One-step, large-scale synthesis of isotruxene

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A concise procedure for the one-step synthesis of isotruxene has been developed. Isotruxene is obtained in around 60% yield on a 150-gram scale through acid-catalysed cyclotrimerisation of equimolar amounts of 1-indanone and 2-indanone. The separation procedure is convenient and is based on different solubilities between isotruxene and side products.

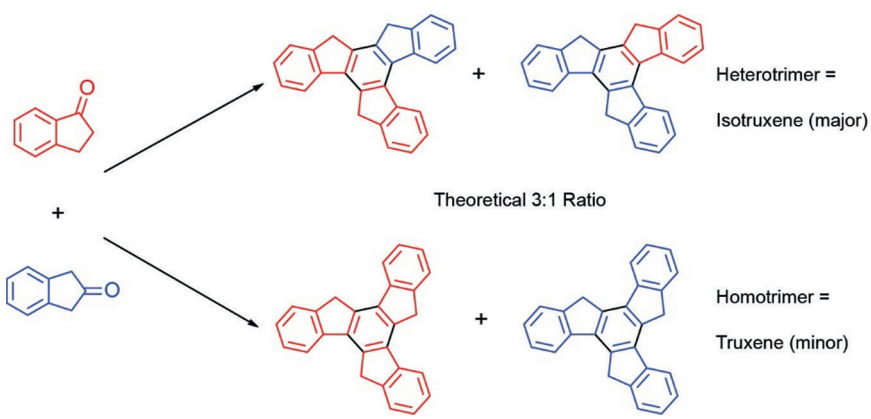
Keywords: truxene, oligofluorene, cyclotrimerisation, large-scale synthesis of isotruxene

Isotruxene is an isomer of truxene (structures in Scheme 1). These two isomers have a similar 2D-extented oligofluorene skeleton but different arrangements of the phenylene groups and thus different conjugation effects.[1,2] Although truxene and its derivatives have been widely applied in the field of organic electronics,[3–8] the potential of isotruxene in this field is much less explored,[9–11] mostly due to the limited synthetic methods. Lang *et al*. reported a synthetic procedure for isotruxene more than 50 years ago.[12] However, the harsh conditions (20 atm and 350 °C) applied in the procedure severely limited its application both in the laboratory and in industry. Yang *et al*. developed a synthetic procedure by oxidative cyclotrimerisation of indene under relatively mild conditions in 2006.[13] The yield was 18% after careful flash chromatography. After that, they reported three modified multistep approaches in 2009.[14] The total yields were improved to 27–36% on a 10-gram scale. Later, two more multistep approaches were reported by Wu and co-workers[15] and Liu *et al*.[16] and the total yields were 18 and 31% on 100-milligram and 1-gram scales respectively. We report here a one-step facile synthesis of isotruxene on a 150-gram scale from commercially available starting materials.

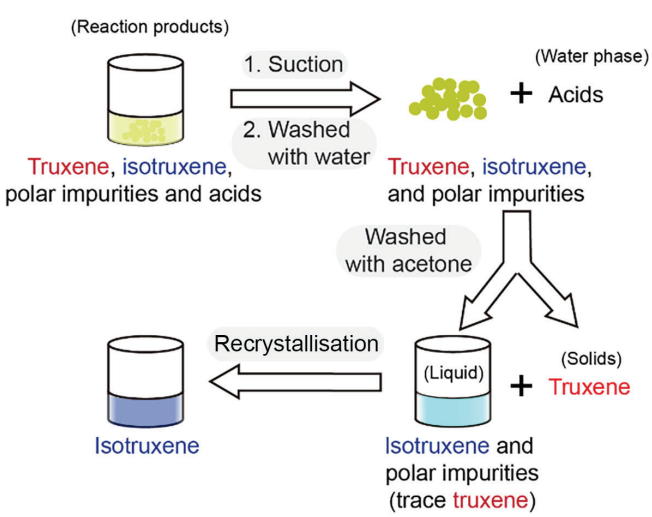
Results and discussion

Inspired by the well-developed synthetic procedure for truxene through cyclotrimerisation of 1-indanone in acetic acid and aqueous HCl, we designed a strategy for the synthesis of isotruxene (Scheme 1).[17] Specifically, equimolar amounts of 1-indanone and 2-indanone, both commercially available, were mixed and subjected to the acidic condensation conditions (HOAc/concentrated aqueous HCl). If the reactivities of the carbonyl groups in both 1-indanone and 2-indanone are equal, the ratio of heterotrimer to homotrimer should be 3:1, thus making isotruxene the major product and truxene the minor product. To our delight, isotruxene indeed formed as the major product after a one-day reflux of the mixture.

The purification procedure was relatively convenient (Scheme 2). The solid residue was easily separated by suction and washed three times with water. Then, after thorough washing



Scheme 1 Truxene-inspired synthetic strategy to isotruxene.



Scheme 2 Purification of isotruxene and truxene.

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with acetone, isotruxene was enriched in the eluent with little truxene and other polar impurities. This crude product was briefly purified through a short column over silica gel, then recrystallised from toluene or xylene, giving isotruxene as a light orange solid in 61% yield. Its ^{1}H and ^{13}C NMR spectra were in accordance with those in the literature.[13,14] High-performance liquid chromatography showed that the purity of the product was over 95%. In addition, truxene was enriched in the filter cake (15%). The as-obtained light-yellow solid of truxene was also pure as confirmed by ^{1}H NMR.[18]

Conclusion

Isotruxene was synthesised on a 150-gram scale simply by one-step cyclotrimerisation of commercially available 1-indanone and 2-indanone and easily separated based on different solubilities between isotruxene and side products. We believe that this tremendous improvement in the synthesis of isotruxene will facilitate the research of isotruxene as a building block for organic electronics, supramolecular chemistry, *etc.* The synthetic and separation strategy may also be applied for other C_{3h} symmetric polycyclic aromatic hydrocarbons and their isomers.

Experimental

Melting points were determined with a Büchi M-565 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX 400 or Bruker Advance 500 spectrometers in the indicated solvents at room temperature (298 K). Mass spectra were obtained on an Agilent 5973N spectrometer or a Waters Micromass GCT Premier spectrometer.

Synthesis of isotruxene; general procedure

1-Indanone (10.0 g, 75.7 mmol) and 2-indanone (10.0 g, 75.7 mmol) were suspended in acetic acid (60 mL) in a 250 mL flask. Hydrochloric acid (20 mL, 6 M) was added under magnetic stirring and the mixture was heated to 100 °C for 12 h. After cooling, the precipitate was filtered off, washed with water and extracted with acetone (100 mL in total). The organic phase was concentrated and the crude product was briefly purified through a short column over silica gel and then recrystallised from xylene to afford isotruxene as a light yellow solid [yield 10.5 g (61%)]. The filter cake was washed with toluene and collected to afford truxene as a yellow solid [yield 2.59 g (15%)].

For 150-gram scale synthesis, 1-indanone (150 g, 1.13 mol) and 2-indanone (150 g, 1.13 mol) were suspended in acetic acid (1 L) and hydrochloric acid (500 mL, 6 M) in a 3 L flask and a mechanical stirring device was used. The mixture was heated to 100 °C for 24 h and the workup procedure was similar to that described above, affording isotruxene as a light yellow solid [yield 150 g (58%)] and truxene as a yellow solid [yield 31.1 g (12%)].

Isotruxene: M.p. 219–221 °C (lit.[13,14] 218–220 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.60 (t, J = 8.0 Hz, 2 H), 7.94 (d, J = 7.2 Hz, 1 H), 7.71 (d, J = 7.2 Hz, 1 H), 7.64 (t, J = 7.2 Hz, 2 H), 7.51–7.45 (m, 3 H), 7.42–7.34 (m, 3 H), 4.28 (s, 2 H), 4.01 (s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.1, 144.0, 143.9, 142.4, 142.0, 141.8, 139.1, 137.5, 136.8, 136.5, 136.1, 135.7, 126.9, 126.8, 126.5, 126.3, 126.2, 126.1, 125.2, 125.1, 125.0, 123.5, 123.3, 122.1, 36.6, 35.9, 35.7; MS (EI) *m/z* 342 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{27}H_{18}^+$: 342.1409; found: 342.1411.

Truxene: M.p. 370–372 °C (dec.) [lit.[18] 368–369 °C (dec.)]; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.97 (d, J = 7.5 Hz, 3 H), 7.71 (d, J = 7.5 Hz, 3 H), 7.51 (t, J = 7.5 Hz, 3 H), 7.40 (t, J = 7.5 Hz, 3 H), 4.30 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.8, 141.7, 137.1, 135.3, 126.9, 126.3, 125.1, 121.9, 36.6; MS (EI) *m/z* 342 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{27}H_{18}^+$: 342.1409; found: 342.1405.

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