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ORIGINAL PAPER

Interesting Reactivity in the Thermolysis and Photolysis of 2,3-Diphenyl-1-naphthol

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Abstract 2,3-Diphenyl-1-naphthol (**1**) undergoes two unexpected reactions under different conditions. Compound (**1**) was heated in DMSO-d_6 and underwent a Pummerer type thermal reaction to give two isomeric products, 1-(methylthio)methoxy-2,3-diphenyl naphthol-d_5 which crystallized in the space group $P\bar{1}$ with $a = 7.1610(9)$ Å, $b = 11.2795(15)$ Å, $c = 12.8905(17)$ Å, $\alpha = 114.049(2)°$, $\beta = 96.589(2)°$, and $\gamma = 102.945(2)°$, and 2-(methylthio)methyl-2,3-diphenyl 1(2H)-naphthalenone-d_5 which crystallized in the space group $P\bar{1}$ with $a = 8.5981(5)$ Å, $b = 10.4374(6)$ Å, $c = 11.1078(6)$ Å, $\alpha = 78.748(2)°$, $\beta = 67.709(2)°$, and $\gamma = 83.184(2)°$. Photolysis (254 nm) of (**1**) resulted in 2,2′,3,3′-tetraphenyl-1,1′-bi-2-naphthol which crystallized in the space group $P2_1/c$ with $a = 26.3616(11)$ Å, $b = 10.1707(4)$ Å, $c = 23.3376(9)$ Å, and $\beta = 99.034(2)°$.

Keywords X-ray analysis · Pummerer thermal reaction · Photolysis

Introduction

During our studies of the thermal and photochemical properties of 2,3-diphenyl-1-naphthol (**1**) we set out to identify solvents in which it would be stable. It was soon discovered that upon heating in DMSO-d_6, (**1**) [1] converted into two unanticipated isomers, 1-(methylthio)methoxy-2,3-diphenyl naphthol-d_5, (**2**), and 2-(methylthio)methyl-2,3-diphenyl 1(2H)-naphthalenone-d_5, (**3**), whose structures were elucidated using X-ray crystallography (Fig. 1). Unfortunately, this very interesting new reaction proved to not be general. With 1-naphthol a large variety of products resulted, and it was clear that the presence of two large groups, here phenyls, was responsible for the simplicity of the reaction course.

To further test the reactivity of (**1**), the compound was irradiated in THF with ultraviolet light at 254 nm to yield another unexpected product, 2,2′,3,3′-tetraphenyl-1,1′-bi-2-naphthol (**4**) whose structure was also established by X-ray crystallography (Fig. 1).

In addition to structural analysis, all products have been characterized by ^{1}H NMR spectroscopy and melting point measurement. Since all products were unexpected the use of single crystal X-ray analysis was critical in determining the structures.

Experimental

Z-1,2-Diphenylacrylonitrile

A mixture of 7.26 g (62 mmol) of benzylcyanide, 6.58 g (62 mmol) of benzaldehyde and 10.28 g (75 mmol) of potassium carbonate was refluxed in 120 mL of methanol for 4 h in a N_2 atmosphere. The reaction mixture was then poured into 500 mL of water and extracted with dichloromethane (4 × 50 mL). The combined organic phase was washed with water (2 × 50 mL), dried with sodium sulfate and the solvent was removed on a rotary evaporator. The residue was recrystallized from 90 mL of heptane. Yield: 10.3 g (81%), m.p. 81–83 °C (lit m.p. [2] 82–84 °C).

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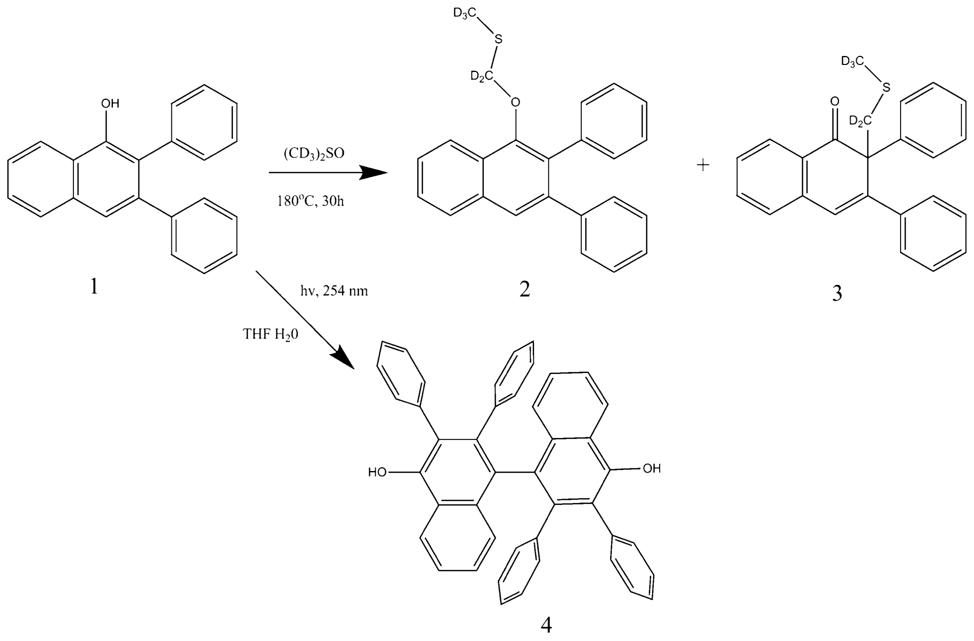

Fig. 1 Reactions of compound (**1**)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.36–7.50 (m, 6H); 7.53 (s, 1H), 7.65–7.69 (m, 2H); 7.87–7.90 (m, 2H).

1,2,3-Triphenylbutyronitrile

To a solution of benzylmagnesium chloride, prepared from 12.21 g (0.50 mol) of magnesium and 63.6 g (0.50 mol) of benzylchloride in 300 mL of anhydrous ether in a N$_2$ atmosphere, was added 400 mL of anhydrous THF. The solution was then cooled to −40 °C. Cuprous (I) iodide, 3.0 g (16 mmol) was added and the reaction mixture was stirred for 10 min. A solution of 79.4 g (0.39 mol) of Z-1,2-diphenyl acrylonitrile in 250 mL of anhydrous THF was added dropwise, while maintaining temperature at −40 °C. When the addition was completed, the reaction mixture, cooled to room temperature, was then refluxed for 3 h. The reaction mixture was then poured into a mixture of 3 L of water and 60 mL of concentrated HCl, stirred for 20 min and extracted with dichloromethane (5 × 300 mL). The organic phase was washed with water (3 × 300 mL), dried with sodium sulfate and the solvent was removed on a rotary evaporator. The residue, which spontaneously crystallized, was recrystallized from 900 mL of ethanol. Forty grams of product, m.p. 129–131 °C, was obtained. Concentration of the mother liquors afforded a second crop, which was recrystallized from 300 mL of ethanol to yield 38.0 g, m.p. 128–130 °C (lit[3] m.p. 130–132 °C). The total yield was 78.0 g (68%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.14–3.30 (m, 3H); 4.03–4.05 (m, 1H); 6.91–6.95 (m, 2H); 7.00–7.05 (m, 2H); 7.17–7.25 (m, 9H); 7.28–7.33 (m, 2H).

1,2,3-Triphenylbutyric Acid

A mixture of 78.0 g (0.26 mol) of 1,2,3-triphenylbutyronitrile, 112 g (2.0 mol) of potassium hydroxide and 1,200 mL of ethylene glycol was refluxed for 12 h in a N$_2$ atmosphere. After cooling, the mixture was poured into 4 L of water and 200 mL of concentrated HCl and extracted with dichloromethane (4 × 200 mL). The organic phase was washed with water (3 × 300 mL), dried with sodium sulfate and the solvent was removed on a rotary evaporator. The residue was dissolved in 400 mL of boiling ethanol and left to stand overnight. The crystals that formed were filtered and washed sparingly with cold ethanol. Yield: 29.4 g (36%), m.p. 139–142 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.48–2.56. (dd, 1H, $J = 11$ Hz and 13.2 Hz); 2.69–2.74 (dd, 1H, $J = 3.3$ Hz and 13.2 Hz); 3.45–3.54 (td, 1H, $J = 3.3$ Hz and 11.2 Hz); 3.86–3.89 (d, 1H, $J = 11.7$ Hz); 6.64–6.67 (m, 2H); 7.00–7.14 (m, 8H); 7.30–7.42 (m, 3H); 7.48–7.51 (m, 2H). The melting point corresponds to one of the known diastereomers [3]. The mother liquor on evaporation afforded a residue, weighing 60 g. This was crystallized from 850 mL of heptane-toluene (4/1). The crystals were filtered, washed with pentane and air dried. Yield: 47.5 g (57.2%), m.p. 155–157 °C. The ^{1}H NMR spectrum indicated this to be the second diastereomer contaminated with 5% of the first one. The pure sample obtained by recrystallization from cyclohexane and melted at 159–160 °C corresponding to the literature [3]. ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.89–2.97 (dd, 1H, $J = 13.3$ Hz and 10.1 Hz); 3.16–3.22 (dd, 1H, $J = 3.6$ Hz and 13.3 Hz); 3.60–3.69 (td, 1H, $J = 3.6$ Hz and 10.8 Hz);

3.93–3.96 (d, 1H, $J = 11.1$ Hz); 6.82–6.84 (m, 2H); 6.92–7.18 (m, 13H). The overall yield was 76.9 g (93%). Because it is known [3], that the higher melting diastereomer of 1,2,3-triphenylbutyric acid gives better yields during cyclization to tetralone, the lower melting diastereomer (28 g) was equilibrated to the 1/1 mixture (as determined by NMR) of both diastereomers by refluxing with potassium hydroxide in ethylene glycol and working up as described above. After fractional crystallization as described above 10 g of the lower melting diastereomer was obtained along with 14 g of the higher melting isomer.

Trans-2,3-diphenyltetralone

To a solution of 50.0 g (0.16 mol) of 1,2,3-triphenylbutyric acid (the 95% pure higher melting diastereomer with 5% of the low melting one) in 1,200 mL of benzene was added 35.9 g (0.17 mol) of phosphorus pentachloride and the reaction mixture refluxed for 2 h. Vigorous evolution of HCl gas was observed. After 2 h 43.6 g (0.16 mol) of stannic tetrachloride was added. The reaction mixture was refluxed overnight, poured into mixture of 4 L of ice cold water and 300 mL of concentrated HCl, stirred for 30 min and extracted with dichloromethane (5 × 200 mL). The organic phase was washed with 5% aqueous potassium hydroxide (3 × 300 mL) and water (4 × 300 mL). The aqueous and alkaline washings were combined, acidified and again extracted with dichloromethane (2 × 100 mL). The organic phase was washed with water (3 × 100 mL) and combined with the main organic phase which was then dried with sodium sulfate and the solvent was removed on a rotary evaporator. The residue was dissolved in 1,400 mL of boiling ethanol and then 800 mL removed by distillation. Crystals formed after 48 h and were filtered and washed with cold ethanol. Yield: 25.5 g, m.p. 148–151 °C. The combined mother liquors were refluxed, and then ethanol was again distilled leaving a final volume of 150 mL. This solution was seeded with a crystal of product and left to crystallize overnight. The crystals were filtered and washed with cold ethanol. The second crop was weighing 5.05 g, m.p. 148–150 °C (lit[3] m.p. 143–147 °C). Total yield: 30.55 g (65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.20–3.27. (dd, 1H, $J = 4.2$ Hz and 16.3 Hz); 3.40–3.48 (dd, 1H, $J = 11.4$ Hz and 16.3 Hz); 3.67–3.76 (td, 1H, $J = 4.2$ Hz and 11.8 Hz); 3.99–4.03 (d, 1H, $J = 12.0$ Hz); 6.96–7.00 (m, 2H); 7.01–7.21 (m, 8H); 7.28–7.30 (d, 1H, $J = 7.5$ Hz); 7.36–7.41 (t, 1H, $J = 7.5$ Hz); 7.52–7.57 (td, 1H, $J = 1.2$ Hz and 7.5 Hz); 8.10–8.13 (dd, 1H, $J = 1.5$ Hz and 8.0 Hz).

2-Bromo-2,3-diphenyltetralone

To solution of 14.2 g (48 mmol) of trans-2,3-diphenyltetralone in 750 mL of glacial acetic acid was added dropwise 10.7 g (67 mmol) of bromine in 100 mL of glacial acetic acid. The reaction mixture was stirred at room temperature for 24 h, poured into 4 L of water and extracted with dichloromethane (5 × 300 mL). The organic phase was washed with 10% sodium bisulfite solution (500 mL), water (4 × 500 mL), dried with sodium sulfate and the solvent was removed on a rotary evaporator. The residue was dissolved into 100 mL of hot cyclohexane and left to crystallize overnight. The crystals were filtered, washed sparingly with cold cyclohexane and air-dried. Yield: 15.3 g (85%), m.p. 115–117 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.10–3.17 (dd, 1H, $J = 3.6$ Hz and 16.8 Hz); 3.54–3.60 (dd, 1H, $J = 3.6$ Hz and 11.7 Hz); 3.78–3.88 (dd, 1H, $J = 11.7$ Hz and 16.8 Hz); 6.89–6.92 (m, 2H); 7.08–7.21 (m, 8H); 7.33–7.35 (d, 1H, $J = 7.5$ Hz); 7.42–7.47 (t, 1H, $J = 7.5$ Hz); 7.56–7.61 (td, 1H, $J = 1.5$ Hz and 7.5 Hz); 8.28–8.30 (dd, 1H, $J = 1.2$ Hz and 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.1; 34.8; 54.4; 127.6; 127.7; 127.8; 127.9; 128.0; 129.0; 129.4; 129.5; 129.9; 130.3; 134.3; 138.2; 138.3; 142.5; 191.3.

2,3-Diphenyl-1-naphthol (**1**)

To solution of 6.90 g (18.3 mmol) of 2-bromo-2,3-diphenyltetralone in 200 mL of DMF were added 400 mg (4.60 mmol) of lithium bromide and 1.5 g (20 mmol) of lithium carbonate. The reaction mixture was heated for 2 h at 100 °C under nitrogen, poured into 1,000 mL of water and 20 mL of concentrated HCl and extracted with ethyl acetate (4 × 100 mL). The organic phase was washed with water (3 × 100 mL) dried with sodium sulfate and the solvent was removed on rotary evaporator. The residue was crystallized from acetic acid and then from heptane. Yield: 3.90 g (72%), m.p. 130–131 °C (lit[1] m.p. 127–128 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.04–7.26 (m, 10H); 7.46 (s, 1H); 7.49–7.55 (m, 2H); 7.88–7.93 (m, 1H); 8.25–8.29 (m, 1H); 8.97 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 121.2, 122.7, 123.5, 125.7, 126.6, 127.1, 127.7, 127.8, 128.0, 129.4, 130.0, 131.4, 133.9, 135.5, 139.9, 141.5, 148.6.

Synthesis of 1-(Methylthio)methoxy-2,3-diphenyl naphthol-d_5 (**2**) and 2-(Methylthio)methyl-2,3-diphenyl 1(2H)-naphthalenone-d_5 (**3**)

A solution of 200 mg (0.67 mmol) of 2,3-diphenyl-1-naphthol (**1**) in 4.0 mL of DMSO-d_6 was heated at 180 °C in a N_2 atmosphere. After 30 h no trace of naphthol (**1**) was detected by ^{1}H NMR. The reaction mixture was then poured into 150 mL of water, extracted with ethyl acetate (4 × 20 mL), the combined organic phase washed with water (4 × 20 mL), dried with sodium sulfate and the solvent was removed on a rotary evaporator. The residue was purified by column chromatography (1.9 × 30 cm silica gel) with hexane–ethyl acetate (20/1) as an eluent. Compounds (**2**) and (**3**) were obtained and recrystallized from hexane–ether. Slow crystallization afforded crystals suitable for X-ray. Compound (**2**): Yield: 80 mg (40%), m.p. 115–117 °C. ^{1}H NMR (300 MHz, DMSO-d$_6$, 25 °C) δ 7.09–7.31 (m, 10H); 7.57–7.64 (m, 2H), 7.78 (s, 1H); 8.00–8.03 (m, 1H); 8.17–8.20 (m, 1H). Compound (**3**): Yield: 90 mg (45%), m.p. 145–147 °C. ^{1}H NMR (300 MHz, DMSO-d$_6$, 25 °C) δ 7.02–7.05 (m, 2H); 7.22–7.46 (m, 10H), 7.62–7.65 (d, 1H, $J = 7.5$ Hz); 7.72–7.81 (m, 2H).

Photochemical Rearrangement of 2,3-diphenyl-1-naphthol to the 2,2′,3,3′-Tetraphenyl-1,1′-bi-2-naphthol (4)

A solution of 450 mg (1.51 mmol) of 2,3-diphenyl-1-naphthol (**1**) in 180 mL of 50% aqueous THF was irradiated at 254 nm in a Rayonet-type reactor for 30 h. During irradiation a slow stream of nitrogen was passed through the reaction mixture. The reaction mixture was cooled and extracted with dichloromethane (4 × 20 mL). The combined organic phase was dried with sodium sulfate and the solvent was removed with a rotary evaporator. The residue was chromatographed (1.9 × 30 cm silica gel column) with hexane–ethyl acetate (25/1) as the eluent. The 10 mL fractions contained naphthol (**6**) (300 mg, 67%) and then 63 mg (14%) of slightly impure binaphthyl product as a yellow solid. The impurity was removed by washing with 0.50 mL of refluxing hexane. The solid was filtered and dried in vacuum affording a slightly yellow powder. Yield: 40 mg (8.9%), m.p. 274–276 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.51 (s, 1H); 5.80 (br s, 1H), 6.62–6.80 (m, 6H); 7.00–7.32 (m, 4H); 7.37–7.54 (m, 3H); 8.32–8.35 (d, 1H, $J = 9$ Hz). ^{13}C NMR (75 MHz, CDCl$_3$) δ 122.2; 122.6; 123.2; 125.3; 125.7; 126.3; 127.1; 127.5; 127.8; 127.9; 128.6; 129.2; 130.5; 132.2; 135.5; 136.0; 139.4; 139.8; 147.9. IR (Soln. in CHCl$_3$, NaCl) 3584, 3537, 3155, 3061, 2985, 2902, 2360, 2253, 1793, 1731, 1648, 1601, 1471, 1379.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC+300 and Varian MercuryPlus 300 (300 MHz) spectrometers using using DMSO-d$_6$ and CDCl$_3$ as solvents. The melting points are uncorrected. The progress of reactions and the purity of products were monitored by TLC on Merck 60 F254 plates using hexane and ethyl acetate. Tetrahydrofuran and diethyl ether were distilled over sodium diphenylketyl prior to use. Silica gel Merck 60 (0.040–0.063 mm) was used for column chromatography.

X-ray Analysis

A colorless crystal of compound (**2**) with approximate dimensions 0.31 × 0.30 × 0.27 mm^3, a colorless crystal of compound (**3**) with approximate dimensions 0.42 × 0.40 × 0.35 mm^3, and a yellow crystal of compound (**4**) with approximate dimensions 0.25 × 0.11 × 0.04 mm^3 were selected under oil under ambient conditions and attached to the tip of a MiTeGen Micromount©. The crystals were mounted in a stream of cold nitrogen at 100(2) K for compound (**2**) and 102(1) K for compounds (**3**) and (**4**) and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection for compound (**2**) were performed on a Bruker CCD-1000 diffractometer with Mo K$_\alpha$ ($\lambda = 0.71073$ Å) radiation and the diffractometer to crystal distance of 4.9 cm. The crystal evaluation and data collection for compounds (**3**) and (**4**) were performed on a Bruker SMART APEXII diffractometer with Cu K$_\alpha$ ($\lambda = 1.54178$ Å) radiation and the diffractometer to crystal distance of 4.03 cm.

The initial cell constants for compound (**2**) were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3° in a 6° range about ω with the exposure time of 20 s per frame. A total of 125 reflections were obtained. The initial cell constants for compounds (**3**) and (**4**) were obtained from three series of ω scans at different starting angles. Each series consisted of 50 frames collected at intervals of 0.5° in a 25° range about ω with the exposure time of 5 s per frame. The reflections were successfully indexed by an automated indexing routine. The final cell constants were calculated from a set of 5352 strong reflections for compound (**2**), a set of 9893 strong reflections for compound (**3**), and a set of 9815 strong reflections for compound (**4**) from the actual data collection.

The data for compound (**2**) were collected by using a complete sphere collection routine. The reciprocal space was surveyed to the extent of a full sphere to a resolution of 0.71 Å. A total of 13243 data were harvested by collecting three sets of frames with 0.36° scans in ω and one set with 0.45° scans in ϕ with an exposure time 18 s per frame. The data for compounds (**3**) and (**4**) were collected by using the full sphere data collection routine to survey the reciprocal space to a resolution of 0.82 Å. For compound (**3**) a total of 14440 data were harvested by collecting 19 sets of frames with 0.5° scans in ω with an exposure time 5 s per frame. For compound (**4**) a total of 96941 data were harvested by collecting 19 sets of frames with 0.5° scans in ω with an exposure time 20 s per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [4, 5].

Structure Solution and Refinement

The systematic absences in the diffraction data for both compound (**2**) and compound (**3**) were consistent for the

Table 1 Crystal data and structure refinement

Identification code	Compound (**2**)	Compound (**3**)	Compound (**4**)
CCDC code	678263	678262	678946
Empirical formula	$C_{24}H_{20}OS$	$C_{24}H_{20}OS$	$C_{44}H_{30}O_2$
Formula weight	356.46	356.46	590.68
Temperature	100(2) K	102(1) K	102(1) K
Wavelength	0.71073 Å	1.54178 Å	1.54178 Å
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Unit cell dimensions	$a = 7.1610(9)$ Å	$a = 8.5981(5)$ Å	$a = 26.3616(11)$ Å
	$b = 11.2795(15)$ Å	$b = 10.4374(6)$ Å	$b = 10.1707(4)$ Å
	$c = 12.8905(17)$ Å	$c = 11.1078(6)$ Å	$c = 23.3376(9)$ Å
	$\alpha = 114.049(2)°$	$\alpha = 78.748(2)°$	$\alpha = 90°$
	$\beta = 96.589(2)°$	$\beta = 67.709(2)°$	$\beta = 99.034(2)°$
	$\gamma = 102.945(2)°$	$\gamma = 83.184(2)°$	$\gamma = 90°$
Volume	901.5(2) Å^3	903.51(9) Å^3	6179.6(4) Å^3
Z	2	2	8
Density (calculated)	1.313 mg/m^3	1.310 mg/m^3	1.270 mg/m^3
Absorption coefficient	0.189 mm^{-1}	1.648 mm^{-1}	0.593 mm^{-1}
$F(000)$	376	376	2480
Crystal size	0.31 × 0.30 × 0.27 mm^3	0.42 × 0.40 × 0.35 mm^3	0.25 × 0.11 × 0.04 mm^3
Theta range for data collection	2.04–30.06°	4.32–72.30°	1.70–69.97°
Index ranges	$-9 \le h \le 10, -15 \le k \le 15, -17 \le l \le 17$	$-10 \le h \le 10, -12 \le k \le 12, -12 \le l \le 13$	$-32 \le h \le 31, -12 \le k \le 12, -28 \le l \le 27$
Reflections collected	13243	14440	96941
Independent reflections	4985 [R(int) = 0.0584]	3292 [R(int) = 0.0188]	11534 [R(int) = 0.0300]
Completeness to theta	94.4%	92.1%	98.4%
Absorption correction	Multi-scan with SADABS	Multi-scan with SADABS	Empirical with SADABS
Max. and min. transmission	0.9507 and 0.9437	0.545 and 0.596	0.9767 and 0.8658
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4985/0/236	3292/0/236	11534/0/845
Goodness-of-fit on F^2	1.007	1.019	1.012
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0449$, $wR2 = 0.1181$	$R1 = 0.0327$, $wR2 = 0.0899$	$R1 = 0.0460$, $wR2 = 0.1171$
R indices (all data)	$R1 = 0.0576$, $wR2 = 0.1247$	$R1 = 0.0327$, $wR2 = 0.0900$	$R1 = 0.0542$, $wR2 = 0.1227$
Largest diff. peak and hole	0.526 and −0.205 e Å^{-3}	0.276 and −0.318 e Å^{-3}	0.826 and −0.216 e Å^{-3}

space groups $P\bar{1}$ and $P1$. The E-statistics strongly suggested the centrosymmetric space group $P\bar{1}$ that yielded chemically reasonable and computationally stable results of refinement [4]. The systematic absences in the diffraction data for compound and the E-statistics for compound (**4**) were uniquely consistent for the space group $P2_1/c$ that yielded chemically reasonable and computationally stable results of refinement [6].

A successful solution by the direct methods provided most non-hydrogen atoms from the E-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms except the hydroxyl hydrogen atoms in compound (**4**) were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The hydroxyl hydrogen atoms were located in the difference map and refined independently. In the case of compound (**4**) there are two chemically equivalent but symmetry independent molecules in the asymmetric unit.

The final least-squares refinement for compound (**2**) of 236 parameters against 4985 data resulted in residuals R (based on F^2 for $I \ge 2\sigma$) and wR (based on F^2 for all data) of 0.0449 and 0.1247, respectively. The final least-squares refinement for compound (**3**) of 236 parameters against 3292 data resulted in residuals R (based on F^2 for $I \ge 2\sigma$)

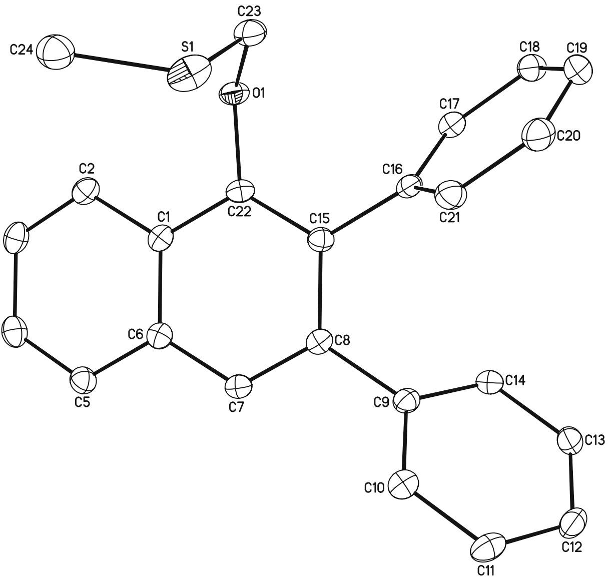

Fig. 2 Compound (**2**) drawn with 50% probability ellipsoids. All hydrogen and deuterium atoms were omitted for clarity

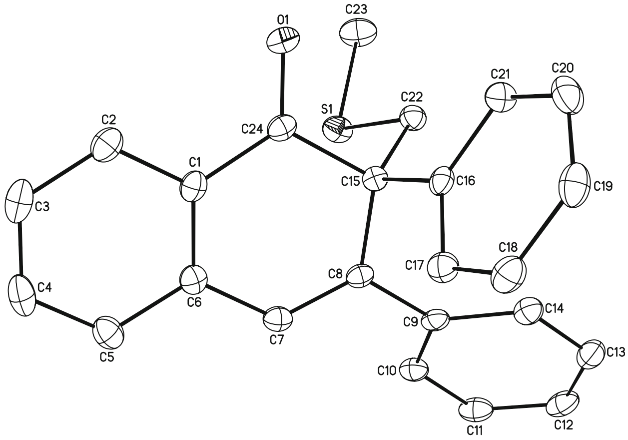

Fig. 3 Compound (**3**) drawn with 50% probability ellipsoids. All hydrogen and deuterium atoms were omitted for clarity

and *wR* (based on F^2 for all data) of 0.0327 and 0.0900, respectively. The final least-squares refinement for compound (**4**) of 845 parameters against 11534 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0460 and 0.1227, respectively. The final difference Fourier maps were featureless for all compounds.

CCDC 678263 (compound (**2**)), CCDC 678262 (compound (**3**)), and CCDC 678946 (compound (**4**)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: +44(0)1223-336033 (see Table 1).

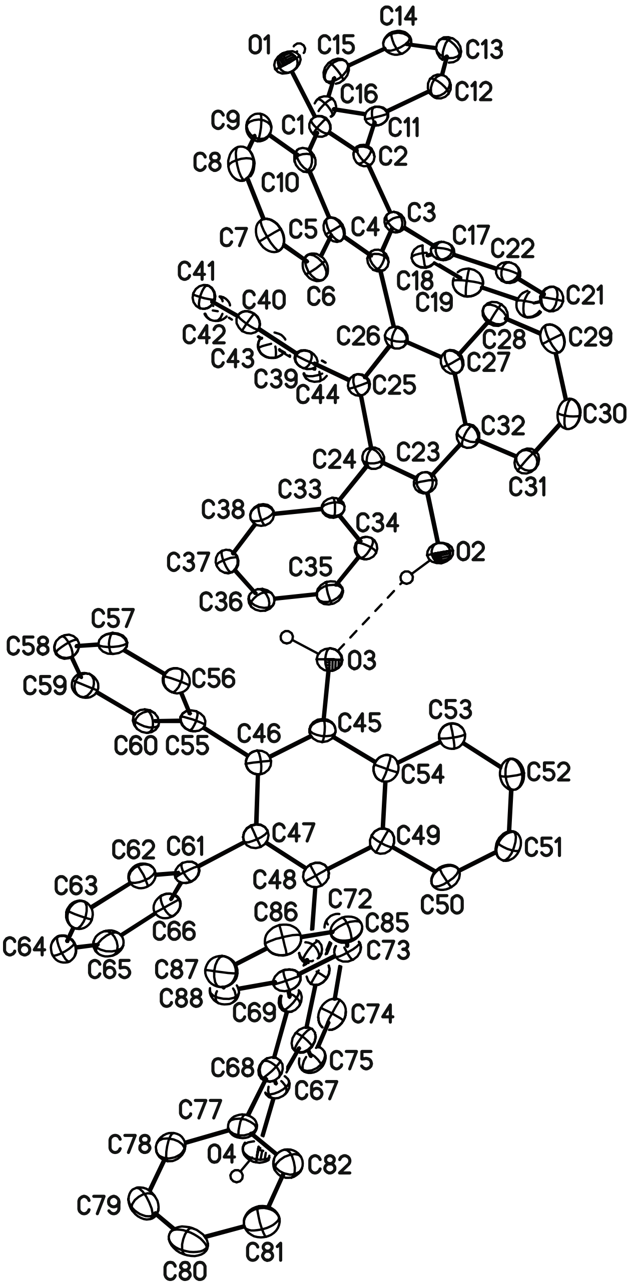

Fig. 4 Compound (**4**) drawn with 50% probability ellipsoids. All hydrogen and atoms attached to carbon atoms were omitted for clarity. The hydrogen bond is shown with a dashed line

Results and Discussion

The structures (**2**) and (**3**) were not well-defined by NMR analysis and thus we turned to X-ray crystallography to determine the structures of the products. Based on the unequivocal crystallographic data simple mechanistic considerations suggest that the products result from reaction of the $CD_2 = S^+\text{-}CD_3$ species with the conjugate base of the naphthol via a Pummerer-like thermal reaction.

Compounds (**2**) (Fig. 2) and (**3**) (Fig. 3) are structural isomers, compound (**3**) being a racemic mixture. In both compounds there is a naphthalene entity with two phenyl groups attached at positions 2 and 3. Both structures also include an oxygen atom and a CH_2–S–CH_3 group but differ in the attachment of the oxygen and CH_2–S–CH_3 groups to the naphthalene yielding different bonding patterns within the naphthalene.

In compound (**2**) the CH_2–S–CH_3 group bonds to atom O1 while in compound (**3**) the CH_2–S–CH_3 group bonds to a chiral carbon atom in the naphthalene group and the O1 atom is doubly bonded to a carbon atom forming a ketone. Resultantly, in compound (**2**), all carbon atoms, C1–8, C15 and C22, in the naphthol 6-membered rings are sp^2 hybridized and coplanar within 0.03 Å. The dihedral angles between the least squares planes defined by the phenyl rings C9–C14 and C16–C21 and the naphthol group are 53.89(3)° and 60.25(3)°.

In compound (**3**), two of the carbon atoms in the naphthalenone group, C15 and C24, are sp^3 hybridized. Atom C15 is now a chiral atom and the crystals of compound (**3**) contain a racemic mixture. Thus the carbon atoms in the naphthalenone rings, C1 to C8, C15 and C24, are no longer as planar as in compound (**2**). The atoms have a rms deviation of 0.06 Å from the best fit least squares plane. Applying the Cremer and Pople [7] ring puckering analysis using PLATON [8] to the C1, C6, C7, C8, C15 and C24 six-membered ring yields puckering coordinates as follows: puckering amplitude $Q = 0.13$ Å, $\theta = 60.49°$, and $\phi = 278.93°$. These coordinates indicate that the ring is only slightly puckered with a conformation intermediate between E_6 (envelope with C24 slightly below the plane) and $^5S_6$ (screw-boat with C15 slightly above the plane and C24 slightly below the plane) [9]. Dihedral angles between the planes of the naphthalenone ring and the phenyl rings C9–C14 (37.25(4)°) and C16–C21 (85.98(3)°) differ from the corresponding angles in compound (**2**).

Both (**2**) and (**3**) exhibit three C–H···π interactions in total which help stabilize the packing of the compounds. These interactions exhibit H···centroid of the phenyl ring distances less than the sum of the van der Waals radii for a phenyl ring perpendicular to the plane of the ring and hydrogen atoms. They also have C–H···centroid angles ranging between 142.30° and 168.33°. In compound (**2**) atom H24B forms an intermolecular contact with the C1–C6 ring, and atom H10 forms an intermolecular contact with the C1–C6 ring. In compound (**3**) atom H3 forms an intermolecular contact with the C16–C21 ring. In addition in compound (**3**) some non-classic, intermolecular hydrogen bonding interactions occur between H12 and O1, and H19 and O1 which also influence crystal packing. The interactions have H···O distances shorter than the sum of the van der Waals radii of the two elements and C–H···O angles range between 149.37° and 162.29°.

Compound (**4**) consists of dimers of the starting material (**1**) (Fig. 4). There are two chemically equivalent but symmetry independent molecules in the asymmetric unit. There is one strong hydrogen bonding interaction, O2–H2O···O3, between the two symmetry independent molecules. This hydrogen bond has a donor acceptor distance of 2.9524(17) Å and a O2–H2O···O3 angle of 153(2)°.

The naphthol groups are coplanar within 0.02 Å for atoms C1–C10, within 0.02 Å for atoms C23–C32, within 0.03 Å for atoms C45–C54, and 0.04 Å for atoms C67–C76. The two symmetry independent molecules have similar arrangements in space with a rms deviation of 0.05 Å when the naphthalene groups were fit to each other (Fig. 5). The angle between the least squares planes of the naphthlene groups in the dimers is on average 76.9(8)° which is statistically similar to the angle of 70(18)°

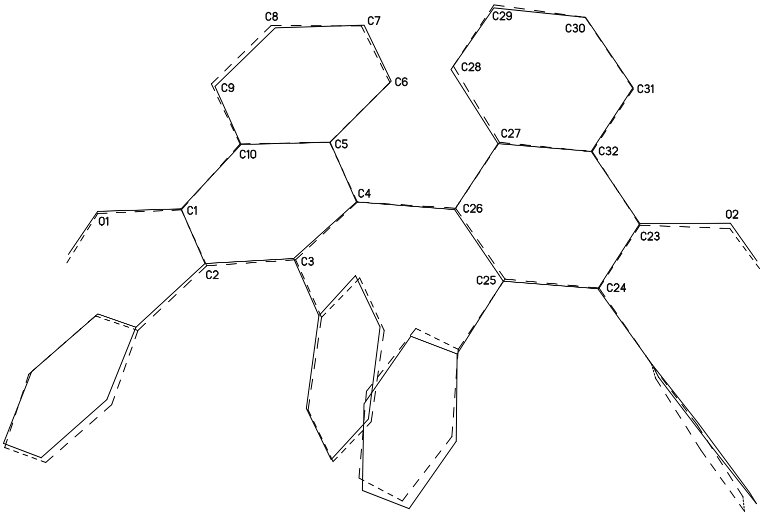

Fig. 5 Overlap diagram of the two symmetry independent molecules in the asymmetric unit of compound (**4**). All hydrogen atoms attached to carbon atoms were omitted for clarity. The atoms in the naphthalene rings were fitted to each other

between the naphthalene groups in dimers of 1639 relevant compounds in the Cambridge Structural Database [10]. The four averages of the eight angles (corresponding angles in the two symmetry independent dimers were averaged) between the least squares planes of the naphthalene and phenyl groups are 73(3)°, 54.01(4)°, 58(2)°, and 61.7(4)°.

Conclusion

Heating of 2,3-diphenyl-1-naphthol with deuterated DMSO yields isomers (**2**) and (**3**) in an 8:9 ratio via the Pummerer rearrangement. These compounds differ in the attachment of the CH_2–S–CH_3 group and O1 atom to the naphthalene ring. This results in all the carbon atoms in the naphthalene ring of compound (**2**) to be sp^2 hybridized while one carbon atom in the ten-membered ring of the racemic compound (**3**) is sp^3 hybridized. The photochemical rearrangement resulting from irradiating 2,3-diphenyl-1-naphthol with UV light yields dimer (**4**) that crystallizes with two symmetry independent molecules in the asymmetric unit. Subsequent to irradiation the presumed dihydro product had undergone air oxidation.

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