Journal of Photochemistry and Photobiology A: Chemistry 198 (2008) 26–33

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Intramolecular charge transfer in photoexcited hydroxyterphenyls: Evidence for formation of terphenyl quinone methides in aqueous solution

Musheng Xu, Christy Z. Chen, Peter Wan*

Department of Chemistry, Box 3065, University of Victoria, Victoria, BC V8W 3V6, Canada

ARTICLE INFO

Article history:
Received 23 November 2007
Received in revised form 9 February 2008
Accepted 17 February 2008
Available online 10 March 2008

Keywords:
Terphenyl quinone methide
Photosolvolysis
Photodehydroxylation
Photosolvolysis
Excited state proton transfer

ABSTRACT

The photochemistry of a number of *p*-terphenyls substituted with hydroxy and hydroxymethyl substituents at the terminal benzene rings has been studied in aqueous solution. Previous work has shown that a simple hydroxyl group can strongly activate appropriately substituted benzenes or biphenyls towards dehydroxylation, via its highly electron-donating nature upon deprotonation in S_1. The intermediates formed are the corresponding quinone methides (QMs) or biphenyl quinone methides (BQM). We show in this work that the methodology also works for appropriately substituted *p*-terphenyls. Thus, a number of *p*-terphenyls with the appropriate substituents at the terminal benzene rings were synthesized via consecutive Suzuki-type coupling reactions from commonly available starting materials. Although these terphenyls are much less soluble than their simpler biphenyl analogs, they were sufficiently soluble in aqueous CH_3CN or CH_3OH for their photosolvolytic reactivity to be studied by product studies and fluorescence measurements which are consistent with formation of terphenyl quinone methides (TQMs) as intermediates. Their quantum yields of formation are attenuated compared to the corresponding biphenyl and benzene analogs and one possible reason is the highly fluorescent nature of both phenol and phenolate forms.

1. Introduction

Continuing studies from our laboratory [1a–m] and from Freccero [1n–q] have shown that efficient photosolvolysis (e.g., Eq. (1)), photocyclization (e.g., Eq. (2)), and proton exchange via photogenerated biaryl quinone methides (BQM), can be induced in biphenyls and biaryls in general, using an hydroxy group as an electron donating substituent and carrier of an acidic proton (in S_1), taking advantage of the propensity of biaryls to twist to a more planar geometry on electronic excitation. In these and related reactions, the enhanced acidity of the phenol moiety in S_1 is essential as the corresponding methoxy derivatives are either much less reactive or not reactive at all. In addition, it is proposed that the S_1 reactive state of these compounds have highly polarized electronic distributions (at least in aqueous solution, a very polar solvent), from the phenol moiety to the attached (adjacent) aromatic ring, which nicely explains the chemistries observed: either photosolvolytic reaction or excited state intramolecular proton transfer (ESIPT) from phenol OH to carbon [1].

In view of the interest in materials properties and applications of rod-like oligo-*p*-phenylenes [2] and our own curiosity as to how far the photoinduced charge transfer can be effected through a conjugated π system of phenyl rings, we have synthesized a number of hydroxyterphenyls **1**–**6** and a related diphenylacetylene system **7**. These compounds were designed to test whether photoexcitation results in significant charge transfer through the π system of the phenyl rings (with electron donation from the hydroxyl of the phenol), which might induce solvolytic reactivity at the benzylic alcohol moiety at the other end of the molecule, and hence possibly formation of terphenyl quinone methides (TQMs), analogous to what has been observed for similar biphenyl derivatives [1]. We find that based on products studies, all systems display charge transfer character in S_1 sufficient for photosolvolytic or photohydrolytic reactivity although in all cases the reactivity (as measured by quantum yields for product formation) are significantly lower than similar biphenyl derivatives.

2. Experimental details

2.1. General

^{1}H NMR spectra were recorded on a Bruker AC-300 (300 MHz) instrument in $CDCl_3$ or $(CD_3)_2CO$. UV–vis spectra were recorded on a Cary 1 or Philips PU 8740 spectrophotometer. Low resolution mass spectra were obtained on a Finnigan 3300 instrument (CI) and high resolution mass spectra (HRMS) were determined with a

* Corresponding author. Tel.: +1 250 721 8976; fax: +1 250 721 7147.
E-mail address: pwan@uvic.ca (P. Wan).

1010-6030/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2008.02.012

Kratos Concept H (EI) instrument. Melting points were obtained on a Gallenhamp melting point apparatus. Thin layer chromatography (TLC) was carried out on Analtech silica gel GF Uniplates. CH_3CN used for the fluorescence studies was dried over CaH_2 and distilled before use. Readily available inorganic and organic reagents were purchase from Aldrich and used as received.

2.2. Materials

2.2.1. o,p-Methyl and p-methoxyphenylboronic acids

The general procedure for the synthesis of these boronic acids is described as follows. The bromotoluene or *p*-bromoanisole was first converted to the corresponding Grignard reagent in anhydrous diethyl ether using standard procedure. The solution was then filtered into a dropping funnel and added drop-wise into a solution of $B(OMe)_3$ (2 times excess) in anhydrous diethyl ether (0.1 mol per 20 mL) over 2 h at −78 °C (acetone-dry ice bath) under N_2. The mixture was then warmed to room temperature and stirred for 2 h. Finally, 10% HCl solution was added and the mixture was stirred for 30 min. The aqueous layer was extracted with diethyl ether. The organic extract was dried over $MgSO_4$ and the solvent was removed to give the boronic acid (white solid) in ca. 85% yield. The pure products were obtained after crystallization from toluene/hexane.

p-Methylphenylboronic acid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H, CH_3), 7.32 (d, 2H, J = 7 Hz, ArH), 8.18 (d, 2H, J = 7Hz, ArH), no OH peak observable.

o-Methylphenylboronic acid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.82 (s, 3H, CH_3), 7.20–7.36 (m, 2H, ArH), 7.45 (dd, 1H, J = 7.1 Hz, ArH), 8.20 (d, 1H, J = 7 Hz, ArH), no OH peak observable.

p-Methoxyphenylboronic acid, ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (s, 3H, OCH_3), 7.00 (d, 2H, J = 7 Hz, ArH), 8.15 (d, 2H, J = 7 Hz, ArH), no OH peak observable.

2.2.2. 4-Hydroxy-4″-hydroxymethyl-p-terphenyl (**1**) and 4-hydroxy-2″-hydroxymethyl-p-terphenyl (**2**)

To a stirred solution of *p*-iodobromobenzene (1 mmol) in DME (100 mL) under nitrogen was added $Pd(PPh_3)_4$ (0.06 mmol). After 15 min, 12 mL of aqueous Na_2CO_3 (6 mmol, 2 M) and 1 mmol of *o* or *p*-$CH_3PhB(OH)_2$ dissolved in a minimum volume of EtOH were sequentially added. The mixture was refluxed for 24 h and then cooled to room temperature and treated again with 1 mmol of *p*-$CH_3OPhB(OH)_2$ dissolved in a minimum amount of EtOH. The solution was then refluxed for another 24 h. The hot solution was filtered immediately through a Celite pad. As the filtrate was cooled to room temperature, some of the biphenyl anisoles precipitated as shining crystals which were isolated from the solution and the liquid portion was concentrated and extracted with Et_2O to recover residual product. The Et_2O extract was washed successively with H_2O, 5% aq NaOH, 10% aq HCl, sat. $NaHCO_3$, and brine, dried over Na_2SO_4, and evaporated under reduced pressure to give a solid residue which was purified by recrystallization from MeOH. The overall yield was ca. 70%. *4-Methoxy-4″-methyl-p-terphenyl*, ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 2.38 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 7.03 (d, 2H, J = 7 Hz, ArH), 7.28 (d, 2H, J = 7 Hz, ArH), 7.55–7.70 (m, 8H, ArH). MS (CI) *m*/*z* (relative intensity): 275 (M+1) (100). *4-Methoxy-2″-methyl-p-terphenyl*, ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 2.38 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 6.98 (d, 2H, J = 7Hz, ArH), 7.22–7.28 (m, 4H, ArH), 7.36 (d, 2H, J = 7Hz, ArH), 7.54–7.62 (m, 4H, ArH). MS (CI) *m*/*z* (relative intensity) 275 (M+1) (100).

To a solution of the above synthesized biphenyl anisoles (4 mmol) in 120 mL CCl_4, a slurry of NBS (4.1 mmol) in 80 mL CCl_4 was added followed by 0.04 g of benzoyl peroxide. The mixture was refluxed for 30 h (the bromination was followed by TLC) and allowed to cool to room temperature and filtered. The solution was washed with H_2O (3 × 50 mL) and then dried over $MgSO_4$. The crude terphenyl bromide was obtained in ca. 90% yield after removal of the solvent and demethylated with BBr_3 without further purification, as follows: a solution of the substrate (1 equivalent) in CH_2Cl_2 (70 mL per 10 mmol) was added drop-wise into a solution of BBr_3 (1.2–2.5 equivalent, 0.1–0.2 M in CH_2Cl_2). The solution was stirred at room temperature for 3 h. The reaction was then quenched by addition of water. The aqueous layer was extracted by Et_2O (twice). The combined organic extract was dried over $MgSO_4$ and the solvent was evaporated on the rotary evaporator to give a pale yellow solid which was used directly in the next hydrolysis step. The bromide $ArCH_2Br$ was refluxed in 1:1 acetone–water (ca. 50 mL per g of bromide, with or without added $NaHCO_3$) overnight. The solution was then cooled to room temperature and extracted with CH_2Cl_2 (twice) then extracted with Et_2O (once). The extracts were combined and dried over $MgSO_4$. The crude product was obtained upon evaporation of the solvent. Recrystallization in toluene/THF/hexanes provided pure **1**: m.p. (decomp.) 296 °C. ^{1}H NMR (360 MHz, $(CD_3)_2CO$) δ 4.22 (t, 1H, J = 5 Hz, exchangeable with D_2O, OH), 4.68 (d, 2H, J = 5 Hz, CH_2), 6.94 (d, 2H, J = 7 Hz, ArH), 7.45 (d, 2H, J = 7 Hz, ArH), 7.55 (d, 2H, J = 7 Hz, ArH), 7.62–7.76 (m, 6H, ArH), 8.45 (s, 1H, exchangeable with D_2O, ArOH); HRMS: observed: 276.1151, calculated for $C_{19}H_{16}O_2$: 276.1146. Recrystallization in toluene/hexanes provided pure **2**: m.p. (decomp.) 214 °C. ^{1}H NMR (360 MHz, $(CD_3)_2CO$) δ 4.25 (t, 1H, J = 5 Hz, exchangeable with D_2O, OH), 4.52 (d, 2H, J = 5 Hz, CH_2), 6.83 (d, 2H, J = 7 Hz, ArH), 7.22–7.34 (m, 3H, ArH), 7.4 (d, 2H, J = 7 Hz, ArH), 7.49 (d, 2H, J = 7 Hz, ArH), 7.57–7.63 (m, 3H, ArH), 8.45 (s, 1H, exchangeable with D_2O, ArOH); ^{13}C NMR δ 31.0, 62.5, 116.4, 126.8, 127.4, 127.8, 128.5, 128.8, 130.2, 130.4, 132.5, 140.0, 140.8, 141.5; HRMS: observed: 276.1149, calculated for $C_{19}H_{16}O_2$: 276.1146.

2.2.3. 4-Hydroxy-4″-(α-hydroxybenzyl)-p-terphenyl (**3**) and 4-hydroxy-2″-(α-hydroxybenzyl)-p-terphenyl (**4**)

4-Hydroxybenzophenone or 2-hydroxybenzophenone (Aldrich, 10 g, 51 mmol) was dissolved in 200 mL of distilled CH_2Cl_2 in a 500 mL 2-neck round bottom flask. After addition of 15 mL of pyridine (52 mmol) the solution became clear and was cooled down to 0 °C and trifluoromethylsulfonic acid anhydride (Aldrich, 13 mL, 77 mmol, 1.5 eq) in a 70 mL of distilled CH_2Cl_2 was added via a 100 mL dropping funnel over 20 min. The solution was then allowed to warm up to room temperature and stirred overnight. The reaction was worked up by pouring the organic solution into 200 mL ice-water and then extracted with 200 mL dichloromethane twice and washed with water. The organic layers were combined and dried with anhydrous magnesium sulfate. After removal of the solvent and pyridine (the latter under vacuum), a brown yellow oil was obtained which was taken to the next step (coupling reaction) without purification, as described below.

4-Methoxyphenylboronic acid (12.5 g, 82 mmol, 1.6 eq) was dissolved in 250 mL of deoxygenated toluene in a 500 mL 3-neck round bottom flask containing 18 g (130 mmol, 2.5 eq) K_2CO_3 and 17 g (52 mmol, 1 eq) of 2 or 4-benzoylphenyltriflate as synthesized above. The flask was fitted with a reflux condenser and a stirring bar. After flushing with N_2 1.5% mole (based on the benzoylphenyltriflate) of $Pd(PPh_3)_4$ was added through the side arm. The mixture was then purged again with N_2 and refluxed overnight. The solution was cooled and any inorganic precipitate was removed by vacuum filtration. After decolorizing with charcoal followed by filtration, a clear yellow toluene solution was obtained. Removal of solvent gave a light yellow solid which was recrystallized from toluene/hexane, producing a white solid (5.1 g, 55%). *4-(4′-Methoxyphenyl)benzophenone*, ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (s, 3H, $-OCH_3$), 7.08 (d, J = 8.1 Hz, 2H, ArH), 7.55 (t, 2H, ArH), 7.70 (m, 3H, ArH), 7.81 (m, 6H, ArH); MS (CI, *m*/*z*) 289 (M^++1). *2-(4′-Methoxyphenyl)benzophenone*, ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.68 (s,

3H, –OCH_3), 6.62 (dd, J = 8.1 Hz, 1.8 Hz, 2H, ArH), 7.14 (d, J = 7.8 Hz, 2H, ArH), 7.21 (t, J = 4.2 Hz, 2H, ArH), 7.38 (m, 4H, ArH), 7.42 (m, 1H, ArH), 7.56 (dd, J = 1.9 Hz, 8.1 Hz, 2H, ArH); MS (CI, m/z) 289 (M^++1).

The 2 or 4-(4′-methoxyphenyl)benzophenone was treated with BBr_3 in 100 mL CH_2Cl_2 at room temperature for 2 h after which the reaction was quenched with addition of water and the organic component was extracted with 100 mL dichloromethane twice and combined. After removal of the solvent, the crude product was a light yellow solid (yield 94%). Pure *4-(4′-hydroxylphenyl)benzophenone* (**8**) was obtained by recrystallization from toluene/hexane. ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 6.95 (dd, J = 2.2 Hz, 8.1 Hz, 2H, ArH), 7.60 (m, 5H, ArH), 7.80 (m, 6H, ArH), 8.64 (s, 1H, exchangeable with D_2O, ArOH); MS (CI, m/z): 275 (M^++1). *2-(4′-Hydroxyphenyl)benzophenone*, ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 6.70 (dd, J = 1.8 Hz, 8.0 Hz, 2H, ArH), 7.15 (d, J = 8.1 Hz, 2H, ArH), 7.26 (t, J = 7.6 Hz, 2H, ArH), 7.43 (m, 4H, ArH), 7.61 (m, 3H, ArH), 8.39 (s, 1H, exchangeable with D_2O, ArOH); MS (CI, m/z): 275 (M^++1).

Using an identical protocol as already described above, these hydroxyphenyl benzophenones were triflated using trifluoromethylsulfonic acid anhydride, coupled to *p*-methoxyphenylboronic acid using Suzuki coupling, demethylated using BBr3, and reduced with $NaBH_4$ or $LiAlH_4$ to give either **3** or **4**. Typical yields in each step was > 90%. Terphenyl **3** was recrystallized from toluene, ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 4.90 (d, 1H, exchangeable with D_2O, –OH), 5.91 (d, J = 2.2 Hz, 1H, ArCH), 6.95 (d, J = 8.3 Hz, 2H, ArH), 7.21 (m, 1H, ArH), 7.25 (m 2H, ArH), 7.45 (m, 6H, ArH), 7.64 (m, 6H, ArH), 8.45 (s, 1H, exchangeable with D_2O, ArOH); HRMS $C_{25}H_{20}O_2$: calc. 352.1463, found 352.1458. Terphenyl **4** was recrystallized from 9:1 toluene/hexane, ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 4.78 (d, J = 3.5 Hz, 1H, exchangeable with D_2O, –OH), 6.02 (d, J = 3.2 Hz, 1H, ArCH), 6.95 (dd, J = 1.9 Hz, 8.1 Hz, 2H, ArH), 7.20 (m, 6H, ArH), 7.38 (m, 4H, ArH), 7.60 (m, 5H, ArH), 8.45 (s, 1H, exchangeable with D_2O, ArOH); HRMS $C_{25}H_{20}O_{2:}$ calc. 352.1463, found 352.1478.

2.2.4. 4-Hydroxy-2″-benzyl-p-terphenyl (*12*)

A photochemical method was employed for the synthesis of **12**, by photolysis of **4** in the presence of $NaBH_4$, presumably via the intermediate TQM. A solution of 100 mg of **4** and excess NaBH4 (about 80 mg) dissolved in 80 mL 1:1 H_2O–CH_3CN was irradiated at 254 nm in a Rayonet photochemical reactor for 12 min. The solution was then extracted with CH_2Cl_2 which gave a colorless solid on evaporation of the solvent. This material was purified by prep. TLC (silica gel, 5% ethyl acetate in CH_2Cl_2) followed by crystallization in 9:1 toluene/hexane to give 86 mg (90%) of pure **12**, ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.00 (s, 2H, $ArCH_2$), 4.78 (s, 1H, Ar–OH), 6.85 (d, J = 8.1 Hz, 2H, ArH), 6.95 (d, J = 8.3 Hz, 2H, ArH), 7.20 (m, 5H, ArH), 7.23 (m, 4H, ArH), 7.45 (m, 4H, ArH); HRMS $C_{25}H_{20}O$, calc. 336.1514, found 336.1501.

2.2.5. 4-Hydroxy-4′-(hydroxymethyl)diphenylacetylene (*7*)

The required 4-ethynylbenzaldehyde (**9**) was synthesized from trimethylsilylacetylene (Aldrich) and *p*-bromobenzaldehyde, according to the procedure reported by Austin et al. [4]. The subsequent coupling with 4-iodophenol followed a procedure of Li et al. [5] using as catalyst tri-(2-furyl)phosphine and $Pd_2(dba)_3$ (tris(dibenzylideneacetone)dipalladium(0)). The crude material was purified by column chromatography (silica gel, 3:7 hexane/CH_2Cl_2), to give pure *4-hydroxy-4′-formyldiphenylacetylene* (***10***), ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.81 (dd, J = 2.1Hz, 8.2 Hz, 2H, ArH), 7.35 (dd, J = 2.2 Hz, 8.3 Hz, 2H, ArH), 7.59 (d, J = 8.1 Hz, 2H, ArH), 7.70 (s, 1H, ArOH), 7.79 (dd, J = 2.2 Hz, 8.2 Hz, 2H, ArH), 9.95 (s, 1H, –CHO). Treatment of **10** with $NaBH_4$ in CH_3OH readily gave **7**, ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 2.86 (d, J = 2.0 Hz, 1H, –OH), 4.61 (d, J = 8.3 Hz, 2H, ArH), 6.72 (dd, J = 2.1 Hz, 8.3 Hz, 2H, ArH), 7.28 (m, 4H, ArH), 7.38 (d, J = 8.1 Hz, 2H, ArH), 7.92 (s, 1H, ArOH); HRMS $C_{15}H_{12}O_2$: calc. 224.0837, found 224.0837.

2.3. Product studies

A solution of the compound was transferred to a 100 or 200 mL quartz vessel with a water-cooled cold finger (ca. 15 °C) and purged with argon (via a stainless steel syringe needle) for approximately 15 min before and during irradiation in a Rayonet RPR 100 photochemical reactor using 254 nm (or 300 nm) lamps. After photolysis, NaCl was added to the solution and extracted with CH_2Cl_2. The organic extract was dried with $MgSO_4$ and the solvent removed under aspirator vacuum.

2.3.1. Photolysis of *1*

A solution of **1** (10 mg) in 3:7 H_2O–MeOH (100 mL) was photolyzed (254 nm × 8 lamps) in a quartz tube for 2.5 min by the above general procedure. ^{1}H NMR showed that the product mixture contained ca. 13% of methyl ether **11** and 87% of starting material **1**; no side products were detectable. Preparative TLC (silica, 5% EtOAC–CH_2Cl_2) was used for the isolation of *4-hydroxy-4″-(methoxymethyl)-p-terphenyl* (***11***), ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 3.35 (s, 3H, OCH_3), 4.48 (s, 2H, CH_2), 6,94 (d, 2H, J = 7 Hz, ArH), 7.45 (d, 2H, J = 7 Hz, ArH), 7.55 (d, 2H, J = 7 Hz, ArH), 7.62–7.76 (m, 6H, ArH), 8.45 (s, 1H, exchangeable with D_2O, ArOH); HRMS, calculated for $C_{20}H_{18}O_2$, 290.1302, observed 290.1303.

2.3.2. Photolysis of *2*

A solution of **2** (10 mg) in 1:1 H_2O–MeOH (100 mL) was photolyzed (254 nm × 8 lamps) in a quartz tube for 2.5 min. ^{1}H NMR showed that the product mixture contained ca. 25% of the corresponding methyl ether and 75% of starting material **2**. Prep. TLC (silica, 5% EtOAC–CH_2Cl_2) was used for the isolation of the product, *4-hydroxy-2″-(methoxymethyl)-p-terphenyl*, ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 3.18 (s, 3H, OCH_3), 4.22 (s, 2H, CH_2), 6.83 (d, 2H, J = 7 Hz, ArH), 7.22–7.34 (m, 3H, ArH), 7.4 (d, 2H, J = 7 Hz, ArH), 7.49–7.63 (m, 5H, ArH), 8.45 (s, 1H, exchangeable with D_2O, ArOH); HRMS, calculated for $C_{20}H_{18}O_2$, 290.1302 observed, 290.1302.

2.3.3. Photolysis of *3*

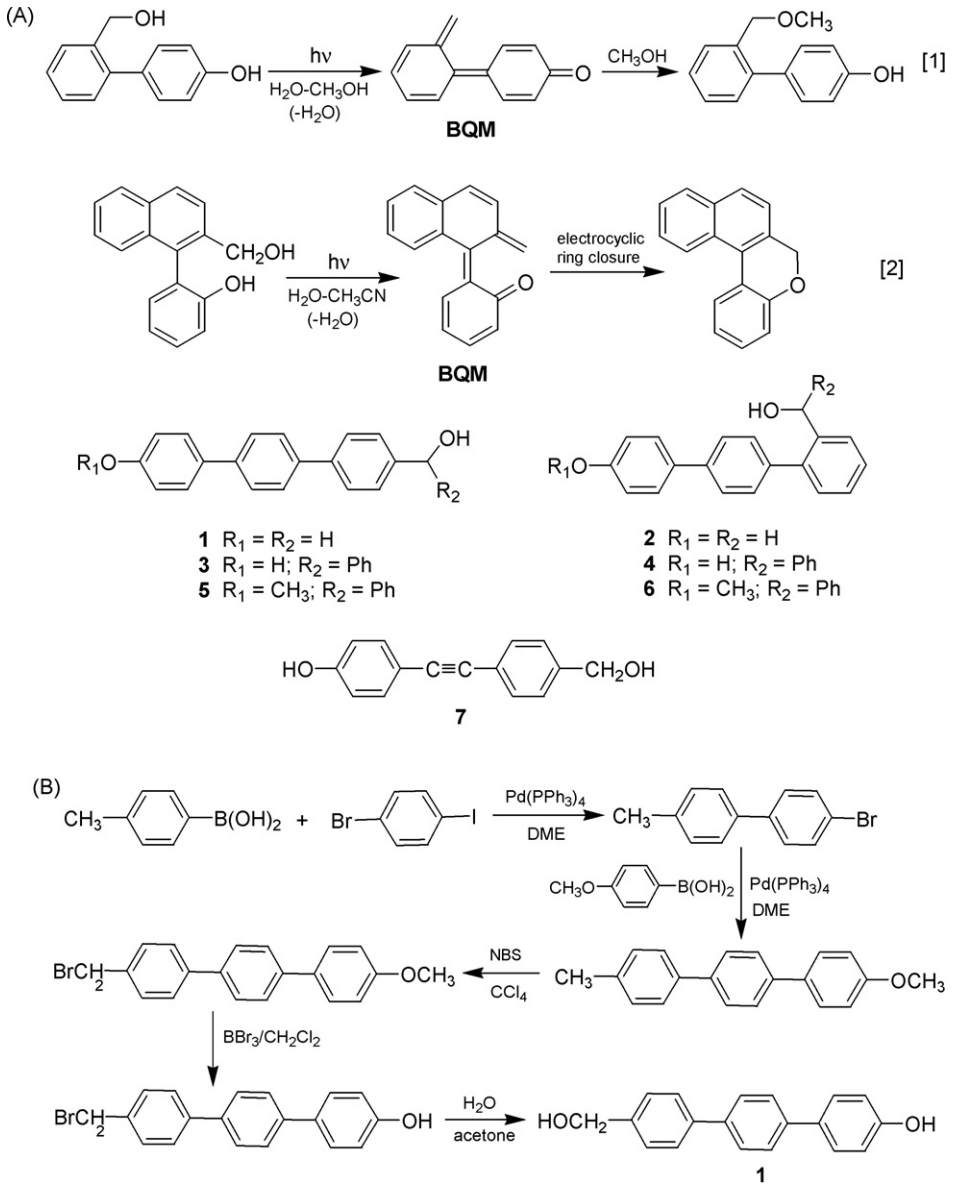
A solution of **3** (20 mg) in 1:1 H_2O–CH_3OH in 80 mL was irradiated for 25 min. ^{1}H NMR of the white crude product showed a 8% conversion 8% to the corresponding methyl ether. Purification was accomplished by prep. TLC (silica, CH_2Cl_2) to give pure *4-hydroxy-4″-(α-methoxybenzyl)-p-terphenyl*, ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 3.25 (s, 3H, –OCH_3), 5.40 (s, 1H, –CH–), 6.93 (d, J = 8.3 Hz, 2H, ArH), 7.20 (m, 1H, ArH), 7.25 (m, 2H, ArH), 7.45 (m, 6H, ArH), 7.64 (m, 6H, ArH), 8.40 (s, 1H, exchangeable with D_2O, ArOH); MS (FAB), 366.1 (M^+, 99%), 335 (M^+ –OCH_3, 66%), (M^+-$HOCH_3$, 54%), (M^+ –OCH_3–Ph, 100%).

2.3.4. Photolysis of *4*

Photolysis as above gave ca. 10% yield of the corresponding methyl ether, which was purified by prep. TLC (silica, CH_2Cl_2), to give *4-hydroxy-2″-(α-methoxybenzyl)-p-terphenyl*, ^{1}H NMR δ (300 MHz, $CDCl_3$) δ 3.08 (s, 3H, –OCH_3), 5.28 (s, 1H, –CH–), 6.80 (d, J = 8.3 Hz, 2H, ArH), 7.20 (m, 6H, ArH), 7.45 (m, 4H, ArH), 7.64 (m, 5H, ArH), 7.76 (br, 1H, ArOH); MS (FAB): 366.1 (M^+).

2.3.5. Photolysis of *7* in 1:1 H_2O–CH_3OH or 1:1 H_2O–CH_3CN

A solution of **7** (10 mg) was dissolved in 80 mL of the appropriate solvent and irradiated at 300 nm for 20 min. Separation and purification by prep. TLC (silica, CH_2Cl_2) gave **13** as the major product, ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.11 (s, 2H, $ArCH_2$–), 4.72 (s, 2H, $ArCH_2O$–),



Scheme 1.

6.70 (d, 2H, J = 7.8 Hz, Ar–H), 7.0 (d, 2H, J = 7.9 Hz, Ar–H), 7.38 (d, 2H, J = 8.2 Hz, Ar–H), 7.89 (d, 2H, Ar–H, J = 8.0 Hz); MS (FAB) 242.2 (M^+).

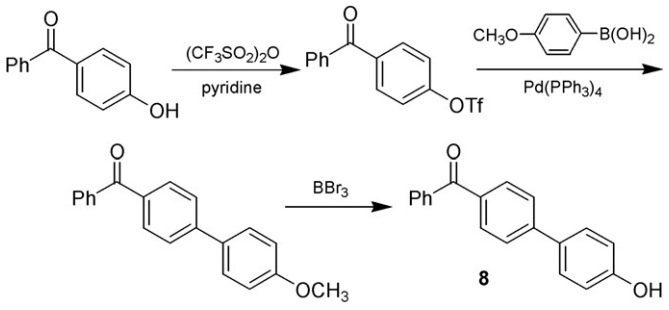
2.4. Steady-state fluorescence measurements

Fluorescence emission spectra (corrected) were taken in 3.0 mL quartz cuvettes at $\sim 10^{-4}$ M on a Photon Technology International (PTI) A-1010 instrument at ambient temperature ($22 \pm 2\,^{\circ}C$) with a slit width of 2 nm. Samples were initially deaerated by argon purging prior to measurement.

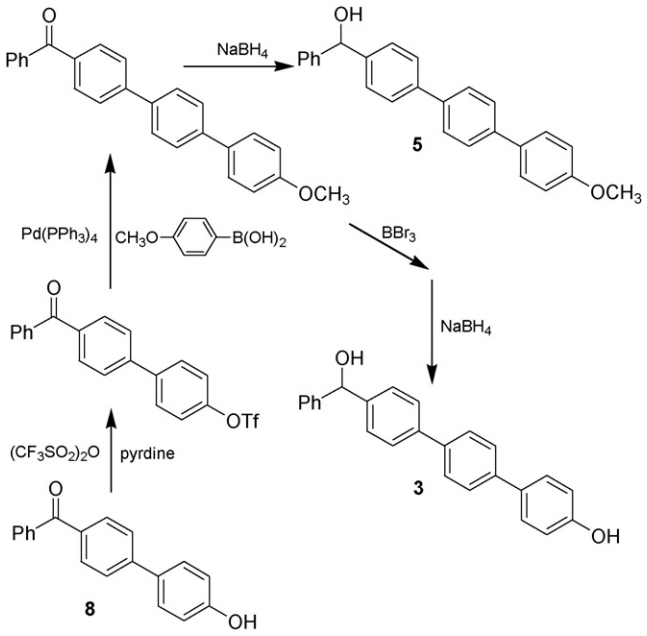
3. Results and discussion

3.1. Synthesis of terphenyls and related compounds

Terphenyls **1** and **2** were readily synthesized using consecutive Suzuki cross-coupling reactions [3], as shown in Scheme 1 for terphenyl **1**. The overall yield was typically 10–20%. The method employed did not allow ready access to the corresponding methoxy derivatives (in place of phenol OH) so these "control" compounds were not studied in this series. However, they were readily available in the α-phenyl-substituted series as follows. The α-phenyl terphenyl derivatives **3–6** were made using a slightly different method but still employing Suzuki cross-coupling methodology, as shown in Schemes 2 and 3 for **3** and **5**. Commercially available 4-hydroxylbenzophenone



Scheme 2.



Scheme 3.

(or 2-hydroxybenzophenone for the analogous synthesis of **4** and **6**) was first converted to its triflate using trifluoromethylsulfonic anhydride (Scheme 2). This was then cross-coupled with 4-methoxyphenylboronic acid to give the corresponding methoxybiphenyl derivative. Subsequent demethylation using BBr_3 or pyridinium HCl gave 4-(4′-hydroxyphenyl)benzophenone (**8**), which served as the critical precursor for the synthesis of **3** and **5** shown in Scheme 3 in which the same set of reactions are used again, with added $NaBH_4$ reduction steps to make the target benzylic alcohols. Overall yields were acceptable (5–10%).

The synthesis of diphenylacetylene **7** involved a palladium-catalyzed cross-coupling of known 4-ethynylbenzaldehyde (**9**) [4] with 4-iodophenol, by adapting a procedure reported by Li et al. [5], to give **10**, which was readily reduced to give the desired diphenylacetylene alcohol **7** (15% overall yield) (Scheme 4).

Although X-ray crystal structures were not available for terphenyls **1**–**6**, simple molecular modelling (Chem 3D, AM1) shows that each phenyl ring is twisted by about 60° (dihedral angle) from each other (Fig. 1). This ensures that there is minimal electronic communication between the phenol and the benzyl alcohol moieties in these compounds in the ground state. Indeed, they are thermally unreactive with respect to solvolysis in neutral and moderately acidic and basic media.

3.2. Product studies

Photolysis of ~10^{-4} M terphenyls **1–4** in 1:1 H_2O–CH_3OH (3:7 H_2O–CH_3OH for **1**) (Rayonet RPR 100 photochemical reactor, 254 nm lamps, ~15 °C, argon purged and stirred) gave clean

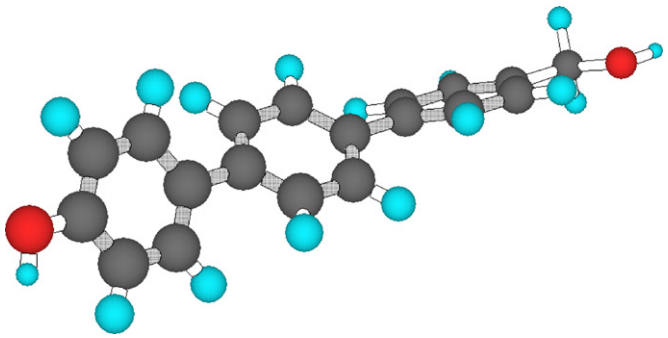
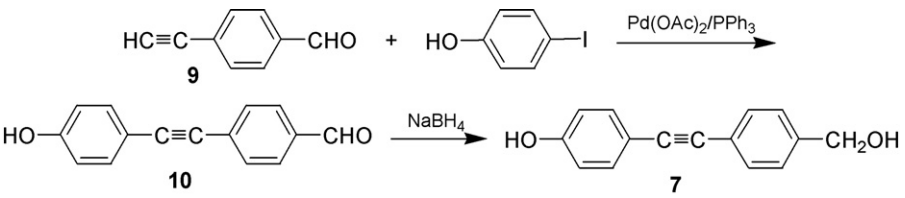


Fig. 1. Calculated minimized (Chem 3D) structure for terphenyl **1** showing the twisting between phenyl rings (about 60°) in the ground state.

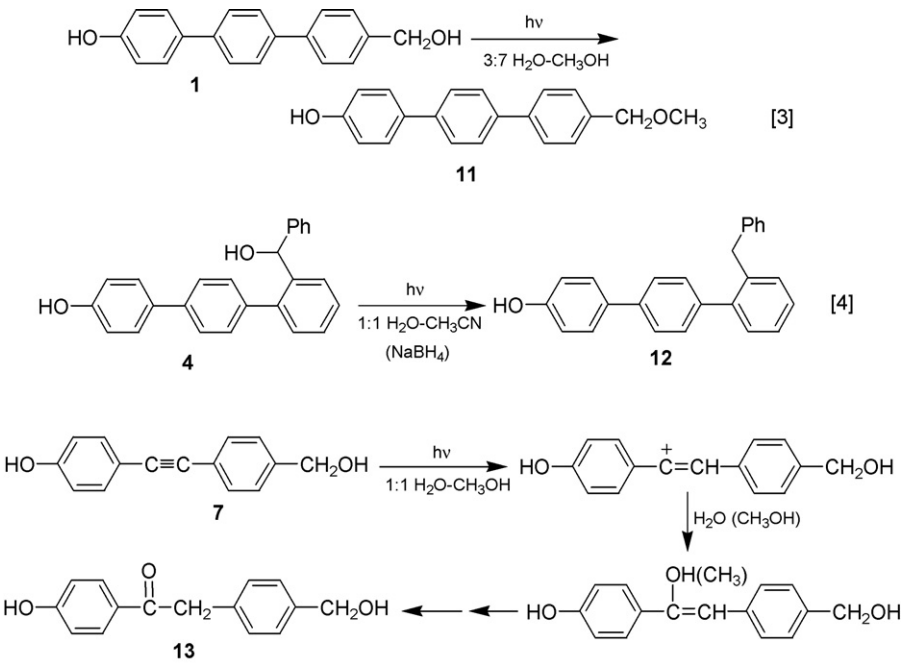
conversion to the corresponding methyl ethers in low-conversion experiments (<15%), as shown for **1**, which gave **11** (Eq. (3)). Methyl ether formation was easily monitored by growth of the sharp singlet at δ 3.1–3.4 for the benzylic methoxy group. No reactions were observed in the dark. Photolysis of methoxyterphenyls **5** and **6** under identical conditions resulted in only recovery of starting material. Photolysis of **4** in 1:1 H_2O–CH_3CN gave no reaction but photolysis in the presence of 10 equiv. $NaBH_4$ gave up to 90% yield of the reduced terphenyl product **12**. Again, no reaction was observed in the absence of irradiation. The reduced product **12** was also observed on extended photolysis of **4** in 1:1 H_2O–CH_3OH. Previous work has shown this is due to photoreduction of the initially formed methyl ether product, via initial C–OCH_3 bond homolysis followed by disproportionation of the radical pair [1]. All of these product studies are consistent with the essential requirement of the phenol moiety for photosolvolysis reaction and hence involvement of quinone methide-type intermediates as already demonstrated for related biphenyl systems [1].

The solution pH had only minor effect on the photomethanolysis yields of these terphenyl alcohols. For example, in the case of **2**, photolysis was carried out in 1:1 H_2O–CH_3OH in pH range of 1–12 (water portion). At pH 1, the yield for methyl ether formation only increased by about 20% compared to pH 7 whereas the yield was constant in the pH 4–12 range. The enhancement of yield at pH 1 suggests the operation of a competitive acid-catalyzed photosolvolysis pathway. These results are different from what has been observed for analogous biphenyl systems in which photosolvolysis was more efficient at pHs > $pK_a(S_o)$ of the phenol OH and there is also some reduction in yield at lower pHs, below the expected $pK_a(S_1)$ [1].

Product quantum yield (Φ_p) for formation of methyl ether products from photolysis of hydroxyterphenyl methanols **1–4** were measured at low conversion (<15%) in aqueous methanol. The quantum yield for methyl ether formation for 4-hydroxy-4′-hydroxymethylbiphenyl (Φ_p = 0.027 [1i]) was employed as a secondary actinometer. All quantum yields for the terphenyl systems were lower than for similar biphenyl systems, by as much as an order of magnitude. The quantum yields for methyl ether formation were 0.016 for **1** (in 3:7 H_2O–CH_3OH); 0.034 for **2** (in 1:1 H_2O–CH_3OH); ca. 0.01 for **3** and **4** (both in 1:1 H_2O–CH_3OH).



Scheme 4.



Scheme 5.

Photolysis of diphenylacetylene **7** in 1:1 H_2O–CH_3OH or 1:1 H_2O–CH_3CN gave a mixture of products in which the major isolable one (by prep. TLC) was ketone **13**. No product with a distinctive $ArCH_2OCH_3$ fragment could be discerned in the product mixture indicating that simple photosolvolysis of the benzylic alcohol moiety (as observed for **1**–**4**) was not an important pathway for this compound. Product **13** is consistent with simple photohydration of the alkyne moiety, a known reaction pathway for diphenylacetylenes [6] (Scheme 5). Because evidence for significant charge transfer to from the phenol to the benzyl alcohol moiety at the other end of the molecule was lacking in this system, no further studies were pursued for this compound.

3.3. Fluorescence measurements

A major photophysical difference between biphenyls and terphenyls is that the latter compounds are generally very fluorescent [7]. Thus, it was important to undertake fluorescence measurements that might help understand reactivity differences observed between biphenyls vs. terphenyl systems that are designed for photogenerating BQM/TQMs. Fluorescence emission spectra of **1–4** and **12** (the latter compound being unreactive) were taken in CH_3CN as a function of water content. All five terphenyls gave similar intense fluorescence emission in neat CH_3CN solution with λ_{max} at 350–370 nm (λ_{ex} 285 nm). Fluorescence quantum yields for **1** and **2** were measured using 2-aminopyridine as a standard ($\Phi_f = 0.60$ [8]) and were 0.62 (for **1**) and 0.59 (for **2**) confirming the highly fluorescent terphenyl chromophore in these compounds. For comparison, biphenyls of similar structure have Φ_f of about 0.2 [1i]. In the presence of water, the fluorescence emission of all five compounds were gradually quenched by increased water content with a slight red shift on initial addition of water, with formation of a new significantly red-shifted emission band at 470–490 nm. This new band was identified as emission from the corresponding phenolate ion, by comparison with authentic phenolate emission obtained by exciting the same compounds at pH 12 (Figs. 2 and 3). Although there are minor differences in the extent of quenching by added water and band shapes, all compounds, including the unreac-

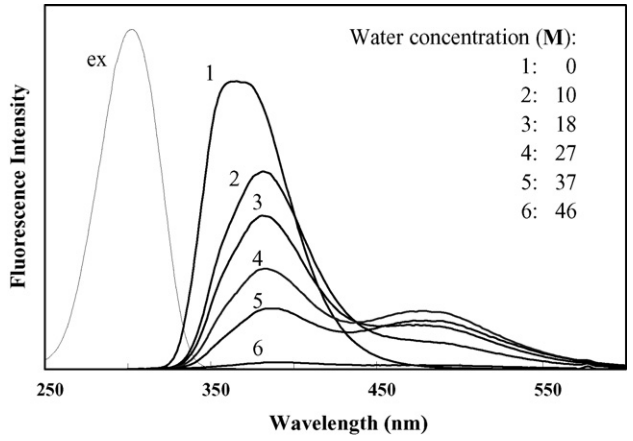


Fig. 2. Effect of added water (in CH_3CN) on the fluorescence emission of terphenyl **3** (λ_{ex} 285 nm).

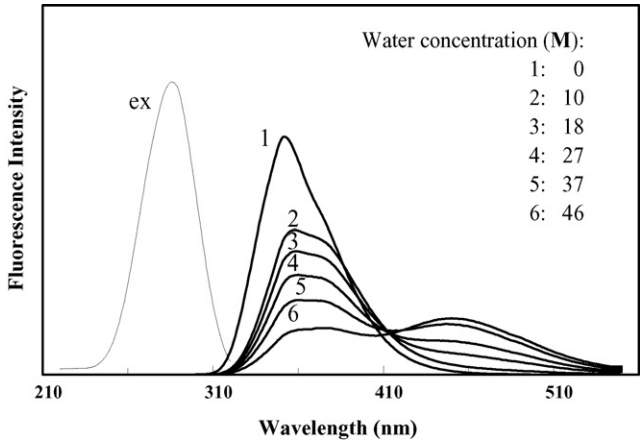


Fig. 3. Effect of added water (in CH_3CN) of the fluorescence emission of terphenyl **4** (λ_{ex} 285 nm).

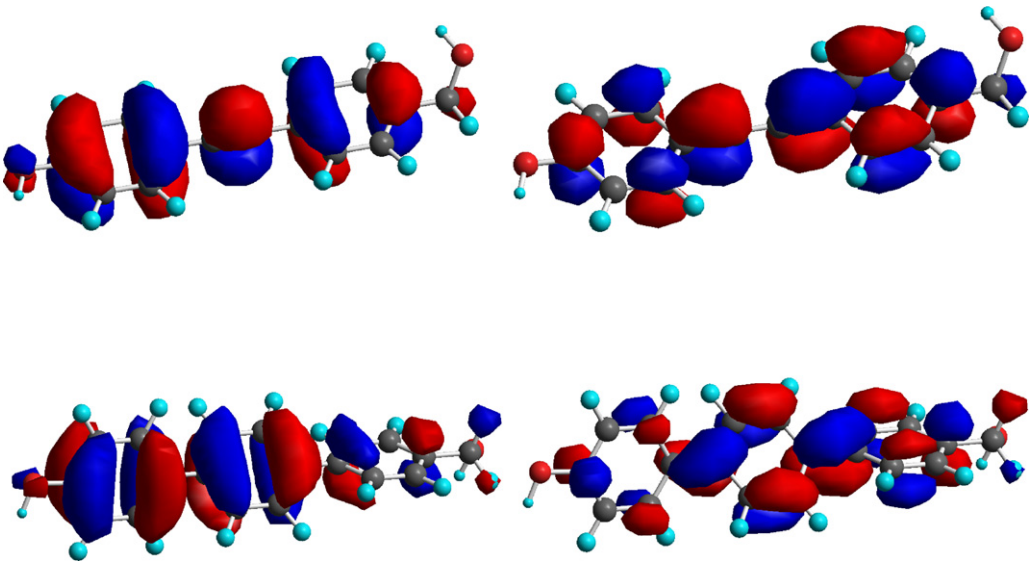


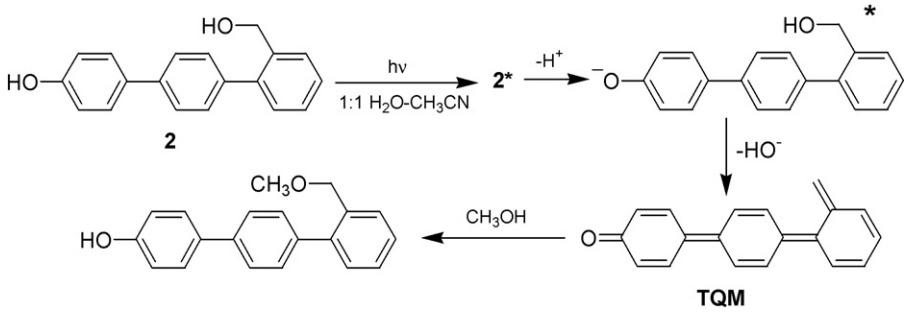
Fig. 4. Calculated HOMOs (left) and LUMOs (Chem 3D, AM1) for diphenylacetylene **7** (top) and terphenyl alcohol **3** (bottom).

tive terphenyl behaved similarly, viz., water quenched fluorescence emission and that the phenolate ion is emissive for all compounds. This latter observation is in contrast to what is observed for the corresponding biphenyls [1i] where reactive biphenyls do not have emissive phenolate ions whereas the non-reactive ones do. These observations are consistent with the observation that the reactive terphenyls have low quantum yields of reaction (to form TQMs) that do not significantly affect the fluorescence efficiency in either phenol or phenolate forms. That is, terphenyls favour radiative decay rather than undergo heterolytic cleavage of the benzylic C–OH bond that would give rise to TQMs. One possible explanation is that the extent of charge transfer from the phenol ring to the third ring of the terphenyl is not as significant as to the adjacent ring thereby reducing reaction efficiency. This is confirmed at least in HOMO/LUMO calculations (vide infra).

3.4. Mechanisms of reaction

It is instructive to examine calculated HOMO/LUMO coefficients (Chem 3D, AM1) for **7** and **3**, the latter as representative for the hydroxyterphenyl series, to see whether the expected charge transfer (from phenol to the adjacent rings) can be predicted using simple theory (Fig. 4). The electronic distribution of the excited state can be qualitatively predicted by examining changes in HOMO/LUMO coefficients since the simplest picture of an electronically excited state can be visualized as being obtained by promotion of an electron from the HOMO to the LUMO. Based on this simple argument, one would predict that for **7** the extent of charge transfer to the second benzene ring would be small if any and that most of the charge migration form the phenol ring ends up on the acetylenic carbons. This is consistent with the observed photochemistry of this compound in aqueous solution. For **3** one would predict that (1) there will be a tendency to planarize all three benzene rings on excitation since there is bonding character between all the carbon atoms joining the rings in the LUMO but not in the HOMO (this is required for TQM formation); and (2) there is extensive charge migration on electronic excitation with most of the charge ending up on the adjacent benzene ring and not on the third ring as would be required for efficient photosolvolysis of our hydroxyterphenyls. The latter is consistent with the observed results in which the quantum yields of TQM formation are significantly lower than those of BQM formation already reported.

Although there was no pH effect on photosolvolysis quantum yield of the hydroxyterphenyls in the pH 4–12 region, we believe that the most likely mechanism for photosolvolysis is formation of excited state phenolate followed by dehydroxylation, to give TQMs as shown in Scheme 6 for **2**. This is supported by lack of reaction of the methoxy derivatives **5** and **6**. We believe that the low quantum efficiency for reaction is a prime reason for lack of observable sensitivity to pH. The fact that both phenol and phenolate forms were observable in fluorescence studies support the notion that excited state deprotonation is not 100% efficient under the conditions employed. This discounts the possibility that all phenols are depro-



Scheme 6.

tonated in S_1 in all the pHs studied (i.e., a very strong photoacid), and hence absence of a pH effect on reaction efficiency. We have carried out preliminary studies of these compounds by nanosecond laser flash photolysis to see whether long-wavelength transients assignable to high-conjugated TQMs are formed. Although we were able to discern triplet states being formed and weak transients in the 500–700 nm region, we were not able to unequivocally assign them to TQMs since non-reactive terphenyls also gave very similar spectra. The main problem in these experiments in due to the low quantum efficiency of TQM formation as indicated in the product studies. Until we are able to design more efficient terphenyls that can generate TQMs more efficiently, characterization of the interesting intermediates by laser flash photolysis remains elusive.

4. Conclusions

In summary, we have synthesized a number of hydroxyterphenyls and investigated the possibility of TQM generation on photolysis in aqueous solution. Although we were unable to directly observe TQMs using laser flash photolysis, product studies support the intermediate of TQMs for these compounds. These studies also support the notion that hydroxyterphenyls have polarized excited states in which the charge from the hydroxyphenyl ring is donated to the second and third rings on photoexcitation. The lower reactivity of these hydroxyterphenyls allows direct observation of fluorescence from the excited singlet of the phenolate in aqueous solution which is not possible for similar biphenyl systems. Additional studies are necessary in order to design more reactive terphenyl systems towards TQMs formation.

Acknowledgments

Support of this research by NSERC (Canada) and the University of Victoria is gratefully acknowledged. We thank Matthew Lukeman for help in exploratory nanosecond laser flash photolysis experiments.

References

[1] (a) C.-G. Huang, K.A. Beveridge, P. Wan, J. Am. Chem. Soc. 113 (1991) 7676;
(b) Y. Shi, P. Wan, J. Chem. Soc., Chem. Commun. (1995) 1217;
(c) P. Wan, B. Barker, L. Diao, M. Fischer, Y. Shi, C. Yang, Can. J. Chem. 74 (1996) 465;
(d) Y. Shi, P. Wan, J. Chem. Soc., Chem. Commun. (1997) 273;
(e) Y. Shi, A. MacKinnon, J.A.K. Howard, P. Wan, J. Photochem. Photobiol. A 113 (1998) 271;
(f) M. Lukeman, P. Wan, J. Am. Chem. Soc. 124 (2002) 9458;
(g) M. Lukeman, P. Wan, J. Am. Chem. Soc. 125 (2003) 1164;
(h) M. Flegel, M. Lukeman, L. Huck, P. Wan, J. Am. Chem. Soc. 126 (2004) 7890;
(i) Y. Shi, P. Wan, Can. J. Chem. 83 (2005) 1306;
(j) M. Xu, M. Lukeman, P. Wan, Photochem. Photobiol. 82 (2006) 50;
(k) N. Basarić, P. Wan, J. Org. Chem. 71 (2006) 2677;
(l) N. Basarić, P. Wan, Photochem. Photobiol. Sci. 5 (2006) 656;
(m) M. Flegel, M. Lukeman, P. Wan, Can. J. Chem. 86 (2008) 161;
(n) D. Verga, S.N. Richter, M. Palumbo, R. Gandolfi, M. Freccero, Org. Biomol. Chem. 5 (2007) 233;
(o) S.N. Richter, S. Maggi, S. Colloredo-Mels, M. Palumbo, M. Freccero, J. Am. Chem. Soc. 126 (2004) 13973;
(p) S. Colloredo-Mels, F. Doria, D. Verga, M. Freccero, J. Org. Chem. 71 (2006) 3889;
(q) F. Doria, S.N. Richter, M. Nadai, S. Colloredo-Mels, M. Mella, M. Palumbo, M. Freccero, J. Med. Chem. 50 (2007) 6570.
[2] For example:
(a) K. Müllen, G. Wegner (Eds.), Electronic Materials: The Oligomer Approach, Wiley-VCH, Weinheim, 1998;
(b) C.C. Dong, P. Styring, J.W. Goodby, L.K.M. Chan, J. Mater. Chem. 9 (1999) 1669;
(c) N. Sakai, N. Majumdar, S. Matile, J. Am. Chem. Soc. 121 (1999) 4284.
[3] (a) N. Miyaura, T. Yanagi, A. Suzuki, Syn. Commun. 11 (1981) 513;
(b) C.M. Unrau, M.G. Campbell, V. Snieckus, Tetrahedron Lett. (1992) 2773.
[4] W.B. Austin, N. Bilow, W.J. Kelleghan, K.S.Y. Lau, J. Org. Chem. 46 (1981) 2280.
[5] F. Li, S.I. Yang, Y. Ciringh, J. Seth, C.H. Martin III, D.L. Singh, D. Kim, R.R. Birge, D.F. Bocian, D. Holten, J.S. Lindsey, J. Am. Chem. Soc. 120 (1998) 10001.
[6] (a) P. Wan, S. Culshaw, K. Yates, J. Am. Chem. Soc. 104 (1982) 2509;
(b) P. Wan, K. Yates, Rev. Chem. Intermed. 5 (1984) 157.
[7] I.B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, second ed., Academic Press, New York, 1971.
[8] D. Eaton, Pure Appl. Chem. 60 (1988) 1107.