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# Solid-State Dehydration of (*o*-Hydroxyaryl)diphenylmethanols. Crystal and Molecular Structures of [1-(2-Hydroxyphenyl)]diphenylmethanol and of [1-(2-Hydroxynaphthyl)]diphenylmethanol[1,2]

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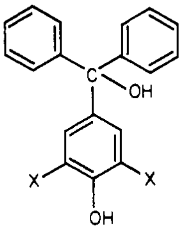
**Abstract:** The rearrangement of [1-(2-hydroxynaphthyl)]diphenylmethanol (**3**) to the corresponding fuchsone (**4**) has been shown to proceed in the solid state (either as a reaction of powders or single crystals) when induced thermally or photochemically. The thermal reaction is comparable in rate to those of the (*p*-hydroxyphenyl)diphenylmethanols studied earlier in spite of the rather different hydrogen-bonding scheme shown by X-ray analysis of the crystal structure of **3**. The thermal reaction can also be nucleated photochemically. Colorless crystals of **3** are monoclinic, $a = 13.097$ (3) Å, $b = 8.402$ (2) Å, $c = 16.877$ (5) Å, $\beta = 115.08$ (2)°; the space group is $P2_1/c$ and the structure has been refined to an $R$ factor of 0.054 on 1887 nonzero reflections. Molecules of **3** have an internal hydrogen bond between the naphtholic and alcoholic groups and, in addition, there is an intermolecular hydrogen bond between the alcoholic hydroxyl group and the naphthol group of an adjacent molecule. The crystals of **6** are monoclinic, $a = 22.408$ (4) Å, $b = 8.630$ (2) Å, $c = 15.989$ (2) Å, $\beta = 107.88$ (1)°; the space group is $C2/c$ and the structure has been refined to an $R$ factor of 0.049 on 2454 nonzero reflections. The hydrogen-bonding pattern is very similar to that found in **3**. Examination of the thermally induced reaction of the related compound (*o*-hydroxyphenyl)diphenylmethanol (**6**) showed that even after long reaction times (113 h) at 65 °C there was no evidence for formation of the ortho fuchsone **4**, and at 110 °C (after melting) infrared spectroscopic examination of the reaction mixture showed absorption attributed to starting material **6** and 9-phenylxanthene (**8**) but no indication of the accumulation of the ortho fuchsone (**7**). The central carbon atom, C(1), lies from the plane defined by its three bonded carbon atoms by distances of 0.421 Å in **3** and 0.463 Å in **6**. The greater tendency toward planarity in **3** may be a factor in the greater solid-state reactivity.

In a previous paper in this series[3] the thermal, photochemical, and photonucleated thermal dehydration reactions in the solid state of (4-hydroxyphenyl)diphenylmethanols (**1**) to the fuchsones (**2**) were discussed in relation to the crystal structures of these substances. In particular, the unsubstituted compound **1a** and its 2,6-dibromo (**1b**) and 2,6-dimethyl derivatives (**1c**) have been shown to have, as a common structural feature, hydrogen-bonded chains connecting the phenolic hydroxyl group of one molecule with the alcoholic hydroxyl group of the next in an orientation suitable for an intermolecular chain dehydration, and evidence was found that solid-state reactivity was related to the presence of such chains. Gomberg and McGill[4] had reported that (*o*-hydroxynaphthyl)diphenylmethanol (**3**) could be made to undergo dehydration to the fuchsone **4**, apparently in the solid state. Since the placement of the hydroxyl in the 2 rather than the 4 position of an aryl ring introduced the possibility of intramolecular hydrogen bonding which might be expected to alter significantly the crystal packing and hence the reactivity, we continued our study with the (*o*-hydroxyaryl)diphenylmethanols.

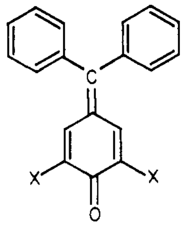
Carbinol **3** had been reported[4] to undergo conversion to the xanthene **5** "after prolonged boiling with acetic acid". The effect of carrying out these reactions in the solid state on the conversion of **3** to **5** as compared to **3** to **4** was therefore of interest.

A more obvious candidate for an (*o*-hydroxyaryl)diphenylmethanol suitable for dehydration in the solid state is the triphenyl compound **6**, which had been reported by Gomberg and Nishida[5] to undergo solid-state dehydration at 100 °C to give not the fuchsone **7** but 9-phenylxanthene (**8**).

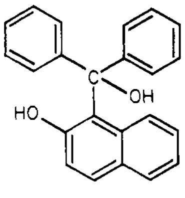
This paper reports on the thermal, photochemical, and photonucleated thermal conversion in the solid state of the compound **3** to **4** and the crystal structure of **3**. The crystal structure of **4** has been reported in a previous publication.[6] The paper also contains a description of our study of the solid-state behavior of **6** and the crystal structure of **6**.



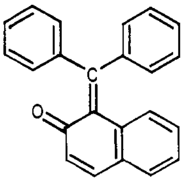
**1a**, X = H
**b**, X = Br
**c**, X = CH$_3$



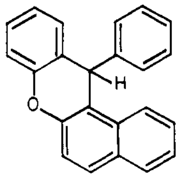
**2a**, X = H
**b**, X = Br
**c**, X = CH$_3$



**3**



**4**



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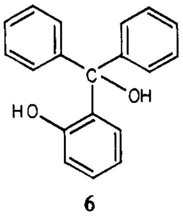
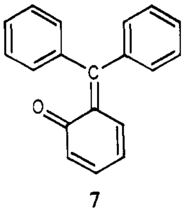
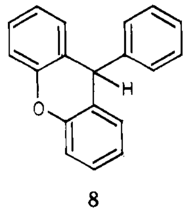


**6**



**7**



**8**

## Experimental Section

See the previous paper[3] for information about instrumentation. Further experimental detail and reproductions of many spectra may be found in ref 1.

**[1-(2-Hydroxynaphthyl)]diphenylmethanol (3)** was prepared from methyl 2-hydroxy-1-naphthoate and phenylmagnesium bromide as a

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(1) Taken in part from the Ph.D Thesis of Terry W. Lewis, submitted to the University of Illinois, 1977, available from University Microfilms, Ann Arbor, Mich.

(2) We are indebted to the National Science Foundation (NSF CHE-76-07620-A02) for support of this work.

(3) T. W. Lewis, D. Y. Curtin, and I. C. Paul, *J. Am. Chem. Soc.*, **101**, 5717 (1979).

(4) M. Gomberg and W. J. McGill, *J. Am. Chem. Soc.*, **47**, 2392 (1925).

(5) M. Gomberg and D. Nishida, *J. Am. Chem. Soc.*, **45**, 190 (1923).

(6) E. N. Duesler, T. W. Lewis, D. Y. Curtin, and I. C. Paul, *Acta Crystallogr., Sect. B*, **34**, 985 (1978).

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white powder: mp 195 °C, turning red at approximately 120 °C (lit.[4] mp 195–198 °C); IR (KBr pellet) 3420 (br, s), 1630 (s), 1470 (m), 1230 (s), 710 (s) cm$^{-1}$; NMR (acetone-$d_6$) $\delta$ 10.9 (1 H, s), 6.87–7.88 (16 H, m), 6.73 (1 H, s), signals at $\delta$ 10.9 and 6.73 diminish on dilution with $D_2O$; UV $\lambda_{max}$ ($Et_2O$) nm (log $\epsilon$), 267 (3.68), 278 (3.76), 290 (3.70), 321 (3.50), 331 (3.53), 335 (3.59); DSC (20 °C/min) endotherm, extrapolated onset ~150 °C with a shoulder centered at 162 °C; melt endotherm, extrapolated onset ~205 °C.

Crystals grown from ether–hexane solution were six-sided tablets elongated along [010] with {001} as the prominent faces. The external morphology of the crystals displayed 2/*m* symmetry. Interfacial angles (deg), ±1° (calcd); (001):(100) 65 (64.95); (001):($\bar{1}$02) 38 (38.8); (001):(110) 76 (75.8); (001):($\bar{1}$11) 78 (78.1); ($\bar{1}\bar{1}$0):(11$\bar{1}$) 154 (153.9); ($\bar{1}$02):($\bar{1}$11) 60.5 (60.5).

**1-($\alpha$,$\alpha$-Diphenylmethylene)-1,2-naphthoquinone (4).**[4] Boiling **3** in a minimal amount of glacial acetic acid for a few minutes gave, upon cooling, red crystals of **4** in essentially quantitative yield. Recrystallization from ether–hexane gave red crystals: mp 199–200 °C (lit.[4] mp 195–198 °C); IR (KBr) 3080 (w), 1655 (s), 1560 (m), 1245 (m), 770 (s), 710 (s) cm$^{-1}$; NMR ($CDCl_3$) $\delta$ 6.67–7.45 (m, 15 H), 6.19 (d, 1 H); UV, nm (log $\epsilon$), 357 (3.99). Crystals grown from ether–hexane solution were rectangular tablets elongated along [010] with {001} as the prominent faces, or six-sided tablets elongated along [010] with {100} as the prominent faces. In both cases, the external morphology of the crystals displayed 2/*m* symmetry. Interfacial angles (deg), ±1° (calcd); (001):(100) 70 (70.7); (100):(1$\bar{1}\bar{1}$) 50 (50.4); (100):(021) 83 (84.5); (001):(0$\bar{2}\bar{1}$) 108 (106.8); (0$\bar{2}$1):(11$\bar{1}$) 132 (133.1); (0$\bar{2}$1):(0$\bar{2}\bar{1}$) 35 (33.7). DSC (25 °C/min) showed no indication of an endotherm or an exotherm until the melting endotherm (extrapolated onset 209 °C).

**Conversion of the Carbinol 3 to 12-Phenyl-12[*H*]-benzo[*a*]xanthene (5).** A solution of 0.14 g of **3** in 15 mL of glacial acetic acid, after boiling for 2 h, stirring at ambient temperature for 16 h, and boiling for 29 h, retained its dark red color and was shown by TLC (toluene eluent) to contain starting material as well as **5** and an uncharacterized oil (not **4**). Continuation of the boiling for 5 days (132 h) gave only a barely perceptible color change. Addition of 5 drops of concentrated hydrochloric acid as boiling was continued for 3 h produced a somewhat lighter solution shown by TLC to contain no starting material. Cooling, filtration, addition of water, and washing with petroleum ether (bp 30–60 °C) gave **5** as a 30% yield of pinkish-white powder. Recrystallization (HOAc/$H_2O$; boiling ethanol) gave white needles: mp 163–165 °C (lit.[4,7] 172–173, 162–163 °C): IR (Nujol) 1640 (w), 1600 (w), 1260 (s), 825 (s), 760 (s) cm$^{-1}$; NMR (acetone-$d_6$) $\delta$ 7.9 (m, 3 H), 7.35 (m, 6 H), 7.1 (m, 6 H), 5.9 (s, 1 H); DSC (10 °C/min) endotherm at 170 °C (extrapolated onset 168 °C).

**(2-Hydroxyphenyl)diphenylmethanol (6)** was prepared by reaction of methyl salicylate with phenylmagnesium bromide. Separation of the crude product from unreacted starting material by column chromatography on silica gel (hexane–ether eluent) and recrystallization from EtOH/$H_2O$ gave **6**: mp 140–141 °C (lit.[5] mp 140 °C); IR (Nujol) 3390 (s), 3165 (m), 1626 (w), 1595 (s), 1499 (s), 1250 (s), 1220 (m), 1155 (w), 1099 (m), 1037 (w), 1010 (s), 931 (s), 906 (s), 823 (m), 763 (s), 758 (s), 752 (s), 746 (s) cm$^{-1}$; UV $\lambda_{max}$ (EtOH) nm (log $\epsilon$) 271 (3.70); ($Et_2O$) 274 (3.47); TLC (toluene) $R_f$ 0.26; NMR (acetone-$d_6$) $\delta$ 8.93 (s), 7.27 (s), 6.83–6.37 (m), 6.23 (s); DSC (20 °C/min) sharp endotherm at 152.8 °C (extrapolated onset 148.5 °C).

**9-Phenylxanthene (8)**,[5] prepared by heating the hydroxycarbinol **6** with acetic anhydride in acetic acid, and recrystallized from boiling ethanol, was obtained as beautiful, colorless crystals: mp 144–145 °C (lit.[5] mp 144–145 °C); IR (Nujol mull) 1613 (m), 1580 (m), 1484 (s, sh), 1326 (m), 1319 (w), 1259 (s), 1218 (m), 1159 (w), 1124 (m), 1103 (w), 1042 (w), 905 (s), 851 (m), 754 (s), 726 (m), 704 (s) cm$^{-1}$; UV $\lambda_{max}$ ($Et_2O$) nm (log $\epsilon$) 246 (3.87), 213 (4.56), 279 (3.38); TLC (toluene) $R_f$ 0.71; NMR (acetone-$d_6$) $\delta$ 7.23 (s, 5 H), 7.17–6.87 (m, 8 H), 5.33 (s, 1 H); DSC (20 °C/min) endotherm at 151.2 °C (extrapolated onset 147.2 °C).

**X-ray Structure Determination of [1-(2-Hydroxynaphthyl)]diphenylmethanol (3).** A suitable crystal (dimensions 0.4 × 0.2 × 0.1 mm) was obtained by slow evaporation of an ether–hexane solution.

**Crystal Data**: $C_{23}H_{18}O_2$; mol wt 326.4; monoclinic; $a$ = 13.097 (3) Å, $b$ = 8.402 (2) Å, $c$ = 16.877 (5) Å, $\beta$ = 115.08 (2)°; $V$ = 1682 Å$^3$; $Z$ = 4; $d_c$ = 1.29 g/cm$^3$; $F(000)$ = 688; $\mu$ = 6.5 cm$^{-1}$; systematic absences, $h0l$ when $l = 2n + 1$, $0k0$ when $k = 2n + 1$; space group $P2_1/c$. Unit cell parameters were determined by a least-squares fit to the settings for 15 accurately centered high-order reflections (Cu K$\alpha$, $\lambda$ = 1.541 78 Å).

Intensity data were collected on a computer-controlled four-angle Syntex $P2_1$ diffractometer (Cu K$\alpha$). Reflections in the range $2\theta$ = 2–130° were measured by a $2\theta$ scan method, using a moving-crystal, moving-counter technique with scan speeds ranging from 2°/min to 10°/min. The intensities of three standard reflections, measured every 50 reflections, did not show any evidence of crystal decay throughout the period of data collection. A total of 1887 nonzero reflections out of a possible 2873 unique reflections was obtained at the 1.96$\sigma$-significance level. No absorption or extinction corrections were applied.

Table I. Final Atomic Coordinates for 3 (Standard Deviations in Parentheses)[a]

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| C(1) | 0.1677 (2) | 0.2255 (3) | 0.3263 (2) |
| C(2) | 0.2389 (3) | 0.3771 (3) | 0.3517 (2) |
| C(3) | 0.2340 (4) | 0.4764 (4) | 0.2846 (3) |
| C(4) | 0.2948 (4) | 0.6164 (5) | 0.3012 (3) |
| C(5) | 0.3629 (4) | 0.6605 (5) | 0.3858 (3) |
| C(6) | 0.3678 (3) | 0.5659 (4) | 0.4534 (3) |
| C(7) | 0.3067 (3) | 0.4243 (4) | 0.4372 (2) |
| C(8) | 0.1652 (2) | 0.1278 (4) | 0.4026 (2) |
| C(9) | 0.1826 (3) | −0.0339 (4) | 0.4087 (2) |
| C(10) | 0.1729 (3) | −0.1212 (4) | 0.4750 (2) |
| C(11) | 0.1470 (3) | −0.0461 (4) | 0.5368 (2) |
| C(12) | 0.1277 (3) | 0.1155 (5) | 0.5306 (2) |
| C(13) | 0.1371 (3) | 0.2017 (4) | 0.4645 (2) |
| C(14) | 0.1996 (3) | 0.1224 (3) | 0.2641 (2) |
| C(15) | 0.1198 (3) | 0.0618 (4) | 0.1865 (2) |
| C(16) | 0.1506 (3) | −0.0202 (4) | 0.1264 (2) |
| C(17) | 0.2600 (3) | −0.0454 (4) | 0.1450 (2) |
| C(18) | 0.4605 (3) | −0.0380 (5) | 0.2488 (3) |
| C(19) | 0.5424 (4) | −0.0056 (5) | 0.3289 (3) |
| C(20) | 0.5136 (3) | 0.0698 (4) | 0.3909 (3) |
| C(21) | 0.4054 (3) | 0.1126 (4) | 0.3708 (2) |
| C(22) | 0.3159 (3) | 0.0836 (3) | 0.2868 (2) |
| C(23) | 0.3466 (3) | 0.0012 (4) | 0.2259 (2) |
| O(1) | 0.0520 (2) | 0.2794 (3) | 0.2749 (2) |
| O(2) | 0.0053 (2) | 0.0704 (3) | 0.1601 (2) |
| H(1) | 0.035 (3) | 0.366 (5) | 0.297 (2) |
| H(2) | −0.003 (3) | 0.133 (5) | 0.193 (2) |
| H(3) | 0.187 (3) | 0.440 (5) | 0.227 (3) |
| H(4) | 0.298 (3) | 0.683 (5) | 0.253 (2) |
| H(5) | 0.402 (3) | 0.757 (5) | 0.398 (2) |
| H(6) | 0.410 (3) | 0.595 (4) | 0.517 (2) |
| H(7) | 0.313 (3) | 0.355 (4) | 0.488 (2) |
| H(9) | 0.204 (3) | −0.094 (4) | 0.365 (2) |
| H(10) | 0.186 (3) | −0.233 (4) | 0.478 (2) |
| H(11) | 0.143 (3) | −0.108 (4) | 0.584 (2) |
| H(12) | 0.112 (3) | 0.163 (4) | 0.574 (2) |
| H(13) | 0.121 (3) | 0.312 (4) | 0.458 (2) |
| H(16) | 0.084 (3) | −0.057 (4) | 0.075 (2) |
| H(17) | 0.286 (3) | −0.094 (5) | 0.107 (2) |
| H(18) | 0.473 (3) | −0.090 (4) | 0.202 (2) |
| H(19) | 0.620 (4) | −0.032 (5) | 0.341 (3) |
| H(20) | 0.572 (3) | 0.092 (4) | 0.449 (2) |
| H(21) | 0.388 (2) | 0.165 (4) | 0.417 (2) |

[a] Hydrogen atoms are given the number of the atoms to which they are attached.

The weights were taken as $1/[\sigma(F_o)^2 + (0.02F_o)^2]$, where $\sigma(F_o)$ is the standard deviation based on counting statistics. The atomic scattering factors were taken from the analytical expressions from the International Tables for X-ray Crystallography.[8]

The structure was solved by using the MULTAN program.[9] Refinement of the positional and anisotropic thermal parameters for all nonhydrogen atoms gave an $R$ value of 0.114. Positions calculated by using standard criteria for the aromatic hydrogen atoms were then included in the model; after further cycles of least-squares refinement varying positional and anisotropic thermal parameters for all nonhydrogen atoms and positional and isotropic thermal parameters for the aromatic hydrogen atoms, a difference map revealed the positions of the hydroxylic hydrogen atoms. Full-matrix least-squares refinement varying positional and anisotropic temperature parameters for all nonhydrogen atoms and positional and isotropic temperature parameters for all hydrogen atoms converged to an $R$ factor of 0.054 and an $R_2$ of 0.056 on all nonzero reflections; the

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(7) G. Wittig, F. Vidal, and E. Bohnert, *Chem. Ber.*, **83**, 359 (1950).

(8) J. A. Ibers and W. C. Hamilton, Eds., "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, pp 71–147.

(9) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).

**Table II.** The Atomic Coordinates for 6

| atom | *x* | *y* | *z* |
|---|---|---|---|
| C(1) | 0.15859 (6) | 0.4992 (2) | 0.72087 (9) |
| C(2) | 0.11381 (7) | 0.6363 (2) | 0.69123 (11) |
| C(3) | 0.12300 (11) | 0.7682 (2) | 0.74357 (14) |
| C(4) | 0.08045 (16) | 0.8901 (3) | 0.72114 (21) |
| C(5) | 0.02945 (15) | 0.8821 (3) | 0.64750 (23) |
| C(6) | 0.01991 (12) | 0.7528 (4) | 0.59519 (19) |
| C(7) | 0.06212 (9) | 0.6292 (3) | 0.61694 (14) |
| C(8) | 0.15766 (6) | 0.3910 (2) | 0.64413 (9) |
| C(9) | 0.13704 (9) | 0.2397 (2) | 0.63962 (11) |
| C(10) | 0.13846 (11) | 0.1444 (2) | 0.57029 (12) |
| C(11) | 0.15941 (10) | 0.2013 (2) | 0.50375 (13) |
| C(12) | 0.17951 (10) | 0.3525 (2) | 0.50713 (13) |
| C(13) | 0.17860 (9) | 0.4468 (2) | 0.57653 (11) |
| C(14) | 0.14411 (7) | 0.4094 (2) | 0.79507 (9) |
| C(15) | 0.18916 (7) | 0.3114 (2) | 0.85057 (9) |
| C(16) | 0.17487 (9) | 0.2219 (2) | 0.91360 (11) |
| C(17) | 0.11558 (9) | 0.2280 (2) | 0.92293 (12) |
| C(18) | 0.07073 (9) | 0.3235 (2) | 0.86990 (13) |
| C(19) | 0.08527 (8) | 0.4144 (2) | 0.80698 (11) |
| O(1) | 0.22171 (5) | 0.5578 (1) | 0.75971 (8) |
| O(2) | 0.24879 (5) | 0.2994 (1) | 0.84364 (8) |
| H(1)[a] | 0.2290 (9) | 0.623 (2) | 0.7222 (13) |
| H(2) | 0.2551 (10) | 0.393 (3) | 0.8130 (14) |
| H(3) | 0.1655 (11) | 0.778 (3) | 0.8009 (16) |
| H(4) | 0.0889 (12) | 0.978 (3) | 0.7613 (17) |
| H(5) | −0.0002 (16) | 0.968 (4) | 0.6351 (21) |
| H(6) | −0.0166 (15) | 0.746 (4) | 0.5431 (21) |
| H(7) | 0.0551 (10) | 0.551 (3) | 0.5790 (15) |
| H(9) | 0.1227 (10) | 0.194 (2) | 0.6891 (14) |
| H(10) | 0.1239 (10) | 0.042 (3) | 0.5661 (14) |
| H(11) | 0.1595 (13) | 0.140 (3) | 0.4532 (18) |
| H(12) | 0.1927 (11) | 0.400 (3) | 0.4594 (16) |
| H(13) | 0.1914 (10) | 0.554 (3) | 0.5787 (13) |
| H(16) | 0.2092 (10) | 0.162 (3) | 0.9539 (14) |
| H(17) | 0.1065 (9) | 0.168 (2) | 0.9687 (13) |
| H(18) | 0.0278 (10) | 0.328 (2) | 0.8760 (13) |
| H(19) | 0.0530 (9) | 0.481 (2) | 0.7681 (13) |

[a] The hydrogen atoms are given the numbers of the atoms to which they are attached.

"goodness of fit" for the model was 1.59.[10]

A final difference map was obtained after refinement of the model was completed and no significant electron density above 0.2 e/Å$^3$ was observed. The final atomic coordinates for **3** are given in Table I.[11]

**X-ray Structure Determination of [1-(2-Hydroxyphenyl)]diphenylmethanol (6).** Crystals suitable for X-ray work were obtained from a 1:1 mixture of diethyl ether and hexane.

**Crystal Data**: $C_{19}H_{16}O_2$; mol wt 276.4; monoclinic, $a = 22.408$ (4) Å, $b = 8.630$ (2) Å, $c = 15.989$ (2) Å, $\beta = 107.88$ (1)°, $V = 2942$ Å$^3$, $Z = 8$; $d_c = 1.25$ g cm$^{-3}$; $F(000) = 1168$; $\mu$(Cu K$\alpha$) = 6.4 cm$^{-1}$. Systematic absences, $hkl$, $h + k = 2n + 1$, $h0l$, $l = 2n + 1$, require the space group $C2/c$ or $Cc$; the former was established by the results of the analysis. The determination of the cell data and the collection of the intensity data were carried out as described for **3**.

Out of a possible 2748 unique reflections with $2\theta \leq 142°$, 2454 were considered significantly above zero at the $1.96\sigma(I)$ level. There was no evidence for crystal deterioration during the period of data collection.

The structure was solved by direct methods, using the MULTAN program.[9] The positions of all the hydrogen atoms were found from difference maps. Full-matrix least-squares refinement of the positional parameters for all atoms, anisotropic thermal parameters for the nonhydrogen atoms and isotropic thermal parameters for the hydrogen atoms, converged to final agreement factors of $R = 0.049$, $R_2 = 0.069$, and the "goodness of fit" = 2.58 on all nonzero reflections.[10] A final difference map contained no peak with a height greater than 0.1 e/Å$^3$.

The final atomic coordinates for **6** are given in Table II.[11]

**X-ray Powder Photograph Analyses.** Debye–Scherrer powder photographs were taken with a camera made by Charles Supper Co., using Ilford Type G film and nickel-filtered Cu K$\alpha$ ($\lambda$ = 1.541 78 Å) radiation. The theoretical powder patterns for **3** and **4** were calculated from the respective unit cell data, using the program DCALC written locally.[12] Each powder line may be indexed to a specific reflection, and good correlations were obtained between the calculated and observed *d* spacings. The powder pattern of a single crystal of **3**, which had been heated for 22 days at 90 °C but not ground before the photograph, was obtained and was visually identical with that of powdered **4** and could be indexed by using the unit cell data of **4**.

**Solid-State Reactions of 3 to Give 4.** All crystals were taken from a batch for which a satisfactory elemental analysis had been obtained.

**Thermal Reaction of 3.** Thermal reactions were carried out with a Mettler or a calibrated Koffler hot stage. Visual observation of crystals heated at 70 °C for 33 h or at 80 °C for 30 h showed no significant change. At 90 °C, reaction was initiated at nucleation sites on the major face as indicated by the formation of red regions which spread through the crystal. Reaction was sometimes observed to be followed by softening or melting on the surface, although the remainder of the crystal retained its original shape.

Gomberg and McGill[4] had reported that powdered carbinol **3** when heated to 80 °C for 24 h had evolved 100% of the theoretical amount of water to be formed in conversion to the fuchsone **4**. In view of the sharp disparity between our results and those of Gomberg and McGill, it seemed possible that visual observation was deceptive because of the possible conversion, as it was formed, of the red fuchsone **4** to the colorless xanthene **5**. Powdered carbinol **3**, prepared by crushing larger crystals, was therefore heated at 80 °C for 24 h on a Mettler hot stage and the IR and NMR spectra were determined. The NMR spectrum in deuterioacetone was similar to that of starting material **3**, although there were peaks characteristic of the fuchsone **4**. A comparison of the doublet at $\delta$ 6.19 characteristic of fuchsone **4** with the spectrum of an authentic sample showed that not more than about 10% of fuchsone had been formed. There was no evidence of the absorption at $\delta$ 5.9 characteristic of the xanthene **5**. Comparison of the IR spectra led to a similar conclusion.

The reaction of single crystals at 90 °C was followed by the UV method described in the following section. Several crystals were shown to be approximately 50% dehydrated to fuchsone **4** after 191 h. In some cases after prolinged heating at 90 °C crystals melted to a red, fused mass. At temperatures above 90 °C partial melting became so frequent as to make an examination of the crystals at such temperatures of no value.

**Thermal Dehydration of (2-Hydroxyphenyl)diphenylmethanol (6). Search for the *o*-Fuchsone 7.** Powders or samples of small crystals of **6** heated at 65 °C for as long as 113 h showed no visible change other than sometimes becoming pink. The IR spectrum (Nujol mull) at the end of that time showed the absorptions at 1595 and 1626 cm$^{-1}$ characteristic of the starting material but no indication of any substantial chemical change. Additional heating at 100 °C for 4.5 h gave no change in appearance or in the IR. Subsequent heating at 110 °C for 5 min gave a brown oil which when cooled became a brown glass. Grinding of the glass gave a white powder which still showed no IR absorption characteristic of either the dienone (there was no absorption between 1630 and 2000 cm$^{-1}$) or of the xanthene **8**. Further heating of the oil at 110 °C for 45 min gave a similar glass which when powdered showed, in addition to the absorptions of the starting carbinol **6**, absorption at 1573 cm$^{-1}$ characteristic of the xanthene **8**. There was still no absorption between 1640 and 2000 cm$^{-1}$ which could be attributed to the fuchsone **7**. Other attempts under a variety of heating times and conditions gave no indication of the accumulation of the fuchsone.

**Photonucleated Reactions.** Irradiation of crystals of **3** with a G.E. sunlamp at a distance of 46–61 cm or with a Mineralight UVSL-25 TLC indicator lamp ($\lambda$ = 366 nm) at a distance of 1.3–1.9 cm gave the same result. (The manufacturer[13] reported a typical intensity for the TLC source of 70 $\mu$W/cm$^2$ at 46 cm). Although the sunlamp gave off a considerable amount of heat (the temperature at the crystal surface rose to approximately 40 °C), the TLC indicator lamp operated at virtually ambient temperature; any effects were therefore due to the UV light rather than heat from the light source. The time of irradiation with either source was 2–3 days or longer.

Crystals of **3** were analyzed for percent reaction by a UV method using UVANL,[14] a modified Dewar–Urch calculation.[15] The 27 wavelengths utilized were selected every 5 nm from 260 to 390 nm in the spectra of mixtures of **3** and **4**. In each case the crystal was dissolved without further purification in the diethyl ether solvent directly in the UV cell. The validity of this method of analysis was determined with three mixtures of known composition with ratios of **3**:**4** varying from 80:20 to 40:60. Satisfactory agreement (±3%) was obtained between the

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(10) $R = \sum||F_o|-|F_c||/\sum|F_o|$, $R_2 = [\sum w|F_o - F_c|^2 / \sum w|F_o|^2]^{1/2}$; "goodness for fit" = $[\sum w|F_o - F_c|^2/(m - n)]^{1/2}$, where $m$ = no. of observations, $n$ = no. of adjustable parameters.

(11) See paragraph at end of paper regarding supplementary material.

(12) D. A. Dieterich, Ph.D. Thesis, University of Illinois, 1973.

(13) Ultra-Violet Products, Inc., San Gabriel, Calif.

(14) D. B. Pendergrass, Jr., Ph.D. Thesis, University of Illinois, 1971.

(15) M. J. S. Dewar and D. S. Urch, *J. Chem. Soc.*, 345 (1957).

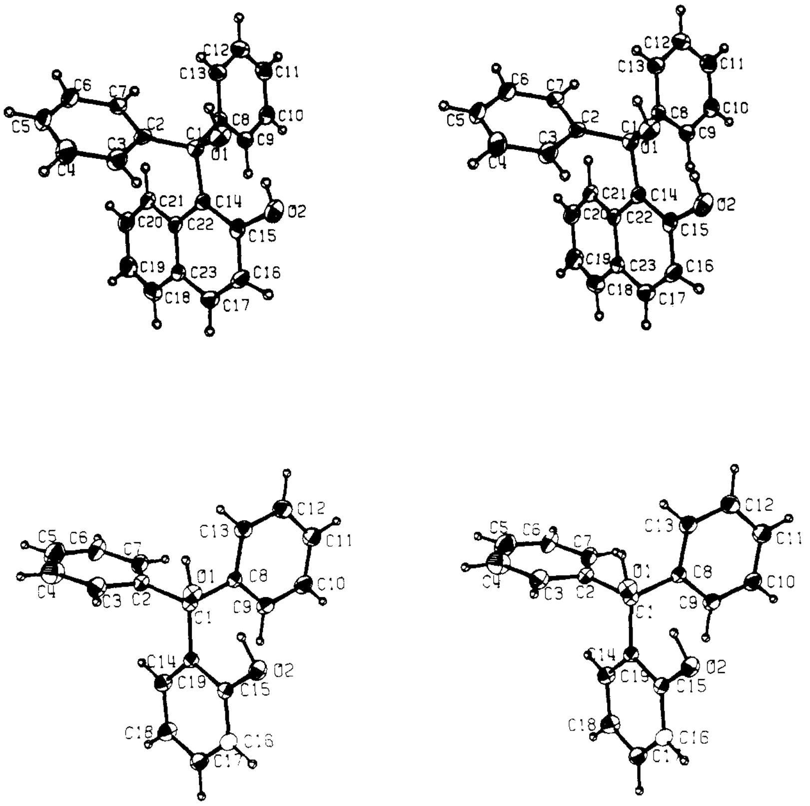


**Figure 1.** Stereoscopic views of the structures of 3 and 6 as determined from the X-ray analysis: (top) a single molecule of the naphthyl alcohol 3; (bottom) a single molecule of the phenyl alcohol 6.

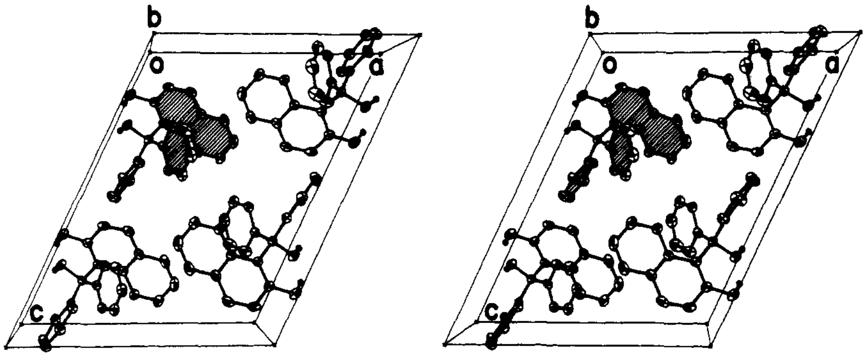


**Figure 2.** A stereoscopic view of the contents of the unit cell in the crystal structure of the naphthyl alcohol 3. The reference molecule (i.e., that whose coordinates are given in Table I) has the aromatic rings shaded.

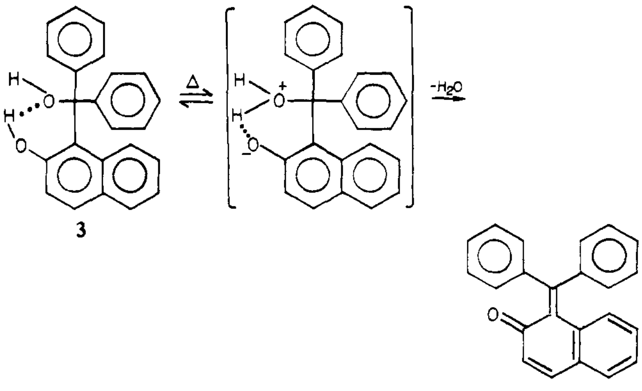
known compositions and those calculated with UVANL.

Prolonged exposure of crystals of 3 to UV light resulted in a very slight coloration of the crystals. The photonucleation of the thermal reaction was demonstrated by covering one-half of a crystal with aluminum foil during irradiation and then heating the entire crystal. Although there was no visible difference between the two halves of the crystal after irradiation, heating (5.5 h, 90 °C) produced selective formation of 4 in the irradiated half of the crystal. There was initially a thin, glass-like red coating in the irradiated half with retention of the optical properties of the crystal. The red coating could be scraped away to reveal unreacted starting material and UV analysis of a crystal at this stage of reaction showed that ≪1% of product 4 had been formed. The glass-like coating remained unchanged on a crystal held for 1 month in the dark at ambient temperature. Upon further heating, the glass-like coating seemed to melt and resolidify and the irradiated region of the crystal became microcrystalline.

## Results and Discussion

The molecular structures of 3 and 6 are shown in Figure 1, while the contents of the unit cells for 3 and 6 are shown in Figures 2 and 3. The determination of the crystal structures of 3 and 6 shows, not unexpectedly, a hydrogen-bonding pattern substantially different from that of the (4-hydroxyphenyl)diphenylmethanols discussed in a previous paper.[3] In the present cases the aromatic hydroxyl is hydrogen bonded to the alcoholic oxygen atom in the same molecule (as indicated for 3 in Scheme I and in Figure 1). In addition, in both structures there is intermolecular hydrogen bonding between the H-donating alcoholic hydroxyl group and

**Scheme I**



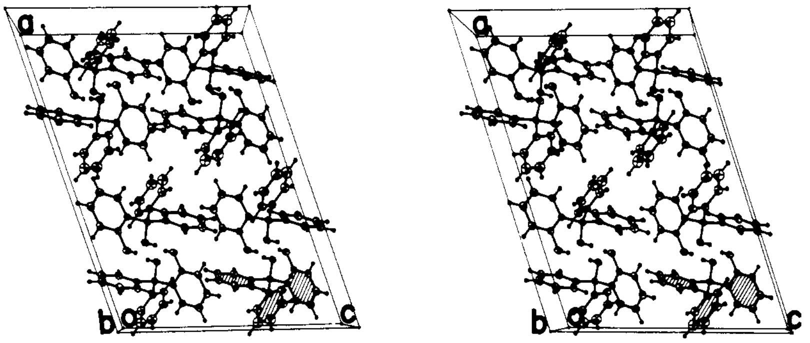


**Figure 3.** Stereoscopic view of the contents of the unit cell in the crystal structure of the phenyl alcohol **6**. The phenyl rings of the reference molecule are shaded.

the H-accepting aromatic group of an adjacent molecule related by the $2_1$ screw axes along *b*. There are thus hydrogen-bonded chains of molecules parallel to *b* (Figure 4) but the intermolecular hydrogen bonds responsible for chain formation seem to be of no particular value in stabilizing the transition state for an elimination reaction. Although the intramolecular hydrogen bond is ideal for a mechanism of the type shown in Scheme I, there is a substantial price to be paid for this advantage since the plane formed by the bonds from the alcohol carbon atom to the two unsubstituted phenyl rings (i.e., the plane defined by C2–C1–C8) is rotated by approximately 80° both from the plane of the adjacent ring of the naphthalene nucleus (i.e., that of C22–C14–C15) in **3** and also from the corresponding plane in **6**, whereas the ideal geometry for ionization of the hydroxyl group should be, from stereoelectronic considerations, approximately 0° (or 180°). The reasons for the different solid-state behavior of **3** (reactive) and **6** (relatively unreactive and then giving a different type of product) must be sought elsewhere than in a variation in hydrogen-bonding pattern.

The proposed intramolecular proton transfer in Scheme I is reminiscent of transfers previously studied by other workers such as those involved in the thermochromism and photochromism of certain anils of salicylaldehyde.[16]

Gomberg and his associates had reported that the 2-hydroxynaphthyl compound **3**, when heated as a solid powder, underwent conversion to the fuchsone **4** at a considerably more rapid rate than the 4-hydroxy-3,5-dibromomethanol **1b** discussed in the previous paper.[3] For example, it was reported[17] that **1b** underwent 4% dehydration at 85 °C in 22 h while **3** underwent 100% dehydration at 80 °C in 24 h. We have found the dehydration of **3** to **4** to be markedly slower than the reaction of the 4-hydroxydibromomethanol **1b** and comparable in reactivity to the 4-hydroxydimethyl compound **1c**. Thus, single crystals of **1b** were 50% converted to **2b** in 2 h at 110 °C, whereas the naphthylmethanol **3** required 191 h at 90 °C for 50% conversion and the 4-hydroxydimethylcarbinol **1c** was only 16% converted to **2c** in 24 h at 110 °C.

In spite of the difficulties inherent in comparing reactivities in the solid state, it seems clear that the difference in packing between the 2-hydroxy compounds exemplified by **3** and the 4-hydroxy compounds such as **1a–c** does not have a controlling effect on their rates of dehydration.

When heated single crystals were viewed through a microscope, the reaction of **3** appeared to begin at randomly distributed nucleation sites and there was no evidence for a preferred direction of spread of the reaction through the crystal. The product **4** of the thermal reaction was shown by melting point and X-ray powder photography to have the same crystal structure as the fuchsone **4** obtained by crystallization. The photochemical reaction was much less evident than had been the case with compounds **1b** and **1c**. Prolonged exposure of single crystals of **3** gave only slight formation of the red color of the fuchsone **4**.[18] The photonucleated thermal reaction of **3** was readily demonstrated, however, by irradiation of one-half of a crystal for 48 h and then heating the entire crystal to 90 °C; the irradiated half showed a very marked preference for thermal reaction. An interesting feature of the behavior of the internally hydrogen-bonded compound **3** was that the boundary between the irradiated and nonirradiated halves of the crystal showed, after heating of the crystal, no streamers of reaction emanating from the reactive region into the clear part of the crystal (along the direction of the hydrogen-bonded chains) as had been the case with form I of the 4-hydroxy compound **1c**. This observation supports the previous conclusion[3] that the streamers are evidence for preferential thermal reaction along the hydrogen-bonded chains linking phenol and

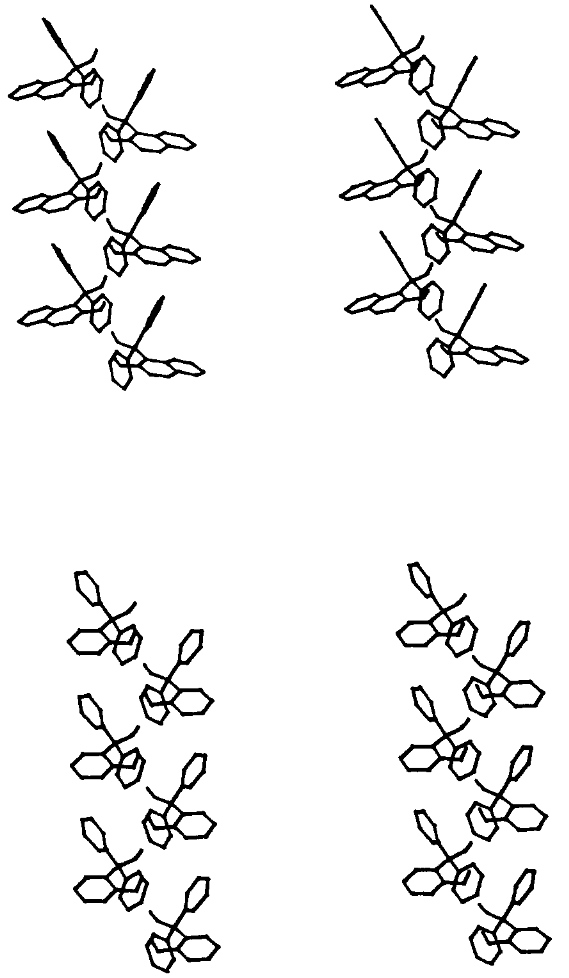


**Figure 4.** Stereoscopic views of the hydrogen-bonded chains in the crystals of **3** and **6**: top, the chain in **3**; bottom, the chain in **6**.

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(16) See, for example, M. D. Cohen and G. M. J. Schmidt, *J. Phys. Chem.*, **66**, 2442 (1962); M. D. Cohen, G. M. J. Schmidt, and S. Flavian, *J. Chem. Soc.*, 2041 (1964).

(17) M. Gomberg and N. E. van Stone, *J. Am. Chem. Soc.*, **38**, 1577 (1916).

(18) It may be noted in this connection that in aqueous solution the ground-state $pK_a$ of β-naphthol is 9.5 but the excited state has $pK_a = 3.1$.[19]

(19) A. Weller, *Z. Phys. Chem. (Frankfurt am Main)*, **3**, 238 (1955).

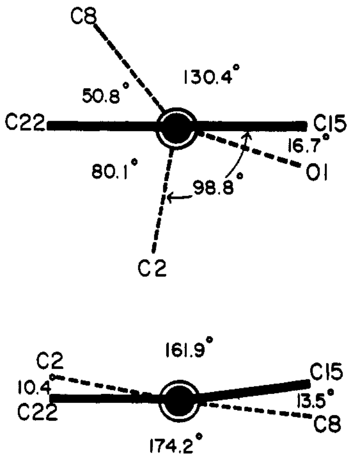

**Figure 5.** Views along the C(14)–C(1) bond in (above) the molecule of **3** and (below) the molecule of **4**. The enantiomer of the molecule of **3** used as the reference molecule in this present paper is shown to correspond to the view of **4** given in ref 6.

alcohol groups of the 4-hydroxy compound **1c**.

The failure of previous workers to synthesize the simpler *o*-fuchsone **7** prompted an investigation of its possible presence as an intermediate in the thermal conversion of the methanol **6** to 9-phenylxanthene (**8**). Carbinol **6** has a characteristic IR absorption at 1595 cm$^{-1}$ while **8** has a corresponding peak at 1580 cm$^{-1}$ and the fuchsone **7** might be expected to have carbonyl absorption near 1655 cm$^{-1}$ in analogy with the naphthalene analogue. Even after 113 h at 65 °C there was no indication from the IR spectrum of either product **7** or **8**. At 110 °C melting occurred and, when the reaction was followed with IR, an absorption characteristic of the starting carbinol **6** gradually disappeared and an absorption characteristic of xanthene **8** appeared, but no absorption in the region where fuchsone **7** might have been expected to absorb was observed. When **6** was heated in the solid state we observed curious color changes analogous to those observed by Gomberg and Nishida.[4]

There remains the puzzle of whether the methanol **6** is converted to xanthene **8** without the intermediate formation of the fuchsone **7**. Comparison of the conformations of **6** and the naphthyl analogue **3** in the crystal (see Figure 1) and also the hydrogen-bonding arrangements in the two crystal structures (Figure 4) provides strong evidence that the difference in their behavior is not due to large conformational variations or to intermolecular orientation by crystal forces. It seems probable then that the low stability of isolated molecules of the *o*-fuchsone is not counteracted by the crystalline environment.

Another factor which may be relevant to the difference of reactivity of **3** and **6** may be found by examination of the geometry at the central carbon atom, C(1). In ideal tetrahedral geometry and with three C–C bonds of length 1.53 Å, a carbon atom will lie 0.51 Å from the plane defined by the three bonded carbon atoms.[20] In triphenylmethanol derivatives, distances as small as 0.33 Å have been found[20] and this tendency toward sp$^2$ character in the central carbon atom has been attributed to intramolecular steric overcrowding. The distances of C(1) from the plane of C(2), C(8), and C(14) are 0.463 Å in **6** and 0.421 Å in **3**. Thus, the greater bulk of the naphthalene nucleus probably results in a flatter, more sp$^2$-character geometry at C(1) in **3** than in **6**. This difference in ground-state geometry for the potential reactants may be a significant factor in the greater solid-state reactivity observed in the case of **3** as compared to **6**. It should be pointed out, however, that, in the case of the (*p*-hydroxyphenyl)diphenylmethanols, solid-state reactivity is observed when the distance of the central carbon lies in the range 0.46–0.48 Å from the plane of its three carbon neighbors,[21] although a somewhat different reaction is being considered in this latter case.

**Molecular and Crystal Structure of (*o*-Hydroxynaphthyl)diphenylmethanol (3) and (*o*-Hydroxyphenyl)diphenylmethanol (6).** The dimensions of the intramolecular and intermolecular hydrogen bonds are of particular interest (Figures 1–4). In **3**, the intramolecular hydrogen bond has an O(2)---O(1) distance of 2.491 (3) Å with O–H and H---O distances of 0.82 (4) and 1.75 (4) Å; for **6**, the corresponding distances are 2.577 (2), 0.98 (2), and 1.71 (2) Å. In **3** the C–O(2)---O(1) and O(2)–H(2)---O(1) angles are 105 (3) and 150 (4)°, respectively, while in **6** they are 84.1 (1) and 146 (2)°.[22] In **3**, the intermolecular hydrogen bond has an O(1)---O(2) ($\bar{x}$, $^1/_2 + y$, $^1/_2 - z$) distance of 2.906 (4) Å with O–H and H---O distances of 0.89 (4) and 2.02 (4) Å, while in **6** the O(1)---O(2) ($^1/_2 - x$, $^1/_2 + y$, $1^1/_2 - z$) distance is 2.861 (2) Å, with O–H and H---O distances of 0.87 (2) and 2.00 (2) Å. In **3** the C–O(1)---O(2) and O(1)–H(1)---O(2) angles are 113.9 (3) and 176 (4)°, respectively, and in **6** they are 112.0 (1) and 169 (2)°.[22] The intramolecular and intermolecular hydrogen bonds lead to chains of molecules running along the *b* axis in both structures as shown in Figure 4. The conformation around the C(1)–C(14) bond in both **3** and **6** is governed primarily by the oxygen–oxygen hydrogen bond with the result that the orientation is highly unfavorable for development of a transition state with a partial C(1)–C(14) double bond (Figure 1). The conformational arrangement along the C(1)–C(14) bond in **3** is shown in Figure 5.[23] For comparison the corresponding arrangement in the fuchsone product **4** is also shown. Not only is extensive rotation around C(1)–C(14) required for progression from **3** to **4** but one of the phenyl rings must rotate through an unfavorable conformation in which it is eclipsed with the naphthalene ring. It will be noted also that the intramolecular O(2)---C(3) and O(2)---C(9) distances in **3** are not at all favorable for the direct formation of an O(2)–C(3) or O(2)–C(9) bond which might lead directly to the xanthene **5**.

The intramolecular bond lengths and angles in both **3** and **6** agree with the values usually found, with the previously noted differences in bond angles at C(1) being a feature of special interest.

**Supplementary Material Available:** A listing of the final thermal parameters, bond lengths and angles, and structure factors for **3** and **6** (33 pages). Ordering information is given on any current masthead page.

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[20] M. J. Sabacky, S. M. Johnson, J. C. Martin, and I. C. Paul, *J. Am. Chem. Soc.*, **91**, 7542 (1969).

[21] See supplementary material associated with ref 3.

[22] If the O–H distances are extended to a more realistic value of 1.00 Å, the H(2)---O(1) intramolecular distance in **3** becomes 1.60 Å and the O(2)–H(2)---O(1) angle is 146°, while the H(1)---O(2) intermolecular distance becomes 1.91 Å and the O(1)–H(1)---O(2) angle is 176°. In **6**, the H(2)---O(1) distance becomes 1.69 Å, and the O(2)–H(2)---O(1) angle is 146°, while the H(1)---O(2) intermolecular distance becomes 1.88 Å and the O(1)–H(1)---O(2) angle is 168°.

[23] The corresponding torsion angles for **6** are C(19)–C(14)–C(1)–C(8) 102°, C(19)–C(14)–C(1)–C(2) -23.6°, C(15)–C(14)–C(1)–O(1) 43°, C(15)–C(14)–C(1)–C(8) -74.6°, and C(15)–C(14)–C(1)–C(2) 160°. It should be noted that these values correspond to the enantiomer of the molecule whose coordinates appear in Table II. As the crystal structure of **7** is not available, there are no values corresponding to those for **4**.