SHORT PAPER

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Synthesis of a pentaerythritol derivative bearing azo functions

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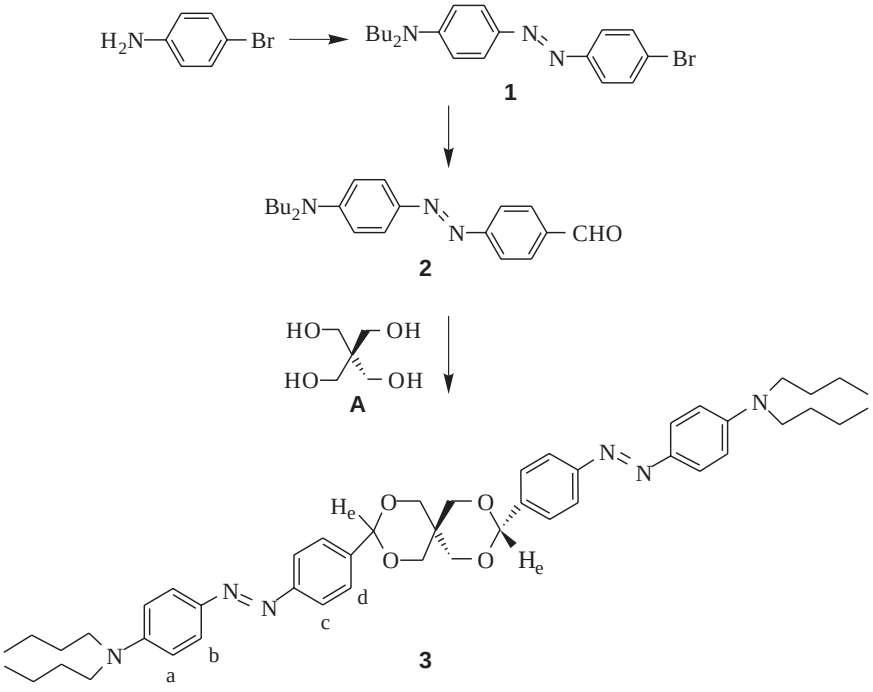
A convenient strategy for synthesis of a pentaerythritol derivative diacetal containing azo functions is presented; NMR data are discussed and are in good agreement with the molecular structure.

Keywords: azo-compound, diacetal, pentaerythritol, chirality, excitonic coupling

We describe here the synthesis of the diacetal **3** (Scheme 1). This molecule, which combines both properties of exciton chirality and photoisomerisable azo functions, constitutes a very promising system. In the chirality field, the great interest for chemists of pentaerythritol derivatives has been largely demonstrated: (i) this type of molecule presents a chirality based on an excitonic coupling, which can be used for absolute stereochemical assignments by the circular dichroism method;[1] (ii) in this context, such diacetals seem to exhibit interesting properties in terms of resolution, since several halogeno-derivatives were resolved by fractional crystallization;[2] (iii) recently, the spiran molecular geometry of the pentaerythritol **A** was used to obtain distorted spiro-polymers, readily soluble in organic solvents.[3] Furthermore azo functions, as optically isomerisable, have a relevant role in different fields of linear and nonlinear optics;[4] in this last field, the nonconjugated dimeric structure of **3** could lead to exalted properties.[5] Preliminary studies of this molecule doping polymers films have also shown its efficiency in all optical-poling (*i.e.* purely optical orientation of dye molecules) and photoinduced second harmonic generation (SHG).[6]

As previously described,[7] the synthesis of the diacetal derivatives is generally performed by condensation of aldehydes and ketones with pentaerythritol **A** using acids in catalytic amount. Lewis acids such as anhydrous ferrous sulfate,[8] and strong protic acids such as *p*-toluenesulfonic acid (PTSA)[9] can be used. The diacetal **3** was obtained in toluene, by condensation of the aldehyde **2** with the pentaerythritol **A** (Scheme 1). In spite of optimised conditions (removal of water and catalyst), a relatively low yield of 45% was obtained for **3**. Different attempts at optimisation of these synthesis conditions with the previously used reactant and catalyst (triethyl orthoformate[2] and $FeSO_4$ [8] respectively) led to lower yields. The deactivation of **2**, by the electron-donating dibutylamino group, could explain these relatively low yields. The intermediate benzaldehyde **2** was prepared in two steps: (i) synthesis of the [4-(4-bromo-phenylazo)phenyl] dibutylamine **1** by an azo coupling reaction from the commercial 4-bromoaniline and *N*,*N*-dibutylaniline, as previously described;[10] (ii) synthesis of **2** with a yield of 78% based on a lithium-bromine exchange,[11] followed by electrophilic attack with the dimethylformamide (DMF).



Scheme 1 Synthesis of the pentaerythritol derivative 3.

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

NMR data are in good agreement with the spiran chirality of **3**, since carbons (C(1) and C(2) of Fig. 1) from each acetal are non-equivalent (71.8 and 71.3 ppm respectively); furthermore, diastereotopic protons H_f and H_g (respectively H_h and H_i of Fig. 1) present a coupling constant of 11.6 Hz in absolute value. These experimental data are consistent with the geometry obtained from the MOPAC package[12] on a simplified diacetyl derivative (Fig. 1), showing that the proton H_f is more influenced by the spatial proximity of the two oxygens of an acetal corroborating its higher NMR chemical shift; when comparing calculated H–O distances in the modelised molecule of Fig. 1, they are predicted to be equal to 2.66 and 2.77 Å in the case of H_f, whereas for H_g, H_h and H_i at least one of these distances is larger than 3.2 Å.

Experimental

4–(4-Dibutylaminophenylazo)benzaldehyde **2**: To a cold solution (–105°C) of the [4-(4-bromophenylazo)phenyl]dibutyl-amine **1** (4 g, 10.3 mmol) in 50 ml of THF, is added dropwise under argon a 2.5 M BuLi solution in pentane (4.7 ml; 11.8 mmol). After 15 min of stirring, DMF (1.03 ml; 13.4 mmol) was added dropwise and the reaction mixture was stirred for 4 hours at –105 °C before hydrolysis by 2 ml of water. After evaporation of the solvent, the crude product was recrystallised (ethanol/water) to yield **2** (2.7 g; 8 mmol, 78%). ^{1}H NMR ($CDCl_3$): δ (ppm) 10.03 (1H, s, C*H*O), 7.96 (2H, d, *J* 8.6 Hz, H_{aro}), 7.90 (2H, d, *J* 8.6 Hz, H_{aro}), 7.86 (2H, d, *J* 9.2 Hz, H_{aro}), 6.68 (2H, d, *J* 9.2 Hz, H_{aro}), 3.37 (4H, t, *J* 7.6 Hz, N–C*H*$_2$–CH$_2$), 1.62 (4H, m, N–CH$_2$–C*H*$_2$), 1,38 (4H, sext. *J* 7,2 Hz, CH$_2$–C*H*$_2$–CH$_3$), 0,97 (6H, t, *J* 7,2 Hz, C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ (ppm) 192.4 (CHO), 157.7 (C_{aro}), 152.0 (C_{aro}), 144.0 (C_{aro}), 136.6 (C_{aro}), 131.3 (CH_{aro}), 126.7 (CH_{aro}), 123.2 (CH_{aro}), 111.8 (CH_{aro}), 51.6 (N–*C*H$_2$–CH$_2$), 30.1 (CH$_2$–*C*H$_2$–CH$_3$), 20.9 (N–CH$_2$–*C*H$_2$), 14.6 (*C*H$_3$). UV-vis (EtOH): λ_{max} (ε) = 467 (33640). m.p. = 86.6°C. Calcd for $C_{21}H_{27}N_3O$: C, 74.80; H 8.19; N, 12.37. Found C. 74.74; H, 8.06; N, 12.45.

3,9-Bis[4-(4-N,N-dibutylaminophenylazo)-phenyl]-2,4,8,10-tetraoxaspiro[5,5] undecane **3:** A mixture of pentaerythritol **A** (115 mg; 0.84 mmol), **2** (500 mg; 1.5 mmol) and of a catalytic amount of *p*-toluenesulfonic acid in toluene 150 ml was stirred at refluxing temperature for 4 h using a Dean-Stark apparatus for water removal. After cooling and evaporation of the solvent to dryness, the resulting residue was purified by chromatography on silica gel (Et_2O/pentane, 3:2). Recrystallisation (CH_2Cl_2/pentane) of the resulting product yields to 262 mg (0.34 mmol, 45%) of the pale orange product. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.83 (4H, d, *J* 8.3, H_b. H_c), 7.57 (2H, d, *J* 8.3 Hz, H_d), 6.68 (2H, d, *J* 8.3 Hz, H_a), 5.50 (1H, s, H_e), 4.89 (1H, d, *J* 11.6 Hz, H_f), 3.87 (2H, d, *J* 11.6, H_g, H_i), 3.67 (1H, d, *J* 11.6 Hz, H_h), 3.35 (4H, t, *J* 7.3 Hz, N–C*H*$_2$), 1.58 (4H, m, N–CH$_2$–C*H*$_2$), 1.37 (4H, m, C*H*$_2$–CH$_3$), 0.96 (6H, t, *J* 7.3 Hz, CH$_3$). ^{13}C NMR ($CDCl_3$): δ (ppm) 154.3 (C_{aro}), 151.3 (C_{aro}), 143.7 (C_{aro}), 139.1(C_{aro}), 127.4 (CH_{aro}), 125.9 (CH_{aro}), 122.7 (CH_{aro}), 111.7 (CH_{aro}), 102.7 (C_{He}), 71.8 and 71.3 (CH$_2$–O), 51.6 (N–*C*H$_2$), 33.2 (C^{IV}), 30.1 (N–CH$_2$–*C*H$_2$), 20.9 (*C*H$_2$–CH$_3$), 14.6 (CH$_3$). UV-vis (EtOH): 424 (55680). m.p. = 139.2°C. Calcd for $C_{47}H_{62}N_6O_4$: C, 72.59; H, 8.08; N, 10.71. Found C, 72.84; H, 8.06; N, 10.84.

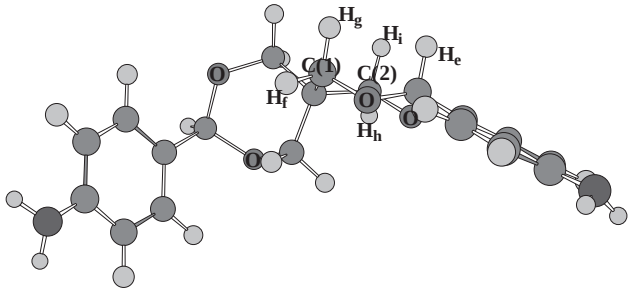

Fig. 1 Modelisation of the diacetal part of compound **3**.

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