Synthesis and Characterization of New Truxenones for Nonlinear Optical Applications

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

Introduction

Truxenone, diindeno[1,2-*a*;1′,2′-*c*]fluorene-5,10,15-trione, and related truxene derivatives have been known for well more than a century[1] 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 formally comprises three fluorenones that share a common central benzene ring and serves as a rigid template for further modification that permits the creation of derivatives with 3-fold rotational symmetry.

Multidimensional chromophores as functional nonlinear optical materials have been the focus of research in two-photon absorption[3] 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 electrooptical 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 as a strong electron-withdrawing unit; 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 nonlinear 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 (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker Avance-400 (400 MHz) or Inova-500 (500 MHz) NMR spectrometer. Chemical shifts for protons are reported in parts per million ($CDCl_3$ δ 7.25). Chemical shifts for carbon are reported in parts per million downfield from added tetramethylsilane. The ^{13}C NMR data are not available for those

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compounds with poor solubility. Elemental analyses for carbon, hydrogen, and nitrogen were determined on a Leco CHNS-932 instrument. 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 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 (300 W) in a pressure vessel provided by CEM.

Materials. Some reagents were obtained from commercial vendors; 5-fluoroindanone was obtained from TCI, whereas the amines and other reagents were purchased from Sigma Aldrich, Acros, or Lancaster. All the reagents were 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 (3 Å). The flash chromatographies were performed on silica gel (60 Å, 70−230 mesh).

2,2-Dibromoindan-1-one. In a 100 mL round-bottom flask with a magnetic stir bar, 1-indanone (5.00 g, 37.9 mmol) was dissolved in 100 mL of chloroform. Under strong agitation, bromine (12.10 g, 75.8 mmol) diluted in chloroform (5 mL) was slowly added, and stirring was continued for an additional 1 h. Any excess of bromine was removed by bubbling nitrogen through the solution for 1 h. The solvent was removed under vacuum, and the solid product was washed with a small quantity of ethanol. Yield: 9.0 g (82%). ^{1}H NMR ($CDCl_3$): δ 7.97 (d, J = 7.6 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 7.6 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 $(M + H)^+$. 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 a magnetic stir bar were mixed P_2O_5 (1.20 g, 8.5 mmol) and methanesulfonic acid (12.00 g, 125.0 mmol), and the mixture was heated at 110 °C for 30 min. Next, 3-(3,4-dimethoxyphenyl)-propionic acid (2.00 g, 9.5 mmol) was added all at once, and stirring was continued for 15 min. After being cooled 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). Yield: 1.25 g (68%). ^{1}H 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 Hz, 2H), 2.68 (t, J = 5.4 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 $[M + H]^+$. MS-MS (193.0): *m*/*z* 151.0.

2,2-Dibromo-5,6-dimethoxyindan-1-one. In a 100 mL round-bottom flask with a magnetic stir bar was dissolved 5,6-dimethoxy-indan-1-one (1.00 g, 5.2 mmol) 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 h. The excess of bromine was removed by bubbling nitrogen through the solution during 1 h. The solvent was removed under vacuum, and the product was recrystallized from methanol. Yield: 1.04 g (58%). ^{1}H 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 $[M + H]^+$. MS-MS (350.8): *m*/*z* 269.9, 271.8, 191.0. Calcd for $C_{11}H_{12}Br_2O_3$: C, 37.53; H, 3.44. Found: C, 38.00; H, 3.03.

5,6-Dimethoxyindan-1,3-dione. In a 100 mL round-bottom flask with a magnetic stir bar was dissolved 5,6-dimethoxyindan-1-one (1.00 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 (3.68 g, 36.8 mmol) was added in small portions over 1 h; the cooling bath was then removed, and the mixture was stirred for an additional 24 h. 2-Propanol (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 (2 × 100 mL). The solvent was removed under vacuum to give the product, which was used without further purification. Yield: 0.56 g (52%). ^{1}H NMR ($CDCl_3$): δ 7.34 (s, 2H), 4.04 (s, 6H), 3.20 (s, 2H). ^{13}C NMR ($CDCl_3$): 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 a magnetic stir bar was dissolved α,α,α′,α′-tetrabromo-*o*-xylene (30.00 g, 71.0 mmol) in dry DMF (150 mL); 2-cyclopenten-1-one (5.82 g, 71.0 mmol) and NaI (70.00 g, 466.6 mmol) were then added. The reaction mixture was heated at 80 °C overnight. After being cooled to room temperature, the solution was poured into an ice−water mixture (400 mL) and decolorized by the addition of sodium bisulfite. A brown-yellow precipitate appeared that was removed by suction filtration. The crude product was purified by flash chromatography. Yield: 2.92 g (23%). ^{1}H NMR ($CDCl_3$): δ 8.31 (s, 1H), 7.97 (m, 1H), 7.88 (s, 1H), 7.85 (m, 1H), 7.58 (m, 1H), 7.49 (m, 1H), 3.31 (m, 2H), 2.79 (m, 2H). ^{13}C NMR ($CDCl_3$): 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 ($-H_2O$), 155.0 ($-CO$), 141.0 ($-CH_2CO$).

2,2-Dibromo-3-hydrocyclopenta[*b*]naphthalen-1-one. In a 100 mL round-bottom flask with a magnetic stir bar was dissolved 2,3-dihydrocyclopenta[*b*]naphthalen-1-one (1.00 g, 5.5 mmol) 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 h. The excess bromine was removed by bubbling nitrogen through the solution for 1 h. The solvent was removed under vacuum, and the product was recrystallized from ethanol. Yield: 1.1 g (59%). ^{1}H NMR ($CDCl_3$): δ 8.55 (s, 1H), 8.03 (d, J = 7.5 Hz, 1H), 7.89 (d, J = 7.5 Hz, 1H), 7.82 (s, 1H), 7.69−7.57 (m, 2H), 4.43 (s, 3H). ^{13}C NMR ($CDCl_3$): 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 ($-Br$). Calcd for $C_{13}H_8Br_2O$: C, 45.92; H, 2.37. Found: C, 46.40; H, 2.48.

Dimethyl 2,3-Naphthalenedicarboxylate.[12] In a 100 mL round-bottom flask with a magnetic stir bar was dissolved 2,3-naphthalenedicarboxylic acid (1.50 g, 7.0 mmol) in methanol (15 mL), and thionyl chloride (3.30 g, 28.0 mmol) was added slowly. The reaction mixture was heated under reflux for 2 h, and after being cooled to room temperature, the solvent was removed under reduced pressure. The mixture was dispersed in water (200 mL) and extracted with

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ethyl acetate. The solvent was removed under vacuum, and the product (a colorless oil that solidified after standing at 4 °C) was used without further purification. Yield: 1.66 g (98%). ^{1}H NMR ($CDCl_3$): δ 8.28 (s, 2H), 7.95−7.93 (m, 2H), 7.66−7.64 (m, 2H), 3.98 (s, 6H). ^{13}C NMR ($CDCl_3$): 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%, 0.50 g, 10.4 mmol) was placed in a two-neck flask under nitrogen. A solution of dimethyl 2,3-naphthalenedicarboxylate (1.66 g, 7.0 mmol) in ethyl acetate (10 mL) was slowly added, and the reaction mixture was heated under reflux for 4 h. After being cooled to room temperature, the solid was filtered off, washed with a mixture of ethanol/diethyl ether (1/1, 10 mL); it was then dispersed into a hot solution of hydrochloric acid (2%, 200 mL) and stirred for a few minutes during decarboxylation. After being cooled to room temperature, the solid crude product was filtered off and purified by flash chromatography (hexane/ethyl acetate). Yield: 0.69 g (52%). ^{1}H NMR ($CDCl_3$): δ 8.53 (s, 2H), 8.16−8.13 (m, 2H), 7.77−7.74 (m, 2H), 3.40 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 197.7, 138.2, 136.4, 130.7, 129.7, 124.3, 46.7. IR (cm^{-1}): 2964, 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 100 mL round-bottom flask with a magnetic stir bar was dissolved 5-fluoroindan-1-one (1.00 g, 6.7 mmol) in 25 mL of chloroform. Under strong agitation, bromine (2.13 g, 13.3 mmol) was slowly added, and stirring was continued for 1 h. The excess bromine was removed by bubbling nitrogen through the solution for 1 h. The solvent was removed under vacuum, and the product was washed with a small amount of ethanol. Yield: 1.38 g (70%). ^{1}H NMR ($CDCl_3$): δ 7.98 (dd, $J = 8.4$ Hz, $J' = 5.2$ Hz, 1H), 7.22 (m, 1H), 7.11 (m, 1H), 4.30 (s, 2H). (Lit. 7.87−7.81 (m, 1H), 7.49−7.41 (m, 2H) 3.49 (s, 2H)).[13] ^{13}C NMR ($CDCl_3$): δ 191.0, 169.6, 167.0, 150.1 (d, $J = 41.6$ Hz), 129.2 (d, $J = 33.6$ Hz), 117.4 (d, $J = 80.0$ Hz), 113.0 (d, $J = 70.0$ Hz), 56.1, 52.2. (Lit. in DMSO-d_6: 192.39, 168.87 ($J = 257.0$ Hz), 130.12 ($J = 10.9$ Hz), 128.44 ($J = 10.9$ Hz), 126.10 ($J = 1.7$ Hz), 118.66 ($J = 23.9$ Hz), 114.84 ($J = 23.6$ Hz), 58.56, 52.26).[13] IR (cm^{-1}): 2924, 1727, 1393, 1334, 1253. Mp: 130 °C (Lit. 274−275 °C, dec).[13] MS: *m*/*z* 306.80, 308.8, 310.7. MS-MS (308.80): *m*/*z* 227.90, 229.8 (−HBr), 149.0 (−Br). Calcd for $C_9H_5Br_2FO$: C, 35.10; H, 1.64. Found: C, 35.18; H, 1.67.

2,2,5-Tribromoindan-1-one.[7] In a 100 mL round-bottom flask with a magnetic stir bar was dissolved 5-bromoindan-1-one (2.00 g, 9.5 mmol) in 30 mL of chloroform. Under strong agitation, bromine (3.04 g, 19.0 mmol) was slowly added, and stirring was continued for 1 h; nitrogen was then passed through the reaction mixture for 1 h. Residual solvent was removed under vacuum, and the yellowish solid product was washed with a small amount of ethanol. Yield: 2.35 g (67%). ^{1}H NMR ($CDCl_3$): δ 7.83 (d, $J = 7.5$ Hz, 1H), 7.67 (d, $J = 7.5$ 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 °C).[11] 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 a magnetic stir bar was added indan-1,3-dione (2.50 g, 17.0 mmol) and methanesulfonic acid (40 mL). The mixture was heated at 110 °C for 3 h. After being cooled 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 being cooled was isolated by suction filtration. This material was then recrystallized from 2-picoline. Yield: 1.73 g (79%). ^{1}H NMR ($CDCl_3$): δ 9.32 (d, $J = 7.2$ Hz, 3H), 7.90 (d, $J = 7.2$ Hz, 3H), 7.72 (t, $J = 7.2$ Hz, 3H), 7.60 (d, $J = 7.2$ Hz, 3H). IR (cm^{-1}): 2922, 2856, 1703, 1606, 1567, 1459, 1317, 1271. Mp: >400 °C (Lit. mp >350 °C).[14] MS: *m*/*z* 384.9 $[M + H]^+$. MS-MS (384.9): *m*/*z* 356.0, 191.0.

4,9,14-Trifluorotruxenone. *Method A.* 2,2-Dibromo-5-fluoroindan-1-one (0.25 g, 0.8 mmol) was placed in an adapted microwave vessel and irradiated for 2 min at maximum power (300 W). After being cooled to room temperature, the reaction mixture was mixed with dichloromethane (2 × 10 mL) and the product was filtered off. Yield: 19.6 mg (16.6%)

Method B. 2,2-Dibromo-5-fluoroindan-1-one (1.00 g, 3.3 mmol) 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 h). The mixture was cooled to room temperature, dispersed in dichloromethane (25 mL), and sonicated for 5 min; the product was then filtered off and washed two more times with dichloromethane (25 mL). The product obtained was used without further purification. Yield: 97.2 mg (20.6%).

^{1}H NMR ($CDCl_3$): δ 9.06−9.02 (m, 1H), 8.00−7.97 (m, 1H), 7.10−7.00 (m, 1H). 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. Calcd for $C_{27}H_9F_3O_3$: C, 73.98; H, 2.07. Found: C, 73.80; H, 2.06.

4,9,14-Tribromotruxenone.[7] 2,2,5-Tribromoindan-1-one (3.00 g, 8.1 mmol) 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. 1.5 h). The mixture was cooled to room temperature, dispersed in dichloromethane (25 mL), and sonicated for 5 min; the product was then filtered off and washed two more times with dichloromethane (25 mL). The product obtained was used without further purification. Yield: 0.51 g (30%). ^{1}H NMR ($CDCl_3$): δ 9.39 (s, 1H), 8.36 (d, $J = 7.6$ Hz, 1H), 7.72 (d, $J = 7.6$ Hz, 1H). 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. Calcd for $C_{27}H_9Br_3O_3$: C, 52.21; H, 1.46. Found: C, 51.70; H, 1.47.

4,9,14-Tris(pyrrolidino)truxenone. In a 25 mL round-bottom flask with a magnetic stir bar were placed 4,9,14-trifluorotruxenone (90 mg, 0.2 mmol), potassium carbonate (ca, 2 g), 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 being cooled to room temperature, the reaction mixture was poured into water (200 mL); the precipitated product was filtered off and dried. Yield: 61.6 mg (51%). ^{1}H NMR ($CDCl_3$): δ 8.73 (d, $J = 2.4$ Hz, 3H), 7.67 (d, $J = 8.0$ Hz, 3H), 6.49 (dd, $J = 8.0$ Hz, $J' = 2.4$ Hz, 3H), 3.60−3.57 (m, 12H), 2.12−2.01 (m, 12H). HRMS: calcd for $[M + Na]^+$, *m*/*z* 614.2420; found, *m*/*z* 614.2421.

4,9,14-Tris(diethylamino)truxenone. In a 25 mL round-bottom flask with a magnetic stir bar were placed 4,9,14-trifluorotruxenone (100 mg, 0.23 mmol), potassium carbonate (ca. 3 g), and anhydrous dimethyl sulfoxide (10 mL). Diethylamine (2 mL, 20.0 mmol) was added, and the reaction mixture was heated at 100 °C under nitrogen overnight. After the solution was cooled to room temperature and extracted several times with dichloromethane, the product was obtained as a dark red solid. Yield: 27.8 mg (20%). ^{1}H NMR ($CDCl_3$): δ 8.73 (d, $J = 2.4$ Hz, 3H), 7.67 (d, $J = 8.0$ Hz, 3H), 6.49 (dd, $J = 8.0$ Hz, $J' = 2.4$ Hz, 3H), 3.57 (q, $J = 7.2$ Hz, 12H), 1.27 (t, $J = 7.2$ 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,

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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* 598.2. Calcd for $C_{39}H_{39}N_3O_3$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.40; H, 6.25; N, 7.64.

4,9,14-Tris(dibutylamino)truxenone. In a 25 mL round-bottom flask with a magnetic stir bar were placed 4,9,14-trifluorotruxenone (44 mg, 0.1 mmol), potassium carbonate (ca. 3 g), and anhydrous dimethyl sulfoxide (10 mL). Dibutylamine (2 mL, 12.0 mmol) was added, and the reaction mixture was heated at 100 °C under nitrogen overnight. After being cooled 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. Yield: 21.4 mg (27%). ^{1}H NMR ($CDCl_3$): δ 8.94 (d, J = 2.4 Hz, 3H), 7.69 (d, J = 8.0 Hz, 3H), 6.61 (dd, J = 8.0 Hz, J′ = 2.4 Hz, 3H), 3.55 (t, J = 7.6 Hz, 12H), 1.77−1.72 (m, 12H), 1.54−1.48 (m, 12H), 1.03 (t, J = 7.6 Hz, 18H). ^{13}C NMR ($CDCl_3$): 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. Calcd for $C_{51}H_{63}N_3O_3$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.45; H, 8.26; N, 5.85.

4,9,14-Tris(dihexylamino)-truxenone. In a 25 mL round-bottom flask with a magnetic stir bar were placed 4,9,14-trifluorotruxenone (100 mg, 0.2 mmol), potassium carbonate (ca. 3 g), and anhydrous dimethyl sulfoxide (10 mL). Dihexylamine (3 mL, 13.0 mmol) was added, and the reaction mixture was heated at 100 °C under nitrogen overnight. After being cooled 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. Yield: 35.1 mg (16%). ^{1}H NMR ($CDCl_3$): δ 8.92 (d, J = 2.0 Hz, 3H), 7.66 (d, J = 8.0 Hz, 3H), 6.59 (dd, J = 8.0 Hz, J′ = 2.0 Hz, 3H), 3.55−3.51 (m, 12H), 1.77−1.72 (m, 12H), 1.50−1.37 (m, 18H), 0.93 (t, J = 7.6 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, 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. Calcd for $C_{63}H_{87}N_3O_3$: C, 80.98; H, 9.38; N, 4.50. Found: C, 80.35; H, 9.29; N, 4.41.

4,9,14-Tris-(*S*)-(+)-2-pyrrolidinemethanol-truxenone. In a 100 mL round-bottom flask with a magnetic stir bar were placed 4,9,-14-trifluorotruxenone (100 mg, 0.2 mmol), potassium carbonate (ca. 2 g), and anhydrous dimethyl sulfoxide (30 mL). (*S*)-(+)-2-Pyrrolidinemethanol (1 mL, 10 mmol) was added, and the reaction mixture was heated at 100 °C under nitrogen overnight. After being cooled to room temperature, the reaction mixture was poured into water (200 mL); the precipitated product was filtered off, washed with hot 2-picoline, and dried. Yield: 141 mg (92%). This compound was used for subsequent reactions without further purification. ^{1}H NMR (d_6-DMSO): δ 8.42 (s, 3H), 7.34 (d, J = 8.4 Hz, 3H), 6.53 (d, J = 8.4 Hz, 3H), 4.89 (b, 3H), 3.90 (s, 3H), 3.58−3.40 (m, 6H), 2.11−2.01 (m, 18H). IR (cm^{-1}): 3368, 2951, 2874, 1679, 1607, 1572, 1496, 1363, 1275, 1226, 1153, 1104, 1040, 1008, 883, 802, 760, 667, 570. Mp: 201 °C. MS: *m*/*z* 682.0.

4,9,14-Tris-(*S*)-(+)-(2-hexyloxymethyl-pyrrolidin-1-yl)-truxenone. In a two-neck flask were dispersed 4,9,14-tris-(*S*)-(+)-2-pyrrolidinemethanol-truxenone (0.10 g, 0.2 mmol) and NaH (50% in mineral oil) (0.10 g, 2.0 mmol) in dry THF (20 mL) under N_2; 1-iodohexane (1.0 mL, 6.7 mmol) was then slowly added, and the reaction mixture was heated under reflux overnight. After being cooled to room temperature, the excess NaH was neutralized by the addition of water. The mixture was then poured into water, extracted with dichloromethane, and purified by flash chromatography on silica gel (CH_2Cl_2/EtOAc is 9/1), giving a red gel. Yield: 55 mg (39%). ^{1}H NMR ($CDCl_3$): δ 8.76 (d, J = 1.6 Hz, 3H), 7.62 (d, J = 8.4 Hz, 3H), 6.59 (dd, J = 1.6 Hz, J′ = 8.4 Hz, 3H), 4.20 (s, 3H), 3.75−3.41 (m, 18H), 2.21−2.06 (m, 12H), 1.61 (m, 6H), 1.40−1.28 (m, 18H), 0.91 (t, J = 6.8 Hz, 9H). ^{13}C NMR ($CDCl_3$): δ 190.5, 152.6, 145.0, 144.7, 132.1, 125.7, 124.3, 112.7, 112.2, 71.7, 70.2, 58.6, 48.9, 31.7, 29.8, 28.8, 25.8, 23.1, 22.7, 14.1. IR (cm^{-1}): 3114, 2926, 2856, 1684, 1606, 1575, 1497, 1468, 1363, 1320, 1275, 1224, 1184, 1160, 1101, 1005, 974, 889, 801, 761, 725, 667, 581. MS: *m*/*z* 934.1 $[M + H]^+$. MS-MS (934.1): *m*/*z* 850.1, 766.0, 708.0. Calcd for $C_{60}H_{75}N_3O_6$: C, 77.14; H, 8.09; N, 4.50. Found: C, 76.93; H, 8.47; N, 4.02.

4,9,14-Tris-(*R*)-(+)-pyrrolidinotruxenone. In a 100 mL round-bottom flask with a magnetic stir bar were placed 4,9,14-trifluorotruxenone (0.20 g, 0.5 mmol), potassium carbonate (ca. 8 g), and anhydrous dimethyl sulfoxide (60 mL). (*R*)-(+)-3-Hydroxy-pyrrolidine (1.0 g, 11.5 mmol) was added, and the reaction mixture was heated at 100 °C under nitrogen overnight. After being cooled to room temperature, the reaction mixture was poured into water (800 mL); the brown precipitated product was filtered off, washed with hot 2-picoline and ethanol, respectively, and then dried in a vacuum. Yield: 0.26 g (89%). The product was used for alkylation reaction without further purification. ^{1}H NMR (d_6-DMSO): δ 8.55 (s, 3H), 7.53 (b, 3H), 6.57 (b, 3H), 5.07 (b, 3H), 4.51 (s, 3H), 3.59 (m, 6H), 3.35 (m, 6H), 2.16−2.03 (m, 6H). IR (cm^{-1}): 3339, 2915, 2853, 1672, 1606, 1569, 1503, 1470, 1379, 1329, 1274, 1226, 1164, 1098, 1011, 978, 880, 853, 800, 759, 663. Mp: >400 °C. MS: *m*/*z* 640.0 M^+.

4,9,14-Tris-(*R*)-(+)-(3-propoxy-pyrrolidin-1-yl)truxenone. In a two-neck flask were 4,9,14-tris-(*R*)-(+)- pyrrolidinotruxenone (0.10 g, 0.2 mmol) and NaH (50% in mineral oil) (0.10 g, 2.0 mmol) in dry THF (20 mL) under N_2; 1-iodopropane (1.0 mL, 10.0 mmol) was then slowly added, and the reaction mixture was heated under reflux overnight. After the solution was cooled to room temperature, the excess NaH was neutralized by the addition of water. The mixture was then poured into water, extracted with dichloromethane, and purified by flash chromatography on silica gel (CH_2Cl_2/EtOAc is 9/1), giving a red solid. Yield: 73 mg (59%). ^{1}H NMR ($CDCl_3$): δ 8.68 (d, J = 2.0 Hz, 3H), 7.64 (d, J = 8.4 Hz, 3H), 6.51 (dd, J = 2.0 Hz, J′ = 8.4 Hz, 3H), 4.27 (s, 3H), 3.77−3.61 (m, 12H), 3.50 (t, J = 6.8 Hz, 6H), 2.29−2.16 (m, 6H), 1.64 (m, 6H), 0.95 (t, J = 7.6 Hz, 9H). ^{13}C NMR ($CDCl_3$): δ 190.4, 152.5, 144.9, 144.5, 132.0, 125.7, 124.8, 113.0, 112.3, 78.0, 71.0, 46.8, 31.1, 23.2, 10.7. IR (cm^{-1}): 2960, 2931, 2854, 1683, 1607, 1574, 1504, 1470, 1380, 1332, 1274, 1229, 1179, 1102, 1011, 976, 883, 799, 760, 664, 610, 580. Mp: 258 °C. HRMS: calcd for $[M + H]^+$, *m*/*z* 766.3856; found, *m*/*z* 766.3858.

4,9,14-Tris(dibutylamino)-1,6,11-tris(dicyanomethlylene)-truxane. In a 100 mL round-bottom flask with a magnetic stir bar were dispersed 4,9,14-tris(dibutylamino)truxenone (100 mg, 0.1 mmol) and malononitrile (100 mg, 1.5 mmol) into dry chlorobenzene (30 mL); the mixture was placed under nitrogen. $TiCl_4$ (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 h 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 was removed under reduced pressure. The product was purified by flash chromatography (hexane/dichloromethane). Yield: 78.0 mg (66%). ^{1}H NMR (CDCl3): δ 8.25 (d, J = 9.2 Hz, 3H), 6.96 (d, J = 2.4 Hz, 3H), 6.68 (dd, J = 9.2 Hz, J′ = 2.4 Hz, 3H), 3.54−3.39 (m, 12H), 1.79−1.69 (m, 12H), 1.53−1.42 (m, 12H), 1.05 (t, J = 7.2 Hz, 18H). ^{13}C NMR ($CDCl_3$): δ 162.1, 152.0, 142.4, 142.3, 134.8, 128.0, 123.7, 115.4, 114.8, 113.2,

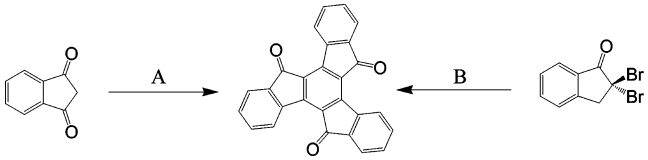


Figure 1. Two main precursors for the preparation of the truxenone derivatives: indane-1,3-dione (method A) or 2,2-dibromoinden-1-one (method B).

110.4, 77.3, 68.8, 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. HRMS: calculated for $[M + H]^+$, *m*/*z* 910.5284; found, *m*/*z* 910.5266.

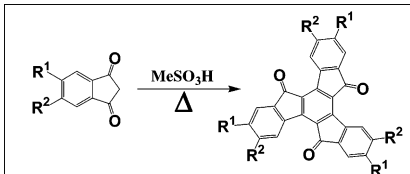
Synthesis

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-dione[15] (directly or from an indane-1,3-dione precursor or dimer,[16] method A) and, second, the condensation or trimerization of an inden-1-one derivative (often involving a dihalogenated precursor,[17,18] method B).

The functionalization of the benzene rings in truxenones may result from the condensation/trimerization of already prefunctionalized precursors, such as the conversion of 5-bromoindan-1-one to 4,9,14-tribromotruxenone.[7] Surprisingly, the postfunctionalization of the benzene ring(s) in truxenone appears to not 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.[19] 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.[20]

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 being 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 5-methoxyindan-1,3-dione could result in four different truxenone isomers, which would be very difficult to separate).

Table 1. Overview of All the Truxenones Synthesized Here from Indan-1,3-dione Derivatives in Methanesulfonic Acid (110 °C, 3 h)



R^1	R^2	Yield
OMe	OMe	-
H	H	79%
o-phenylene		21%

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] 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 known,[14] the most common being trimerization of the indan-1,3-dione in sulfuric acid.[21] We have found that substituting methanesulfonic acid for sulfuric acid often provides better results. Whereas 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 (R^1 and R^2 = *o*-phenylene in Table 1) was successful, this method, unfortunately, 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 in behavior.

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 20−30% (Table 2). The halogenated materials employed in this study could be synthesized from the 3-halodihydrocinnamic acids because of 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. When we prepared the precursor 2,2-dibromo-5-fluoroindan-1-one, we noted that Tatsugi and Izawa[13] obtained this compound from the bromination and oxidation of indan-1-one with NBS-DMSO when they prepared indane-1,2,3-triones. However, the mp and NMR data between our compounds are not consistent (see the Experimental Section). An X-ray crystallographic analysis showed our compound has the expected structure.[22]

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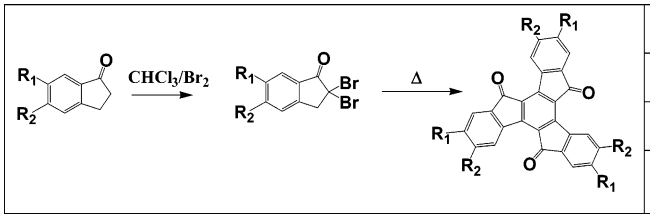
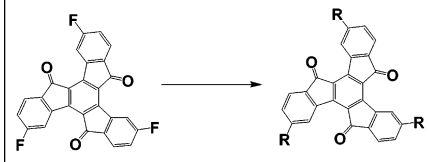
(22) The crystal structure will be published separately.

Table 2. Summary of the Attempts to Prepare Truxenones from Inden-1-one Derivatives via a Sequence of Bromination (Br_2) and Pyrolysis (220 °C)



R_1	R_2	Yield
OMe	OMe	-
H	Br	30
H	F	21

Table 3. Overview of All the 4,9,14-Tris(dialkylamino)truxenones Obtained by Nucleophilic Substitution of the 4,9,14-Trifluorotruxenone



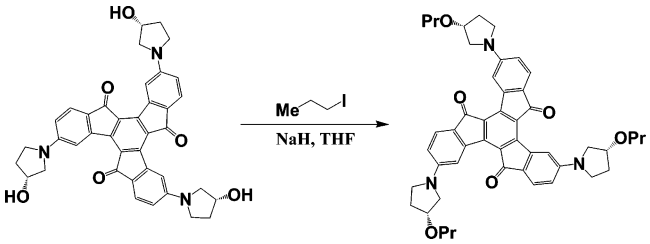
R	Yield
NEt_2	20
NBu_2	27
$NHex_2$	16
	51
	92
	68

The ability to synthesize the truxenones substituted by fluorine at positions 4, 9, and 14, combined with the fact that the carbonyl-substituted central ring activates aromatic nucleophilic substitution,[23−25] 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.

The difference in 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 its nucleophilic activity. On the other hand, the presence of shorter tail lengths results in lower solubility of the product in common organic solvents, which 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 because of increased electron donation.[26] Unfortunately, simple pyrrolidines also result in a dramatic decrease in 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*-Propyliodide



For any ultimate use as nonpolar electrooptic 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 their propeller-shaped derivatives, would appear to be good candidates for forming discotic liquid crystals that will self-assemble to provide the desired macroscopic organization. Currently, liquid crystals with a planar truxenone core (carbonyl groups at positions 5, 10, and 15) appear to be unknown, but there are numerous examples of discotic liquid crystals that contain the truxene core (three methylene groups at positions 5, 10, and 15); these include a series of 2,3,7,8,12,13-hexaesters[27] and 2,3,7,8,12,13-hexaethers.[28] 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.[29] Such molecules typically relax quickly and thermally between the two enantiomers (right-handed and left-handed propellers). Whereas such enantiomers can be synthesized and then resolved, for example, by chemical reactions in a chiral environment, the only example we know

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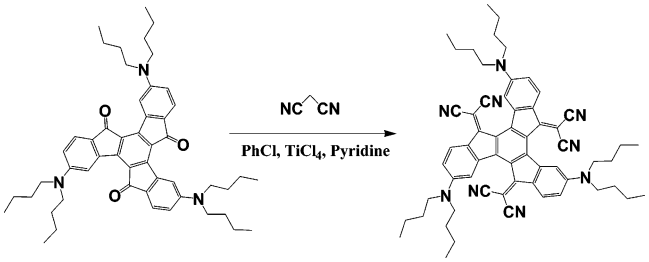
Figure 2. Left: Nearly planar truxenone core (AM1 geometry optimization). Right: Dicyanomethylene substituents (which replace the ketones in the truxenone) interact with the adjacent benzene rings and twist the molecule into a propeller geometry (RHF optimization using SBKJC basis). For simplicity, both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

of that has been resolved in this way has a chromophore that does not have sufficiently large hyperpolarizability to result in interesting nonlinear optical susceptibilities.[30] Other discotic liquid crystals with thioether tails are nonplanar, but the distortions in the aromatic part of the molecule are small.[31]

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 truxenone[32] as well as for the tris-5,10,-15-(fluorinylidene) compound.[33] The dicyanomethylene group is a well-known acceptor group in NLO materials; as such, it could serve a dual role here as an acceptor group and also the source of nonplanarity because of 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; the results confirmed that the equilibrium geometry is nonplanar. These optimization calculations were done with GAMESS,[34] using the SBKJC basis with an effective core potential and assuming a 3-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/mol) 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−$TiCl_4$ system.[35] This method has been applied here to the

Scheme 2. Transformation of the 4,9,14-Tris(dibutylamino)truxenone (Trux-3NBu$_2$) to Its Tris(dicyanomethylene) Derivative (Trux-6CN-3NBu$_2$) by the Reagent System Pyridine−$TiCl_4$



tris(dibutylamino)truxenone in order to prepare its tris-(dibutylamino) tris(dicyanomethylene) derivative in 66% yield (see Scheme 2). This derivative now has the requisite propeller symmetry and 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 because of decomposition.

Linear and 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.[36] 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° hyper-Rayleigh scattering, which (generally) results in only two numbers that are then interpreted as giving the vector and octupolar Kleinman-allowed components.

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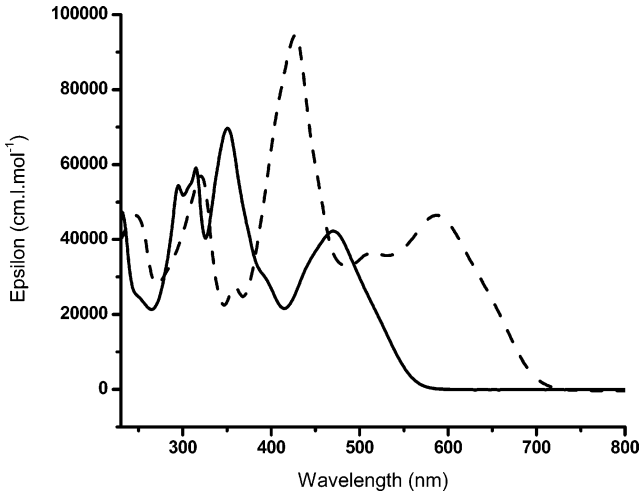

Figure 3. Absorption spectra of **Trux-3NBu$_2$** (solid line) and **Trux-6CN-3NBu$_2$** (dashed line) obtained in dichloromethane solution.

The solubility of many truxenones in most common solvents is so small that measurements with our HRS setup 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 homologues, for which the amino groups are diethylamino (**Trux-3NEt$_2$**), dibutylamino (**Trux-3NBu$_2$**), prolinoxypropyl (**Trux-3POPr**), and 3-pyrrolidinoxyhexyl (**Trux-3POHex**), and one tris(dicyanomethylene) derivative (**Trux-6CN-3NBu$_2$**).

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-3NBu$_2$** (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-3NBu$_2$**).

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 being relatively weak. This relatively weak lowest-lying absorption in **Trux-3NBu$_2$**, which seems to be a mixture of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, is also observed in the parent 9H-fluoren-9-one molecule[37] and 3-(dimethylamino)-9H-fluoren-9-one.[38] In addition, weak, low-lying $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions are confirmed by our own ZINDO calculations on this molecule. Results of a ZINDO/S all singly excited configuration interaction calculation (done with Gaussian03[39]) on **Trux-6CN-3NBu$_2$** suggest that the weak low-lying absorptions are due to $\pi \rightarrow \pi^*$ transitions only. For both truxenone molecules mentioned above, the weak $\pi \rightarrow \pi^*$ transitions result mainly from poor HOMO−LUMO overlap. The calculations on **Trux-6CN-3NBu$_2$** 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 state 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 for 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 confirms that the most strongly absorbing degenerate (E-type) states are not the lowest-lying excited states. For good Kleinman-allowed nonlinear optical behavior, strongly absorbing low-lying E-type states are preferred. For efficient Kleinman-disallowed nonlinear optical behavior (β_{2mm} second-rank tensor susceptibility), such low-lying states, preferably with an additional strongly absorbing nondegenerate 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 show that this is an oversimplified 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 1560 nm. The experimental setup and analysis, which determine the four rotational invariants of the hyperpolarizability β tensor, are discussed in a previous paper.[36] Although the selected truxenones have good solubility in most common solvents, we have preferred to make the measurements in benzene rather than halogenated solvents such as 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 a difference in the 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.

Because the hyperpolarizabilities of the solvents are too small to be measured in our setup, the external reference method[40] has been used here. Disperse Red 1 (DR1) was

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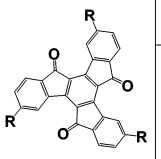
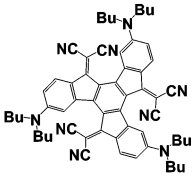
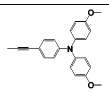
Table 4. Structure of All the Truxenones and the Tris(dicyanomethylene) Measured by KD-HRS in This Study as well as the Phenylethynyl-Bridged Truxenone Synthesized by Lambert et al.

Truxenones		Tris(dicyanomethylene) derivative
	R=  Trux-3NEt$_2$	 Trux-6CN-3NBu$_2$
	 Trux-3NBu$_2$	
	 Trux-3POHex	
	 Trux-3POPr	
	 Lambert's compound	

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, $\beta_{1ss} = \sqrt{\sqrt{3}/5}\ \beta_{EFISH}$. The β_{1ss} and β_{3ss} are the well-known polar and octupolar figures of merit, respectively. Previous EFISH measurements gave the hyperpolarizability value as $\beta_{EFISH} = 125 \times 10^{-30}$ esu at 1360 nm (see ref 38, p 489). A two-level model has been used to estimate the β value of DR1 at 1560 nm.[40] 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 values of β increase when we change from dibutylamino or diethylamino to pyrrolidino derivatives. In fact, it is well-known that among dialkylamino groups, pyrrolidine provides one of the strongest donor effects, which we anticipated would slightly lower the transition energies and increase the transition moments relative to the derivatives with an acyclic amino group. For this reason, the Kleinman-allowed hyperpolarizabilities of the compounds containing this cyclic amino group were expected to be larger than the compounds containing an acyclic amino group, as both these effects would increase the sum over states expression for the Kleinman-allowed hyperpolarizabilities, particularly in the region for which both the fundamental and second harmonic are below the lowest-lying absorption energy of the molecule. Contrary to our expectations, linear absorption data suggest that the low-lying ground-to-excited-state transition moments are slightly decreased (by ~5% on average) when going from the acyclic to cyclic amino donors, and there is virtually no change in energy. Thus, there must be some other cause for the increase in the hyperpolarizabilities of the pyrrolidino derivatives, most probably an increase in transition moments between excited states. The similar value obtained for **Trux-3POPr** and **Trux-3POHex** indicates that the alkoxy chains introduced to improve the solubility of the compounds, as anticipated, have little influence on the NLO properties. The large improvement observed between **Trux-3NBu$_2$** and **Trux-6CN-3NBu$_2$** was also expected, because of the fact that the substitution of the carbonyls by dicyanomethylene groups will enhance the withdrawing influence of the central ring; by consequence, this should lower the excitation energies and increase the transition moments. The twisting of the core because of the dicyanomethylene group will offset some of the gain in the transition moments polarized in the plane (E-type), but will increase transition moments polarized along the C_3 axis (A-type), hence increasing all of the rotationally invariant components of the hyperpolarizability tensor.

The large vector components (β_{1ss} and β_{1mm}) suggest nonplanar structures with a nonzero dipole. The large β_{2mm} components, which require a special axis in the molecule (more precisely, a nonzero second-rank traceless symmetric pseudotensor), are of interest for second-order nonlinear optics in uniaxially aligned chiral media.[36] 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 3-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, to result in these nonzero root-mean-square (RMS) averages. These fluctuations seem to be intrinsic to the triketone molecules, as the HRS for the **Trux-3NEt$_2$** has very comparable vector and pseudotensor contributions in two different solvents, benzene and 1,4-dioxane.

In fact, quantum chemistry calculations suggest that, whereas the ring system is very close to planar, the amines are somewhat nonplanar, 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 nonplanar; the small deviations from planarity primarily involve optically nonresponsive 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

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Table 5. Rotational Invariants (in units of 1×10^{-30} esu) Measured by KD-HRS at 1560 nm

sample	$\|\|\beta_{1ss}\|\|$	$\|\|\beta_{1mm}\|\|$	$\|\|\beta_{2mm}\|\|$	$\|\|\beta_{3ss}\|\|$	depolarization ratio[a] D_{zz}^{xz} calcd	depolarization ratio[a] D_{zz}^{xz} exp
DR1 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

[a] The calculated depolarization ratio is determined from KD-HRS measurements,[36] whereas the experimental depolarization ratio is directly determined from 90° HRS measurements.

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° HRS experiment, the depolarization ratio is defined as $D_{zz}^{xz} = I_{\perp}/I_{||}$, where $I_{\perp}$ and $I_{||}$ represent the second harmonic scattering intensity when the incident and outgoing polarization states are orthogonal and parallel to each other, respectively. In the KD-HRS experiment we can express $I_{\perp}$ and $I_{||}$ in terms of the rotational invariants and therefore calculate the depolarization ratio.[36] In Table 5, we compare the value calculated in this manner from KD-HRS measurements to those determined directly from 90° 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 2/3. This overall disagreement with this expected value is another reflection of the fluctuations away from the putative symmetry leading to nonzero 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 ($\beta_{\text{unpolarized}}$)[36] and then compare our results with those in the literature. In fact, Lambert et al. also found large hyperpolarizabilities in similar phenylethynyl-bridged truxenone derivatives[7] (which gives $\beta_{\text{ref}} = \sqrt{8/21} \times 355 \times 10^{-30}$ esu $= 219 \times 10^{-30}$ 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 scattering.

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

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}). Because our measurements are done at 1560 nm and theirs at 1500 nm, 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 lowest-energy peaks, because all the truxenones have multiple absorption peaks.

Table 6. Characteristics of Different Truxenone Derivatives

sample	$\lambda_{\max}$[a] (nm)	$\beta_{\text{unpolarized}}$[b] ($\times 10^{-30}$esu)	$\beta_{\text{unpolarized}}/\beta_{\text{ref}}$[c]
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

[a] $\lambda_{\max}$ = Maximum absorption of the lowest-energy absorption peak. [b] $\beta_{\text{unpolarized}}$ = Unpolarized hyperpolarizability values calculated from rotational invariants by the relation (*I*). [c] $\beta_{\text{unpolarized}}/\beta_{\text{ref}}$ = ratio between the unpolarized hyperpolarizability values of the compound and that of Lambert's compound.

If the results obtained for **Trux-3NBu$_2$** and **Trux-3NEt$_2$** are similar, the three other compounds show a large improvement in the β value and in 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 because, in general, it seems that states that 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 that 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 that contribute strongly to the linear absorption also contribute strongly to the nonlinear hyperpolarizability, it is not clear that the lowest-energy 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 confirm 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 nonlinear optical properties.

Conclusion

The synthesis of several new truxenones substituted by different amino groups at positions 4, 9, and 14 has been accomplished by exploiting aromatic nucleophilic substitution reactions of the new fluorotruxenone precursors. One of these aminotruxenones was successfully converted to its nonplanar dicyanomethylene derivative. For representative materials in this series, we carried out a complete characterization of NLO properties 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. Because of 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. Further effort dedicated to the interesting and challenging optical resolution of the diastereomeric materials remains to be pursued in order to fully exploit these materials. 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 for 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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