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Third-Order Nonlinear Optical Response of Some Tetrasubstituted Cumulenes

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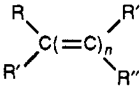
Third-order nonlinear optical properties of several tetrasubstituted cumulenic compounds were studied using subpicosecond degenerate four-wave mixing (DFWM) in the forward geometry. Mean values of the second molecular hyperpolarizability $\langle \gamma \rangle$ of an ensemble of randomly oriented molecules were obtained by comparing the conjugate signal from a solution of the molecules with the signal from a reference liquid (THF). The estimated effective values of $\chi^{(3)}$, the third-order optical susceptibility, of cumulenic compounds with extended conjugation of the π-electron system are high, partly due to the strong nonlinear optical response of the molecules in their ground state and partly due to the resonance enhancement at the operating wavelength, 602 nm.

Introduction

In the past there has been considerable interest in the third-order nonlinear optical properties of organic compounds with extended π-conjugation.[1] Polyenes,[2] polyenynes (polydiacetylenes),[3] polyynes,[4] aromatic and heteroaromatic conjugated polymers,[5] and miscelaneous structures (e.g., poly(*p*-phenylenevinylene),[6]) have been studied experimentally. Ab initio calculations of longitudinal polarizabilities have been performed for the case of cumulenes.[7,8] It follows from the calculations that cumulenes should possess high polarizability and are thus promising candidates for efficient optically nonlinear compounds. Preliminary experimental study of the third-order optical nonlinearity of some cumulenes has been reported by Ermer et al.[9]

In this paper, attention is focused on the third order nonlinear optical behavior of some cumulenes having general formula


$$\mathrm{RR'C(=C)_{\mathit{n}}R''R'''}$$

where R-R‴ are aryl or *tert*-butyl groups and *n* is 3 (butatrienes) or 5 (hexapentaenes). Synthesis and basic properties of such cumulenes have been reviewed in the past.[10,11] These "rodlike" compounds possess two mutually perpendicular, nearly "independent", π-electron systems.[11] It follows from X-ray measurements[12] that the C=C bonds with an odd *n* are a little longer than those with an even *n* (bond alteration is about 0.007 nm), both still being shorter than a "standard" double bond (0.134 nm). From a comparison of the visible spectra of 1,1,6,6-tetraphenylhexapentaene (compound VII in Scheme I) (the first maximum of absorption at λ_{max} = 480 nm) with that of 1,1,6,6-tetraphenylhexa-1,3,5-triene (λ_{max} = 380 nm)[10] it follows that tetraarylcumulenes with *n* = 5 possess better effective conjugation (narrower bandgap) than the analogous polyenes with the same number of carbon atoms.

A great variety of compounds with cumulenic systems are described in the literature.[10,11] For this study, a representative "set" of cumulenes is chosen for establishing a correlation between structural and/or electronic features of these compounds and their third-order nonlinear optical response.

For the characterization of the third-order nonlinear optical properties, the effective value of the second hyperpolarizability, $\langle \gamma \rangle$, of each compound was determined using the femtosecond degenerate four-wave mixing (DFWM) techniques. Experiments were performed at the wavelength of 602 nm, with the compounds dissolved in THF. Conjugate signals from the solutions were compared with those from a reference liquid.

Experimental Section

1. **Synthesis.** Propynols (I) and butynediols (II) needed for the preparation of cumulenes IV-XV were synthesized using some modifications of already described procedures.[9,10]

Propynols I were prepared by rapid reaction of corresponding ketones with a slight excess of commercially available sodium

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(1) *Materials for Nonlinear Optics: Chemical Perspectives*; Marder, et al., Eds.; ACS Symp. Series No. 455, 1991.

(2) Sinclair, M.; Moses, D.; Akagi, A.; Heeger, A. J. in *Nonlinear Optical Effects in Organic Polymers*; Messier, J., Kajzar, F., Prasad, P., Ulrich, D., Eds.; NATO ASI Series; Kluwer Academic Publishers: Dordrecht, 1989; p 29.

(3) Rao, D. N.; Chopra, P.; Ghoshal, S. K.; Swiatkiewicz, J.; Prasad, P. N. *J. Chem. Phys.* **1986**, *84*, 7049.

(4) Perry, J. W.; Stiegman, A. E.; Marder, S. R.; Coulter, D. R. In *Organic Materials for Non-Linear Optics*; Hann, R. A., Bloor, D., Eds.; Royal Society of Chemistry: London, 1989; p 189.

(5) Zhao, M. T.; Singh, B. P.; Prasad, P. N. *J. Chem. Phys.* **1988**, *89*, 5535.

(6) Singh, B. P.; Prasad, P. N.; Karasz, F. *Polymer* 1988, *29* (11), 1940.

(7) Dory, M.; Bodart, V. P.; Delhalle, J.; Andre, J.-M.; Bredas, J. L. In *Nonlinear Optical Properties of Polymers*; Heeger, A. J.; Orenstein, J.; Ulrich, D. R., Eds.; Materials Research Society, Pittsburgh, 1988; p 239

(8) Chopra, P.; Carlacci, L.; King, H. F.; Prasad, P. N. *J. Phys. Chem.* **1989**, *93*, 7120.

(9) Ermer, S. P.; Lovejoy, S. M.; Leleng, D.; Aetman, J. C.; Avon, K. P.; Spitzer, R.; Hansen, G. A. *SPIE Proceedings* **1990**, *1337*, 89.

(10) Cadiot, P.; Chodkiewicz, W.; Rauss-Godineau, J. *Bull. Soc. Chim. Fr.* **1961**, 2176, and references therein.

(11) Fischer, H. In *The Chemistry of Alkenes*; Patai, S., Ed.; Interscience Publishers: London, 1964; p 1027, and references therein.

(12) Irngartinger, H.; Goetzmann, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 340.

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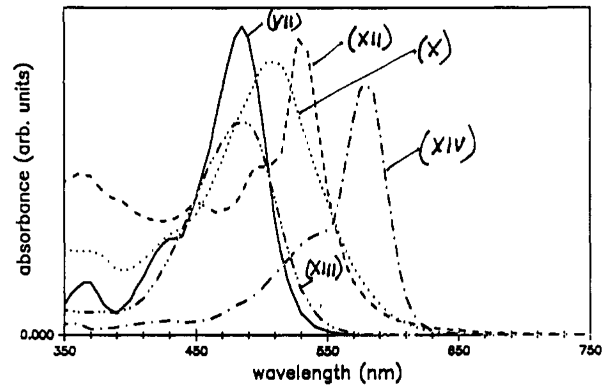

Figure 1. Visible absorption spectra of cumulenes in THF solutions (compound, curve, ϵ at λ_{max} in L cm^{-1} mol^{-1}): VII, solid 107 000; XII, dash 10 900; X, dot 19 200; XIV, dash–dot 118 000; XIII, dash–dot–dot 44 100.

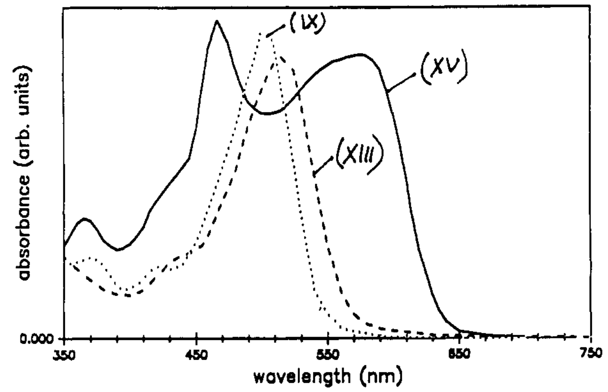

Figure 2. Visible absorption spectra of cumulenes in THF solutions (compound, curve, ϵ at λ_{max} in L cm^{-1} mol^{-1}): XV, solid 59 600 (from the first maximum at 458 nm); IX, dot 32 300; VIII, dash 22 000.

acetylide (Aldrich) in dry DMF at 0–20 °C. After chromatography (in CH_2Cl_2), I were obtained as viscous oils which slowly crystallized. TLC showed a single spot; melting points were in agreement with published data.[10,13]

Symmetric butynediols II needed for the preparation of IV and V were prepared by a 5 h of treatment of corresponding ketones with a 2-fold excess of sodium acetylide in THF at room temperature. Under these conditions, addition of sodium salt of the already formed propyneol to ketone competes with the addition of sodium acetylide, and butynediols II are formed in a "single-pot" synthesis. Asymmetric butynediol necessary for the cumulene VI was obtained using a reaction of propynol I (from *p*-nitrobenzophenone) with *p*-(dodecyloxy)benzophenone in the presence of sodium amide in THF.

Other intermediates and all the cumulenes were prepared in accordance with published procedures.[10,12,13] Purification of final cumulenes involved column or flash chromatography and subsequent recrystallizations. In the case of XIV, which is sparingly soluble in any solvent, thorough extraction of the crude product with cold ether was found to be an efficient purification method.

All cumulenes showed desired IR and UV–vis spectra[10,12] (Figures 1–3) and gave a single spot in various TLC elution systems. Melting points, where lower than 300 °C, were in reasonable agreement with the published data[10,11] but darkening (decay) was frequently observed above 150 °C. Compound XIV was found to be unstable at ambient temperature (some changes in the UV–vis spectra of its solutions in THF or CH_2Cl_2 were observed after several days). When stored in a refrigerator (in solid state), no changes in the spectra of this cumulene were seen even after 5 months.

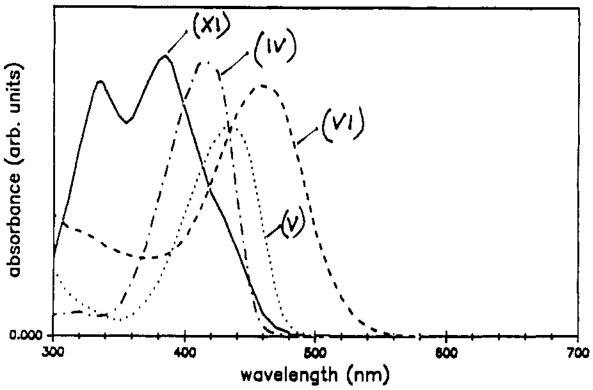

Figure 3. UV–vis absorption spectra of cumulenes in THF solutions (compound, curve, ϵ at λ_{max} in L cm^{-1} mol^{-1}): XI, solid 9 700; VI, dash 24 700; IV, dash-dot 53 100; V, dot 48 800.

2. Apparatus and the Method of Measurement. Subpicosecond, approximately 400 fs wide, pulses were generated by a laser system in which the pulse train from a mode-locked Nd: YAG laser (Spectra Physics Model 3800) were compressed by a pulse compressor (Spectra Physics Model 3690), frequency doubled and used to synchronously pump a dye laser (Spectra Physics Model 375 B). After amplification by a three-stage amplifier (Quanta-Ray PDA-1) pumped at 30 Hz with a Nd: YAG laser (Quanta-Ray DCR-2A), the mean power of the beam of the output pulses was about 10 mW. The operating wavelength was 602 nm, the beam was linearly polarized with the electric vector in the vertical direction.

By the use of two beam-splitters, two pump beams of equal intensity and one weaker probe beam were separated and used in the DFWM experiments. Sample solutions were contained in a glass cuvette (1 mm inner thickness, i.e., more than 10 times the width of the pulses).

Phase conjugate pulse signals were detected by a fast photodiode connected to a digital boxcar averager (EG&G PAR Model 4400). Another photodiode and another channel of the averager were used for simultaneous monitoring of the input pulses.

The experiments were carried out with a setup for the DFWM in the backward geometry, a common arrangement described before.[3,5,14] The two pump beams entered the solution at a small angle through one wall of the cuvette; the probe beam was incident from the opposite wall and in a direction antiparallel to one of the pump beams. The phase conjugate signal was then produced in a direction antiparallel to the other pump beam. The backward geometry, used with success for nonabsorbing materials and for longer pulses, was found inappropriate for measurements on substances which show resonance enhancement, as it artificially favors the DFWM contribution due to the excited state population grating. The main problem lies in the fact that the detected signal consists not only of the phase conjugate part from the region where the three input pulses overlap but also from the probe pulse diffracted by the transient grating left behind the pump pulses. This makes it difficult to quantitatively compare the signals from samples showing electronic one-photon or two-photon resonance with those from reference which is nonresonant. For this reason, the study was finally performed in the forward geometry of DFWM.

In the forward geometry the probe beam entered the cuvette from the same side as the two pump beams but its direction lay slightly off the horizontal plane containing the pump beams. The DFWM signal was then observed also off the horizontal plane. This geometry ensures the constancy of the time delay between the two overlapped pump pulses and the probe pulse during their movement through the whole inner part of the cuvette.

The probe pulses were mechanically delayed in order to see the time evolution of the transient grating created by the two pump pulses. To get the effective $\chi^{(3)}$ of a solution containing the molecules of the studied substance, the values of the signal

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(13) Rauss-Godineau, J.; Chodkiewicz, W.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1966**, 2885.

(14) Prasad, P. N.; Swiatkiewicz, J.; Pfleger, J. *Mol. Cryst. Liq. Cryst.* **1988**, *160*, 53.

from the solution and that from the reference were used at the delay corresponding to the maximal signal from the reference.

If we denote the intensity of the pump beams as I_1 and I_2, the intensity of the probe beam as I_3 and that of the DFWM signal as I_4 and if $I_4 \ll I_3$ (which is usually the case) the intensity I_4 may be expressed as[15,16]

$$I_4 \propto G^3(I_1 I_2 I_3/n^4)l^2[\chi^{(3)}]^2 \qquad (1)$$

where l is the interaction length in the sample, n_0 is the linear refractive index of the solution, and G is a correction factor for the reflection and scattering in the sample.

Measuring the intensity I_4 for the sample and that for the reference, knowing the value $\chi^{(3)}{}_{\text{ref}}$ of the reference and keeping the other parameters of the two measurements as unchanged as possible allows one to get the $\chi^{(3)}$ of the sample, using (1). The best way to fulfil the last mentioned condition in solution measurements is to use the solvent as a reference liquid and to work with small concentrations of the solute. In the case of cumulenes, this conditions could be met in a natural way. The substances have very limited solubility and THF appeared to be their best common solvent. For this reason, THF was also chosen as the reference liquid.

In the case of absorbing substances, the intensity I_4 from the sample solution had to be corrected for absorption. The correction factor is known.[17,18] It was only necessary to determine the extinction coefficient by a separate measurement, to know the concentration of the solution and the thickness of the inner part of the cuvette.

As the amplitudes of the individual pulses from the employed system have a very broad distribution, it can not be assumed that the signals I_4 of the reference and of the sample belong to the same input pulse intensity I_0. For this reason, the value of each signal was detected simultaneously with the input pulse monitored. This was repeated at least 500 times at each delay position of the probe pulses. The values of I_4 for both the reference and the sample were found for the same intensity I_0 of the input pulses using the plot of I_4 versus $I_0{}^3$ (as I_1, I_2, and I_3 are all proportional to I_0, $I_4 \propto I_0{}^3$).

Two facts should be mentioned here. First, (1) is valid for intensities, whereas the measurements are performed with very short pulses and, in fact, not the intensity but the energy of pulses is recorded by the detectors. However, the intensity around the maximum of a pulse, which gives the main contribution to the measured signal, may be taken as proportional to the pulse energy as long as the shape of the pulses remains the same. Experimentally observed behavior supports this assumption. Second, (1) is valid for the nonresonant response of the studied material. However, it appeared in the experiments that even for highly absorbing cumulenes in which the resonance enhancement was considerable, the relation $I_4 \propto I_0{}^3$ was valid around the maximum of the dependence of the sample signal on the delay time.

Results

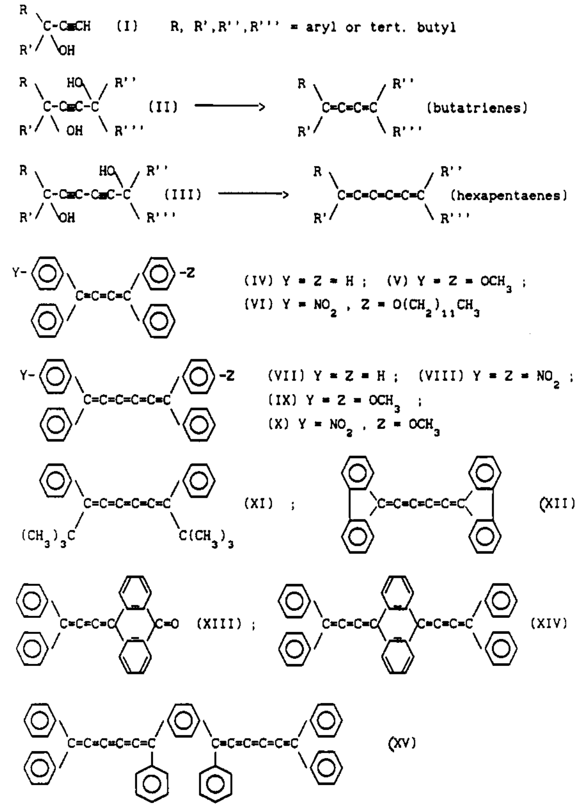
For each studied compound, measurements were performed at several different concentrations. The evaluation of the results was done by the previously described method.[5] The value of the orientationally averaged second hyperpolarizability $\langle\gamma\rangle$ was obtained from the concentration dependence of the ratio $I_4/I_{4\text{ref}}$ by a least-squares fitting method. It was assumed that the molecules of the solvent and those of the solute contribute additively to the effective value of $\chi^{(3)}$ of the solution and that the Lorentz local field factor was applicable.

Table I. Optical and Third-Order Nonlinear Properties of Tetrasubstituted Cumulenes[a]

compound	$\lambda_{\max}$ (nm)	ϵ at 602 nm (L cm^{-1} mol^{-1})	$\langle\gamma\rangle$ (esu)
IV	417	below resolut	-3×10^{-33}
V	440	below resolut	-7×10^{-33}
VI	460	below resolut	-9×10^{-34}
VII	480	18	-1×10^{-32}
VIII	517	780	-1×10^{-33}
IX	505	140	-4×10^{-33}
X	507	1200	-3×10^{-32}
XI	386	below resolut	-1×10^{-36}
XII	535	600	-2×10^{-32}
XIII	485	16	-1×10^{-33}
XIV	580	48500	-4×10^{-31}
XV	458, 576	40700	-3×10^{-31}

[a] The estimated values are based on the assumption that for THF, the $\chi^{(3)}{}_{\text{THF}} = +3.7 \times 10^{-14}$ esu.

Scheme I



The results obtained for the studied cumulene compounds are presented in Table I. The first column of the table contains the number corresponding to a compound in Scheme I. The second column lists the wavelengths of the lowest energy UV-visible maxima in the absorption curves which characterize the optical bandgaps of the compounds. The third column contains the values of the extinction coefficients of the compounds at the operating wavelength, 602 nm. The next column gives the values of $\langle\gamma\rangle$, the mean effective value of the second optical hyperpolarizability. The value includes the effective sum of all contributions to the nonlinearity at a delay time at which the overlap of all the three input pulses in the solution is the best. The values were calculated on the assumption that $\langle\gamma\rangle$ of THF, the reference in all our measurements, is equal to $+1.5 \times 10^{-36}$ esu, which corresponds to $\chi^{(3)}_{\text{THF}} = +3.7 \times 10^{-14}$ esu. The latter value has been accepted in this laboratory as the most probable

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[15] Fisher, R. A. *Optical Phase Conjugation*; Academic Press: New York, 1983.

[16] Prasad, P. N. In *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N.; Ulrich, D. R., Eds.; Plenum Press: New York, 1988.

[17] Caro, R. G.; Gower, M. C. *IEEE J. Quantum Electron.* **1982**, *QE-18*, 1376.

[18] Zeldovich, Y.; Pilpetsky, N. F.; Shunov, B. *Principles of the Phase Conjugation*; Springer-Verlag: Berlin, 1985.

effective value after a number of comparative experiments with different liquids.[19]

Discussion

Extended delocalization of π-electrons is considered to be one of the most important features of an organic compound which contributes to its high third-order optical nonlinearity.[20,21] In cumulenes delocalization of π-electrons, whose extent is reflected in the position of the longest-wavelength absorption maximum (giving the "bandgap"), is influenced by a number of factors (length of cumulene system, type of the substituents, steric arrangement, etc.). Unfortunately, direct correlation of the delocalization length and/or of the structure with the observed third-order nonlinear optical response is complicated by the presence of resonance enhancement of the response in many cases.

In fact, the structure and nonlinear optical properties of only those compounds can be compared which do not absorb light at the measuring wavelength of 602 nm: IV, V, VI, and XI (see Table I). The third-order nonlinear optical response of diaryl-substituted hexapentaene (XI) is much lower than that of tetraaryl-substituted butatrienes IV, V, and VI. Notably, the position of the bandgap is at about 340 nm for hexapentaenes with fully aliphatic substitution,[11] and at 386 nm for XI and at 480 nm for VII. This comparison reveals a large contribution from aromatic substituents to the delocalization length. It follows from the X-ray measurements of IV,[12] that only two phenyl groups (one on each side of a cumulene), having planes of rings at angles of 16.4 and 28.2° with respect to the plane of the cumulene "odd" π-electron system, contribute significantly to the conjugation, whereas the other phenyls lay at adverse angles of 51.3 and 42.5°. Also in solution, the prevailing conformations of the tetraphenyl-substituted butatrienes or hexapentaenes are probably highly nonplanar. Exact geometry of XI is not known but one can judge from the position of the bandgap that the phenyl groups of this compound influence the length of conjugation only slightly, probably due to the steric hindrances caused by bulky tertiary butyl groups. Actually, the small value of $\langle\gamma\rangle$ of XI is close to the calculated value for unsubstituted ("hydrogen substituted") hexapentaene.[22]

If aromatic rings are substituted by electron-releasing methoxy groups as in (V), some red shift in λ_{max} is observed compared to the unsubstituted tetraphenyl butatriene. One could expect that the change in the electron density of a conjugated system caused by this substitution will have some influence on the optical nonlinearity. In special type "push-pull" molecules, represented by VI, the distribution of electron density is asymetric which also may change the nonlinear properties. As can be seen (Table I), however, the enhancement of the third-order nonlinear optical response caused by substitution in V is only small and the "push-pull" compound shows even some decrease of the signal.

All other cumulenes investigated in this study absorb light at the measuring wavelength and their nonlinear optical response is resonantly enhanced. The enhancement of $\langle\gamma\rangle$ increases with increasing extinction at 602 nm: XIV > XV > X > XII > IX > VIII = XIII (with only one exception represented by hexapentaene VII). In these cases, it is difficult to draw any correlation between the molecular structure and nonlinear optical response.

In inorganic materials, resonant third-order optical processes provide the most effective nonlinearity.[23] It seems that the situation is similar for the highly absorbing cumulene compounds (Table I). Even with the subpicosecond pulses, the resonance contribution cannot be separated from the electronic nonlinear response of the molecules in their ground state using the time delay of the probe pulse. From the time-resolved measurements one can only observe that the contribution caused by the transient grating of excited molecules persists for longer time delays.

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(19) Samoc, A.; Samoc, M.; Prasad, P. N.; Willand, C. S.; Williams, D. J. Nonlinear optical properties of halomethanes studied by subpicosecond degenerate four-wave mixing and electric-field-induced second harmonic generation.

(20) Agrawal, G. P.; Cojan, C.; Flytzanis, C. *Phys. Rev.* **1978**, *B17*, 776.

(21) Prasad, P. N. In *Organic Materials for Non-Linear Optics*; Hann, R. A., Bloor, D., Eds.; Royal Society of Chemistry: London, 1989; p 264.

(22) Preliminary results of ab initio calculation made in this laboratory.

(23) *Optical nonlinearities and instabilities in semiconductors*; Haug, H., Ed.; Academic Press: London, 1988.