Push–Pull Polyenes and Carotenoids: Synthesis and Non-linear Optical Properties

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The series of polyenes and carotenoids (**1**)—(**4**) bearing a common donor group and different acceptor groups (**a**)—(**f**) at the ends of the chain, have been synthesized; some of these compounds have been found to display efficient optical second harmonic generation.

Modification of natural carotenoids[1] provides direct access to the molecular engineering of polyolefinic chains yielding molecules of interest for the development of molecular devices or of new materials. Thus, the symmetrically substituted bis-pyridinium carotenoids, the caroviologens, represent an approach to a molecular wire.[2] Unsymmetrical modification by introduction of a donor group D at one end and of an acceptor group A at the other end of the polyenic chain, would yield push–pull carotenoids. Such highly polarizable molecules may display interesting photophysical properties. They may function as electrochromic dyes and polarity probes for membrane potentials,[3] present analogies with the visual pigment retinal in rhodopsin,[4] and yield materials displaying semi-conducting[5] or non-linear optical properties.[6,7] We report here the synthesis of three series of such push–pull polyenes (**1**)—(**3**) and carotenoids (**4**) of increasing length, as well as some of their photophysical properties.

The design of these molecules rests on the combination of an electron donor, a long conjugated chain, and a series of electron acceptor groups. A benzodithia group was chosen as donor; such units are also present in the tetrathiafulvalenes which yield organic metals.[8] The acceptor groups comprise aldehyde (**a**), dicyanomethylene (**b**), pyridine (**c**), *N*-methylpyridinium (**d**), *p*-cyanophenyl (**e**), and *p*-nitrophenyl (**f**). Push–pull ω-dimethylaminocarbonyl polyenes,[9] diphenylhexatriene,[10] and oligoacetylenes[11,12] have been reported.

The benzodithia-polyene-aldehydes (**2a**), (**3a**), and (**4a**) were prepared by condensation of the dialdehydes (**5**), (**6**), and (**7**),[13] respectively, with 1 equiv. of the Wittig or Wittig–Horner[14,15] reagents generated from the corresponding precursors W or WH,[16] by treatment with butyl-lithium in tetrahydrofuran (THF) at −78 °C, or in phase transfer [liquid–liquid (LLPT) or solid–liquid (SLPT)]‡ conditions at room temperature. Polyenes (**2a**)—(**4a**) were isolated and purified by careful chromatography on silica gel under argon (eluent CH_2Cl_2): (**2a**), WH/BuLi (50% yield) or W/LLPT (80% yield), cryst. EtOH, m.p. 179—180 °C; (**3a**), WH/BuLi (30% yield) or W/LLPT (50% yield), cryst. CH_2Cl_2–EtOH, m.p. 197 °C (decomp.); (**4a**), W/LLPT (30% yield) or WH/SLPT (50% yield), cryst. CH_2Cl_2–EtOH, m.p. 216 °C (decomp.).

Reaction of (**1a**)[19]—(**4a**) with malononitrile (EtOH, catalytic amount of piperidine),[20] gave, respectively, the dicyanomethylene derivatives (**1b**) (98% yield, cryst. EtOH, m.p. 254 °C), (**2b**) [80% yield, cryst. $MeOCH_2CH_2OH$, m.p. 235 °C (decomp.)], (**3b**) (75% yield, m.p. decomp.), (**4b**) (65% yield, m.p. decomp.).

Wittig–Horner condensation of 4-(CH_2POPh_2)pyridine[2] with the aldehydes (**1a**)[19]—(**4a**) in SLPT conditions (NaH, 18-crown-6, THF, room temp.) afforded the 4-pyridyl derivatives (**1c**) (90% yield, cryst. CH_2Cl_2–cyclohexane, m.p. 183 °C), (**2c**) [75% yield, cryst. CH_2Cl_2–EtOH, m.p. 205 °C (decomp.)], (**3c**) [75% yield, cryst. CH_2Cl_2–EtOH, m.p. 230 °C (decomp.)], (**4c**) [50% yield, cryst. $CHCl_3$, m.p. 238 °C (decomp.)].

The methyl iodides (**1d**)—(**4d**) were obtained by treatment of the corresponding pyridine derivatives (**1c**)—(**4c**) with neat methyl iodide at 20 °C. They were purified by crystallization from ethanol.

The reagents (p-CN)$C_6H_4CH_2PO(OEt)_2$ and (p-NO_2)$C_6H_4CH_2PO(OEt)_2$ (ref. 21) were condensed with the aldehydes (**1a**), (**2a**), and (**3a**) in SLPT conditions, to give, respectively, the cyanophenyl and nitrophenyl derivatives: (**1e**), 77% yield, cryst. EtOH, m.p. 201 °C; (**2e**), 90% yield, cryst. EtOH, m.p. 223 °C (decomp.); (**3e**), 75% yield, cryst. CH_2Cl_2–EtOH, m.p. 230 °C (decomp.); (**1f**), 80% yield, cryst. EtOH, m.p. 212 °C; (**2f**), 70% yield, cryst. CH_2Cl_2–EtOH, m.p. decomp.; (**3f**), 70% yield, cryst. CH_2Cl_2–EtOH, m.p. 230 °C (decomp.).§

Compounds (**1**)—(**4**) exhibit broad and intense absorption bands in the visible region, characteristic of internal charge transfer[22,23] (Table 1). Each series (**a**)—(**f**) displays a bathochromic effect with increasing number of conjugated double bonds as reported for diphenylpolyenes[24] and carotenoids.[25] The absorption spectra of most compounds also show solvatochromism. One may expect the conjugated chain to play the role of a molecular wire connecting the D and A groups, as in the caroviologens[2] and in push–pull oligoacetylenes.[11,12]

During the last fifteen years, non-linear optics has been emerging as a promising area for optical signal processing.[26]

Table 1. Electronic absorption data for compounds (**1**)—(**4**), (**a**)—(**f**).[a]

	$\lambda_{max.}$/nm (log ε)			
	(**1**)	(**2**)	(**3**)	(**4**)
(**a**)	372 (4.23)	456 (4.66)	466 (4.68)	500 (4.88)
(**b**)	446 (4.66)	562 (4.75)	540 (4.58)	588 (4.83)
(**c**)	394 (4.60)	457 (4.77)	452 (4.76)	505
(**d**)[b]	476 (4.54)	534 (4.66)	493 (4.68)	540
(**e**)	410 (4.58)	465 (4.80)	457 (5.30)	
(**f**)	452 (4.40)	488 (4.60)	467 (4.88)	

[a] In chloroform solution at 20 °C. [b] In dimethyl sulphoxide solution at 20 °C.

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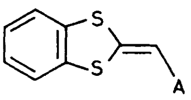
† ER 285 of the CNRS.

‡ LLPT conducted in conditions (CH_2Cl_2–NaOH) similar to those used for the condensation of PhCHO with $PhCH_2PPh_3{}^+Cl^-$, see ref. 17. SLPT conducted in conditions (NaH, 18-crown-6, THF) similar to those used for the reaction of PhCHO with $PhCH_2PO(OEt)_2$, see ref. 18.

§ All new compounds had spectral (${}^1H$ n.m.r., i.r.) and microanalytical properties in agreement with the assigned structures. Determination of the melting points by differential scanning microcalorimetry indicated that some compounds decomposed immediately after melting set in, while others decomposed before or at melting (m.p. decomp.). (**2f**) showed correct spectra but was rather unstable and difficult to purify.



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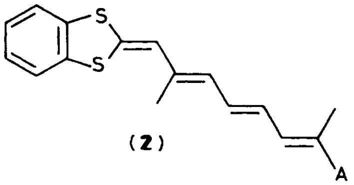

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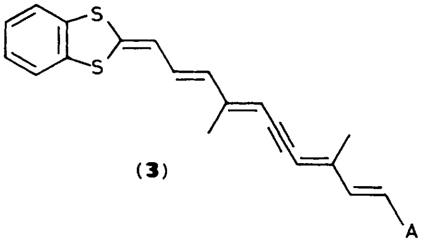

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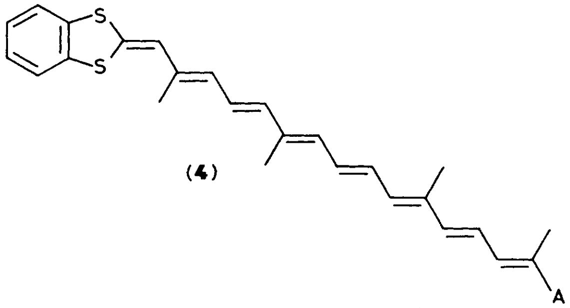

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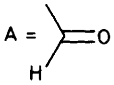

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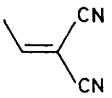

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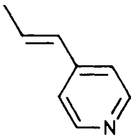

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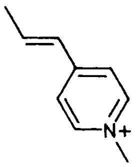

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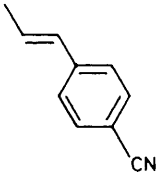

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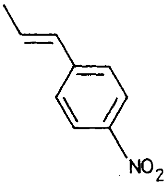

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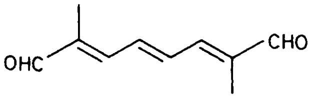
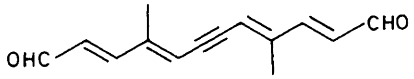
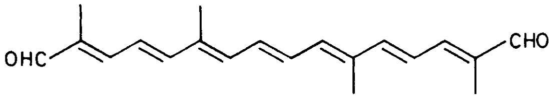


(5)



(6)



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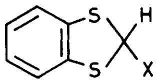

W ; X = $\mathrm{PPh_3^+\ BF_4^-}$
WH ; X = $\mathrm{PO(OEt)_2}$

Some organic materials exhibit efficiencies at least one order of magnitude above that of classical inorganic materials such as potassium dihydrogen phosphate (KDP).[6,7] Moreover, they possess comparatively high damage thresholds to laser irradiation and a great variety of available chemical modifications. Experimental results as well as theoretical models[7] have shown that molecules containing highly disymmetric conjugated π electronic systems (*i.e.* conjugation and intramolecular charge transfer, as in 4-nitroaniline for instance) exhibit efficient second-order effects such as second harmonic generation. The second-order polarizability or hyperpolarizability β depends on the length of push–pull conjugated π systems.[27,28] An extension of the conjugation path between the D and A groups results in a substantial increase in the value of β; for example, 4-amino-4′-nitro-*trans*-stilbene has a hyperpolarizability which is at least 10 times that of 4-nitroaniline.[29] Push–pull polyenes have a much larger hyperpolarizability than the corresponding polyphenyls.[28]

We investigated the second harmonic generation (SHG) efficiencies of the series of push–pull polyenes (**1**)—(**4**) increasing in length up to nine conjugated double bonds, by means of the Kurtz powder technique.[30] This is a convenient method for screening large numbers of powdered materials for non-linear optical activity, by observing the light emitted from a powdered sample on laser irradiation. The SHG efficiency was determined relative to reference compounds. The power samples of compounds (**1**)—(**4**) were irradiated at 1.06 μm and/or 1.32 μm with an home-made Q-switched YAG : $\mathrm{Nd^{3+}}$ laser delivering i.r. pulses having the following characteristics: energy per pulse a fraction of mJ, pulse duration 10 ns at 1.06 μm, and 70 ns at 1.32 μm, repetition rate 10 Hz. The SHG powder efficiences were calibrated with respect to the second harmonic signal (wavelength 530 nm for irradiation at 1.06 μm and 660 nm for irradiation at 1.32 μm) emitted by a standard urea powder.[31]

The results (presented in Table 2) must be taken cautiously because SHG powder efficiency depends on both the molecular (β) and the bulk polarizabilities (best represented by the second-order non-linear susceptibility $\chi^{(2)}$, a macroscopic parameter). The ability of a *solid* compound to generate SH

Table 2. Second harmonic generation efficiencies of powdered samples of compounds (**1**)—(**4**), (**a**)—(**f**).[a]

	(**1**)		(**2**)		(**3**)		(**4**)	
(**a**)	—	0	f	0	f	0	0	0
(**b**)	—	0	ε	0	—	0	0	0
(**c**)	f	0	5	0	10	30	12	13
(**d**)	0	0	ε	0	ε	0	—	0
(**e**)	f	0	f	0	f	0		
(**f**)	1	13	0	0	0	0		

[a] For each compound the second harmonic signal is given relative to that of urea for irradiation at 1.06 μm (left) and 1.32 μm (right); f: two-photons fluorescence; ε: SHG signal between those of KDP and urea; 0: no detectable signal; —: not measured.

radiation depends on the β value but also indicates that it crystallizes in a non-centrosymmetric space group, since second-order susceptibility vanishes for centrosymmetric crystals. Compounds of series (**b**), (**c**), (**d**), and (**f**) gave SHG effects, (**2c**), (**3c**), (**4c**), and (**1f**) displaying by far the most intense signals, much stronger than that of urea. The compounds of series (**c**), containing a pyridine ring as acceptor, exhibit both large SHG efficency and a chain length dependence. The lack of SHG for (**2f**) and (**3f**) could be caused by bulk effects. Several compounds [the aldehydes (**2a**), (**3a**) and the phenylcyanides (**2e**), (**3e**)] showed an interesting luminescence corresponding to the absorption of two photons at 1.06 μm and the emission of red light. Taking into account the possible annihilation of SHG by bulk effects, the present results, albeit qualitative, indicate that the push–pull polyenes and carotenoids (**1**)—(**4**) are good candidates for further optical studies, such as d.c.-electric field induced SHG (allowing quantitative measurement of β),[32] as well as incorporation into organized assemblies.

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