

Preparation of 4-(*N,N*-dihexylamino)-4'-nitrostilbene (DHANS)

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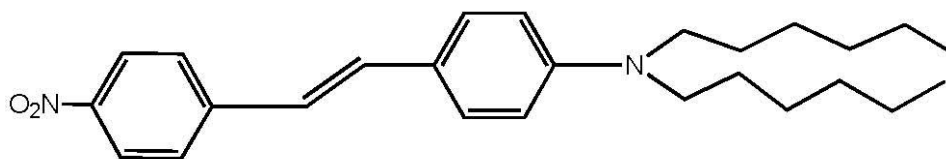
Abstract

A rational preparation of the NLO-dye (*E*)-4-(*N,N*-Dihexylamino)-4'-nitrostilbene (DHANS), using adapted standard procedures, is described. The target compound has been for the first time fully characterized by elemental analysis and spectroscopic data.

Keywords: NLO-properties, wave guiding polymers, dye preparation

Introduction

Like analogous stilbenes or azo dyes^{1,2}, the title compound is of interest in the preparation of non linear optical wave guiding polymer films^{3,4} or in studies of its influence on the thermodynamic properties of liquid crystalline 4'-pentylbiphenyl-4-carbonitrile⁵, but a procedure for its preparation does not seem to have ever appeared in the literature.



DHANS

In the references cited one finds either statements about a private source^{3,4} or simply that „the substance had been prepared“ in the respective research group⁵.

The Beilstein file refers to lit.⁵ but also does not list details of its preparation or physical and spectral data. In view of the interest in this kind of dyes this situation is felt to be unsatisfactory and therefore a rational procedure for the preparation of DHANS from readily available starting

materials is presented here.

Preparative work

Adapted standard procedures were used throughout. First, aniline was *N,N*-bis-hexylated using 1-bromohexane and potassium hydroxide.⁶ It is important to carefully purify the product by separating off all monoalkylated by-product and verifying its purity by ¹H NMR control. Vilsmeier formylation using dimethylformamide instead of *N*-formylaniline^{7,8} gave rise to 4-(*N,N*-dihexylamino)benzaldehyde, which was used in a Wadsworth-Emmons olefination reaction⁹ following analogous procedures^{10,11} to give the target substance, which was fully characterized by ¹H NMR-, IR, mass- and UV-spectra as well as elemental analysis.

Experimental Section

General Procedures. Unless stated otherwise, the preparations have been carried out in standard three-necked flasks equipped with mechanical stirrer, interior thermometer, dropping funnel and reflux condenser and immersed in either an oil or ice water bath as required. - UV spectra were taken on a Perkin Elmer 554 spectrophotometer, IR spectra on a Perkin-Elmer 983 instrument. ¹H NMR Spectra (CDCl₃ as solvent, TMS as internal standard) were recorded on Jeol JNM-PM X60 SI (60 MHz) and Bruker WM 300 instruments (300 MHz). The mass spectrum was taken on an AMD 604 mass spectrometer in the EI mode.

***N,N*-Dihexylaniline.** The literature procedure⁶ was upscaled to the fourfold size. A 500 ml flask was charged with 46.4 g (0.50 mol) of aniline and 56.1 g (1.0 mol) of powdered potassium hydroxide, which was then liquified by stepwise addition of 20 mL of water with external cooling. With rapid stirring, 168 g (143 mL, 1.05 mol) of 1-bromohexane were added within 30 min. The mixture was stirred and heated to 130 °C and kept at that temperature for 40 h.

After cooling to room temperature, 100 mL of water were added. The upper phase was decanted and washed with 100 mL of water and dried to give 111 g of an oil, showing a ¹H NMR integral ratio of aryl-H: other H \approx 1:6, which was subject to repeated distillation *in vacuo* to give, besides lower boiling foreruns, 58.7 g (45%) of an oil constantly boiling at 130 °C/ 1.33 mbar, ²⁰
n_D²⁰ 1.5067 (lit.^{D6} bp 172-173 °C/15 Torr, yield 55%). - ¹H NMR (60 MHz) δ 7.40 - 7.10 (m, 2H), 6.80 - 6.45 (m, 3H), 3.50 - 3.10 (m, 4H), 1.90 - 1.70 (22H).

The lower boiling fractions contain the monoalkylated amine as well as residual bromohexane and may be recycled. - For the following step, only fractions showing the correct integral ratio of 5H (aryl): 4H (2 x CH₂): 22H (2 x C₅H₁₁) being free of NH resonances around 3.66 ppm should be used.

4-(*N,N*-Dihexylamino)benzaldehyde. A 500 mL three-necked flask was charged with 44g (0.17 mol) of *N,N*-dihexylamine and 37 g (39.2 mL, 0.51 mol) of *N,N*-dimethyl-formamide. With external cooling, 26 g (0.17 mol) of phosphorus oxychloride were added dropwise at such a rate

that the temperature did not rise above 20 °C. The mixture was stirred at 20 °C for one h, subsequently heated to 100 °C, stirred at that temperature for 3 h and allowed to cool to room temperature. Crushed ice (200 g) was added slowly with efficient stirring, the mixture adjusted to pH 6 by addition of 5 N NaOH and extracted with 3 x 80 mL of diethyl ether.

The combined extracts were washed with saturated sodium hydrogen-carbonate solution, dried (Na₂SO₄) and concentrated. The residue (39.9 g) was distilled *in vacuo* to yield 28.2 g (57%) of a main fraction boiling at 163 °C/1.6 x 10⁻² mbar (lit.⁷ 205-207 °C/2 Torr). - ¹H NMR (60 MHz) δ 9.76 (1H, CHO), AA'BB' (δ_{AA'}, 7.76, δ_{BB'}, 6.66), 3.35 (mc, 2 x CH₂) 1.9 - 0.7 (m, 22 H). - Only fractions showing the correct integral ratios should be used.

***O,O*-Diethyl 4-nitrobenzylphosphonate.** A 100 mL flask connected to a 15 cm Vigreux column, distillation bridge and condenser was charged with a few boiling chips, 40 g (185 mmol) of 4-nitrobenzylbromide and 28 g (29 mL, 169 mmol) of triethylphosphite and then warmed gradually by an external oil bath.

A vigorous reaction, starting at 130 °C bath temperature, persisted for a few minutes and approximately 18.4 g (mainly bromoethane) were distilled off. At 155 °C bath temperature, no more volatiles were collected and the column was replaced by a distillation head. Low boiling fractions between 135 °C and 150 °C at 2.9 x 10⁻² mbar were discarded. A main fraction of 26.1 g (57%) of an oil, bp 166 °C/ 3 x 10⁻² mbar was collected, n_D²⁰ 1.5250 (lit.^{D12} bp 148-153 °C/ 0.1 mm, n_D²⁰ 1.5220). - ¹H NMR (60 MHz) AA'BB' (δ_{AA'}, 8.20, δ_{BB'}, 7.77), 4.30 (two superimposed q, 4H, *J* = 7.2 Hz), 3.52 and 3.13 (benzyl CH₂), 1.30 (t, *J* = 7.2 Hz, 6H, CH₃).

***(E)*-4-(*N,N*-Dihexylamino)-4'-nitrostilbene (DHANS).** In a 500 mL flask 25.9 g (94.8 mmol) of diethyl 4-nitrobenzylphosphonate and 27.4 g (94.8 mmol) of 4-(*N,N*-dihexylamino)benzaldehyde were dissolved in 120 mL of CaH₂-dried 1,2-dimethoxyethane. Equimolar amounts of sodium hydride (2.3 - 4 g depending on quality) were added in small portions to the stirred solution while the contents of the flask were kept at room temperature by external cooling. A deep red color developed immediately after the first addition of NaH. When all hydride had been added, the mixture was warmed up to 70 °C and allowed to cool off to room temperature again.

Water (200 mL) was added in small portions and the mixture extracted with 300 mL and thereafter 200 mL of chloroform. The combined extracts were washed with 300 mL of water, dried (Na₂SO₄) and concentrated to give 38.2 g of a deep red solid which was crystallized twice from hexane to give 27.4 g (71%) deep orange-red leaflets, mp 87 - 88 °C.

The mother liquor's residue was worked up by column chromatography using silica gel (0.2 - 0.5 mm) and cyclohexane/ethyl acetate (9:1) discarding the first lightly colored eluate and dark polar materials moving behind the intensely red colored zone, from which a second crop of 3.3 g (8.5 %) was obtained.

By the same procedure, the precrystallized material may be refined to be free of traces of contaminants as demonstrated by tlc. - ¹H NMR (300 MHz) AA'BB' (δ_{AA'} 8.16, δ_{BB'} 7.53, *J*_{AB} ≈ 10.9 Hz), AA'BB' (δ_{AA'} 7.39, δ_{BB'} 6.62, *J*_{AB} ≈ 8.9 Hz), AB (δ_A 7.18, δ_B 6.88, ³*J*_{AB} = 16.2 Hz),

3.29 (m, 4 H, N(CH₂)₂, 1.52 (m, 4 H), 1.37 (m, 12 H), 0.90 (t, $J = 6.7$ Hz, 6 H, 2 x CH₃). - IR (KBr), ν/cm^{-1} : 2954, 2927, 2858, 1605, 1584, 1506, 1335, 1186, 1106, 967, 958, 870, 852, 836. - MS (70 eV, 170 °C) m/z (%) 408 (52, M⁺) 378 (10), 337 (100, M⁺ - C₅H₁₁), 307 (9), 267 (66), 253 (11), 237 (10), 221 (5), 178 (9), 118 (5), 43 (26), 41 (7). - UV, λ/nm (lg ϵ): (Ethanol) 440 (broad max, onset 600 nm, 4.48), 350 (min, 3.66), 304 (max, 4.17), 256 (max, 3.83). - (Hexane): 452 (sh, 4.24), 424 (max, 4.42) 404 (sh, 4.37), 340 (min, 3.51), 294 (max, 4.37), 232 (min, 3.88), 205 (max, 4.43) - Anal. calcd. for C₂₆H₃₆N₂O₂ (408.58): C, 76.43; H, 8.88; N, 6.86. Found: C, 76.50, 76.41; H, 8.88, 8.86; N, 6.85, 6.82.

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