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Synthesis of 1-Vinylidene-naphthofurans: A Thermally Reversible Photochromic System That Colors Only When Adsorbed on Silica Gel

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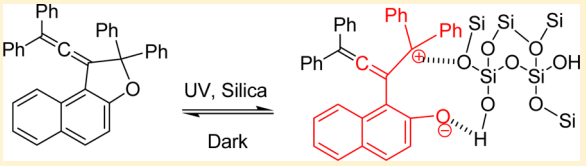
Supporting Information

ABSTRACT: A set of new 1-vinylidene-1,2-dihydro-naphtho[2,1-*b*]furans were unexpectedly obtained in the reaction of 2-naphthol with readily available 1,1,4,4-tetraarylbut-2-yne-1,4-diols. Surprisingly, when adsorbed in silica gel, these compounds exhibit photochromism at room temperature, whereas not in solution and in the solid state. UV or sunlight irradiation leads, in a few seconds, to the formation of intense pink/violet to green colors that bleach completely in a few minutes in the dark. These new compounds also exhibit reversible acidochromic properties in solution: addition of TFA leads to the opening of the furan ring and addition of a proton to the allene function, leading to a conjugated and violet tertiary carbocation that returned immediately to the uncolored allenic structure upon addition of a weak base.



INTRODUCTION

Over the last decades, interest in photochromic compounds has been growing.[1] These molecules are able to switch between two states, usually exhibiting different colors, under the action of light and have been applied with success in ophthalmic photochromic lenses that reversibly darken under sunlight.[2] Because other properties, such as the refractive index, dielectric constant, and geometry, can be switched upon irradiation with light, these molecules have an enormous potential to be used in other applications that do not require necessarily a color change, such as optical data storage devices,[3] electronic display systems,[4] logic gates,[5] and molecular imaging.[6] The most important classes of thermally reversible photochromic compounds include naphthopyrans, spiropyrans, spiroxazines, fulgides, and azo compounds, but new structures are now and then discovered.[7] The UV or visible light activation of these compounds promotes a chemical reaction leading to the formation of one or more species with a different absorption spectrum, which, in the absence of light, returns thermally, with variable speed, to the initial form. The phenomenon occurs typically in solution or when the molecules are dispersed in polymeric matrixes, although the kinetics of the process is highly affected by the nature of the host matrix.[8] A wide range of chemically different matrixes, where the organic photochrome is dispersed or covalently linked, have been investigated: purely organic medium, for example, poly(methyl methacrylate) (PMMA),[9] hybrid inorganic−organic composites (ormosils),[10] or purely inorganic silicate matrixes.[11] In some cases, the photochromism was also detected in the solid state.[12]

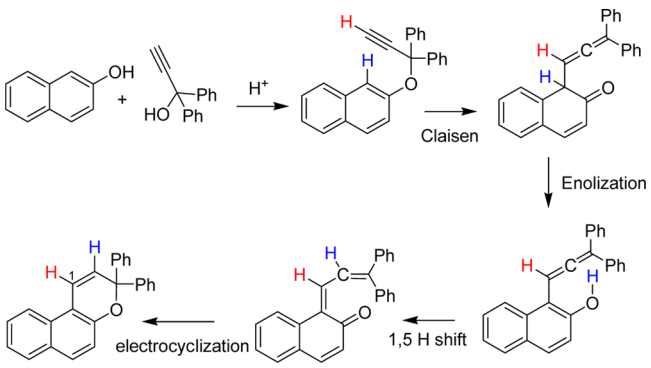
Because of the versatility of the naphthopyran entity, there has been an intense research on this class of molecules: naphthopyrans are easy to prepare, they show a high resistance to photodegradation, different colors can be produced after UV activation, and the thermal relaxation kinetic can be controlled by introducing proper substituents in the structure.[13]

Naphthopyrans are usually prepared through the reaction of naphthols with 1,1-diarylpropynols in acid media at reflux.[14] The mechanism involves the acid-catalyzed formation of an ether, followed by Claisen rearrangement, enolization, 1,5-hydrogen shift, and electrocyclization (Scheme 1).[15] The reaction is compatible with various substituents and has been used for the synthesis of hundreds of different naphthopyrans.

RESULTS AND DISCUSSION

Synthesis. In the course of our studies on the photochromism of naphthopyrans substituted in the pyran-double bond,[16] we explored the reaction of 2-naphthol **1** with the readily

Scheme 1. Mechanism for the Acid-Catalyzed Synthesis of Naphthopyrans from Naphthols and 1,1-Diarylpropynols



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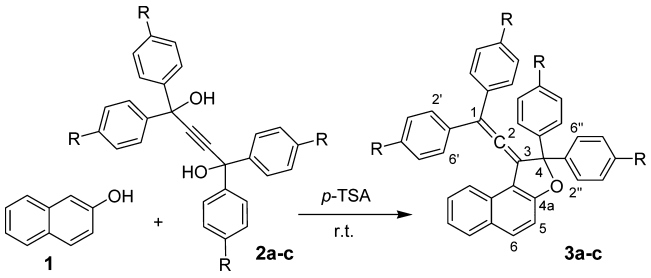
available 1,1,4,4-tetraarylbut-2-yne-1,4-diols **2a–2c**[17] (Scheme 2), which could afford directly a naphtho[2,1-*b*]pyran possessing

Scheme 2. Synthesis of 1-Vinylidene-naphtho[2,1-*b*]furans 3a–3c (a: R = H; b: R = F; c: R = OCH_3)

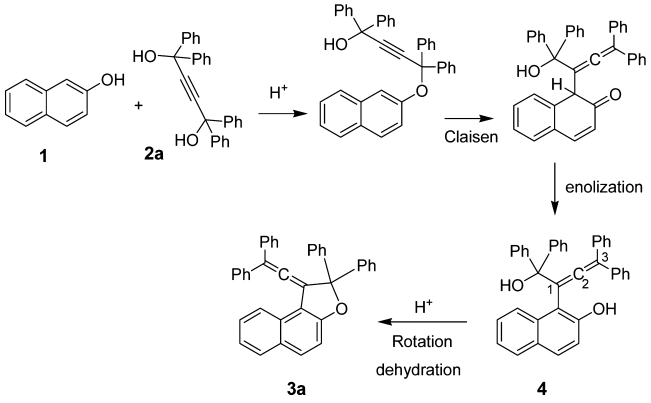


a reactive alcohol function as substituent in position 1. In fact, treating 2-naphthol **1** with diol **2a** (Ar = Ph) in $CHCl_3$ in the presence of an acid catalyst (*p*-TSA) led to the complete disappearance of the starting materials after 60 min, at room temperature, with the formation of a new photochromic compound. However, the absence of any ethylenic-pyran hydrogen in the ^1H NMR spectrum, the presence of a low-field signal at 202.9 ppm in the ^{13}C NMR spectrum, and a shift of the typical pyran sp^3 carbon atom, usually around 80 ppm, but here at 95.1 ppm, excluded a naphthopyran structure and pointed to the formation of a completely different structure: the naphthofuran **3a** (47% yield) presenting a substituted allene function (Scheme 2).

The structure of this new compound was unambiguously established using 2D NMR experiments. In particular, $^1H-^{13}C$ long-range scalar correlations (HMBC) were measured between protons H-2′/H-6′ at 7.16 ppm and C-1 at 117.7 ppm (^3J) and C-2 at 202.9 ppm (^4J) that proved the allene structure. Carbon C-3 at 114.9 ppm showed no correlation through 2, 3, and 4 bonds. The sp^3 carbon C-4 at 95.1 ppm is correlated with protons H-2″/H-6″ at 7.47 ppm (^3J), and finally, the furan carbon C-4a at 157.9 ppm is correlated with H-5 at 7.29 ppm (^2J) and H-6 at 7.82 ppm (^3J).

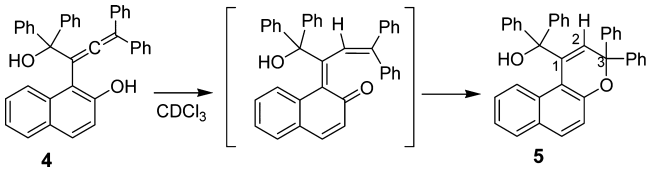
Starting from substituted diols **2b–2c** (R = F, OMe), we obtained the corresponding 1-vinylidene-1,2-dihydro-naphtho-[2,1-*b*]furans **3b** (19%) and **3c** (46% yield). When the reaction between **1** and diol **2a** was quenched after 10 min, the formation of the expected 1-vinylidene-naphtho[2,1-*b*]furan **3a** was detected by TLC along with a small amount of another compound **4**, with lower R_f, that showed similar photochromic properties and was also isolated and characterized (Scheme 3). The structure elucidation of this compound showed that it has two OH groups and an allene function, characterized by the carbon resonances of 109.2 ppm (C-1), 112.2 ppm (C-3), and 208.3 ppm (C-2), being similar to the allene intermediate in the naphthopyran synthesis (Scheme 1). The allenylnaphthol **4** is clearly an intermediate in this reaction since, in the presence of *p*-TSA, it is completely converted into the 1-vinylidene-naphtho-[2,1-*b*]furan **3a**, and the photochromic behavior, observed in the TLC plates, is probably due to its conversion into compound **3a** promoted by the silica. The isolation of a small amount of this allenylnaphthol from the reaction mixture indicates that the reaction between 2-naphthol **1** and diol **2a** follows, very likely, the same mechanism leading to naphthopyrans, shown in Scheme 1, except that the intermediate **4** after rotation and dehydration is converted into the 1-vinylidene-naphtho[2,1-*b*]furan **3a** (Scheme 3).

Scheme 3. Mechanism for the Formation of 1-Vinylidene-naphtho[2,1-*b*]furan 3a and the Allenylnaphthol 4



The allenylnaphthol **4** is stable in the solid state, but not in solution, being completely converted to the naphthopyran **5** after a few days in a $CDCl_3$ solution (Scheme 4). The formation of the

Scheme 4. Thermal Evolution of Allenylnaphthol 4 into Naphthopyran 5 in $CDCl_3$ Solution



naphthopyran structure **5** was confirmed by the appearance in the ^1H NMR spectrum of a singlet at 5.82 ppm, characteristic of the ethylenic-pyran proton H-2, and the typical sp^3 pyran carbon C-3, observed at 82.9 ppm in the ^{13}C NMR spectrum. $^1H-^{13}C$ scalar correlation between proton H-2 and carbon C-3 was measured in HMBC experiments, which confirmed structure **5**.

Photochromic Properties. The 1-vinylidene-naphtho[2,1-*b*]furans **3a–3c** are not photochromic in the solid state or in solution using polar (CH_2Cl_2, Et_2O, $CHCl_3$, CH_3CN, DMSO, EtOH, CH_3CO_2H) or apolar (toluene) solvents, even at low temperature (toluene or acetone at −80 °C). Nevertheless, they show reversible photochromic properties when adsorbed in silica gel at room temperature:[18] when silica gel was added to a solution of 1-vinylidene-naphthofurans **3a** in CH_2Cl_2 and the solvent was removed by evaporation at atmospheric pressure, we obtained a white powder of silica gel doped with compound **3a** that turned pink/violet when exposed to UV light/sunlight for 15 s and faded back completely to white, in the dark, in less than 5 min (Figure 1).

Figure 1. Photographs of silica gel doped with compound **3a**, in an aluminum sheet, before and after UV irradiation (365 nm) for 15 s.

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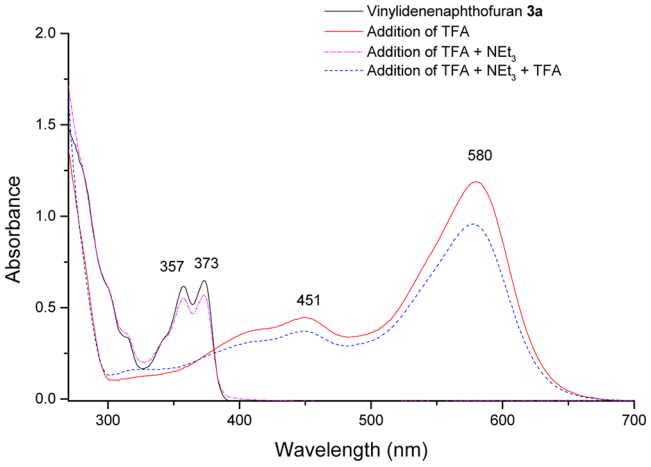

Figure 2. Absorption spectra of (black) naphthofuran **3a**, (red) after the addition of CF_3COOH, (pink) after the addition of $CF_3COOH + NEt_3$, and (blue) after subsequent addition of CF_3COOH.

The photochromic behavior of compounds **3a**–**3c** is reproducible and can be repeated several times without any sign of degradation: TLC analysis of compounds **3a**–**3c** after 10 UV/dark cycles showed that they remained unchanged. The color change is dependent on the amount of water in the silica gel and does not occur in hydrated silica, but the photochromic behavior can be recovered after heating a sample of hydrated silica doped with compound **3a** (oven, 60 °C, 1 day). On the other hand, after UV activation of the doped silica powder, the addition of any solvent leads to the immediate disappearance of the color, indicating that the compound is no longer adsorbed in the silica. The behavior observed with silica gel could not be extended to other oxides (Al_2O_3, SnO_2, MgO, TiO_2) or pure SiO_2 (quartz), which means that the terminal OH groups present in the silica gel are probably necessary for the observation of the phenomenon.

Acidochromic Properties. These compounds show also acidochromic properties. Addition of TFA to a $CHCl_3$ uncolored solution of compound **3a** leads to the appearance of a violet color, characterized by two bands in the visible spectrum (λ_{max} = 451 and 580 nm) that bleached when NEt_3 was added to the solution (Figure 2). The process is completely reversible, and upon subsequent addition of acid, the violet coloration appears again. The same reversible behavior was observed with compounds **3b** (λ_{max} = 448 and 588 nm) and **3c** (λ_{max} = 503 and 658 nm) with a notable bathochromic shift of both bands in the latter due to the presence of the dimethoxy substituents in the aromatic rings. This reaction was also followed by NMR: addition of TFA to a $CDCl_3$ solution of **3a** led to a complete change in the aromatic part of the ^1H NMR spectrum, and upon addition of NEt_3, the signals of the naphthofuran **3a** appeared again (Figure 3).

The ^1H NMR spectrum of the colored solution suggests that an addition of H^+ to the allene function occurred with the opening of the furan ring and formation of a tertiary carbocation. This assumption was confirmed by ^{13}C NMR with the disappearance of the low-field allenic signal at 202.9 ppm (C-2) and the appearance of two signals at 185.9 and 186.7 ppm assigned, respectively, to a carbonyl (C-4a) and a tertiary carbocation (C-4). The chemical shifts of H-2′, H-3′, and H-4′ at 6.59, 6.92, and 7.11 ppm, respectively, are more shielded than those in compound **3a**. This strong upfield effect can be explained by π stacking between the phenyl and the naphthalene part in the opened form. Moreover, the 1D NOESY spectrum showed dipolar correlations between the ethylenic proton H-2 at 7.31 ppm and the aromatic protons H-2b/H-2c at 7.45–7.49 ppm, which confirmed the structure of this opened structure (Scheme 5).

The visible spectra of these colored species present two absorption maxima. The band around 450 nm resembles the absorption band of a merocyanine dye (open form of the naphthopyran), while the second maxima, between 580 and 658

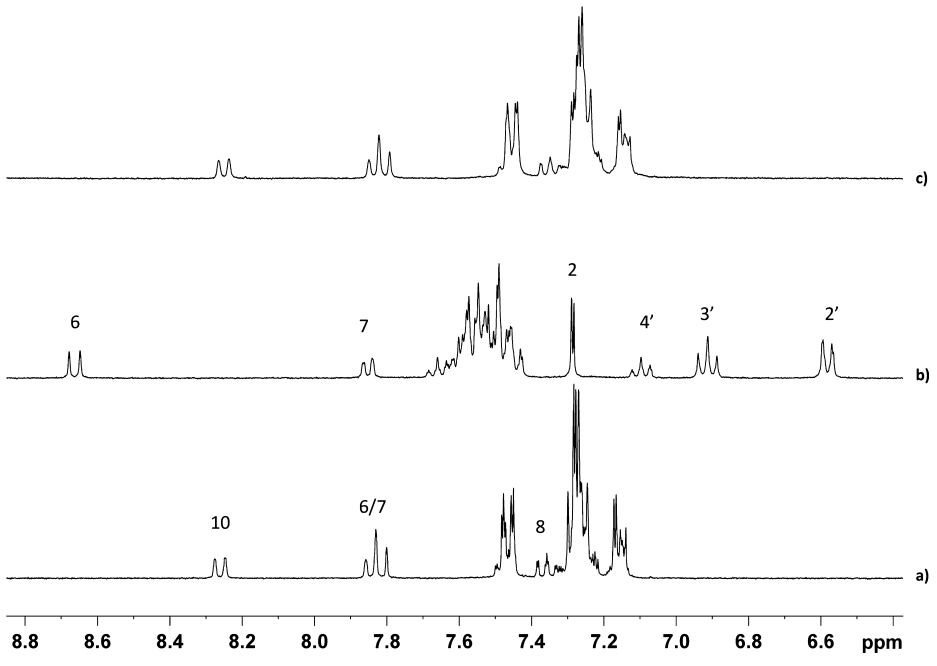

Figure 3. ^1H NMR spectra of (a) **3a** in $CDCl_3$, (b) after addition of CF_3COOH, and (c) after subsequent addition of NEt_3.

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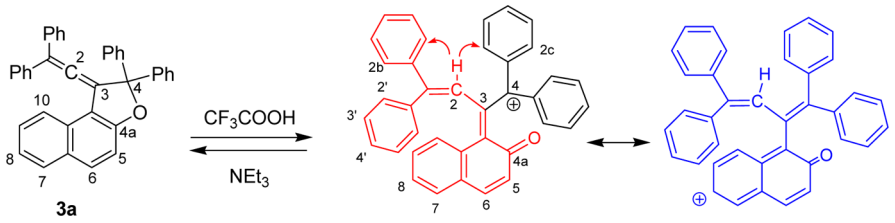
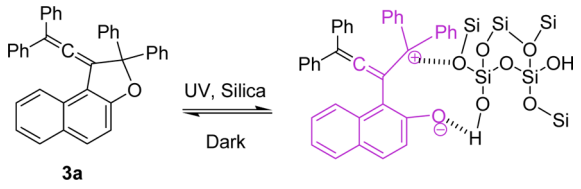
Scheme 5. Acidochromism of Naphthofuran 3a and Dipolar Correlations between H-2 and H-2b/H-2c



nm, may be justified by the extension of the conjugation between the merocyanine and the carbocation.[19]

The formation of this conjugated opened species in an acidic medium suggests that the UV irradiation of compound **3a**, dispersed in silica gel, may also lead to a heterolytic cleavage of the C−O bond with formation of a conjugated zwitterionic species stabilized by the polar OH terminal groups of the silica gel (Scheme 6). This type of stabilization of a zwitterionic

Scheme 6. Photochromic Equilibrium for 1-Vinylidenenaphtho[2,1-*b*]furan 3a



colored form through hydrogen bonding by the residual acidic silanol groups has also been observed in spiropyrans and spirooxazines.[20] The structure of this zwitterionic species is different from the one observed upon addition of acid but allows also the extended conjugation between the naphthalene and the phenyl rings.

Kinetic Studies. For the measurement of the color of the doped silica solid after UV irradiation and kinetic analysis of the thermal decoloration process, we used a colorimeter that characterizes the color developed in terms of their tonality, luminosity, and saturation using the $L^*a^*b^*$ color space coordinates (L^* is the luminosity, $+a^*$ indicates toward the red, $-a^*$ toward the green, $+b^*$ direction yellow, $-b^*$ direction blue). The silica gel doped with naphtho[2,1-*b*]furans **3a**−**3c** is white before irradiation, and it has nearly the same color coordinates as the pure silica gel. After irradiation with UV light (6 W, 365 nm) for 15 s, all the color coordinates change and the doped powder acquired pink/violet (**3a**, **3b**) or green (**3c**) colorations that bleached in the dark and returned to the initial white coloration with variable kinetics depending on the nature of the aryl substituents (Table 1).

The time evolution of the three color coordinates L^*,a^*,b^* during the thermal decoloration of compound **3a** is shown in Figures 4 and 5. These curves can be very closely fitted to a monoexponential equation, suggesting that, most likely, a single colored species is formed after light activation.

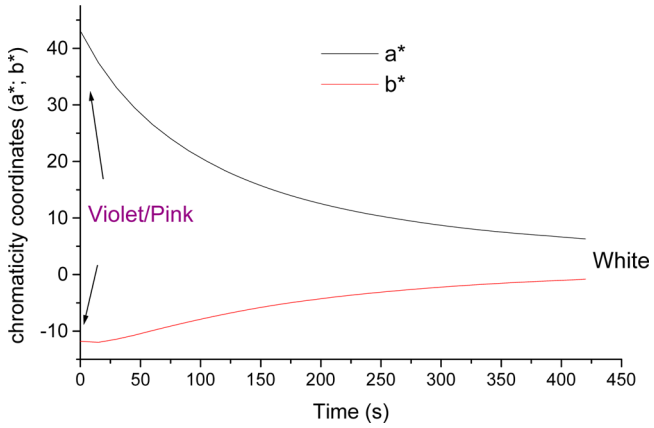


Figure 4. Color space coordinates evolution (a^* and b^*) during the thermal fading of compound **3a**.

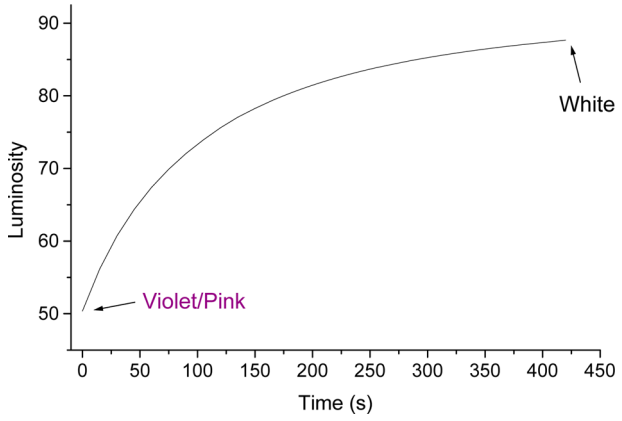


Figure 5. Color space coordinate L^* (luminosity) evolution during the thermal fading of compound **3a**.

For naphtho[2,1-*b*]furan **3a**, a lifetime of 76 s of the violet/pink opened form was measured at 20 °C. The introduction of electron acceptor fluoro atoms in the *para* position of the aryl substituents (compound **3b**) led to an increase of the bleaching

Table 1. Color Space Coordinates ($L^*a^*b^*$) before and after UV Irradiation, Bleaching Rate Constants, and Half-Life Time for Compounds 3a−3c Adsorbed in Silica Gel

compound	before UV light	after UV light	k (s^{-1})	$t_{1/2}$ (s)
3a (R = H)	90.64; 3.13; 1.32 (white)	53.35; 41.61; −0.72 (violet/pink)	0.0091	76
3b (R = F)	92.65; 0.76; 3.59 (white)	75.54; 20.15; −2.40 (violet/pink)	0.020	35
3c (R = OMe)	84.88; −7.12; 8.55 (white)	46.04; −23.35; 8.17 (green)	0.0012	577
silica gel	92.31; 0.70; 2.37 (white)			

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rate ($t_{1/2}$ = 35 s), while electron-donating methoxy groups in the same position (compound **3c**) promoted the formation of more stable opened forms with a green coloration and a much higher lifetime ($t_{1/2}$ = 577 s). These results are in accordance with the zwitterionic character proposed for the structure of the colored forms (Scheme 6).

The easiness of the synthesis of these new 1-vinylidene-1,2-dihydronaphthofurans and their photochromic performance, under UV or sunlight irradiation, at room temperature when adsorbed in silica gel, make them good candidates for new photochromic materials with thermally reversible behavior.

CONCLUSION

A new photochromic system with a 1-vinylidene-naphthofuran structure was discovered. These compounds were easily obtained in the reaction of 1-naphthol with 1,1,4,4-tetraarylbut-2-yne-1,4-diols at room temperature and show photochromic properties only when they are adsorbed in silica gel. Sunlight irradiation of silica gel doped with these compounds generates in a few seconds a deep pink/green color that fades thermally within a few minutes in the dark. The 1-vinylidene-naphthofurans also show acidochromic properties: addition of TFA to an uncolored solution of compound **3a** leads to the immediate development of an intense violet coloration that bleaches immediately when a weak base (NEt_3) is added. NMR studies on these solutions show that, in an acid medium, the heterolytic opening of the furan ring and addition of a proton to the allene occur, leading to a highly conjugated cationic species that reverts completely to the initial allenic structure in a weak basic medium. The UV irradiation of compound **3a** in silica gel may lead also to a heterolytic cleavage of the C−O bond with formation of a conjugated zwitterionic species stabilized by the polar OH terminal groups of the silica gel.

EXPERIMENTAL SECTION

General Methods. The reactions were monitored by thin-layer chromatography on aluminum plates precoated with silica gel 60 F254 (0.25 mm). Column chromatography (CC) was performed on silica gel 60 (70−230 mesh). The new compounds were determined to be >95% pure by ^{1}H NMR spectroscopy. NMR spectra in $CDCl_3$ were recorded at 298 K using spectrometers (ν_0 (^{1}H) = 300, 400, and 500 MHz). Chemical shifts (δ) are reported in parts per million. IR spectra were obtained using KBr disks (wavenumbers in cm^{-1}).

1,1,4,4-Tetraphenylbut-2-yne-1,4-diol (2a). *n*-Butyllithium (15 mL, 1.6 M in hexanes) was slowly added (ca. 15 min) to a cold (0 °C) stirred solution of 1,1-diarylprop-2-yn-1-ol (2.50 g, 12 mmol) in anhydrous tetrahydrofuran (25 mL). On completion of the addition, the cold solution was stirred for 30 min. The benzophenone (2.41 g, 30 mmol) was added in a single portion to the solution, and the resulting mixture was stirred at room temperature for 22 h and controlled by TLC (the reaction was not complete). Three-fourths of the solvent was removed under reduced pressure, and aqueous HCl (5%, 50 mL) was added to afford a suspension of diol **2a** that was filtered. The crystals were then recrystallized from ethyl acetate/petroleum ether to give pure **2a** as white crystals (3.80 g, 81% yield). mp 201.4−203.0 °C. IR (KBr, cm^{-1}): 3532, 3456, 3061, 3019, 2918, 2843, 2364, 2339, 1600, 1499, 1448, 1331, 1213, 1138, 1070, 1028, 995, 911, 886, 776, 743, 693, 642, 609. ^{1}H NMR (400 MHz, $CDCl_3$): 7.59 (d, *J* = 7.9 Hz, 8H), 7.39−7.23 (m, 12H), 2.86 (s, 2H, OH). EI-MS (TOF) *m*/*z* (%): 372 (32), 371 (11), 370 (14), 356 (28), 344 (22), 267 (22), 265 (27), 252 (11), 208 (10), 207 (14), 182 (64), 181 (10), 179 (13), 178 (17), 165 (19), 05 (100), 77 (50). HRMS: calcd for $C_{28}H_{20}O$ (M − H_2O): 372.1514. Found: 372.1503

Synthesis of Diols (2b and 2c). The suspension of the lithium acetylide−ethylene diamine complex (90%, 2.475 g, 26.9 mmol) and 1.5 equiv of 4,4′-difluorobenzophenone or 4,4′-dimethoxybenzophenone in dry THF (50 mL) was stirred at room temperature for 3 days. The mixture was then filtered with Celite, and the solvent was removed under reduced pressure. The residue was diluted with water (50 mL) and extracted with AcOEt (2 × 40 mL). The organic phase was dried over Na_2SO_4, and a part of the solvent was removed under reduced pressure. During the solvent evaporation, the ketone, a white solid, is removed by fractionation precipitation. The remaining oil is composed mainly of the diol and can now be easily purified

*1,1,4,4-Tetra(4-fluorophenyl)but-2-yne-1,4-diol (**2b**).* The crude product was precipitated with CH_2Cl_2, and the crystals were filtered and washed with petroleum ether to afford **2b** as white crystals (0.437 g from 8.80 g of 4,4′-difluorobenzophenone, 5% yield). mp 158.4−165.4 °C. IR (KBr, cm^{-1}): 3553, 3448, 1606, 1504, 1413, 1345, 1231, 1156, 1095, 997, 845, 822, 735, 573. ^{1}H NMR (400 MHz, $CDCl_3$): 7.50 (m, 8H), 7.48 (t, *J* = 8.9 Hz, 8H), 2.82 (s, 2H, OH). EI-MS (TOF) *m*/*z* (%): 444 (2), 428 (10), 416 (5), 321 (6), 243 (4), 218 (70), 214 (11), 123 (100), 95 (61), 75 (22). HRMS calcd for $C_{28}H_{16}OF_4$ (M − H_2O): 444.1137. Found: 444.1127.

*1,1,4,4-Tetra(4-methoxyphenyl)but-2-yne-1,4-diol (**2c**).* The crude product was purified by flash chromatography (0−50% AcOEt/petroleum ether) to afford pure **2c** as yellow crystals (1.42 g from 9.76 g of 4,4′-dimethoxybenzophenone, 56% yield). mp 136.5−138.0 °C. IR (KBr, cm^{-1}): 3398, 2959, 2934, 2833, 1585, 1613, 1511, 1460, 1414, 1362, 1249, 1175, 1106, 1032, 987, 832, 588. ^{1}H NMR (400 MHz,$CDCl_3$): 7.48 (d, *J* = 8.7 Hz, 8H), 6.83 (d, *J* = 8.7 Hz, 8H), 3.77 (s, 12H, OCH_3), 2.80 (s, 2H, OH). EI-MS (TOF) *m*/*z* (%): 492 (11), 490 (10), 476 (23), 464 (14), 243 (10), 242 (81), 211 (33), 135 (100), 107 (15), 92 (19), 77 (19). HRMS calcd for $C_{32}H_{28}O_5$ (M − H_2O): 492.1937. Found: 492.1936.

Synthesis of 1-Vinylidene-1,2-dihydro-naphtho[2,1-*b*]furans (3a−3c). 4-Toluenesulfonic acid monohydrate (5 mg) was added to a stirred solution of 2-naphthol (280 mg) and diol **2a**−**2c** (1 equiv) in $CHCl_3$ (10 mL), and the violet solution thus formed was maintained at room temperature until TLC examination indicated that no diol remained (about 1 h). After addition of water (60 mL), the organic phase was separated and the aqueous phase was extracted with $CHCl_3$ (2 × 40 mL). The combined organic extracts were dried (Na_2SO_4), and the solvent was removed under reduced pressure to give an oil that was purified by column chromatography and recrystallization.

*1,2-Dihydro-1-(2,2-diphenyl)vinylidene)-2,2-diphenylnaphtho-[2,1-b]furan (**3a**).* The product was purified by column chromatography (5−10% ethyl acetate/petroleum ether) and then recrystallized from petroleum ether to afford white crystals of **3a** (0.455 g from 0.758 g of diol **2a**, 47% yield). mp 193.4−195.9 °C. IR (KBr, cm^{-1}): 3060, 3027, 1626, 1592, 1516, 1457, 1440, 1269, 1247, 1180, 1017, 962, 806, 751, 696. ^{1}H NMR (300 MHz, $CDCl_3$): 8.26 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.43−7.51 (m, 5H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.20−7.31 (m, 13H), 7.16 (d, *J* = 7.9 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 95.1, 112.6, 113.7, 114.9, 117.5, 122.4, 123.9, 127.5, 127.9, 128.0, 128.1, 128.3, 128.6, 128.9, 129.3, 130.0, 130.3, 132.0, 136.6, 143.2, 157.9, 202.9. EI-MS (TOF) *m*/*z* (%): 499 (11), 498 (43), 497 (11), 496 (29), 469 (16), 468 (76), 467 (11), 454 (11), 421 (32), 420 (10), 392 (20), 391 (100), 389 (32), 387 (16), 376 (11), 331 (13), 315 (10), 313 (20). HRMS calcd for $C_{38}H_{26}O$: 498.1984. Found: 498.1989.

*1,2-Dihydro-1-(2,2-di(4-fluorophenyl)vinylidene)-2,2-di(4-fluoro-phenyl)naphtho[2,1-b]furan (**3b**).* The product was purified by column chromatography (3% ethyl acetate/petroleum ether) and then recrystallized from petroleum ether to afford white crystals of **3b** (0.216 g from 0.445 g of diol **2b**, 19% yield). mp 124.4−127.7 °C. IR (KBr, cm^{-1}): 3061, 1634, 1604, 1505, 1460, 1271, 1236, 1156, 1012, 962, 832, 797, 748, 573. ^{1}H NMR (300 MHz, $CDCl_3$): 8.18 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.34−7.46 (m, 5H), 7.28 (d, *J* = 8.9 Hz, 1H), 7.12 (dd, *J* = 8.6 Hz, *J* = 5.4 Hz, 4H), 6.89−7.06 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): 93.8, 112.4, 112.9, 115.1, 115.3, 115.6, 115.9, 121.9, 124.0, 128.1, 129.1, 129.3, 129.6, 130.1, 130.2, 132.0, 132.3, 138.6, 157.6, 160.9, 164.2, 202.1. ^{19}F NMR (282 MHz, $CDCL_3$): −113.51 (tt, *J* = 8.4 Hz, *J* = 5.4 Hz, 1F), −113.92 (tt, *J* = 8.5 Hz, *J* = 5.4 Hz, 1F). EI-MS (TOF) *m*/*z* (%):570 (100), 476 (10), 475 (51), 474 (11), 445 (14), 367 (18), 351 (16), 349 (14), 201 (14). HRMS calcd for $C_{38}H_{22}OF_4$: 570.1607. Found: 570.1605.

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*1,2-Dihydro-1-(2,2-di(4-methoxyphenyl)vinylidene)-2,2-di(4-methoxyphenyl)naphtho[2,1-b]furan (**3c**).* The product was purified by column chromatography (15−20% ethyl acetate/petroleum ether). The compound was then dissolved in CH_2Cl_2, and charcoal was added. The suspension was heated for 30 min at 60 °C and filtered, and the solvent was removed under reduced pressure. Recrystallization from petroleum ether afforded slightly yellow crystals of **3c** (0.550 g from 0.970 g of diol **2c**, 46% yield). mp 71.9−74.9 °C. IR (KBr, cm^{-1}): 2954, 2931, 2833, 2359, 2337, 1607, 1511, 1458, 1248, 1170, 1030, 833, 811, 584. ^{1}H NMR (300 MHz,$CDCl_3$): 8.25 (d, J = 8.3 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 7.39 (d, J = 8.8 Hz, 4H), 7.34 (t, J = 8.0 Hz, 1H), 7.25 (d, J = 8.8 Hz, 1H), 7.11 (d, J = 8.8 Hz, 4H), 6.78 (d, J = 8.7 Hz, 4H), 6.75 (d, J = 8.8 Hz, 4H), 3.83 (s, 6H, OCH_3), 3.80 (s, 6H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 55.3, 94.5, 112.5, 113.4, 113.7, 113.8, 114.8, 116.3, 122.2, 123.5, 127.7, 128.7, 129.0, 129.1, 128.8, 129.9, 130.0, 131.4, 135.7, 157.7, 159.2, 159.3, 202.0. EI-MS (TOF) m/z (%): 618 (47, M^+), 617 (29), 616 (100), 589 (12), 588 (43), 587 (12), 557 (13), 511 (12), 510 (11), 482 (14), 481 (55), 350 (3), 287 (3), 227 (3), 135 (4). HRMS calcd for $C_{42}H_{34}O5$: 618.2406. Found: 618.2402.

1-(1-Hydroxy-1,1,4,4-tetraphenylbuta-2,3-dien-2-yl)-naphthalen-2-ol (4). ^{1}H NMR (500 MHz, CDCl3): 3.22 (s, 1H), 7.00 (broad, 4H), 7.14 (d, J = 8.6 Hz, 1H), 7.14 (ddd, J = 8.4 Hz, J = 6.9 Hz, J = 1.4 Hz, 1H), 7.20−7.28 (m, 9H), 7.29−7.33 (m, 4H), 7.53 (s, 1H), 7.57 (broad, 4H), 7.61 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 83.0, 109.2, 112.1, 114.3, 118.6, 123.1, 125.2, 126.3, 127.0, 127.8, 128.0, 128.1, 128.4, 128.6, 129.0, 130.1, 133.9, 135.5, 144.4, 152.1, 208.3. EI-MS (TOF) m/z (%): 516 (5), 514 (16), 500 (53), 499 (99), 498 (100), 437 (64), 422 (50), 421 (96), 420 (73), 393 (25), 333 (80), 332 (83), 331 (90), 315 (73), 302 (80), 289 (44), 255 (57), 226 (44), 167 (75), 165 (82). HRMS calcd for $C_{38}H_{28}O_2$: 516.2089. Found: 516.5084.

1-(Hydroxydiphenylmethyl)-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (5). ^{1}H NMR (500 MHz, $CDCl_3$): 3.37 (s, 1H), 5.82 (s, 1H), 6.99 (ddd, J = 8.5 Hz, J = 7.1 Hz, J = 1.4 Hz, 1H), 7.17 (ddd, J = 7.9 Hz, J = 7.0 Hz, J = 0.9 Hz, 1H), 7.19−7.27 (m, 8H), 7.32 (d, J = 7.7 Hz, 4H), 7.37 (t, J = 7.8 Hz, 4H), 7.39 (d, J = 8.9 Hz, 1H), 7.53 (d, J = 7.4 Hz, 4H), 7.57 (d, J = 8.7 Hz, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.72 (d, J = 8.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 82.9, 83.2, 116.7, 119.4, 123.4, 125.8, 126.2, 127.3, 127.5, 127.7, 127.89, 127.92, 128.1, 128.9, 130.0, 130.3, 130.9, 135.1, 141.3, 143.8, 147.9, 153.1. EI-MS (TOF) m/z (%): 516 (9), 515 (13), 514 (30), 500 (43), 499 (39), 498 (79), 437 (100), 421 (56), 409 (54), 334 (87), 333 (75), 315 (32), 302 (44), 289 (30), 257 (64), 255 (34), 226 (31), 191 (32), 182 (39). HRMS calcd for $C_{38}H_{28}O_2$: 516.2089. Found: 516.5082.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra of all new compounds and the colored species and kinetic studies for compounds **3a**−**3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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