 465.3270. Found: 465.3243.

Characterizing data for **3**: Yield, 37%. M.p., 296–300 °C. ¹H and ¹H COSY NMR (CD₂Cl₂) δ 1.03 (s, 6H), 1.47 (m, 2H), 1.62 (m, 2H), 1.72 (s, 3H), 1.98 (s, 3H), 1.99 (s, 3H), 2.00 (s, 3H), 2.03 (m, 2H), 2.07 (s, 3H), 6.14 (d, 1H, *J* 15.90 Hz), 6.16 (d, 1H, *J* 9.08 Hz), 6.21 (d, 1H, *J* 16.22 Hz), 6.28 (d, 1H, *J* 10.61 Hz), 6.35 (d, 1H, *J* 10.49 Hz), 6.37 (d, 1H, *J* 14.87 Hz), 6.47 (d, 1H, *J* 11.50 Hz), 6.52 (d, 1H, *J* 14.84 Hz), 6.63 (d, 1H, *J* 15.95 Hz), 6.66 (dd, 1H, *J* 10.74, 14.18 Hz), 6.70 (m, 1H), 6.71 (dd, 1H, *J* 11.26, 14.62 Hz), 6.72 (dd, 1H, *J* 10.80, 14.23 Hz), 7.09 (d, 1H, *J* 15.77 Hz), 7.56 (dm, 2H, *J* 8.61 Hz), 8.16 (dm, 2H, *J* 8.83 Hz). Satisfactory elemental analyses were obtained. High resolution EIMS, *m/z* calc. for C₃₇H₄₅NO₂: 535.3442. Found: 535.3450.