# Synthesis, (Non)Linear Optical and Redox Properties of a Donor-Substituted Truxenone Derivative

**Christoph Lambert,* Gilbert Nöll, Elmar Schmälzlin, Klaus Meerholz, and Christoph Bräuchle**

**Abstract:** A two-dimensional NLO chromophore (**7**) with three donor-substituted branches and truxenone as the central coupling unit was synthesised from tribromotruxenone by Stille coupling with *N*,*N*-di(4-methoxyphenyl)-4′-(tributylstannylethynyl)phenylamine. UV/visible spectroscopy and hyper-Rayleigh scattering measurements prove the truxenone moiety to be a far stronger electron acceptor than, for example, a nitro group. In addition, coupling of excited states leads to an enhanced quadratic hyperpolarisability of **7** compared with one-dimensional reference chromophores. The large redox-potential separation of about 400 mV of the three reductive waves in the cyclic voltammetry also indicates strong electronic coupling of the truxenone unit. Semiempirical computations at AM1-CI level were used to explain the strong coupling; these calculations also suggest a quartet high-spin state for the truxenone trianion. UV/visible spectroelectrochemical investigations of the oxidation and the first reduction of **7** show that both processes weaken the CT excitation so as to modulate the NLO properties.

**Keywords:** cross coupling · cyclic voltammetry · cyclotrimerisation · nonlinear optics · semiempirical calculations

## Introduction

In conventional push–pull-substituted, nonlinear optic (NLO) chromophores the quadratic nonlinearity is associated with a one-dimensional optical charge transfer (CT) along the molecular axis.[1] In these systems, the magnitude of the first order hyperpolarisability is directly related to the inverse square of the absorption CT energy.[2] Hence, the lower the CT excitation is, the higher is the hyperpolarisability. This efficiency–transparency trade-off makes red-absorbing chromophores practically useless for, for example, frequency-doubling applications, due to self absorption of light of the second-harmonic generation (SHG). The search for better, more efficient and at the same time more transparent NLO chromophores has lead to the development and investigation of new, alternative chromophore types during the recent years.[3] One promising strategy is to extend the charge-transfer dimension from one to two or even to three dimensions.[4–7] Compared with conventional dipolar chromophores with second-order nonlinear optical properties, two- and three-dimensional (2D and 3D) chromophores with $C_3$, $D_3$ or $T$ symmetry[6, 7] (often termed octopolar) have several advantages: they are inherently more transparent, since the lack of a dipole moment often results in negligible solvatochromism; the coupling of excited states can lead to enhanced nonlineartities compared with one-dimensional (1D) reference chromophores at practically no cost of transparency; the zero dipole moment should enhance the chance of non-centrosymmetric space groups in crystalline materials, a necessity for practical applications.[4, 8]

Recently, we have synthesised and investigated 1D and 3D phosphonium ions with *weakly* interacting chromophore branches and we found the above mentioned enhancement of quadratic nonlinearity.[7d] In the present study, donor branches were connected with a *strongly* coupling central electron-acceptor unit in order to investigate the effect on the quadratic hyperpolarisability. Wolff et al.[6l] have used 1,3,5-triazine for this purpose and achieved high nonlinearities with very transparent chromophores. Other, more coloured examples are crystal violet[6d,e,h,k] or a donor-substituted triphenylcyclopropenyl cation.[6e]

We chose truxenone (**1**) as the central connecting moiety because it should be a good electron acceptor, and its $C_{3h}$

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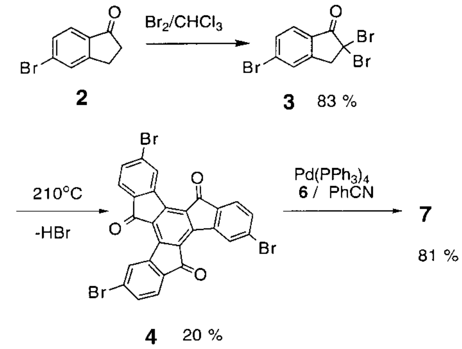
symmetry allows the connection of three chromophore branches. In addition, the planar π-electron system of the truxenone moiety might lead to strong electronic coupling of CT excitations involving the attached substituents.

Since the first synthesis of truxenone in 1877 by Gabriel and Michael,[9] a large number of papers have been devoted to truxenone syntheses, of which the most straightforward methods have been achieved by Jonescu.[10] In contrast, attempts to synthesise substituted derivatives have not been very fruitful owing to solubility problems of truxenone and its derivatives, and the concomitant problems of purification.[11] However, very recently some studies again dealt with the synthesis of truxenone derivatives, since they might serve as starting materials for the total synthesis of $C_{60}$.[12] Most of these attempts use the truxenone parent compound and enlarge the carbon skeleton by attack at the C=O double bond. One very recent synthesis by Plater and Praveen[12e] starts from *o*-methylacetophenone followed by a Wirth cyclotrimersisation and subsequent multistep transformation to the truxenone parent compound. It was claimed (though not proven) that in this way ring-substituted derivatives should be obtainable.

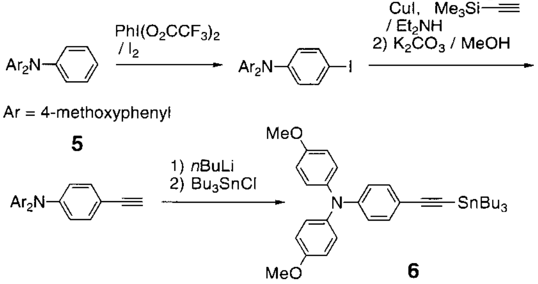
In the following, we describe a new and quite general synthetic route to ring-substituted truxenones. The linear and nonlinear optical properties were investigated by UV/visible and hyper-Rayleigh scattering (HRS); the redox properties were studied by cyclic voltammetry. UV/visible spectroelectrochemical methods were used to assess the spectral properties of the charged chromophore species. Comparison is made with computed values at semiempirical AM1-CI level.

## Results and Discussion

**Synthesis**: Our truxenone synthesis starts from 5-bromoindanone (**2**), which is easily available by known procedures.[13] α Bromination with bromine in $CHCl_3$ leads to the geminal dibromo derivative **3** in high yield. Pyrolysis of **3** at approximately 210 °C gives tribromotruxenone **4** in 20% yield (Scheme 1). The generation of HBr was observed during pyrolysis. Compound **4** is even less soluble in common organic solvents than truxenone itself, but can be recrystallised from boiling nitrobenzene. In order to connect the bromo derivative **4** by a Stille cross-coupling reaction with a donor-substituted tributylstannylacetylene, we synthesised **6** in four steps by Hagihara cross-coupling from known *N*,*N*-di(4-methoxyphenyl)phenylamine **5** (Scheme 2). Cross coupling of **4** and **6** was accomplished by $Pd(PPh_3)_4$ catalysis in benzonitrile. This solvent is decisive for it allows low but sufficient solubility of **4** at elevated temperature in order to promote threefold coupling to **7** in high yield. Other solvents did not dissolve **4** sufficiently (xylene) or lead to oxidative homocoupling of the tributylstannylacetylene (nitrobenzene). The donor-substituted **7** is a dark red solid that readily dissolves in moderately polar solvents such as $CH_2Cl_2$, $CHCl_3$, THF, toluene and benzene.



Scheme 1. Reaction scheme for the formation of **7**.



Scheme 2. Reaction scheme for the formation of **6**.

**Linear and nonlinear optical properties**: The UV/visible spectra of **7** were recorded in $CHCl_3$ ($\lambda_{max} = 509$ nm, $\varepsilon = 34\,300\,\text{M}^{-1}\,\text{cm}^{-1}$), $CH_2Cl_2$ ($\lambda_{max} = 508$ nm) and DMSO ($\lambda_{max} = 500$ nm) and differ only marginally (Figure 1). We attribute the long-wavelength absorption at 509 nm ($CHCl_3$) to a charge transfer from the diarylamine donors to the central truxenone acceptor. For symmetry reasons, this excitation is degenerate (*E*). AM1-CI(6,3) calculations proved this assumption (see Experimental Section).

**Abstract in German:** *Ein zweidimensionaler NLO-Chromophor (**7**), der aus donorsubstituierten Seitenarmen und Truxenon als zentraler Kupplungseinheit besteht, wurde ausgehend von Tribromtruxenon und N,N-Di(4-methoxyphenyl)-4′-(tributylstannylethynyl)phenylamin durch Stille-Kupplung synthetisiert. UV-Vis-Spektroskopie sowie Hyper-Rayleigh-Streuungsmessungen ergeben, daß die Truxenoneinheit ein weit besserer Elektronenacceptor ist als z. B. eine Nitrogruppe. Zusätzlich führt die Kopplung angeregter Zustände zu einer Erhöhung der quadratischen Hyperpolarisierbarkeit von **7**, verglichen mit eindimensionalen Referenzchromophoren. Die großen Potentialtrennungen von ca. 400 mV der drei Reduktionswellen im Cyclovoltammogramm weisen ebenfalls auf eine starke elektronische Wechselwirkung im Truxenongerüst hin. Semiempirische Berechnungen auf AM1-CI-Niveau dienen zur Erklärung der starken Kopplung und legen einen Quartett-Grundzustand für das Truxenon-Trianion nahe. Die UV-Vis-spektroelektrochemischen Untersuchungen der Oxidation und der ersten Reduktion von **7** zeigen, daß beide Prozesse die CT-Anregung schwächen, was zur Modulierung der NLO-Eigenschaften genutzt werden kann.*

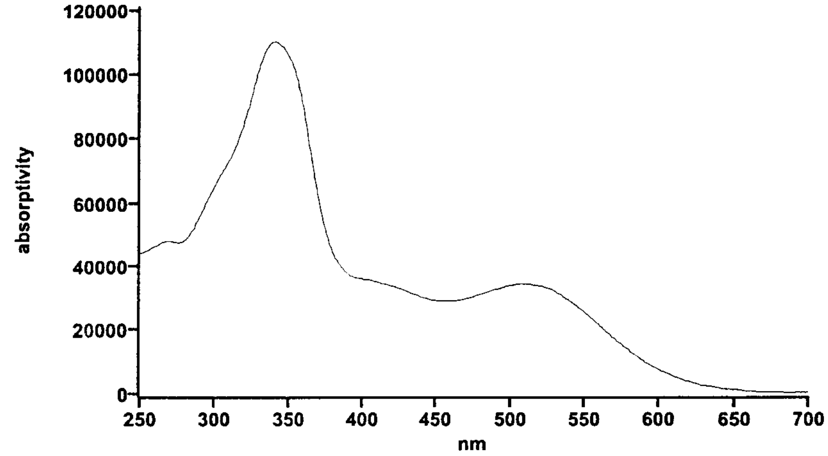
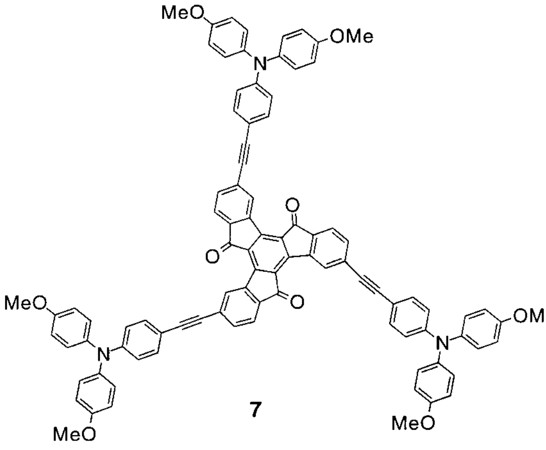
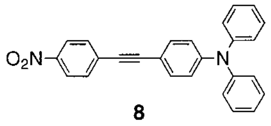


Figure 1. UV spectrum of **7** in $CHCl_3$.

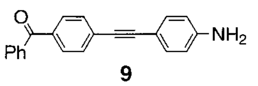
The choice of an appropriate 1D reference system for comparison of linear and nonlinear optical properties is difficult and to some extent arbitrary since the connecting moiety, truxenone, is strongly coupling and cannot reasonably be divided into subunits. Therefore, we have not undertaken attempts to synthesise 1D reference systems, but rather use literature values of similar aminotolanes. For example, 4,4′-(*N*,*N*-diphenylamino)nitrotolane (**8**)[14a] and 4,4′-amino(phenylcarbonyl)nitrotolane (**9**)[14b] have absorption maxima at 418 nm and at 352 nm in $CHCl_3$, respectively. The bathochromic absorption of **7** shows that the truxenone moiety is a far stronger electron acceptor than a single carbonyl functionality and even more than a nitro group.



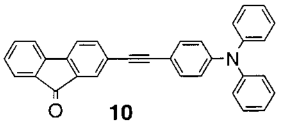
**7**



**8**



**9**



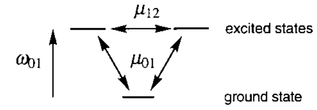
**10**

HRS measurements[15] were performed with $CHCl_3$ solutions of **7** at 1500 nm with an optical parametric power oscillator (OPPO) system.[16] The unpolarised second-harmonic (750 nm) was detected. The experimental set-up and data evaluation is described in ref. [16]. *p*-Dimethylaminocinnamaldehyde was chosen as the reference compound ($\beta_{zzz}^{1500} = 35 \times 10^{-30}$ esu[14b, 17]). The $\beta^{B*}$ convention by Willets et al.[18] is adopted in the present paper. Although **7** has actually $C_3$ symmetry owing to twisting of the diphenylamino groups, we assume $D_{3h}$ symmetry for the data evaluation as this is the approximate symmetry of the localised transition moments of the chromophore branches. In this case, there are only two nonzero $\beta$ tensor elements, $\beta_{xxx} = -\beta_{xyy}$, if Kleinman symmetry is valid.[19]

For $D_{3h}$ symmetric molecules, $\beta_{xxx}$ can be approximated by a three-level model [Eq. (1) and Scheme 3], in which $\mu_{01}$ denotes the transition moment from the ground state to the

$$\beta_{xxx} = \frac{1}{\hbar^2} \times \mu_{01}^2 \frac{\mu_{12}}{\omega_{01}^2} \times \frac{\omega_{01}^4}{(\omega_{01}^2 - 4\,\omega^2)(\omega_{01}^2 - \omega^2)} \tag{1}$$

first degenerate excited states, $\mu_{12}$ is the transition moment connecting these excited states, $\omega_{01}$ is the CT energy and $\omega$ is the energy of the incident laser light.[6b]



Scheme 3. Scheme showing transitions between ground and excited states.

The HRS measurement of **7** gave $\beta_{xxx} = 355 \times 10^{-30}$ esu at 1500 nm and, by extrapolation with the three-level model [Eq. (1)], $\beta_{xxx}^0 = 169 \times 10^{-30}$ esu (Table 1). Although this value might be resonantly enhanced to a minor extent, since **7** has a nonzero extinction coefficient at the SHG (750 nm) of about $100\,\text{M}^{-1}\text{cm}^{-1}$, $\beta^0$ is much higher than that of **8** ($28.2 \times 10^{-30}$ esu[14a]) or of **9** ($16 \times 10^{-30}$ esu[14b]). This enhancement cannot solely be explained by the red shift of the absorption maximum of **7** versus **8** or **9**, since from the three-level term of Equation (1) one can estimate the contribution of the bathochromic absorption ($\omega_{01}$) to $\beta$ only to be roughly 100%. In addition, the extinction coefficient of **7** ($\varepsilon = 34\,300\,\text{M}^{-1}\,\text{cm}^{-1}$) is less than three times as large as most push–pull-substituted tolane derivatives.[20] Hence, a possibly enhanced $\mu_{01}^2$ (which is proportional to the extinction coefficient) in Equation (1) can also not account for the high $\beta$ value.

Table 1. Experimental (HRS in $CHCl_3$), AM1-TDHF computed (gas phase), and theoretical (tensor addition) absolute and relative quadratic hyperpolarisabilities.[a]

| | $\lambda_{max}$ [nm] | $\beta_{xxx}^0$ (HRS) [$10^{-30}$ esu] | $\beta_{xxx}^0$ (AM1-TDHF) [$10^{-30}$ esu] | $\beta_{xxx}^0$ (theor.) | $\beta_{xxx}^0/M$ (HRS) [$10^{-30}$ esu mol g$^{-1}$] |
|---|---|---|---|---|---|
| **7** | 509 | 169 (6.04) | 28.8 (1.08) | (0.49) | 0.124 |
| **8** | 418 | 28.2[b] (1) | 27.9 (1) | | 0.072 |
| **9** | 352 | 16[c] (0.57) | | | 0.054 |
| **10** | | | 18.2 (0.65) | (0.65) | |
| **CV** | 584 | 30[d] (1.06) | | | 0.074 |

[a] Values in parentheses are relative values for each method. The conversion factor to SI units is $1 \times 10^{-30}$ esu $= 3.713 \times 10^{-51}\,\text{cm}^3\,\text{V}^{-2}$. [b] Ref. [14a]. [c] Ref. [14b]. [d] Ref. [6h].

Quadratic hyperpolarisabilities calculated by the AM1-TDHF (time-dependent Hartree-Fock) method are quite reliable when relative values between similar compounds without excited state electron-correlation contributions are compared.[7d, 21] Hence, we computed $\beta^0$ of **7**, **8**, and a 1D model compound **10** with a fluorenone acceptor functionality. The AM1-computed relative $\beta^0$ values of **7**:**8**:**10** are 1.08:1:0.65. Assuming negligible interaction between chromophore branches, one can construct the $\beta$ tensor of a composite chromophore by tensor addition from the 1D subchromophores.[7d, 19] By this method, a $\beta^0$ ratio for **7**:**10** of 0.75:1 (=0.49:0.65, see Table 1) is expected. The AM1-computed $\beta^0$ enhancement of **7** versus **10** (1.08:0.65) by about 110% relative to the ratio calculated by the tensor addition method (0.49:0.65) reveals that truxenone cannot directly be compared with fluorenone, because it is a much better electron acceptor. The experiment shows that **7** has an even higher $\beta^0_{xxx}$ value than the computed relative value with respect to **8** or **10**: $\beta^0(\mathbf{7})$:$\beta^0(\mathbf{8}) = 6.04$:1. As in the case of tri- and tetrasubstituted phosphonium ions we attribute this additional $\beta^0_{xxx}$ enhancement to a strong transition moment ($\mu_{12}$) coupling the degenerate excited states [Eq. (1)].[7d] The high $\beta^0_{xxx}$ value of **7** and the bathochromic shift with respect to **8** and **9** demonstrate the strong electron-withdrawing and coupling capabilities of truxenone. Compared with, for example, crystal violet, (**CV**, $\beta^0_{xxx} = 30 \times 10^{-30}$ esu, $\lambda_{\max} =$ 584 nm in $CHCl_3$),[6h] **7** has a much higher $\beta^0_{xxx}$ at distinctly smaller absorption wavelength. All experimental data and computed values are compiled in Table 1 together with the experimental $\beta^0_{xxx}$ divided by the molecular mass. This value might serve as a relative measure of efficiency.

**Redox properties**: Cyclic voltammetry measurements were carried out in $CH_2Cl_2$ in order to study the influence of the central coupling unit on the redox properties of **7**. The voltammogram (Figure 2) shows one pair of reversible waves for the oxidation of the triarylamine moieties that comprises the transfer of three electrons. The separation of peak potentials is 66 mV; this proves the amine redox centres to be practically independent of each other. On the reductive side there are three waves for the reduction of the central truxenone moiety, the first two are reversible (at a scan rate of 20 mV s$^{-1}$) and the third is quasi reversible at a scan rate of 1000 mV s$^{-1}$. In contrast to the oxidation, a series of the three reductive processes is separated by about 400 mV (Table 2), emphasising the strong electronic coupling in the central unit.[22]

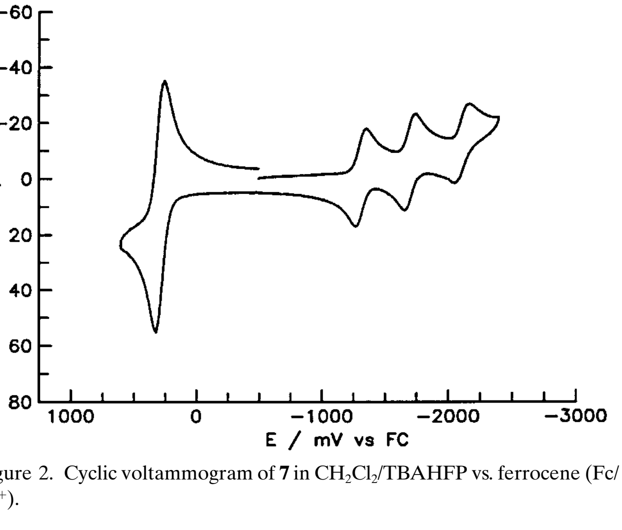


Figure 2. Cyclic voltammogram of **7** in $CH_2Cl_2$/TBAHFP vs. ferrocene (Fc/Fc$^+$).

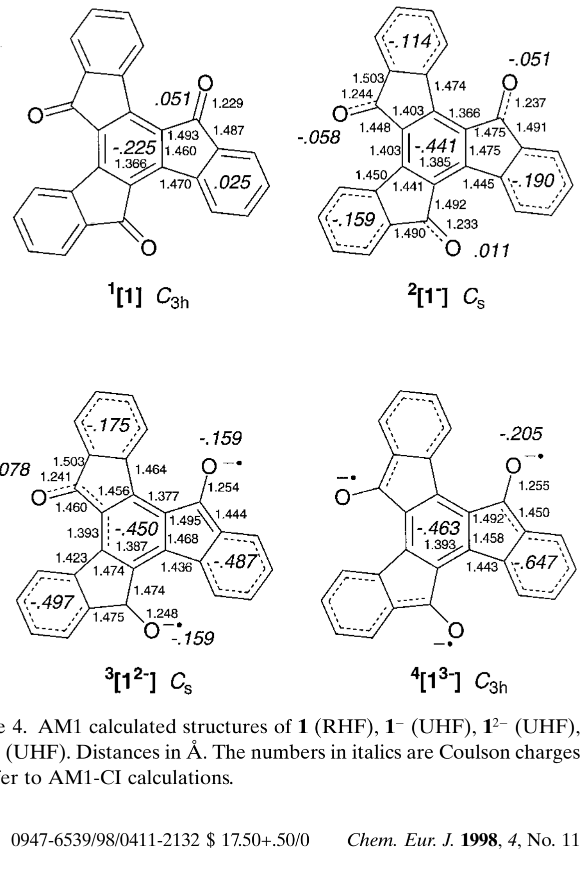
Table 2. Half-wave redox potentials and peak-potential differences of **7** in $CH_2Cl_2$/TBAHFP vs. Fc/Fc$^+$ at 1000 mV s$^{-1}$; $n$ is the number of electrons transferred.

| $n$ | 3 | 1 | 1 | 1 |
|---|---|---|---|---|
| $E_{1/2}$ [mV] | 290[a] | – 1310[a] | – 1700[a] | – 2105[b] |
| $\Delta E$ [mV] | 66 | 80 | 84 | 116 |

[a] Reversible at 20 mV s$^{-1}$. [b] Irreversible at slower scan rates than 1000 mV s$^{-1}$.

We used AM1-CI calculations to investigate the spin multiplicities and charge distributions of truxenone radical anions generated during the reduction of **7**.[23] For simplicity, we only calculated the radical ions of truxenone itself, because we assume that the reductive behaviour of **7** will be qualitatively mirrored by its parent compound. The structures were optimised at UHF or at RHF level, respectively, according to the most stable spin state found in the CI calculations. Subsequently, we performed CI single-point calculations using the UHF (RHF) geometries (Scheme 4). These computations gave a doublet state for $\mathbf{1}^{-}$, a triplet for $\mathbf{1}^{2-}$, and a quartet state for $\mathbf{1}^{3-}$.

For better comparison, the calculated Coulson charges were grouped together for the central $C_6$ unit, the three $C_6H_4$ units



Scheme 4. AM1 calculated structures of **1** (RHF), $\mathbf{1}^{-}$ (UHF), $\mathbf{1}^{2-}$ (UHF), and $\mathbf{1}^{3-}$ (UHF). Distances in Å. The numbers in italics are Coulson charges and refer to AM1-CI calculations.

and the three CO moieties (Scheme 4). The charge population and geometrical analysis of the CI results shows that the extra charge in $\mathbf{1}^-$ is largely localised at the central $C_6$ ring, whereas $\mathbf{1}^{2-}$ is a triplet ground state ($\Delta E_{S\text{-}T} = +2.7$ kcal mol$^{-1}$) with the two extra electrons distributed over two carbonyl centres, the central $C_6$ ring and two $C_6H_4$ moieties (Scheme 4). The charge distribution is reflected, for example, by the longer C–O distances of the two carbonyl groups. The asymmetric charge density results in symmetry reduction to $C_s$. However, in $\mathbf{1}^{3-}$ three electrons are delocalised over the π-electron system leading to $C_{3h}$ symmetry. The negative charge is mainly centred at the three $C_6H_4$ groups and at the CO moieties. Ferromagnetic coupling leads to a quartet ground state and to two degenerate doublets as the first excited states ($\Delta E_{D\text{-}Q} = +4.0$ kcal mol$^{-1}$). This is reasonable as 1,3,5-substituted benzene triradical systems should favour the high-spin state as the ground state.[24] Recent ESR measurements by Lazana et al.[25] in glassy MTHF proved the existence of a quartet state for a reduced truxenone species. These authors ascribe $\mathbf{1}^{3-}$ to the quartet state.

The small but significant changes in geometry and the strong changes of electron-density distribution between the different radical anions ($\mathbf{1}^- \rightarrow \mathbf{1}^{2-} \rightarrow \mathbf{1}^{3-}$, see Scheme 4) again emphasise the strong coupling in the truxenone moiety and explain the quite different observed redox potentials between $\mathbf{7}^-$, $\mathbf{7}^{2-}$ and $\mathbf{7}^{3-}$.

**UV spectroelectrochemistry**: The UV-spectral properties of $\mathbf{7}^{3+}$, $\mathbf{7}^-$ and $\mathbf{7}^{2-}$ were examined in $CH_2Cl_2$ by UV-spectroelectrochemical experiments in a thin-layer cell. Upon oxidation of **7** to $\mathbf{7}^{3+}$ a very intense band appears at 775 nm, characteristic of triarylamine radical cations.[26] At the same time, the CT band at 508 nm decreases (Figure 3a). A similar effect is observed during reduction of **7** to $\mathbf{7}^-$ (Figure 3b): here again, the CT band at 508 decreases and new bands at 436 and at 690 nm appear. We assign the former band to a new CT excitation that is at higher energy compared with neutral **7**, because the acceptor strength of the truxenone moiety is reduced in $\mathbf{7}^-$. The latter, low-intensity band at 690 nm is very likely to be a π–π* excitation localised at the truxenone moiety. The semiempirical computations of $\mathbf{1}^-$ show that the extra electron in $\mathbf{7}^-$ is more or less localised at the central $C_6$ ring of the truxenone system rather than localised in just one $C_6H_4$ ring. This means that reduction of the **7** to $\mathbf{7}^-$ influences the degenerate CT from all three donor-chromophore branches. Hence, further reduction of $\mathbf{7}^-$ to $\mathbf{7}^{2-}$ has only marginal effect on the spectrum in the 300–700 nm region, but slightly alters the π–π* excitation within the truxenone unit: a weak band at 769 arises (not shown). Due to chemical instability the spectra of the third reduction could not be recorded.

The UV spectroelectrochemistry shows that both the oxidation of the remote triarylamine centres as well as the reduction of the central truxenone moiety weaken the long-wavelength CT excitations strongly. Since the CT excitations are responsible for the second-order NLO effects, the latter can be switched electrochemically. In this way, reversible modulation of NLO properties at a molecular level might be achievable.

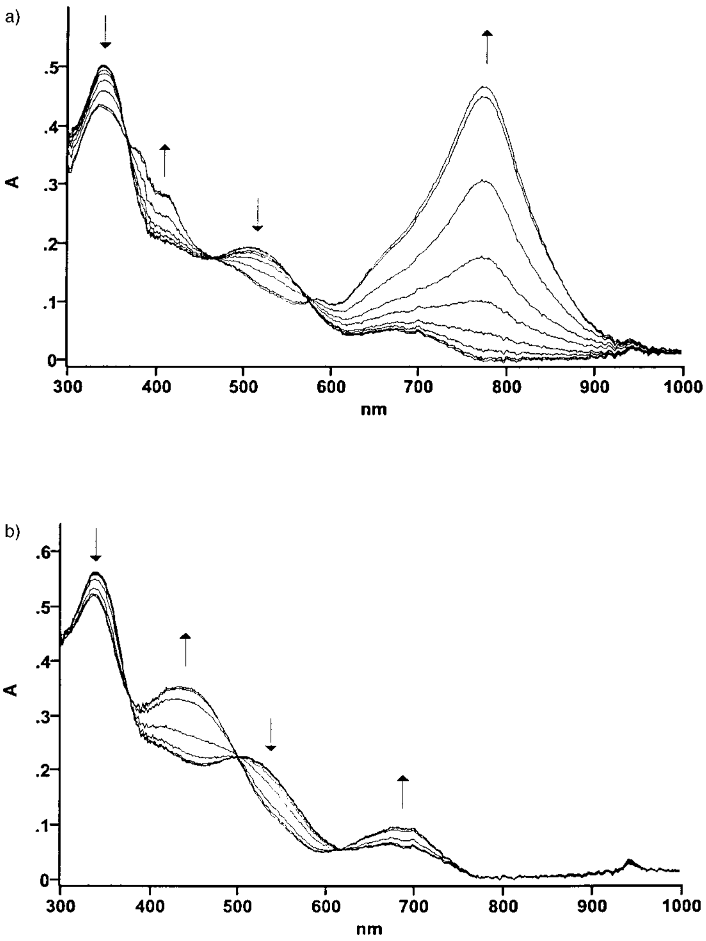


Figure 3. Spectroelectrochemistry of **7** in $CH_2Cl_2$. a) Oxidation ($\mathbf{7} \rightarrow \mathbf{7}^{3+}$). b) First reduction ($\mathbf{7} \rightarrow \mathbf{7}^-$). The band at 680 nm of neutral **7** is a higher order signal as a result of uncorrected diffraction of the spectrometer grid.

## Conclusion

The synthesis of truxenone derivative **7** is straightforward and should allow the preparation of similar systems by $Pd^0$ catalysed cross coupling of various $R{-}SnBu_3$, ROH or $R_2NH$ groups to tribromotruxenone.[27] The linear optical properties (bathochromic shift in the UV/visible spectrum compared with, e.g., **8**), the nonlinear properties (enhancement of quadratic nonlinearity) as well as the redox properties (very different reduction potentials) nicely demonstrate the strong electronic coupling of the central truxenone moiety of **7** in the electronic ground state. The extremely large $\beta$ enhancement (more than is expected due to the bathochromic shift) also indicates that there is strong coupling of the degenerate excited states. The $\beta^0_{xxx}$ value is a factor 2–4 higher than for 1D NLO chromophores with diphenylamino donors ($\beta^0$ ca. $60 \times 10^{-30}$ esu),[14a] and has a comparable absorption wavelength although at a cost of about three times the molecular weight. The quartet state of $\mathbf{1}^{3-}$ suggests that truxenone derivatives such as **7** could be used as high-spin molecules in organic ferromagnets. Analysis of the UV-spectroelectrochemical experiments shows that the CT excitations and, consequently, the NLO properties can reversibly be modulated by electrochemical switching. The aforementioned properties make truxenone a very interesting molecule for electro-optic and magnetic applications. Further studies are necessary to assess the properties of truxenone derivatives with smaller chromophore branches and are currently in progress.

## Experimental Section

**2,2,5-Tribromoindanone (3):** Bromine (15.7 g, 98.2 mmol) was added dropwise to a solution of 5-bromoindanone[13] (10 g, 47.4 mmol) in 80 mL of dry $CHCl_3$. After stirring for 1 h, excess $Br_2$ was removed by bubbling $N_2$ through the solution. The solvent was removed in vacuo; the residue was recrystallised from MeOH. Yield 14.47 g (83 %) of a yellowish powder. M.p. 93 °C; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 7.82-7.60$ (m, 3H; $C_6H_3$), 4.26 (s, 2H; $CH_2$); $^{13}C$ NMR (63 MHz, $CDCl_3$): $\delta = 191.5$, 148.5, 132.7, 132.4, 129.3, 127.7, 128.0, 55.8, 51.9; IR(KBr): $\tilde{\nu} = 1735$ cm$^{-1}$ (s, C=O); $C_9H_5Br_3O$ (368.85): calcd C 29.31, H 1.37; found C 29.52, H 1.63.

**4,9,14-Tribromotruxenone (4)**: A 50 mL roundbottom flask with a long neck, charged with **3** (2.156 g, 5.845 mmol) was placed in a preheated oil bath at 210 °C. The reaction was completed after about 45 min when no further HBr gas was observed. The dark brown residue was treated with $CH_2Cl_2$, filtered and washed with $CH_2Cl_2$. The light brown residue was recrystallised from boiling nitrobenzene. The yellow product was treated with boiling $CHCl_3$ in order to remove traces of nitrobenzene. Yield 265 mg (22 %). M.p. >400 °C. The product is not soluble enough to record NMR spectra at RT. IR(KBr):$\tilde{\nu} = 1712$s cm$^{-1}$ (C=O); MS (70 eV, EI, $^{79}$Br): *m/z* (%): 618 (35) [$M^+$], 590 (5) [$M^+ - CO$], 511 (45) [$M^+ - Br - CO$], 432 (15) [$M^+ - 2Br - CO$], 404 (20) [$M^+ - 2Br - 2CO$], 325 (35) [$M^+ - 3Br - 2CO$], 297 (55) [$M^+ - 3Br - 3CO$], 296 (80) [$M^+ - 3Br - 2CO - H$]; $C_{27}H_9Br_3O_3$ (621.08): calcd C 52.22, H 1.46; found C 51.98, H 1.73.

***N,N*-Di(4-methoxyphenyl)-4′-iodophenylamine**: [Bis(trifluoroacetoxy)iodo]benzene (2.95 g, 6.86 mmol) and iodine (1.74 g, 6.86 mmol) were stirred in dry $CHCl_3$ (70 mL) under an $N_2$ inert gas atmosphere for 1 h. This mixture was added dropwise under exclusion of light to a solution of *N,N*-di(4-methoxyphenyl)phenylamine (3.89 g, 12.73 mmol) in dry $CHCl_3$ (100 mL). After stirring at 50 °C for 1 h the mixture was washed with aq. $Na_2S_2O_3$ and dried over $Na_2SO_4$. The solvent was removed in vacuo, and the residue was dissolved in $CH_2Cl_2$ and filtered through a short collum of silica gel. After removing the solvent in vacuo, the residue was recrystallised from boiling EtOH. Yield: 4.65 g (85 %) colourless crystals; m.p. 114–116 °C; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 7.40/6.67$ (m, AA′, 2H/m, BB′, 2H; I–$C_6H_4$–), 7.03–6.82 (m, AA′–BB′, 8H; MeO–$C_6H_4$–), 3.79 (s, 6H; *Me*O–); $^{13}C$ NMR (63 MHz, $CDCl_3$): $\delta = 156.3$, 148.7, 140.5, 137.7, 126.7, 122.3, 114.9, 82.0, 55.5; $C_{20}H_{18}INO_2$ (431.27): calcd C 55.70, H 4.21, N, 3.25; found C 55.56, H 4.13, N 3.12.

***N,N*-Di(4-methoxyphenyl)-4′-(trimethylsilylethynyl)phenylamine**: *N,N*-Di(4-methoxyphenyl)-4′-iodophenylamine (473 mg, 1.1 mmol), trimethylsiliylacetylene (128 mg, 1.3 mmol, 0.18 mL), $PdCl_2(PPh_3)_2$ (35 mg, 5 mol %) and CuI (5 mg, 2,5 mol %) were stirred under an $N_2$ inert gas atmosphere in dry diethylamine (10 mL) at 60 °C for 1 h. After removing the solvent in vacuo, the residue was hydrolysed with water, the aqueous phase was extracted with diethylether and dried over $Na_2SO_4$. After removing the solvent in vacuo the residue was purified by flash chromatography on silica gel (PE/$CH_2Cl_2$ 3.5:1.5). Yield 406 mg (92 %) of an orange oil, which was imediately deprotected.

***N,N*-Di(4-methoxyphenyl)-4′-(ethynyl)phenylamine**: *N,N*-Di(4-methoxyphenyl)-4′-(trimethylsilylethynyl)phenylamine (4.18 g, 10.39 mmol) was dissolved under an $N_2$ inert gas atmosphere in dry MeOH (ca. 320 mL). Potassium carbonate (2.073g, 15 mmol) was added and the mixture was stirred for 18 h. The solvent was removed in vacuo and the residue purified by flash chromatography on silica gel (PE/$CH_2Cl_2$ 3:2). Yield 3.03 g (89 %) of a yellowish oil, which solidified upon standing. M.p. 81–83 °C; $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 7.26/6.82$ (m, AA′, 2H/m, BB′, 2H; CC–$C_6H_4$–N), 7.03–6.82 (m, AA′–BB′, 8H; MeO–$C_6H_4$–), $\delta = 3.79$ (s, 6H; *Me*O–), 2.98 (s, 1H; HCC–$C_6H_4$–); $^{13}C$ NMR (63 MHz, $CDCl_3$): $\delta = 156.5$, 149.3, 140.2, 132.9, 127.22, 119.0, 114.9, 112.8, 84.3, 75.6, 55.5.

***N,N*-Di(4-methoxyphenyl)-4′-(tributylstannylethynyl)phenylamine (6)**: *n*BuLi (0.90 mL of a 1.6 M solution in hexane, 1.43 mmol) was added dropwise to a solution of di(4-methoxyphenyl)-4′-(ethynyl)phenylamine (414 mg, 1.26 mmol) in dry diethylether under an $N_2$ inert gas atmosphere at −78 °C. After stirring at −50 °C for 30 min, a grayish preciptate formed that dissolved upon adding $Bu_3SnCl$ (472 mg, 1.45 mmol) at −78 °C. After 30 min, the mixture was allowed to warm up to RT. The mixture was hydrolised with water and extracted with diethylether. The organic phase was dried over $Na_2SO_4$ and the solvent was removed in vacuo. The product decomposes on silica gel or alumina and, therefore, was not further purified. Yield 622 mg (80 %) of a yellowish oil. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 7.26/6.82$ (m, AA′, 2H/m, BB′, 2H; CC–$C_6H_4$–N), 7.07–6.77 (m, AA′–BB′, 8H; MeO–$C_6H_4$–), 3.78 (s, 6H; *Me*O–), 1.59 (m, 6H; $CH_2$). 1.37 (m, 6H; $CH_2$), 1.05 (m, 6H; $C^{\alpha}H_2$), 0.91 (m, 9H; $CH_3$); $^{13}C$ NMR (63 MHz, $CDCl_3$): $\delta = 156.2$, 148.4, 140.6, 132.7, 126.8, 119.6, 114.8, 110.7, 91.1, 75.5, 55.5, 28.9, 27.0, 13.6, 11.2.

**4,9,14-Tris{4′-[*N,N*-di(4-methoxyphenyl)amino]phenylethynyl}truxenone (7)**: Compound **4** (100 mg, 0.161 mmol), compound **6** (400 mg, 0.65 mmol) and $Pd(PPh_3)_4$ (28 mg, 0.024 mmol 15 mol %) were stirred under an $N_2$ inert gas atmosphere in dry benzonitrile (7 mL) at 90 °C for 2 h. The solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel (PE/$CH_2Cl_2$ 4:1, then pure $CH_2Cl_2$ and finally $CH_2Cl_2$/MeOH 50:1). The product was dissolved in MeOH/$CH_2Cl_2$, the solvent was removed in vacuo until the product precipitated. Yield 151 mg (81 %) of a dark red powder. M.p. 198–201 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 8.99$ (m, unresolved, 3H; trux), 7.57 (d, $J = 7.69$, 3H; trux), 7.44 (dd, $J = 7.69$, $J = 1.28$, 3H; trux), 7.35/6.87 (m, AA′, 6H/m, BB′, 6H; CC–$C_6H_4$–N), 7.10–6.65 (m, AA′-BB′, 24H; MeO–$C_6H_4$), 3.82 (s, 18H; *Me*O–); $^{13}C$ NMR (63 MHz, $CDCl_3$): $\delta = 190.2$, 156.5, 149.3, 146.4, 141.1, 140.2, 134.4, 130.9, 130.0, 134.1, 131.4, 123.6, 133.0, 127.3, 119.0, 114.9, 113.5, 95.3, 88.9, 55.5; IR(KBr): $\tilde{\nu} = 2196$ (s, CC), 1707 cm$^{-1}$ (s, C=O); HR-MS(NI-LSIMS): *m/z* : calcd = 1365.4564; found = 1365.45676; $C_{93}H_{63}N_3O_9$ (1366.54).

**UV/Vis spectra**: Spectra were recorded in spectrograde solvents at $10^{-5}$–$10^{-6}$ M$^{-1}$ concentrations. No deviations of Lambert–Beer's law were observed in this range.

**HRS measurement**: The experimental set-up is described in detail in ref. [16]. Hyper-Rayleigh scattering measurements were done with solutions of **7** in $CHCl_3$ at number densities between $0.15-4.73 \times 10^{18}$ mL$^{-1}$. No fluorescence could be detected of $CHCl_3$ solutions of **7**. Negative deviation of the HRS signal of **7** from linearity was observed above $1.18 \times 10^{18}$ mL$^{-1}$ due to self absorption of the SHG. Only those points obeying a linear correlation and the blank solvent signal were used for the data evaluation. *p*-Dimethylaminocinnamaldehyde was used as the reference under identical experimental conditions. From a plot of SHG intensity vs. number density relative to the reference compound, the isotropic average $\langle\beta^2\rangle$ for **7** was extracted that is correlated to $\beta_{xxx}$ by $\langle\beta^2\rangle = (8/21) \times \beta^2_{xxx}$ for $D_{3h}$ symmetric molecules.[28] The accuracy of the measurements is estimated to be ±15 %. For comparison, disperse red 1 was measured under identical conditions and gave $\beta_{xxx} = 80 \times 10^{-30}$ esu ($\lambda_{max} = 478$ in $CHCl_3$; $\beta^0_{xxx} = 43 \times 10^{-30}$ esu).[14]

**Cyclic voltammetry**: Measurements were performed with a conventional three electrode set-up, with a Pt-disk work electrode and a Ag/AgCl pseudoreference electrode in 0.1 M tetrabutylammoniumhexafluorophosphate (TBAHFP) in $CH_2Cl_2$ under a nitrogen inert gas atmosphere at RT. The internal standard was ferrocene (Fc/Fc$^+$); the scan rate was varied between 20 and 1000 mV s$^{-1}$. The electrochemical stability was checked by thin-layer multisweep experiments at 20 mV s$^{-1}$.

**UV spectroelectrochemistry**: Measurements were carried out in $CH_2Cl_2$ with a thin-layer cell (100 µm) and a Pt-disk electrode described in ref. [29]. This cell was coupled to a diode array spectometer Polytec X-dap (290–1100 nm).

**Semiempirical calculations**: Calculations were performed with the AM1 hamiltonian implemented in the MOPAC93[30] program package. Molecules **1**, **1**$^-$, **1**$^{2-}$ and **1**$^{3-}$ were optimised either at RHF or at UHF level as singlet, doublet, triplet or quartet ground states, according to their spin multiplicity found in the CI calculations. Compound **7** was optimised in $D_3$ symmetry without methoxy groups at the terminal phenyl groups. For **7**, **1**$^-$, **1**$^{2-}$ and **1**$^{3-}$ CI calculations were performed at UHF (RHF) geometries with an active orbital space CI(*n*,*m*), in which *n* = number of orbitals and *m* = number of doubly occupied orbitals. In the case of an odd number of electrons, the reference wave function was allowed to be symmetric by use of the open(*n*,*m*) keyword, in which *n* denotes the number of electrons equally distributed over *m* orbitals. Thus the following parameters were used: **7**: CI(6,3); $\mathbf{1}^-$ CI(8,3), open(1,1); $\mathbf{1}^{2-}$ CI(8,4), open(2,2); $\mathbf{1}^{3-}$ CI(8,2), open(3,3). A maximum of 121 energy selected microstates is limited by the MOPAC program. The S–T and D–Q splitting energies were taken from the CI calculations without reoptimisation of the higher energy spin states because we expect the geometry differences to be minor. The CI wave function of $\mathbf{1}^-$ is dominated by one microstate, whereas the CI wave functions of $\mathbf{1}^{2-}$ and $\mathbf{1}^{3-}$ mainly consist of four and three equally contributing microstates, respectively. No analysis of spin distributions was possible, since the UHF wave functions of all compounds were significantly spin contaminated. The population analyses refer to Coulson charges calculated from the CI wave functions. The quadratic hyperpolarisabilities of **7**, **8** and **10** were calculated by the TDHF routine implemented in MOPAC93.[21a] The absolute $\beta_{xxx}$ values are given in Table 1 in $\beta^{B*}$ convention.[18]

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