Preparation of an unsymmetrically substituted *push-pull*-triphenodioxazine

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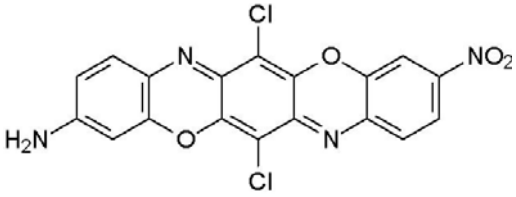
Abstract

The preparation of the NLO dye 3-amino-6,13-dichloro-10-nitrotriphenodioxazine starting from 2-amino-5-nitrophenol and chloranil via 7-acetamido-1,2,4-trichloro-3*H*-phenoxazin-3-one is described. All precursors and new products have been fully characterized.

Keywords: Oxazine dyes, aminophenol - chloroquinone condensation, NMR spectra, fluorescence

Introduction

Triphenodioxazines and triphenodithiazines are of interest in the preparation of non-linear optical wave guiding polymer films.[1–6] Although the preparation of the title compound 3-amino-6,13-dichloro-10-nitrotriphenodioxazine **1** from chloranil **2** and 2-amino-5-nitrophenol **3** via 3-carboxy-6,13-dichloro-10-nitrotriphenodioxazine was described in a patent,[7] no spectroscopic data have been presented therein.



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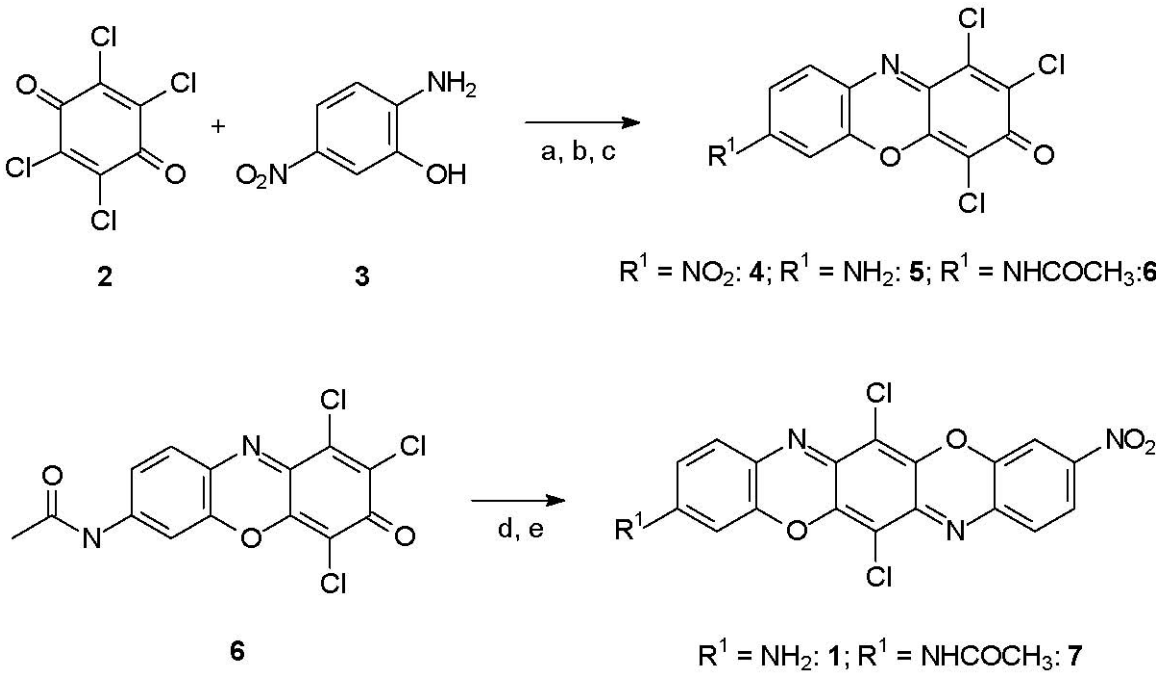
In this paper we describe a somewhat different synthetic access and present full spectroscopic data for **1**.

Results and Discussion

The synthetic route outlined in scheme 1 starts from commercially available 2,3,5,6-tetrachloro-*p*-benzoquinone **2** and 2-amino-5-nitrophenol **3**. The first three steps follow a publication of

Chlenova *et al*.[8] who condensed **2** and **3** in aqueous solution with the aid of a surfactant and sodium acetate as buffer. The resulting 1,2,4-trichloro-7-nitro-3*H*-phenoxazin-3-one **4** is then reduced to the amine **5** by sodium dithionite in aqueous solution. Attempts to condense **5** with **3** remained unsucessful due to the decreased electrophilicity of the carbonyl carbon as well as the reaction of **4** with 2,5-diaminophenol and 2-amino-5-dimethylaminophenol.

Acetylation of **5** with acetic anhydride seems to be more convenient than the procedure applied by Chlenova *et al*.[8] who made use of acetyl chloride in high boiling polychlorobenzenes as solvent. The resulting 7-acetamido-1,2,4-trichloro-3*H*-phenoxazin-3-one **6** is readily reacted with **3** in DMF with sodium acetate and gives rise to the triphenodioxazine **7**. Removal of the acetyl group in boiling aqueous sulfuric acid yields the push-pull dye **1**. The proton NMR of **1** in deuterated sulfuric acid shows the resonances of two independent ABX systems whereas eighteen signals are visible in the ^{13}C NMR, proving the unsymmetrical substitution pattern of **1**. The UV spectrum of **1** exhibits a broad unstructured band in the long wavelength region (604 nm). In contrast to the absorption, the emission spectrum of **1** is well structured and shows a Stokes shift of $\nu = 1004$ cm^{-1} with respect to the absorption maximum. Surprisingly the slightly structured excitation spectrum of **1** does not match the absorption spectrum and is blue-shifted by $\nu = 1996$ cm^{-1} (Figure 1). These findings lead to the conclusion that emission does not occur from the excited state initially reached by absorption showing charge-transfer character.



Scheme 1. Preparation of 3-amino-6,13-dichloro-10-nitrotriphenodioxazine **1**. (a) water, sodium acetate, 70 °C; (b) water, sodium dithionite, ambient temperature; (c) acetic anhydride, reflux; (d) DMF, sodium acetate, 120 °C; (e) 17% (v/v) aqueous sulfuric acid, reflux.

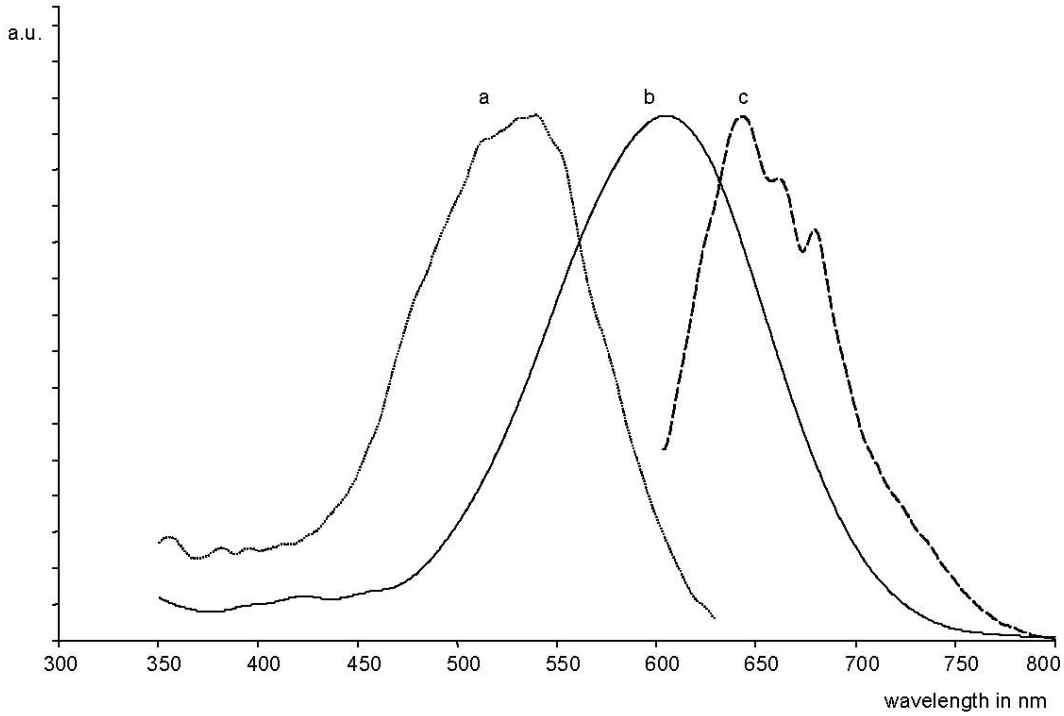


Figure 1. Normalized excitation (a), absorption (b) and fluorescence spectra (c) of **1** in methyl isobutyl ketone at a concentration of 9.6×10^{-6} M

Experimental Section

General Procedures. Melting points (up to 350 °C, uncorrected) were determined on a Kofler melting point microscope, model Reichert Thermovar. All NMR spectra were recorded on a Bruker WM 300 spectrometer at 25 ºC, unless otherwise stated. ^{1}H- and ^{13}C-NMR signals were referenced to tetramethylsilane as internal standard. Coupling constants are given in Hz and without sign. The IR-spectra were recorded (KBr) on a Perkin−Elmer spectrophotometer 983. Mass spectra were recorded on a AMD 604 spectrometer. The UV spectrum of **1** was recorded on a spectrophotometer Perkin–Elmer Lambda 40 in methyl isobutyl ketone. The fluorescence spectrum of **1** was obtained using a Perkin–Elmer luminescence spectrometer LS 50B in the same solvent. Elemental analyzes were performed with an elemental analyzer Carlo Erba 1106.
Materials. Unless otherwise stated, these were commercial samples. All organic solvents were of analytical quality and used as purchased.

1,2,4-Trichloro-7-nitro-3*H*-phenoxazin-3-one (4) was prepared according to ref. 8. Mp. 240 °C (ref. 8: 238–240 °C); ^{1}H-NMR (DMSO-d_6) δ 8.51 (1H, d, *J* = 2.3, 6-H), 8.31 (1H, dd, *J* = 8.8, 2.3, 8-H), 8.23 (1H, d, *J* = 8.8, 9-H); IR ν 3097, 1647, 1627, 1586, 1551, 1522, 1349, 1296, 1271, 1196, 1120, 1091, 1066, 982, 904, 863, 814, 750 cm^{-1}; MS (195 °C) *m/z* (%) 344 (100, M^+), 316 (21), 298 (12), 286 (11), 270 (14), 258 (11), 242 (21), 235 (8), 207 (10), 172 (16), 130 (18).

7-Amino-1,2,4-trichloro-3*H*-phenoxazin-3-one (5) was prepared according to ref 8. No melt below 350 °C; ^{1}H-NMR (DMSO-d_6) δ 7.64 (1H, d, *J* = 8.5, 9-H), 7.49 (2H, broad s, NH_2), 6.91 (1H, d, *J* = 8.6, 8-H), 6.70 (1H, s, 6-H); IR ν 3335, 3194, 1657, 1571, 1513, 1494, 1429, 1429, 1374, 1350, 1322, 1206, 1160, 1080, 981, 939, 921, 832, 776 cm^{-1}; MS (195 °C) *m/z* (%) 314 (100, M^+), 286 (46), 251 (18), 223 (30), 216 (20), 188 (7), 143 (10), 130 (7).

7-Acetamido-1,2,4-trichloro-3*H*-phenoxazin-3-one (6). A mixture of 2.08 g (6.6 mmol) **5** and 30 mL acetic anhydride was refluxed for 24 hours. After cooling water was added and the mixture was heated again for 10 minutes. The resulting solid was collected by filtration and washed with water. Drying gave 1.84 g (78%) **6**. no melt below 350 °C; ^{1}H-NMR (DMSO-d_6) δ 10.78 (1H, s, NH), 8.17 (1H, d, *J* = 1.6, 6-H), 7.99 (1H, d, *J* = 8.7, 9-H), 7.56 (1H, dd, J = 8.7, 1.6, 8-H) 2.09 (3H, s, CH_3); IR ν 3329, 3108, 1715, 1631, 1607, 1588, 1565, 1512, 1490, 1464, 1417, 1390, 1340, 1313, 1288, 1268, 1223, 1187, 1163, 1138, 1080, 987, 953, 921, 877, 843, 784 cm^{-1}; MS (285 °C) *m/z* (%) 358 (55, M^+), 314 (100), 288 (35), 251 (9), 223 (13), 216 (11), 188 (3), 130 (4).

3-Acetamido-6,13-dichloro-10-nitrotriphenodioxazine (7). A suspension of 940 mg (2.6 mmol) **6**, 460 mg (3.0 mmol) 5-nitro-2-aminophenol **3** and 1 g anhydrous sodium acetate in 40 mL DMF was heated to 120 °C for 4 hours. After cooling the precipitate was filtrated and washed with hot water. Drying in a vaccum desiccator yielded 462 mg (39%) **7** which was recrystallized from DMF. no melt below 350 °C; ^{1}H-NMR (D_2SO_4) δ 8.25 (1H, d, *J* = 2.2, 11-H), 8.13 (1H, dd, *J* = 9.2, 2.2, 9-H), 7.90 (1H, d, *J* = 9.1, 1-H), 7.86 (1H, d, *J* = 9.2, 8-H), 7.63 (1H, d, *J* = 2.2, 1-H), 7.49 (1H, dd, *J* = 9.1, 2.2, 2-H), 2.26 (3H, s, Me); ^{13}C-NMR δ 194.22 (C=O), 151.60, 151.47, 151.26, 148.45, 147.67, 143.08, 141.92, 136.56 (quart. C), 128.99 (tert. C), 128.31 (tert. C), 127.13 (quart. C), 126.25, 125.63, 116.22 (tert. C), 110.80, 110.71 (tert. C), 21.23 (Me); IR ν 3323, 3105, 1672, 1630, 1592, 1571, 1527, 1420, 1335, 1294, 1262, 1250, 1121, 1028, 911, 828 cm^{-1}; MS (340 °C) *m/z* (%) 456 (26, M^+), 414 (34), 368 (23), 340 (4), 263 (4); Anal. Calcd for $C_{20}H_9Cl_2N_4O_5$: C, 52.65; H, 1.99; N, 12.28. Found: C, 52.55; H, 2.28; N, 12.07.

3-Amino-6,13-dichloro-10-nitrotriphenodioxazine (1). A sample of 200 mg (0.4 mmol) **7** was dissolved in 8.5 mL conc. sulfuric acid. Under stirring the solution was added dropwise to 50 mL water and was then heated for 4 hours under reflux. The mixture was cooled and the precipitate was filtrated with suction and washed with water. Drying gave 143 mg (79%) **1**. A small sample was recrystallized from DMF and gave analytically pure **1** as small shining green needles, which do not melt below 350 °C; ^{1}H-NMR (D_2SO_4) δ 8.26 (1H, d, *J* = 2.2, 11-H), 8.12 (1H, dd, *J* = 9.2, 2.2, 9-H), 7.91 (1H, d, *J* = 9.1, 1-H), 7.86 (1H, d, *J* = 9.2, 8-H), 7.64 (1H, d, *J* = 2.2, 1-H), 7.50 (1H, dd, *J* = 9.1, 2.2, 2-H); ^{13}C-NMR δ 153.31, 153.18, 152.97, 150.16, 149.38, 144.77, 143.63, 138.26, 130.70 (quart. C), 130.03, 128.84, 128.17 (tert. C), 127.96 (quart. C), 127.33, 118.10, 117.94 (tert. C), 112.52, 112.42 (tert. C); IR ν 3475, 3388, 3095, 1634, 1599, 15710, 1543, 1514, 1435, 1390, 1301, 1278, 1223, 1128, 1071, 1023, 910, 824 cm^{-1}; MS (315 °C) *m/z* (%) 414 (100, M^+), 384 (22), 368 (53), 340 (9), 263 (12); Anal. Calcd for $C_{18}H_6Cl_2N_4O_4$: C, 52.07; H, 1.94; N, 13.49. Found: C, 51.83; H, 2.02; N, 13.41. UV λ (lg ε) 604 (4.5) nm.

Acknowledgements

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