

Synthesis and characterization of new truxenones for nonlinear optical applications

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ABSTRACT: The synthesis of several new truxenones and their tris(dicyanomethylene) derivatives substituted by different amines at positions 4, 9 and 14 are reported. A complete characterization of the NLO properties of representative derivatives was carried out by Hyper Rayleigh Scattering and the major electronic effects and the influence of the structural modifications on the NLO properties have been examined. Due to their C_3 symmetry and their large first hyperpolarizability, the chiral versions of the tris(dicyanomethylene) truxone derivatives are of interest for second-order nonlinear optics in uniaxially aligned chiral media.

KEYWORDS:

Nonlinear optics; Hyper-Rayleigh Scattering, Hyperpolarizability, Multipolar, C_3 symmetry.

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We report the synthesis and the HRS characterization of some new truxenones for NLO applications.

Introduction.

Truxenone, diindeno[1,2-*a*;1',2'-*c*]fluorene-5,10,15-trione, and related truxene derivatives have been known for well over a century¹ but have only relatively recently attracted attention as building blocks for functional materials.² During the last two decades a number of studies have reported the exploitation of different truxenone or truxene derivatives involving their mesomorphic, electrochemical and nonlinear optical properties. A main source of interest in the truxenones as a component or precursor for functional materials derives mainly from the presence of the three identical carbonyl functional groups disposed in the plane of the molecule with overall C_{3h} symmetry. As such, the truxenone molecule is formally comprised of three fluorenones that share a common central benzene ring and serves as a rigid template for further modification permitting creation of derivatives with threefold rotational symmetry.

Multidimensional chromophores as functional nonlinear optical materials have been the focus of research in two-photon absorption³ and parametric nonlinear optics.⁴ The research presented here has been undertaken in order to identify chromophores that can be aligned in thermally stable axially aligned chiral media, which can result in large second order nonlinear optical tensors. Such materials will prove to be valuable alternatives to conventional second order NLO materials such as electro-optical media created by electric field poling. Truxenones and their derivatives are of interest for this and other applications as a consequence of their multidimensionally delocalized electrons and their potential to form columnar liquid crystal media. The central benzene ring in truxenone fused to three carbonyl groups on the five-membered rings functions is a strong electron-withdrawing unit and the substitution of the truxenone in positions 4, 9 and 14 by donor groups will create a multipolar NLO active truxenone. The C_{3h} symmetry gives the truxenones and truxenes an octupolar character, which, as in the case of two-photon absorption, is likely to result in more efficient non-linear optical properties than the corresponding dipolar molecules^{5,6} No synthesis has previously been reported of any truxenone

derivatives with a donor substituent on the immediate periphery of the truxenone unit. Only the study of Lambert et al. reports the preparation and NLO characterization of truxenone derivatives linked to various donor groups via an intervening phenylethynyl bridge.⁷ It is well known that an ethynyl bridge is not very efficient for the transfer of the π electrons, diminishing the NLO potential of this kind of molecule. Here we report the synthesis of some truxenones and derivatives of truxenone that are directly substituted on the immediate periphery by different amine donor groups.

Experimental Section

Instrumentation. Proton nuclear magnetic resonance (¹H NMR) spectra and carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on a Varian Mercury-400 (400 MHz), Inova-500 (500 MHz), or an Inova-600 (600 MHz) NMR spectrometer. Chemical shifts for protons are reported in parts per million (CDCl₃ δ 7.25). Chemical shifts for carbon are reported in parts per million downfield from added tetramethylsilane. Melting points were measured on a TA Instruments DSC 2920 operating at 10 °C/min under nitrogen or by using a polarizing optical microscope equipped with a Mettler FP82HT heating stage attached with a Mettler FP90 temperature controller operating at 10 °C/min. The mass spectroscopy was performed on a Bruker Daltonics Esquire 3000+ with an APCI ion source. The IR spectra were recorded on a Bruker Optics Vector 33. The microwave reactions were performed with the CEM Discover station at maximum power (300W) in a pressure vessel provided by CEM.

Materials. Commercial reagents were purchased from Sigma Aldrich, Acros or Lancaster, and used as received with the exception of pyridine, which was distilled from calcium hydride at 760 Torr and chlorobenzene, which was dried over molecular sieves (3Å).

2,2-dibromoindan-1-one. In a 100 ml round-bottom flask with magnetic stirbar, 1-indanone (5.0 g, 37.9 mmol) was dissolved in 100 ml of chloroform. Under strong agitation, bromine (12.12 g, 76 mmol) diluted in chloroform (5 ml) was slowly added and stirring was continued for an additional 1 hour. Any excess of bromine was removed by bubbling nitrogen through the solution during 1 hour. The solvent was removed under vacuum and the solid product was washed with a small quantity of ethanol. 9.01 g (82%). ¹H NMR (CDCl₃) δ : 7.97 (d, J=7.6Hz, 1H), 7.75 (t, J=7.6Hz, 1H), 7.52 (t, J=7.6Hz, 1H), 7.42 (d,

$J=7.6\text{Hz}$, 1H), 4.31 (s, 2H). ^{13}C NMR (CDCl_3) δ : 192.7; 147.1; 136.9; 129.0; 126.6; 126.0; 56.8; 52.3. IR (cm^{-1}): 2922; 1716, 1598, 1465, 1421, 1266, 1208, 1100. mp: 133 °C (Lit. 131-134 °C)⁸. MS: m/z 288.80, 290.80, 292.80 ($\text{M} + \text{H}$)⁺. MS-MS (290.80), m/z: 209.90, 211.80, 131.1.

5,6-dimethoxyindan-1-one. In a 100 ml round-bottom flask with magnetic stirbar, P_2O_5 (1.20 g, 8.45 mmol) and methanesulfonic acid (12.0 g, 125 mmol) were mixed and heated at 110 °C for 30 min. Next, 3-(3,4-dimethoxyphenyl)propionic acid (2.0 g, 9.52 mmol) was added all at once and stirring was continued for 15 min. After cooling to room temperature, the reaction mixture was poured into 200 ml of water, and extracted with ethyl acetate (200 ml) and dichloromethane (100 ml). The organic layers were combined and dried over magnesium sulfate. The solvent was removed under vacuum and the product was purified by flash chromatography (hexane/ethyl acetate). 1.25g (68 %). ^1H NMR (CDCl_3) δ : 7.18 (s, 1H), 6.89 (s, 1H), 3.97 (s, 3H), 3.91 (s, 3H), 3.06 (t, $J=5.4\text{Hz}$ 2H), 2.68 (t, $J=5.4\text{Hz}$ 2H). ^{13}C NMR (CDCl_3) δ : 155.6, 150.6, 149.5, 130.0, 116.9, 107.6, 104.3, 56.4, 56.2, 36.7, 25.7. IR (cm^{-1}): 2964, 2924, 2852, 1718. mp 117-119 °C (Lit. 118-120 °C)⁹. MS: m/z: 193.0 [$\text{M} + \text{H}$]⁺ MS-MS (193.0), m/z: 151.0.

2,3-dibromo-5,6-dimethoxyindan-1-one. In a 100ml round-bottom flask with magnetic stirbar, 5,6-dimethoxyindan-1-one (1.0 g, 5.2 mmol) was dissolved in 40 ml of chloroform. Under strong agitation, bromine (1.67 g, 10.4 mmol) diluted in chloroform (5 ml) was slowly added and stirring was continued for 1 hour. The excess of bromine was removed by bubbling nitrogen through the solution during 1 hour. The solvent was removed under vacuum and the product was recrystallized from methanol. 1.04 g (58%). ^1H NMR (CDCl_3) δ : 7.32 (s, 1H), 6.80 (s, 1H), 4.24 (s, 2H), 4.01(s, 3H), 3.96 (s, 3H). ^{13}C NMR (CDCl_3) δ : 191.7, 157.5, 150.5, 142.6, 121.4, 107.2, 106.3, 57.2, 56.6, 56.3, 52.3. IR (cm^{-1}): 2963, 2855, 1711, 1568, 1507, 1268, 1222, 1109. mp 131 °C. MS: m/z 348.8, 350.8, 352.70 [$\text{M} + \text{H}$]⁺ MS-MS (350.8), m/z: 269.9, 271.8, 191.0.

5,6-dimethoxyindan-1,3-dione. In a 100 ml round-bottom flask with magnetic stirbar, 5,6-dimethoxyindan-1-one (1.0 g, 5.21 mmol) was dissolved in a mixture of acetic acid (50 ml) and water (10 ml) and the reaction mixture was cooled in an ice bath. Chromium trioxide (3.68g, 36.8 mmol) was

added in small portions over 1 hour and then the cooling bath was removed and the mixture was stirred for an additional 24 hours. Isopropanol (10 ml) was added and the mixture was stirred for an additional 30 min. The reaction mixture was poured into 200 ml of water, and extracted with dichloromethane (2x100 ml). The solvent was removed under vacuum to give the product, which was used without further purification. 0.56g. (52%). ¹H NMR (CDCl₃) δ: 7.34 (s, 2H), 4.04 (s, 6H), 3.20 (s, 2H). ¹³C NMR (CDCl₃) δ: 196.6, 155.8, 138.4, 103.2, 56.7, 44.7. mp: 265 °C dec. (Lit. 267 °C)¹⁰. MS: m/z: 207.0 [M + H]⁺. MS-MS (207.0), m/z: 191.0, 165.0.

2,3-dihydro-cyclopenta[b]naphthalen-1-one. In a 250 ml round-bottom flask with magnetic stirbar, α,α,α',α'-tetrabromo-*o*-xylene (30.0 g, 71 mmol) was dissolved in dry DMF (150 ml) and then 2-cyclopenten-1-one (5.82 g, 71 mmol) and NaI (70 g, 467 mmol) were added. The reaction mixture was heated at 80 °C overnight. After cooling to room temperature, the solution was poured into an ice/water mixture (400 ml), and decolorized by addition of sodium bisulfite. A brown/yellow precipitate appeared which was removed by suction filtration. The crude product was purified by flash chromatography. 2.92 g (23%). ¹H NMR (CDCl₃) δ: 8.31 (s, 1H), 7.97 (d, J=7.5Hz, 1H), 7.88 (s, 1H), 7.85 (d, J=7.5Hz, 1H), 7.58 (t, J=7.5Hz, 1H), 7.49 (t, J=7.5Hz, 1H), 3.31 (t, J=6.3Hz, 2H), 2.79 (t, J=6.3Hz, 2H). ¹³C NMR (CDCl₃) δ: 207.7, 147.9, 137.2, 134.7, 132.3, 130.4, 128.6, 127.9, 126.1, 124.9, 124.4, 58.4, 36.9. IR (cm⁻¹): 3349, 2964, 2924, 2852, 1740, 1680. mp 135 °C (Lit. 140-141 °C)¹¹. MS: m/z 183.0 [M + H]⁺. MS-MS (183.00), m/z: 165.00 (-H₂O), 155.0 (-CO), 141.0 (-CH₂CO).

2,2-dibromo-3-hydrocyclopenta[b]naphthalen-1-one. In a 100 ml round-bottom flask with magnetic stirbar 2,3-dihydrocyclopenta[b]naphthalen-1-one (1.0 g, 5.5 mmol) was dissolved in 30 ml of chloroform. Under strong agitation, bromine (1.76 g, 11.0 mmol) diluted in chloroform (5 ml) was slowly added and stirring was continued for 1 hour. The excess of bromine was removed by bubbling nitrogen through the solution during 1 hour. The solvent was removed under vacuum and the product was recrystallized from ethanol. 1.1 g (59%). ¹H NMR (CDCl₃) δ: 8.55 (s, 1H), 8.03 (d, J=7.5Hz, 1H), 7.89 (d, J=7.5Hz, 1H), 7.82 (s, 1H), 7.69-7.57 (m, 2H), 4.43 (s, 3H). ¹³C NMR (CDCl₃) δ: 192.2 139.8,

138.1, 133.1, 130.7, 130.0, 128.2, 127.2, 124.7, 58.5, 52.1. IR (cm⁻¹): 3021, 2963, 2924, 2855, 1744, 1643, 1367. mp 161 °C. MS: m/z 338.8, 340.8, 342.8 [M + H]⁺. MS-MS (340.80), m/z: 259.90, 261.80 (-HBr), 181.10 (-Br).

Dimethyl 2,3-naphthalenedicarboxylate¹². In a 100ml round-bottom flask with magnetic stirbar, 2,3-naphthalenedicarboxylic acid (1.5g, 7.0mmol) was dissolved in methanol (15 ml) and thionyl chloride (3.30 g, 28.0 mmol) was added slowly. The reaction mixture was heated under reflux for two hours and after cooling to room temperature the solvent was removed under reduced pressure. The mixture was dispersed in water (200 ml) and extracted with ethyl acetate. The solvent was removed under vacuum, and the product (a colorless oil which solidifies after standing at 4 °C) was used without further purification. 1.66 g (98%). ¹H NMR (CDCl₃) δ: 8.28 (s, 2H), 7.95-7.93 (m, 2H), 7.66-7.64 (m, 2H), 3.98 (s, 6H). ¹³C NMR (CDCl₃) δ: 167.57, 133.22, 129.85, 128.77, 128.49, 128.39, 61.49.

2-hydrocyclopenta[b]naphthalen-1,3-dione. Sodium hydride dispersed in mineral oil (60%, 0.5 g, 10.4 mmol) was placed in a two-neck flask under nitrogen. A solution of dimethyl 2,3-naphthalenedicarboxylate (1.66 g, 7 mmol) in ethyl acetate (10 ml) was slowly added and the reaction mixture was heated under reflux for 4 hours. After cooling to room temperature, the solid was filtered off, washed with a mixture of ethanol/ diethyl ether (1/1, 10 ml) and then dispersed into a hot solution of hydrochloric acid (2%, 200 ml) and stirred for a few minutes during decarboxylation. After cooling to room temperature the solid crude product was filtered off and purified by flash chromatography (hexane/ethyl acetate). 0.69 g (52%). ¹H NMR (CDCl₃) δ: 8.53 (s, 2H); 8.16-8.13 (m, 2H); 7.77-7.74 (m, 2H), 3.40 (s, 2H). ¹³C NMR (CDCl₃) δ: 197.7; 138.2; 136.4; 130.7; 129.7; 124.3; 46.7. IR (cm⁻¹): 22964, 2924, 2856, 1706, 1613, 1246, 1183. mp 221 °C (dec). (Lit. 136 °C dec)¹¹. MS: m/z 197.0[M + H]⁺ MS-MS (197.0), m/z: 179.0, 152.1.

2,2-dibromo-5-fluoroindan-1-one. In a 100ml round-bottom flask with magnetic stirbar, 5-fluoroindan-1-one (1.0 g, 6.67 mmol) was dissolved in 25 ml of chloroform. Under strong agitation, bromine (2.13 g, 13.34 mmol) was slowly added and stirring was continued for 1 hour. The excess of bromine was removed by bubbling nitrogen through the solution during 1 hour. The solvent was

removed under vacuum and the product was washed with a small amount of ethanol. 1.38 g (70%). ^1H NMR (CDCl_3) δ : 7.98 (dd, $J=8.4\text{Hz}$, $J'=5.2\text{Hz}$, 1H), 7.22 (ddd, $J=8.8\text{Hz}$, $J'=8.4\text{Hz}$, $J''=2\text{Hz}$, 1H), 7.11 (dd, $J=8.8\text{Hz}$, $J'=2\text{Hz}$, 1H), 4.30 (s, 2H). ^{13}C NMR (CDCl_3) δ : 191.0; 169.6; 167.0; 150.1 (d, $J=41.6\text{Hz}$); 129.2 (d, $J=33.6\text{Hz}$); 117.4 (d, $J=80\text{Hz}$); 113.0 (d, $J=70\text{Hz}$); 56.1; 52.2. IR (cm^{-1}): 2924, 1727, 1393, 1334, 1253. mp 130 °C. MS: m/z 306.80, 308.8, 310.7 MS-MS (308.80), m/z : 227.90, 229.8 (-HBr), 149.0 (-Br).

2,2,5-tribromoindan-1-one.⁷ In 100 ml round-bottom flask with magnetic stirbar, 5-bromoindan-1-one (2.0 g, 9.5 mmol) was dissolved in 30 ml of chloroform. Under strong agitation, bromine (3.04 g, 19.0 mmol) was slowly added and stirring was continued for 1 hour and then nitrogen was passed through the reaction mixture during 1 hour. Residual solvent was removed under vacuum and the yellowish solid product was washed with a small amount of ethanol. 2.35 g (67%). ^1H NMR (CDCl_3) δ : 7.83 (d, $J=8\text{Hz}$, 1H), 7.67 (d, $J=8\text{Hz}$, 1H), 7.62 (s, 1H), 4.28 (s, 2H). ^{13}C NMR (CDCl_3) δ : 191.7, 148.7, 132.7, 129.8, 129.3, 127.7, 126.3, 55.8, 51.9. IR (cm^{-1}): 2962, 2924, 1701, 1506, 1368, 1218. mp: 94 °C (Lit. 93 °C¹¹). MS: m/z 366.7, 368.7, 370.8, 372.8. MS-MS (370.80), m/z : 287.9, 289.7, 291.7, 209.0, 210.9.

Truxenone. In a 100 ml round-bottom flask with magnetic stirbar, indan-1,3-dione (2.5g, 17 mmol) was added to methanesulfonic acid (40 ml). The mixture was heated at 110 °C for 3 hours. After cooling to room temperature, the reaction mixture was dispersed in water (300 ml) and the crude product was filtered off. The product was dissolved in hot propylene carbonate (75 ml) and after cooling was isolated by suction filtration. This material was then recrystallized from 2-picoline. 1.73 g (79%). ^1H NMR (CDCl_3) δ : 9.32 (d, $J=7.2\text{Hz}$, 3H), 7.90 (d, $J=7.2\text{Hz}$, 3H), 7.72 (t, $J=7.2\text{Hz}$, 3H), 7.60 (d, $J=7.2\text{Hz}$, 3H). IR (cm^{-1}): 2922, 2856, 1703, 1606, 1567, 1459, 1317, 1271. mp >400 °C (Lit. mp > 350 °C)¹³. MS: m/z 384.9 [$\text{M} + \text{H}$]⁺. MS-MS (384.9), m/z : 356.0, 191.0.

4,9,14-trifluorotruxenone.

Method A

The 2,2-dibromo-5-fluoroindan-1-one (0.25 g, 0.81 mmol) was placed in an adapted microwave vessel and irradiated for 2 min at maximum power (300 W). After cooling to room temperature, the reaction mixture was mixed with dichloromethane (2x10 ml) and the product was filtered off. 19.6 mg (16.6%)

Method B

The 2,2-dibromo-5-fluoroindan-1-one (1.0g, 3.25mmol) was placed in a 25 ml round-bottom flask equipped with a magnetic stir bar and heated in an oil bath at 220 °C until gas evolution ceased (ca 1 hour). The mixture was cooled to room temperature, dispersed in dichloromethane (25 ml), sonicated for 5 min and then the product was filtered off, and washed two more times with dichloromethane (25 ml). The product obtained was used without further purification. (97.2 mg, 20.6%)

¹H NMR (CDCl₃) δ: 9.06-9.02 (m, 1H); 8.00-7.97 (m, 1H), 7.10-7.00 (m, 1H). ¹³C NMR (CDCl₃) δ: (N/A due to poor solubility). IR (cm⁻¹): 2916, 2851, 1702, 1595, 1572, 1460, 1460, 1212. mp >400 °C. MS: m/z 438.9 [M + H]⁺. MS-MS (438.9), m/z: 410.9.

4,9,14-tribromotru xenone⁷. The 2,2,5-tribromoindan-1-one (3.0 g, 8.13 mmol) was placed in a 25 ml round-bottom flask equipped with a magnetic stirbar, and heated in an oil bath at 220 °C until gas evolution ceased (ca 1.5 hour). The mixture was cooled to room temperature, dispersed in dichloromethane (25 ml), sonicated for 5 min and then the product was filtered off, and washed two more times with dichloromethane (25 ml). The product obtained was used without further purification. 0.51g, (30%). ¹H NMR (CDCl₃) δ: 9.39 (s, 1H), 8.36 (d, J=7.6Hz, 1H), 7.72 (d, J=7.6Hz, 1H). ¹³C NMR (CDCl₃) δ: (N/A due to poor solubility). IR (cm⁻¹): 2924, 2854, 1737, 1601, 1563, 1457, 1375, 1203. mp 395 °C (dec). MS: m/z 618.4, 620.4, 622.4, 624.4. MS-MS (622.4), m/z: 618.4, 620.3, 592.4, 541.6, 513.6.

[3,a,4], [8,a,9], [13,a,14]-Tribenzotru xenone. In a 100 ml round-bottom flask with magnetic stirbar, 2-hydrocyclopenta[*b*]naphthalen-1,3-dione (0.3 g, 1.5 mmol) was added to methanesulfonic acid (40 ml). The mixture is heated at 110 °C for 3 hours. After cooling to room temperature, the reaction mixture

was dispersed in water (300 ml) and the crude product was filtered off. The product was washed first with warm propylene carbonate, then warm 2-picoline and finally with dichloromethane. 58.3 mg (21%)
 ^1H NMR (CDCl_3) δ : 9.02 (s, 3H) 7.66 (d, $J=7.6\text{Hz}$, 1H), 7.36 (d, $J=7.6\text{Hz}$, 1H), 7.21 (t, $J=7.6\text{Hz}$, 1H)
IR (cm^{-1}): 2924, 2856, 1701, 1506, 810. mp $>400^\circ\text{C}$. MS: m/z 534.8 $[\text{M} + \text{H}]^+$. MS-MS (534.8), m/z : 506.8.

4,9,14-Tris(pyrrolidino)truxenone. In a 25 ml round-bottom flask with magnetic stirbar was placed 4,9,14-trifluorotruxenone (90 mg, 0.2 mmol), potassium carbonate (ca 2g) and anhydrous dimethyl sulfoxide (30 ml). Pyrrolidine (1.4 g, 20 mmol) was added and the reaction mixture was heated overnight at 100°C under nitrogen. After cooling to room temperature, the reaction mixture was poured into water (200 ml) and the precipitated product was filtered off and dried. 61.6mg (51%). ^1H NMR (CDCl_3) δ : 8.73 (d, $J=2.4\text{Hz}$, 3H), 7.67 (d, $J=8\text{Hz}$, 3H), 6.49 (dd, $J=8\text{Hz}$, $J'=2.4\text{Hz}$, 3H), 3.60-3.57 (m, 12H), 2.12-2.01 (m, 12H). ^{13}C NMR (CDCl_3) δ : (N/A due to poor solubility) MS: m/z 591.8 $[\text{M} + \text{H}]^+$. MS-MS (591.8), m/z : 563.8.

4,9,14-Tris(diethylamino)truxenone. In a 25 ml round-bottom flask with magnetic stirbar was placed 4,9,14-trifluorotruxenone (100mg, 0.23mmol), potassium carbonate (ca 3 g) and anhydrous dimethyl sulfoxide (10 ml). Diethylamine (2 ml, 20 mmol) was added and the reaction mixture was heated at 100°C under nitrogen overnight. After cooling to room temperature and extraction several times with dichloromethane, the product was obtained as a dark red solid. 27.8mg (20%). ^1H NMR (CDCl_3) δ : 8.73 (d, $J=2.4\text{Hz}$, 3H), 7.67 (d, $J=8\text{Hz}$, 3H), 6.49 (dd, $J=8\text{Hz}$, $J'=2.4\text{Hz}$, 3H), 3.57 (q, $J=7.2\text{Hz}$, 12H), 1.27 (t, $J=7.2\text{Hz}$, 18H). ^{13}C NMR (CDCl_3) δ : 190.2, 153.6, 145.0, 144.9, 132.3, 125.9, 123.7, 111.6, 111.5, 51.8, 31.7, 29.7, 27.5, 26.8. IR (cm^{-1}): 2984, 2923, 2880, 2827, 1683, 1611, 1573, 1484, 1399, 1266, 1228, 1101. mp 300°C (dec). MS: m/z 534.8. MS-MS (534.8), m/z : 506.8.

4,9,14-Tris(dibutylamino)truxenone. In a 25 ml round-bottom flask with magnetic stirbar was placed 4,9,14-trifluorotruxenone (44 mg, 0.1 mmol), potassium carbonate (ca 3 g) and anhydrous dimethyl sulfoxide (10 ml). Dibutylamine (2 ml, 12 mmol) was added and the reaction mixture was

heated at 100 °C under nitrogen overnight. After cooling at room temperature, the reaction mixture was poured into water (200 ml), and extracted with dichloromethane. The product was purified by flash chromatography and recrystallized from hexane. 21.4 mg (27%). ¹H NMR (CDCl₃) δ: 8.94 (d, J=2.4Hz, 3H), 7.69 (d, J=8Hz, 3H), 6.61 (dd, J=8Hz, J'=2.4Hz, 3H), 3.55 (t, J=7.6Hz, 12H), 1.77-1.72 (m, 12H), 1.54-1.48 (m, 12H), 1.03 (t, J=7.6Hz, 18H). ¹³C NMR (CDCl₃) δ: 190.4, 153.8, 145.0, 126.1, 123.8, 111.7, 51.5, 29.8, 20.5, 14.2. IR (cm⁻¹): 3118, 2947, 2903, 2855, 1689, 1613, 1576, 1501, 1460. mp 206 °C. MS: m/z 766.0 [M + H]⁺ MS-MS (766.0), m/z: 710.0, 654.0.

4,9,14-Tris(dihexylamino)-truxenone. In a 25 ml round-bottom flask with magnetic stirbar was placed 4,9,14-trifluorotruxenone (100 mg, 0.23 mmol), potassium carbonate (ca 3 g) and anhydrous dimethyl sulfoxide (10 ml). Dihexylamine (3 ml, 13 mmol) was added and the reaction mixture was heated at 100 °C under nitrogen overnight. After cooling at room temperature, the reaction mixture was poured into water (200 ml), and extracted with dichloromethane. The product was purified by flash chromatography and recrystallized from hexane. 35.1 mg (16%). ¹H NMR (CDCl₃) δ: 8.92 (d, J=2.0Hz, 3H), 7.66 (d, J=8Hz, 3H), 6.59 (dd, J=8Hz, J'=2.0Hz, 3H), 3.55-3.51 (m, 12H), 1.77-1.72 (m, 12H), 1.50-1.37 (m, 18H), 0.93 (t, J=7.6Hz, 18H). ¹³C NMR (CDCl₃) δ: 190.2, 153.6, 145.0, 144.9, 132.3, 125.9, 123.7, 111.6, 111.5, 51.8, 31.7, 29.7, 27.5, 26.8, 22.7, 14.1. IR (cm⁻¹): 3077, 2946, 2902, 2856, 1689, 1613, 1576, 1501, 1460. mp 137 °C. MS: m/z 934.1 [M + H]⁺ MS-MS (934.1), m/z: 850.1, 766.0, 708.0.

4,9,14-Tris-(S)-(+)-2-Pyrrolidinemethanol-truxenone. In a 25 ml round-bottom flask with magnetic stirbar was placed 4,9,14-trifluorotruxenone (100 mg, 0.2 mmol), potassium carbonate (ca 2 g) and anhydrous dimethyl sulfoxide (30 ml). (S)-(+)-2-Pyrrolidinemethanol (1ml, 10 mmol) was added and the reaction mixture was heated at 100 °C under nitrogen overnight. After cooling to room temperature, the reaction mixture was poured into water (200 ml) and the precipitated product was filtered off and washed with hot 2-picoline and dried. 141 mg (92%). ¹H NMR (d₆-DMSO) δ: 8.37 (s, 3H), 7.31 (d, J=8Hz, 3H), 6.50 (d, J=8Hz, 3H), 4.89 (b, 3H), 3.87 (b, 3H), 3.59-3.20 (m, 12H), 2.14-1.90 (m, 12H)

3.60-3.57 (m, 12H), 2.12-2.01 (m, 12H). IR (cm⁻¹): 3412, 2978, 2878, 2832, 1681, 1611, 1574, 1488, 1372, 1279. mp 201 °C. MS: m/z 934.1 [M + H]⁺ MS-MS (934.1), m/z: 850.1, 766.0, 708.0.

4,9,14-Tris(dibutylamino)-1,6,11-tris(dicyanomethylene)-truxane. In a 100 ml round-bottom flask with magnetic stirbar, 4,9,14-tris(dibutylamino)truxenone (100 mg, 0.13 mmol) and malonitrile (100 mg, 1.5 mmol) were dispersed into dry chlorobenzene (30 ml) and placed under nitrogen. TiCl₄ (0.3 ml, 2.7 mmol) and a solution of pyridine (2 ml) in chlorobenzene (10 ml) were slowly added to the reaction mixture at room temperature. The reaction mixture was heated under reflux and the reaction progress was followed by TLC. After 6 hours of heating, the reaction was cooled, poured into water (200 ml) and extracted with dichloromethane. The organic layer was dried over magnesium sulfate and the solvent removed under reduced pressure. The product was purified by flash chromatography (hexane/dichloromethane). 78.0 mg (66%). ¹H NMR (CDCl₃) δ: 8.25 (d, J=9.2Hz, 3H), 6.96 (d, J=2.4Hz, 3H), 6.68 (dd, J=9.2Hz, J'=2.4Hz, 3H), 3.54-3.39 (m, 12H), 1.79-1.69 (m, 12H), 1.53-1.42 (m, 12H), 1.05 (t, J=7.2Hz, 18H). ¹³C NMR (CDCl₃) δ: 162.1, 152.0, 142.4, 134.8, 128.0, 123.7, 115.4, 114.8, 113.2, 110.4, 77.7, 51.7, 29.7, 20.4, 13.9. IR (cm⁻¹): 2980, 2925, 2879, 2831, 2212, 1601, 1534, 1404, 1357, 1222. mp 323 °C (dec). MS: m/z 910.0 MS-MS (910.0), m/z: 853.9, 797.9, 726.9.

Synthesis

A variety of methods are known to prepare the parent truxenone molecule but the majority of them fall into two main categories as seen in Figure 1: first, the trimerization of an indane-1,3-dione¹⁴ (directly or from an indane-1,3-dione precursor or dimer,¹⁵ method A) and, second, the condensation or trimerization of an inden-1-one derivative (often involving a dihalogenated precursor^{16,17} method B).

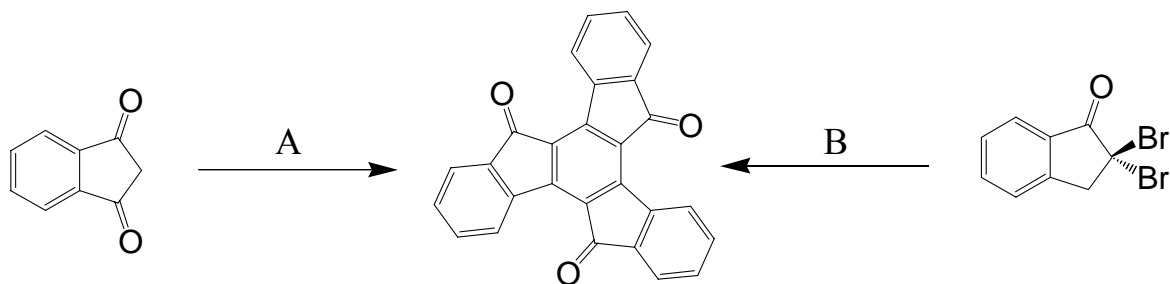


Figure 1. The two main precursors for the preparation of the truxenones derivatives: an indane-1,3-dione (method A) or the 2,2-dibromoindan-1-one (method B).

The functionalization of the benzene rings in truxenones may result from the condensation/trimerization of already pre-functionalized precursors, such as the conversion of 5-bromoindan-1-one to 4,9,14-tribromotruxenone⁷. Surprisingly, the post-functionalization of the benzene ring(s) in truxenone appears not to have been reported. The preparation of ring annulated truxenones by trimerization of ring annulated indan-1-one or indan-1,3-dione derivatives is rare.¹⁸ Such systems with extra annulated rings usually arise by the condensation/trimerization of the same types of precursors but with the extra rings already present, as in the case of the preparation of 6H-trinaphtho[2,3-*a*:2',3'-*f*:2'',3''-*k*]trindene-6,13,20-trione or from conversions of other polycyclic aromatics with the appropriate symmetry, as in the case of the oxidation of decacyclene to give 1,6,11-truxone tricarboxylic acid.¹⁹

In addition to our main objective, which is the preparation of truxenones substituted in positions 4, 9 and 14 by amine donor groups, we have also made several attempts to incorporate alkoxy groups about the periphery of the truxenone. Both 5,6-dimethoxyindan-1-one and 5,6-dimethoxyindan-1,3-dione were considered as appropriate precursors as the presence of two alkoxy groups may provide several advantages: first, they can increase the solubility of the final truxenone, as well as the propensity to form liquid crystalline phases, and second, in the case of the preparation of the truxenone by method A, the number of isomers produced is limited to one (by comparison, trimerization of the 5-methoxyindan-1,3-dione could result in four different truxenone isomers which would be very difficult to separate). The 5,6-dimethoxyindan-1-one is prepared via intramolecular Friedel-Crafts acylation of the 3-(3',4'-dimethoxyphenyl)propionic acid by a known procedure.⁹ The 5,6-dimethoxyindan-1-one can then be

directly converted to the 5,6-dimethoxyindan-1,3-dione by benzylic oxidation with a Cr⁺⁶ reagent in good yield (52%).¹⁰ Numerous systems for the conversion of an indan-1,3-dione to a truxenone are known¹³, the most common being trimerization of the indan-1,3-dione in sulfuric acid.²⁰ We have found that substituting methanesulfonic acid for sulfuric acid often provides better results. While the application of this approach to 2-hydrocyclopenta[*b*]naphthalene-1,3-dione to produce [3,*a*,4], [8,*a*,9], [13,*a*,14]-tribenzotruxenone (R¹ and R² = *o*-phenylene in Table 1) was successful, unfortunately this method failed when applied to 5,6-dimethoxyindan-1,3-dione. In either acidic or basic media the 5,6-dimethoxyindan-1,3-dione could not be converted to the truxenone as the starting material was either completely degraded (acid media) or recovered (basic media). In this last case, the deactivation of the carbonyl group by the presence of a donor (methoxy groups) could explain this difference of behavior.

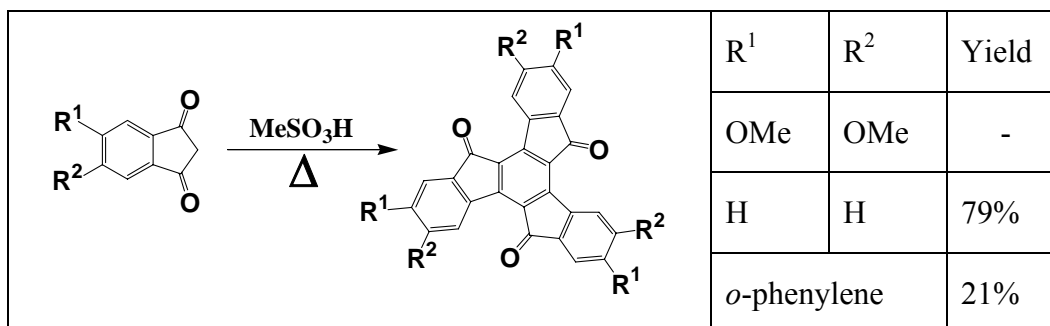


Table 1. Overview of all the truxenones synthesized here from indan-1,3-dione derivatives in methanesulfonic acid (110 °C, 3 hours).

All attempts to create the desired hexaalkoxytruxenones from the halogenated dialkoxyindan-1-one precursors were also not productive. When we used 2,2-dibromo-5,6-dimethoxyindanone or 2,2-dibromo-3-hydrocyclopenta[*b*]-6',7'-dimethoxynaphthalen-1-one as truxenone precursors, the analysis of the reaction mixture by mass spectroscopy showed the complete consumption of the starting material, but without any formation of the corresponding truxenone.

In contrast, in the case of the 2,2-dibromo-5-haloindan-1-ones, the reaction does provide the corresponding 4,9,14-trihalotruxenones, albeit in a modest yield of 20 to 30%. The halogenated materials employed in this study could be synthesized from the 3-halodihydrocinnamic acids due to a preference in the regiochemistry of the intramolecular acylation. With the appropriate 5-haloindan-1-ones in hand, they were converted to a 2,2-dibromo-5-halo derivatives, which were subsequently pyrolyzed by the method described by Lambert *et al*⁷ to give the respective trihalotruxenone.

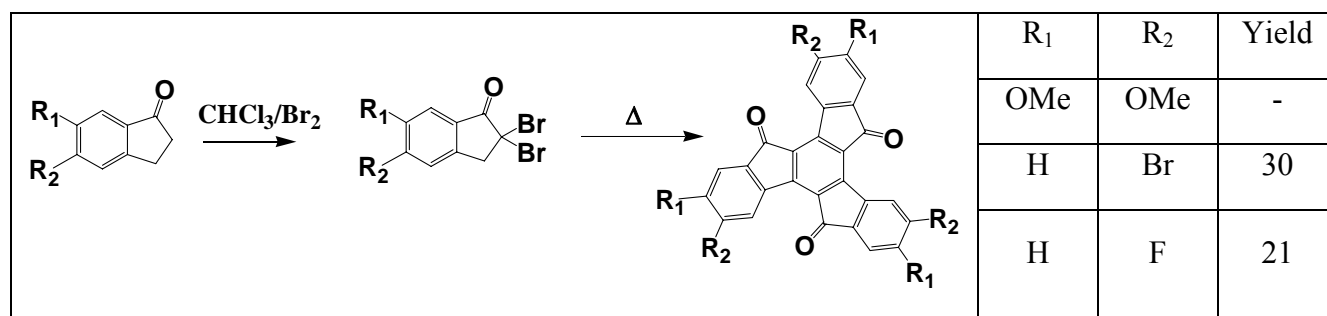


Table 2. Summary of the attempts to prepare truxenones from inden-1-one derivatives via the sequence of bromination (Br₂) and pyrolysis (220 °C).

The ability to synthesize the truxenones substituted by fluorine at positions 4,9,14 combined with the fact that the carbonyl substituted central ring activates aromatic nucleophilic substitution^{21,22,23} provides an alternative route for the preparation of the truxenones substituted by an amine donor group. We have realized the triple nucleophilic substitution of the 4,9,14-trifluorotruxenone with some secondary amines including acyclic versions such as dibutylamine and dihexylamine as well as cyclic amines such as pyrrolidine and the chiral secondary amines L-(+)-prolinol and R-(+)-3-pyrrolidinol. The results obtained are summarized in Table 3.

	R	Yield
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
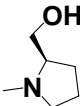
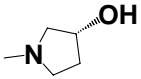
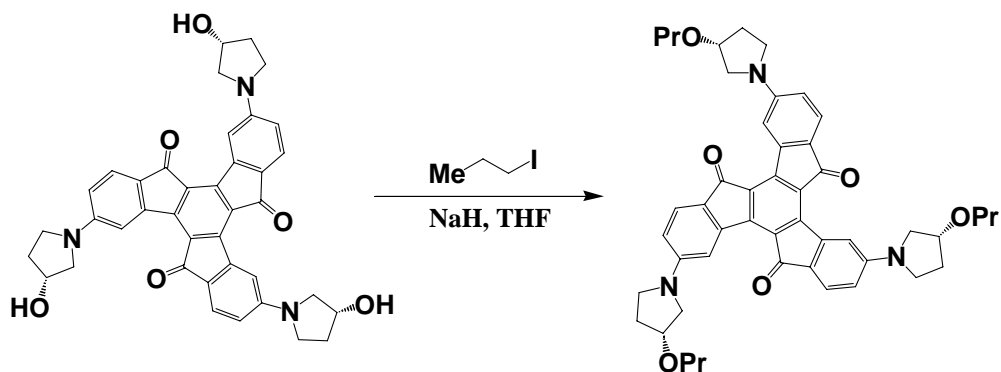
	NEt ₂	20
	NBu ₂	27
	NHex ₂	16
		51
		92
		68

Table 3. Overview of all the 4,9,14-tris(dialkylamino)truxenones obtained by nucleophilic substitution of the 4,9,14-trifluorotruxenone.

The difference of yields from these reactions is due to a number of reasons. On the one hand, the longer the alkyl tail of the secondary amine the lower is its nucleophilic activity. On the other hand, the presence of shorter tail lengths results in lower solubility of the product in common organic solvents that complicates the workup of the reaction.

Substitution of the acyclic dibutylamine and dihexylamine by the different pyrrolidines should provide better NLO properties than their corresponding acyclic secondary amine due to increased electron donation²⁴. Unfortunately, simple pyrrolidines also result in a dramatic decrease of the solubility of the compounds in common organic solvents and complicates their implementation and even the measurement of the NLO properties. To circumvent these problems we used the chiral amino alcohols L-(+)-prolinol and R-(+)-3-pyrrolidinol. The free alcohol group permits the addition of a long alkyl chain by means of an ether linkage so as to increase the solubility as shown in Scheme 1.



Scheme 1. Alkylation of 4,9,14-tris(R-(+)-3-pyrrolidinol)truxenone with *n*-propyl iodide

For any ultimate use as nonpolar electro-optic media at least two further major features are sought from these materials. First of all, the symmetry of the truxenone must be broken to remove a plane of symmetry, i.e., the plane containing the three ketones and the overall π -system of truxenone must be forced into a propeller shape, yielding a chiral character (C_{3h} to C_3). Removal of this plane of symmetry creates two enantiomers, right-handed and left-handed propellers, which ultimately could be separately created by a chiral synthesis or resolved following achiral synthesis. Figure 2 shows how the molecular geometry changes when a truxenone is converted to its tris(dicyanomethylene) derivative. Second, the molecules must have axial alignment. The truxenones, and the propeller shaped derivatives derived from them, would appear to be good candidates to form discotic liquid crystals which will self assemble to provide the desired macroscopic organization. Currently, liquid crystals with a planar truxenone core (carbonyl groups at positions 5,10,15) appear to be unknown but there are numerous examples of discotic liquid crystals that contain the truxane core (three methylene groups at positions 5,10,15); these include a series of 2,3,7,8,12,13-hexaesters²⁵ and 2,3,7,8,12,13-hexaethers²⁶ There are examples of propeller shaped discotic liquid crystals, but those with twisted cores appear to be restricted to metal containing chelates wherein the coordination sphere about the metal establishes the propeller geometry.²⁷ Such molecules typically relax quickly and thermally between the two enantiomers (right-handed propellers and the left-handed propellers). While such enantiomers can be synthesized and then resolved e.g. by chemical reactions in a chiral environment, the only example we know of which has

been resolved in this way has a chromophore which does not have sufficiently large hyperpolarizability to result in interesting nonlinear optical susceptibilities²⁸. Other discotic liquid crystals with thioether tails are nonplanar but the distortions in the aromatic part of the molecule are small.²⁹

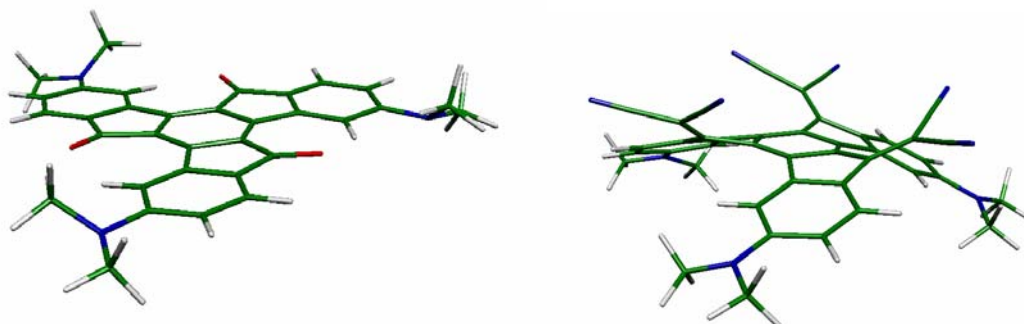
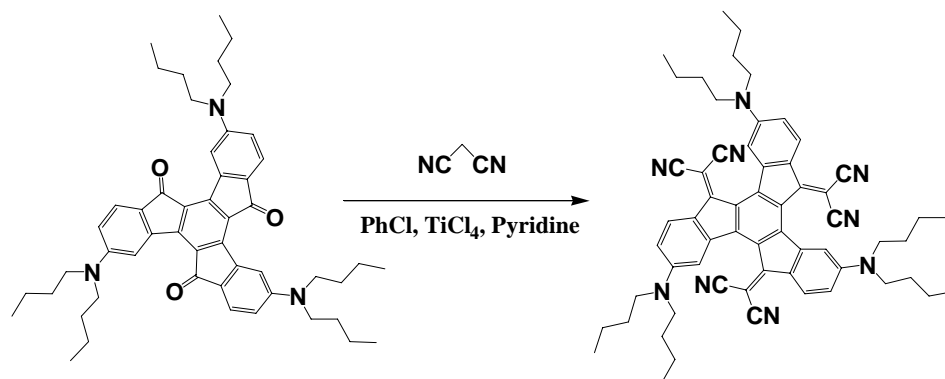


Figure 2: Left: A nearly planar truxenone core (AM1 geometry optimization). Right: The dicyanomethylene substituents (which replace the ketones in the truxenone) interact with the adjacent benzene rings and twist the molecule into a propeller geometry (RHF optimization using SBKJC basis). For simplicity, both molecules are shown with dimethylamino donor groups.

Truxenone itself is a planar C_{3h} molecule wherein there is little or no steric interaction between the carbonyl group(s) and the hydrogen atom(s) on the adjacent rings. However, when methylene carbon atoms bearing additional substituents replace the carbonyl oxygens, the entire molecule becomes distorted and assumes a nonplanar C_3 symmetry. This is the case for the known tris-5,10,15-(dicyanomethylene) derivative of the parent truxenone³⁰ as well as for the tris-5,10,15-(fluorinylidene) compound.³¹ The dicyanomethylene group is a well known acceptor group in NLO materials and as such it could serve a dual role here as an acceptor group and also the source of nonplanarity due to the interactions of the nitrile group(s) with the adjacent donor-substituted ring(s). Quantum chemical Restricted Hartree-Fock (RHF) calculations were carried out to examine the influence of the dicyanomethylene groups and the results confirmed that the equilibrium geometry is nonplanar. These optimization calculations were done with GAMESS³², using the SBKJC basis with an effective core potential and assuming a three-fold rotation axis. It is, in principle, possible to have another isomer of

the tris(dicyanovinyl) compound: not all the dicyanovinyls need to be on the same side of the fused ring structure. Consistent with the observation that only one isomer is obtained; GAMESS calculations (semiempirical AM1) confirm that the unsymmetrical isomer has significantly (7.4 mH or 4.6 kcal/mole) higher energy. This is enough of a difference to make the product predominantly that shown, as is observed experimentally, at least if the reaction is approximately an equilibrium reaction.

The conversion of parent truxenone to its tris(dicyanomethylene) derivative was accomplished using a pyridine-TiCl₄ system.³³ This method has been applied here to some of the tris(dialkylamino)truxenones such as in the conversion of tris(dibutylamino)truxenone to its tris(dibutylamino) tris(dicyanomethylene) derivative in 66% yield. This derivative now has the requisite propeller symmetry and it is a racemic mixture of two propeller enantiomers (or diastereomers in the cases when chiral amines were employed). Unfortunately, none of the amine substituted tris(dialkylamino)truxenones or their tris(dicyanomethylene) derivatives prepared in this study were mesogenic. All these compounds possessed simple crystal to isotropic transitions and in some cases the clearing transition was not reversible due to decomposition.



Scheme 2. Transformation of the 4,9,14-tris(dibutylamino)truxenone (**Trux-3NBu₂**) to its tris(dicyanomethylene) derivative (**Trux-6CN-3NBu₂**) by the reagent system pyridine-TiCl₄.

NLO properties

We have previously described the molecular and bulk properties required for axially aligned chiral second-order nonlinear optical media.⁵ When the molecular first hyperpolarizability tensor β_{ijk} is expanded in terms of rotationally invariant tensor components, the figure of merit of the Kleinman-disallowed component that transforms as a second rank tensor of mixed symmetry contributes to the nonlinear optical response of chiral uniaxial media. We have developed the method of Kleinman-Disallowed Hyper Rayleigh Scattering (KD-HRS) in order to measure the figures of merit for all of the rotationally invariant tensor components.³⁴ As this technique is able to characterize rotationally invariant figures of merit of the hyperpolarizability tensor, it provides considerably more information than electric field induced second harmonic generation (measuring the Kleinman allowed vector component) and 90 degree hyper-Rayleigh scattering which (generally) results in only two numbers which are then interpreted as giving the vector and octupolar Kleinman allowed components.

The solubility of many truxenones in most common solvents is so small that measurements with our HRS set-up were not possible for some of the compounds. For this reason, the characterization of β_{ijk} using KD-HRS was carried out only on the more soluble homologs for which the amino groups are diethylamino (**Trux-3NEt₂**), dibutylamino (**Trux-3NBu₂**), prolinoxypropyl (**Trux-3POPr**) and 3-pyrrolidinoxyhexyl (**Trux-3POHex**), and one tris(dicyanomethylene) derivative (**Trux-6CN-3NBu₂**).

The choice of the wavelength of the probe beam was guided by the absorption spectra of the different compounds. In Figure 3 is seen the UV-Vis spectrum of **Trux-3NBu₂** (truxenone substituted with three dibutylamino groups, which is representative of all the truxenones substituted by an amino group) and the spectrum of its tris(dicyanomethylene) derivative (**Trux-6CN-3NBu₂**).

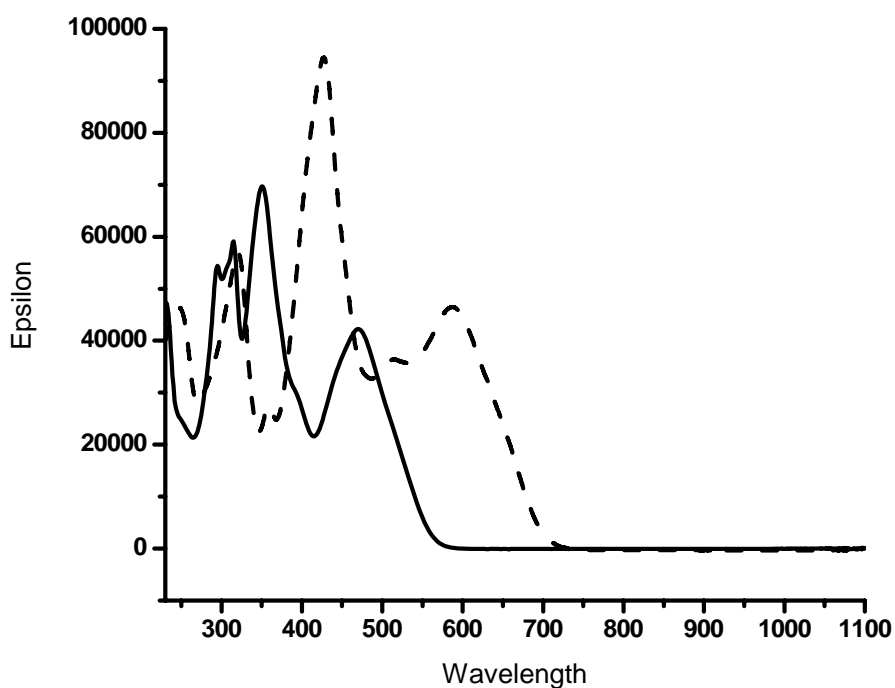


Figure 3. Absorption spectra of **Trux-3NBu₂** (solid line) and **Trux-6CN-3NBu₂** (dashed line) obtained in dichloromethane solution.

Unlike typical dipolar NLO molecules with a single, high transition dipole moment, clear charge transfer band, these spectra are very structured and show multiple absorption peaks, with the lowest lying peak relatively weak. This relatively weak lowest lying absorption, which seems to be a mixture of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions is also observed in the parent 9H-fluoren9-one molecule³⁵ and 3-dimethylamino-9H-fluoren9-one³⁶. In addition this weak, low-lying $\pi \rightarrow \pi^*$ transition is confirmed by our own ZINDO calculations on these and related molecules. Results of a ZINDO/S all singly excited configuration interaction calculation (done with Gaussian03³⁷) on **Trux-6CN-3NBu₂** show two doubly degenerate (E-type) excited states with oscillator strengths greater than 1 in the wavelength range shown in Figure 3. The calculations also predict two more doubly degenerate and one nondegenerate (A-type) excited states with moderate oscillator strengths between 0.3 and 0.6. Many other weak transitions are also predicted in this range. The CIS calculation is not good enough to capture all the richness of the excited states (and thus allow assignments of all of the bands in Figure 3 to be made),

but it does suggest that multiple strongly absorbing excited states are concentrated in a relatively small wavelength band, and also confirms that the most strongly absorbing degenerate (E-type) states are not the lowest lying excited states. For good Kleinman allowed non-linear optical behavior, strongly absorbing low-lying E-type states are preferred. For efficient Kleinman disallowed non-linear optical behavior (β_{2mm} second rank tensor susceptibility), such low-lying states, preferably with an additional strongly absorbing non-degenerate A-type state, are best. These molecules can be thought of as linear chromophores coupled together through the common central ring. Given that the excited states have large amplitude on the (strongly accepting) central ring carbons, the three mutually interacting arms of the molecule yield a complicated excited state structure. The numerous states observed experimentally and in ZINDO calculations clearly shows that this is an over simplified picture: other electronic states must contribute. This suggests that future theoretical and synthetic work can improve the properties of such molecules.

Due to these broadband absorption properties, the KD-HRS experiment cannot be done in the visible wavelength range. Thus, measurements were performed with the fundamental at 1560nm. The experimental setup and analysis, which determine the four rotational invariants of the hyperpolarizability β tensor, are discussed in a previous paper. Although the selected truxenones have good solubility in most common solvents, we have preferred to make the measurements in benzene rather than halogenated solvents like chloroform or dichloromethane. In fact, when the compounds are measured in chloroform solutions, there is an obvious degradation of the compounds with the irradiation time as evidenced by a color change and by a change in two photon fluorescence emission spectra before and after irradiation. When the experiments were carried out in benzene solution, neither degradation nor changes in fluorescence were observed.

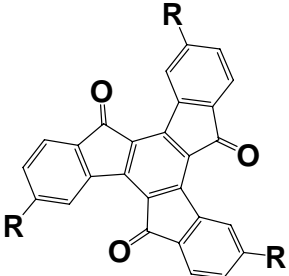
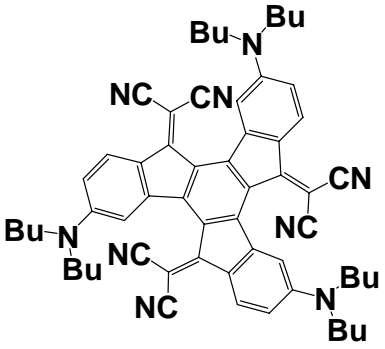

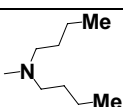
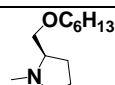
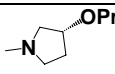
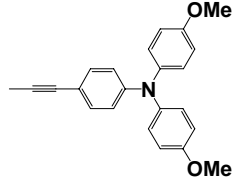
Truxenones		Tris(dicyanomethylene) derivative
	R=	
	 Trux-3NEt ₂	
	 Trux-3NBu ₂	
	 Trux-3POHex	
	 Trux-3POPr	
 Lambert's compound		

Table 4. Structure of all the truxenones and the tris(dicyanomethylene) measured by KD-HRS in this study as well as the pentyne-1-yl bridged truxenone synthesized by Lambert et al.

Since the hyperpolarizabilities of the solvents are too small to be measured in our setup, the external reference method³⁸ has been used here. Disperse Red 1(DR1) was chosen as the reference because it is one of the most studied NLO chromophores and its rotational invariants can be directly related to the EFISH measurements by the relationship, $\beta_{1ss} = \sqrt{3}/5 \beta_{EFISH}$. The β_{1ss} and β_{3ss} are the well-known polar and octupolar figures of merit, respectively. Previous EFISH measurements give the hyperpolarizability

values as $\beta_{EFISH} = 125 \times 10^{-30}$ esu at 1360nm (see ref 38, p. 489). A two-level model has been used to estimate the β value of the Disperse Red 1 at 1560nm³⁸. It is worth noting that the ratio of the octupolar to vector component for DR1 is predicted to be 0.66 within the two level model, and the experimental ratio gives precisely the same value, thus validating the use of the two level model in this case. The rotational invariants of the hyperpolarizability tensors are listed in Table 5.

All the amine substituted truxenones studied show appreciable hyperpolarizability values. The large Kleinman-disallowed components (β_{1mm} and β_{2mm}) indicate breaking of Kleinman symmetry for these multidimensional materials. We also note that the variation in the magnitude of the hyperpolarizability follows our expectations. That is, the values of β increase when we change from dibutylamino or diethylamino to pyrrolidino derivatives. In fact, it is well known that amongst dialkylamino groups that pyrrolidine provides one of the strongest donor effects. For this reason, the Kleinman allowed hyperpolarizabilities of the compounds containing this cyclic amino group are expected to have lower lying excited states and larger electron transfer than the homologs with acyclic dialkylamino groups. Particularly in the energy range for which both the fundamental and second harmonic are below the lowest lying absorption energy of the compounds both these changes should increase the hyperpolarizabilities: Increased electron transfer should increase the numerator in the sum-over-states formula, and the decreased excitation energy should decrease the denominator. The similar value obtained for **Trux-3POPr** and **Trux-3POHex** indicates also that the alkoxy chains introduced to improve the solubility of the compounds have, as anticipated, little influence on the NLO properties. The large improvement observed between **Trux-3NBu₂** and **Trux-6CN-3NBu₂** was also expected, due to the fact that the substitution of the carbonyls by dicyanomethylene groups will enhance the withdrawing influence of the central ring, and by consequence should again lower the excitation energies and electron motion, hence increasing the Kleinman allowed hyperpolarizabilities.

Sample	$\ \beta_{1ss}\ $	$\ \beta_{1mm}\ $	$\ \beta_{2mm}\ $	$\ \beta_{3ss}\ $	Depolarization ratio	
					D_{zz}^{xz}	
					Calculated	Experiment
Disperse Red1 in DMSO	56 ±1	2 ±11	9 ±9	37 ±1	0.35 ±0.02	0.27 ±0.03
Trux-3NBu ₂ in Benzene	62 ±2	79 ±9	43 ±10	65 ±6	0.97 ±0.07	1.19 ±0.16
Trux-3NEt ₂ in Benzene	71 ±3	72 ±5	57 ±4	63 ±4	1.00 ±0.05	0.91 ±0.07
Trux-3POPr in Benzene	94 ±4	82 ±5	72 ±5	75 ±4	0.91 ±0.03	0.83 ±0.05
Trux-3POHex in Benzene	90 ±4	86 ±5	56 ±5	75 ±3	0.89 ±0.05	0.83 ±0.03
Trux-6CN- 3NBu ₂ in Benzene	102 ±2	109 ±6	60 ±8	83 ±4	0.93 ±0.07	1.03 ±0.07

Table 5. Rotational invariants (in units of 10^{-30} esu) measured by KD-HRS at 1560 nm. The calculated depolarization ratio is determined from KD-HRS measurements³⁴ while the experimental depolarization ratio is directly determined from 90 degree HRS measurements.

The large vector components (β_{1ss} and β_{1mm}) suggest non-planar structures with a non-zero dipole. The large β_{2mm} components, which require a special axis in the molecule (more precisely a non-zero second rank traceless symmetric pseudotensor), are of interest for second-order nonlinear optics in

uniaxially aligned chiral media. If the molecules are considered to be planar, the only special axis in these molecules as shown (and as suggested by careful molecular modeling) is the three-fold rotation axis perpendicular through the plane of the central benzene ring, in which plane the electrons contributing the nonlinear optical response move. With the naïve C_{3h} symmetry for the triketone, the additional mirror symmetry is consistent with a traceless symmetric second rank tensor and not a traceless symmetric second rank *pseudotensor*. Thus, there must be conformational or other fluctuations of the ketones away from their putative symmetry, in order to result in these non-zero root mean square (RMS) averages. These fluctuations seem to be intrinsic to the triketone molecules as the HRS for the Trux-3NEt₂ has very comparable vector and pseudotensor contributions in two different solvents: benzene and 1,4-dioxane.

In fact, quantum chemistry calculations suggest that, while the ring system is very close to planar, the amines are somewhat non-planar, with their two alkyl substituents slightly out of the plane of the π system. This small change, which also results in small motions out of plane of other atoms, is *not* expected to make the optically responsive part of these molecules particularly non-planar – the small deviations from planarity primarily involve optically non-responsive atoms. However, there do seem to be rather low energy vibrations in the triketones, which result in out of plane twisting of the molecules. These may be the source of these symmetry-disallowed contributions. These unexpected fluctuations are not expected to contribute to the nonlinear susceptibility in a chiral uniaxial condensed phase so the magnitude of the nonlinear optical tensor in such a phase made from the tris(dicyanomethylenes) is less certain. The large hyperpolarizability components obtained for all these truxenones indicate interest in these molecules for future NLO applications.

The depolarization ratio is often determined in standard HRS measurements. Thus, it is a useful check of results to calculate the depolarization ratio from the rotational invariants in KD-HRS measurements.

In a standard 90 degree HRS experiment the depolarization ratio is defined as $D_{zz}^{xz} = \frac{I_{\perp}}{I_{\parallel}}$, where the I_{\perp} and I_{\parallel} represent the SHG intensity when the incident and outgoing polarization states are orthogonal

and parallel to each other, respectively. In the KD-HRS experiment we can express the I_{\perp} and I_{\parallel} in terms of the rotational invariants and therefore calculate the depolarization ratio.³⁴ In Table 5, we compare the value calculated in this manner from KD-HRS measurements to those determined directly from 90 degree HRS measurements as an internal consistency check on our measurements. The reasonable agreement in Table 5 between the calculated and measured values of this ratio provides confidence in our results. However, the putative symmetry of the triketone compounds would suggest a depolarization ratio of 2. This overall disagreement with this expected value is another reflection of the fluctuations away from the putative symmetry leading to non-zero vector components.

The determination of the rotational invariants and the depolarization ratios allow us, by using the relation (I), to calculate the corresponding β value in nonpolarized Hyper Rayleigh Scattering experiments ($\beta_{\text{unpolarized}}$)³⁴ and then compare our results with those in the literature. In fact, Lambert *et al* also found large hyperpolarizabilities in similar phenylethynyl bridged truxenone derivatives⁷ (which gives $\beta_{\text{ref}} = \sqrt{8/21} \times 355 \times 10^{-30}$ esu = 219×10^{-30} esu at 1500 nm, for a molecule for which the lowest energy absorption maximum is at 508 nm), using unpolarized Hyper Rayleigh Scattering (HRS), i.e. no polarizer for the second harmonic generation.

$$\beta_{\text{unpolarized}} = (\beta_{1ss} \times \sqrt{3} + 2/\sqrt{7} \times \beta_{3ss}) \times \sqrt{(1 + 1/D_{zz}^{xz})} \quad (\text{I})$$

The calculated β values in unpolarized Hyper Rayleigh Scattering (the experimental depolarization ratios are used for calculation) are listed in Table 6 and compared to the previous results obtained by Lambert *et al* (β_{ref}). Since our measurements are done at 1560nm and theirs at 1500nm, a simple calculation using the two-level model gives a reference β_{ref} equal to 204×10^{-30} esu. In Table 6 the absorption peaks refer to the reddest peaks since all the truxenones show multiabsorption peaks.

Sample	λ_{\max} (nm)	$\beta_{\text{unpolarized}} (\times 10^{-30} \text{ esu})$	$\beta_{\text{unpolarized}} / \beta_{\text{ref}}$
Lambert's sample	508	204	1
Trux-3NBu ₂	465	212	1.04
Trux-3Net ₂	461	247	1.21
Trux-3POPr	455	326	1.60
Trux-3POHex	459	316	1.55
Trux-6CN-3NBu ₂	582	327	1.60

Table 6. Characteristics of different truxenone derivatives, where λ_{\max} is the maximum absorption of the reddest (lowest energy) absorption peak; $\beta_{\text{unpolarized}}$ is the unpolarized hyperpolarizability values calculated from rotational invariants by the relation (I), and $\beta_{\text{unpolarized}} / \beta_{\text{ref}}$ is the ratio between the unpolarized hyperpolarizability values of the compound and that of Lambert's compound.

If the results obtained for **Trux-3NBu₂** and **Trux-3Net₂** are similar, the three other compounds show a large improvement of the β value and then of the NLO properties of this kind of material. In general, it would be expected that the closer we get to a resonance the larger the expected hyperpolarizability. This is less clear in these truxones as *in general* it seems that states, which have larger extinction coefficients, also have higher energies. This fact is expected from symmetry and heuristic chemistry and confirmed by ZINDO/S quantum chemistry calculations. If we think of three excited states on each part of the molecule and suppose that these states “spread out” over the molecule in a symmetric way, (e.g. in a way transforming according to the *A* rather than the *E* representation of *C*₃) then in the *C*_{3h} symmetry appropriate to the ketones this state will have no transition dipole moment to the ground state. This, in turn, implies that there is no absorption, or rather that there should be absorption only through symmetry violating transitions, vibrations, etc. Moreover, ZINDO calculations suggest – and this seems likely from the linear absorption data but is harder to discern from heuristic chemistry – even low-lying states which *have* symmetry allowed transitions have relatively small absorption cross-sections: the

strong absorption maximum is associated with a relatively high lying state. As it is generally expected that states which contribute strongly to the linear absorption also contribute strongly to the non-linear hyperpolarizability, it is not clear that the lowest energy / reddest absorption maximum is the peak relevant to understanding the hyperpolarizabilities. Nevertheless we see that all these molecules have in common the fact that they have relatively weak low-lying absorptions. In the end, the larger hyperpolarizabilities of the molecules synthesized for this work confirms our belief that the direct connection between the rigid π system in the center and the donors, rather than the phenylethynyl connection used by Lambert et al results in improved non-linear optical properties.

Conclusion

The synthesis of several new truxenones substituted by different amino groups at positions 4, 9 and 14 has been accomplished exploiting aromatic nucleophilic substitution reactions of the new fluorotruxenone precursors. Some of these aminotruxenones were successfully converted to their nonplanar dicyanomethylene derivatives. For representative materials in this series a complete characterization of NLO properties was carried out by Kleinman-Disallowed Hyper Rayleigh Scattering (KD-HRS). The major electronic effects and the influence of the structural modifications on the NLO properties have been examined experimentally and theoretically. Due to their trigonal symmetry and the large first hyperpolarizabilities that have been determined, these compounds are of interest for second-order nonlinear optics in uniaxially aligned chiral media. In order to fully exploit these materials, further effort dedicated to the interesting and challenging optical resolution of the diastereomeric materials remains to be pursued. We also believe that with appropriate molecular design, e.g. the addition of other donor groups, significant improvements to the hyperpolarizabilities can be made, and the strongly absorbing states can be shifted closer to the lowest lying absorptions, or the lowest lying absorptions can be made to absorb more strongly. The addition of such donor groups, with appropriate alkyl chains, should also allow the formation of liquid crystalline states, which are of interest for our ultimate goal of forming chiral axial phases by self-assembly. Such alignment is particularly of interest for resolved

chiral chromophores as this would allow the unambiguous measurement of Kleinman disallowed average nonlinear optical susceptibilities.

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TOC Graphic and Summary

Data for the TOC:

Authors and Title

Lionel Sanguinet, Jarrod C. Williams, Robert J. Twieg*,

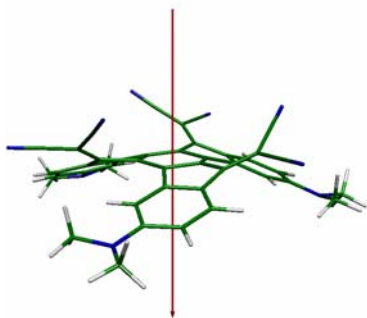
Guilin Mao, Kenneth D. Singer, Greg Wiggers, Rolfe G. Petschek

Synthesis and characterization of new truxenones for nonlinear optical applications

Summary

The synthesis of new truxenones and their tris(dicyanomethylene) derivatives with amine donors is described. Characterization of the NLO properties was carried out by Hyper Rayleigh Scattering and the major electronic effects and the influence of the structural modifications on the NLO properties have been examined.

Graphic (actual size no larger than 1.75 x 2")



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