安田女子大学紀要　38，267-284　2010.

# The Novel Spirolactones of Dibenzo[c,h]xanthene and Xanthene, and Its Interesting Molecular Packing in Unit Cell : On the Base of the Molecular Structures Elucidated by X-ray Structure Analysis

Michio KIMURA

# 新規Dibenzo[c,h]xanthene及びXanthene Spirolactonesの合成，分子構造，及び特徴的な結晶構造 ―― X線構造解析により解明された分子構造，及び結晶構造を基にして ――

木　邑　道　夫

The novel condensation reaction of 1-naphtol with oxalic and sulfuric acids yielded the novel compound, spiro[7H-dibenzo[c,h]xanthene- 7,1'(2'H)-naphtho[1,2-b]furan]-2'-one(2a) by one step process, whose molecular structure was determined by X-ray diffraction methods. In addition, it was found that this novel condensation reactions gives the corresponding novel spirolactones(2b-2h) of xanthene when this reaction is carried out by utilizing phenol derivatives in place of 1-naphtol. The reaction appears to have some generality for 1-naphtol and phenol derivatives. In addition, these spirolactones possess the interesting properties that they form solvates with the aromatic solvent molecules used for recrystallization. The spirolactones form the specific cabities that captures aromatic molecules in the unit cell of single crystals. The various novel spirolactones utilizing 1-naphthol (1a) or phenol derivatives (1b-1h) with oxalic and sulfulic acids were synthesised, and also the crystal and molecular structures of the nitrobenzene solvate of 2a and 2h were established by the X-ray diffraction methods.

## I. Introduction

Previous papers[1,2] from our laboratory have described that the reaction of 1-naphthol (1a) with oxalic and sulfuric acids gives a novel spirolactone 2a of dibenzo[*c*,*h*]xanthene in one step process. This novel reaction forms 2a in an excellent yield (70-75%) with the accompanying loss of four molecules of water (Figure 1 and 2). As the molecular structure of 2a could not be well established on the basis of the chemical and spectroscopic data, it has been determined by the X-ray diffraction method as shown in Figure 3. An extension of the study to the reaction has been attempted in order to increase the examples of the novel spirolactones related to 2a and to learn more about the scope of the interesting reaction. It was found that analogous spirolactones 2b-h of xanthene are formed when this reaction is carried out by utilizing the substituted phenols 1b-h in place of 1-naphthol. That is, the novel reaction appears to have some generality

for 1-naphthol and phenol derivatives. In addition, these spirolactones possess the interesting properties that they form solvates with the aromatic solvent molecules used for recrystallization. This paper is concerned with synthesis of the novel spirolactones of xanthene and dibenzo[*c,h*]xanthene utilizing 1-naphthol (1a) or phenol derivatives 1b-h with oxalic and sulfuric acids, and also the crystal and molecular structures of the nitrobenzene solvate of 2a and 2d was established by the X-ray diffraction method. The reaction mechanism to lead to the spirolactones was elucidated from the base of the molecular structure determined by the X-ray analysis.

## II. Formation of the spirolactones of dibenzo[c,h]xanthene and xanthene

The spirolactones 2a-h prepared in this study are summarized in Table 1 and their syntheses are outlined in Figure 1. In this condensation reaction, a Friedel-Crafts type reaction between 1-naphthol or substituted phenols and oxalic acid may be included initially to form the oxalophenols 3 as described in Figure 2. The reaction was carried out by treating 1 mole of 1-naphthol (1a) or a substituted phenol 1b-h with a 2.6 mole excess of oxalic acid in the presence of 1 mole of sulfuric acid at 130-145° for 3-5 hours. The reaction was also successfully carried out by using mesitylene or xylene as solvents, but generally these solvents did not produce good yields of the desired spirolactones 2a-h. The spirolactones were detected easily by tlc after the reaction, because of the high $R_f$ values as mentioned in the experimental. The resulting reaction mixtures were purified by column chromatography on silica gel using chloroform or ethyl acetate as the eluent, or by preparative tlc (silica gel with chloroform as the eluent) and then recrystallized from xylene, toluene, or nitrobenzene. Regarding the formation of 2b-h, the yields were high except for some cases of sterically hindered substituents or halides on the phenol ring. The methyl groups attached to the 3- or the 4-position of the phenol ring did not have any particular influences on the formation of 2b-h. However, the desired spirolactone was not obtained if the unsubstituted phenol was used, because the sulfonation reaction of phenol proceeded initially. In addition, bulky substituents in phenol ring, such as ethyl, propyl, t-butyl, trimethylene, and phenyl groups prevent the formation of the desired spirolactones. In contrast, electron-withdrawing groups (such as Cl and Br) decrease the yield of the formation of the spirolactones. Some of

**Table 1 Physical Data for Spirolactones 2a-h**

| Spirolactone | R1 | R2 | R3 | mp (℃) | IR ($cm^{-1}$) C=0 | 13C nmr (δ) Spiro carbon atom | C=0 | Yield (%) |
|---|---|---|---|---|---|---|---|---|
| 2a | naphthalene | | | 296-298 | 1790 | 53.42 | 177.09 | 75 |
| 2b | H | $CH_3$ | H | 164-166 | 1810 | 51.91 | 175.90 | 62 |
| 2c | $CH_3$ | H | H | 205-208 | 1810 | 51.13 | 176.55 | 65 |
| 2d | H | Cl | H | 236-238 | 1800 | 51.69 | 174.51 | 23 |
| 2e | H | Br | H | 227-229 | 1810 | 51.60 | 175.10 | 11 |
| 2f | $CH_3$ | Cl | H | >300 | 1800 | 51.08 | 174.99 | 45 |
| 2g | $CH_3$ | $CH_3$ | H | 273-275 | 1800 | 51.20 | 176.23 | 75 |
| 2h | $CH_3$ | H | $CH_3$ | 294-296 | 1800 | 49.72 | 177.50 | 36 |

the compounds 2a-h have interesting properties resulting in the formation of solvates with the aromatic solvent molecules from which 2a-h were recrystallized (for example, toluene, xylene and nitrobenzene, etc.). Three isolated solvates of 2a and 2b are summarized in Table 2.

The structures of 2a-h were confirmed by ir, $^{1}H$, and $^{13}C$ nmr spectroscopy as well as mass spectrometry after isolation of the products. The ir spectra of 2a-h showed the strong absorption (1790-1810 $cm^{-1}$) which characterizes the lactone moiety. In the $^{1}H$ nmr spectra, the presence of sharp singlet signals in the range δ2.0-2.5 confirmed the methyl groups on the benzene rings. For the aromatic ring protons of 2b-h a singlet or a doublet at about δ7-9 was observed, which are indicative of one or two substituents on the benzene rings. Even though the substituent $R_1$ is different from $R_3$ as in compounds 2c, 2f, and 2g, the molecular structures could be established unambiguously by means of these $^{1}H$ nmr spectra. That is, the methyl groups of $R_1$ in 2c, 2f, and 2g were observed in the range δ2.32-2.49, which could be clearly distinguished from other methyl groups on the xanthene moiety. On the other hand, the protons of $R_3$ could be assigned as singlet signals in the range δ7.05-7.09. Accordingly, ring formation by this reaction proceeds to give the spirolactones which possess less sterically hindered substituents for $R_3$. The $^{13}C$ nmr spectra contain three types of signals: the aromatic carbons appear at *ca*. δ105-150, the spiro carbon (C-3) is observed at ca. δ51, and the carbonyl carbon is observed at *ca*. δ175. With regard to mass spectrometry, all the compounds exhibited common fragmentation corresponding to the molecular ion ($M^+$), $M^+ - CO$, and $M^+ - CO\text{-}OH$ which assisted in confirming the structures. The elemental analyses and high resolution mass spectra of the spirolactones 2a-h were in good agreement with the calculated values. But the molecular structures of the spirolactones(2a-2d) could not be well established on the basis of the 1H nmr, $^{13}C$ nmr and ir spectra.

**Table 2 Crystallographic Data for Spirolactones**

| | Nitrobenzene solvate of 2a $C_{32}H_{18}O_3 \cdot C_6H_5NO_2$ | *p*-Xylene solvate of 2a $C_{32}H_{18}O_3 \cdot C_8H_{10}$ | *p*-Xylene solvate of 2b $C_{23}H_{18}O_3 \cdot C_8H_{10}$ | 2d [1] $C_{20}H_9Cl_3O_3$ |
|---|---|---|---|---|
| Recrystallization solvent | nitrobenzene | Xylene [a] | Xylene [a] | Xylene [a] |
| mp/℃ | 312 | 297 | 165 | 237 |
| Crystal system | triclinic | triclinic | monoclinic | monoclinic |
| Space group | Pï | Pï | C2/c | C2/c |
| a/Å | 11.296 (1) | 11.760 (4) | 21.736 (4) | 21.316 (9) |
| b | 13.050 (2) | 13.064 (9) | 17.387 (1) | 17.267 (4) |
| c | 11.138 (1) | 11.239 (4) | 9.211 (3) | 9.158 (6) |
| α/ ° | 113.43 (1) | 69.59 (4) | | |
| β | 94.18 (1) | 106.14 (3) | 95.13 (2) | 94.05 (5) |
| g | 107.95 (1) | 111.94 (4) | | |
| Z | 2 | 2 | 8 | 8 |
| V/ $Å^3$ | 1397 (1) | 1479 (1) | 3467 (1) | 3362 (3) |
| Dc/$gcm^{-3}$ | 1.363 | 1.250 | 1.718 | 1.594 |
| Do [b] | 1.364 | 1.252 | 1.716 | 1.593 |

[a] Purchased xylene of boiling range 138.5-141.5°. [b] Flotation in aqueous potassium iodide.

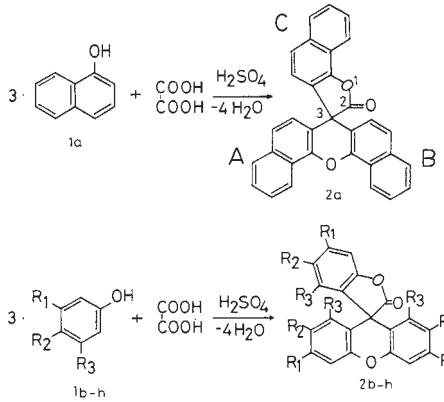


**Figure 1. Spirolactones of dibenzo[c, h]xanthene and xanthene**
The numbering system of 2a, and 2b-2h are different from that of ORTEP drawing. ($R_1$～$R_3$ in Table 1)

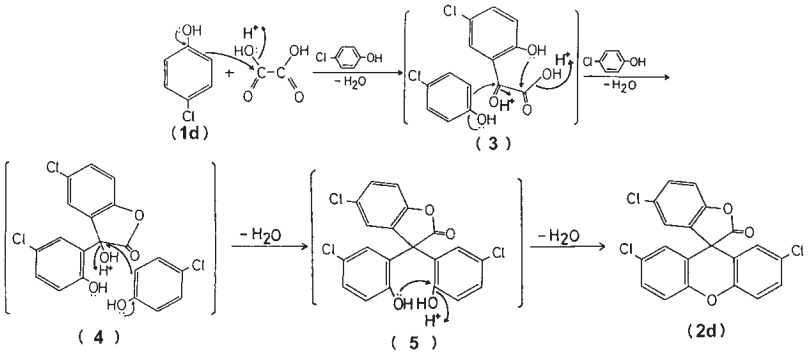


**Figure 2. Reaction mechanism of the novel spirolactones (2d as an example)**

**General procedure for the preparation of compounds (2a, 2b, and 2c) as shown in Figure 1.**

**Spiro[7*H*-dibenzo[*c*,*h*]xanthen-7,3'(2'*H*)-naphtho[1,2-*b*]furan]-2'-one (2a).**

A suspension of 7 g of 1-naphthol (0.049 mole), 3.5 g of oxalic acid (0.039 mole) and 4.4 g of concentrated sulfuric acid (0.046 mole) was heated for 4 hours at 135-140° in an oil bath. The reaction mixture was cooled to room temperature, and poured into hot water. A precipitate was collected, washed with water and a little ethanol, and dried, yielding 16.5 g of 2a (75%), which could be recrystallized from xylene or nitrobenzene, mp 296-298°; ir (potassium bromide): 3050, 1790 (C = O), 1600, 1560, 1500, 1460, 1400, 1360, 1340, 1240, 1200, 1120, 1100, 1040, 1020, 950, 880, 800, 790, 660 $cm^{-1}$; pmr (deuteriochloroform): δ6.68 (d), 7.10 (d), 7.25 (s), 7.42 (d), 7.46-7.91 (m), 8.22 (d), 8.74 (d) (for aromatic ring protons); cmr (deuteriochloroform): δ53.42 (C-3), 112.97, 119.78, 121.53, 121.60, 122.04, 124.08,

124.59, 125.71, 126.78, 127.32, 127.44, 127.80, 128.46, 134.32, 134.69, 146.12, 148.94, 177.09 (C = O); ms: m/z (relative intensity, %) 450 (1.2, $M^+$), 422 (1.0, $M^+$-CO), 421 (0.9), 405 (0.9, $M^+$-CO-OH), 275 (100), 184 (43), 139 (38); high-resolution mass spectra (h r -ms): m/z 450.1269, Calcd. for $C_{32}H_{18}O_3$ 450.1255; tlc (chloroform): Rf 0.70.

*Anal*. Calcd. for $C_{32}H_{18}O_3$: C, 85.29; H, 4.03. Found: C, 85.21; H, 4.28.

**2',5,7'-Trimethylspiro[benzofuran-3(2*H*)-9'-[9*H*]xanthen]-2-one (2b).**

To a mixture of 11 g of 4-methylphenol (0.1 mole) and 8 g of oxalic acid (0.09 mole), 8 g of concentrated sulfuric acid (0.08 mole) was added cautiously, and the resulting mixture was heated gently for 4 hours at 140-145° in an oil bath. After cooling, the reaction mixture was poured into water and extracted with chloroform (150 ml). The organic layer was separated, washed with 5% sodium hydroxide and water, dried over anhydrous sodium sulfate, and concentrated under vacuum. The crude oily products were chromatographed over 300 mg of silica gel (using chloroform as an eluent) to give 21.2 g of 2b (62%), mp 164-166° ; ir (potassium bromide): 2920, 1810 (C = O), 1620, 1510, 1480, 1300, 1280, 1260, 1220, 1140, 1130, 1120, 1060, 960, 900, 820, 810, 790, 660 $cm^{-1}$; pmr (deuteriochloroform): δ2.17 (s, 6H), 2.28 (s, 3H), 6.47 (s, 2H), 6.82 (s, 1H), 7.09 (s, 4H), 7.18 (s, 1H), 7.23 (s, 1H); cmr (deuteriochloroform): δ20.60, 21.11, 51.91 (C-3), 110.44, 117.13, 119.41, 125.76, 127.58, 130.28, 130.48, 133.08, 133.28, 135.25, 148.89, 151.30, 175.90 (C = 0); ms: m/z (relative intensity, %) 342 (30, $M^+$), 313 (42, $M^+ - CO+1$), 299 (100), 141 (15), 28 (17); hr-ms: m/z 342.1261, Calcd. for $C_{23}H_{18}O_3$ 342.1255; tlc (ethyl acetate) $R_f$ 0.67.

*Anal*. Calcd. for $C_{23}H_{18}O_3$: C, 80.68: H, 5.30. Found: C, 80.56; H, 5.53.

**3',6,6'-Trimethylspiro[benzofuran-3(2*H*)-9'-[9*H*]xanthen]-2-one (2c).**

From 11 g of 3-methylphenol (0.1 mole) and 8 g of oxalic acid (0.09 mole) with 8 g of concentrated sulfuric acid (0.08 mole) there was obtained by the same procedure, except isolating by the preparative tlc using chloroform as eluate, 23.3 g of 2c (65%), mp 205-208° ; ir (potassium bromide): 2920, 1810 (C = 0), 1620, 1600, 1500, 1410, 1320, 1250, 1170, 1130, 1060, 1010, 970, 880, 790 $cm^{-1}$; pmr (deuteriochloroform): δ2.31 (s, 6H), 2.42 (s, 3H), 6.50 (d, 2H), 6.72 (d, 2H), 6.84-7.40 (m, 5H); cmr (deuteriochloroform): δ21.09, 21.75, 51.13 (C-3), 108.17, 111.26, 117.20, 117.68, 117.76, 124.59, 124.71, 125.05, 126.15, 126.68, 126.83, 127.20, 129.73, 140.01, 140.11, 140.43, 150.89, 153.86, 176.55 (C = O); ms: m/z (relative intensity, %) 342 (35, $M^+$), 314 (97, $M^+$-CO), 299 (100), 269 (5); hr-ms: m/z 342.1241; Calcd. for $C_{23}H_{18}O_3$ 342.1254; tlc (chloroform) $R_f$ 0.72.

Anal. Calcd. for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.51; H, 5.18.

**2',5,7'-Trichlorospiro[benzofuran-3(2*H*)-9'-[9*H*]xanthen]-2-one (2d).**

From 22 g of 4-chlorophenol (0.17 mole) and 16 g of oxalic acid (0.18 mole) with 16 g of concentrated sulfuric acid (0.16 mole) there was obtained by the same procedure 15.8 g of 2d (23%), mp 236-238°; ir (potassium bromide): 3300, 3150, 1800 (C=O), 1580, 1460, 1410, 1270, 1240, 1110, 1060, 880, 820, 810, 700, 680 $cm^{-1}$; pmr (deuteriochloroform): δ 6.50 (d, 1H), 6.75 (d, 1H) 6.80-7.50 (m, 7H) (for aromatic ring protons); cmr (deuteriochloroform): δ 51.69 (C-3), 112.67, 116,64, 118.22, 119.14, 119.58, 120.07, 125.66, 126.90, 128.56, 129.02, 129.21, 129.31, 129.43, 129.82, 130.38, 130.63, 131.14, 149.16, 174.51 (C=O);

ms: m/z (relative intensity, %) 402 (17, $M^+$), 374 (32, $M^+$-CO), 339 (100, $M^+$-CO-OH-$H_2O$), 276 (15),, 162 (30), 112 (22), 57 (15); tlc (ethyl acetate): $R_f$ 0.76.

Anal. Calcd. $C_{20}H_9Cl_3O_3$: C, 59.51; H, 2.25; Cl, 26.35. Found: C, 59.20; H, 2.32; Cl, 26.35.

**2',5,7'-Tribromospiro[benzofuran-3(2*H*)-9'-[9*H*]xanthen]-2-one (2e).**

From 10 g of 4-bromophenol (0.058 mole) and 5.2 g of oxalic acid (0.058 mole) with 5.7 g of concentrated sulfuric acid (0.058 mole) there was obtained by the same procedure 3.4 g of 2e (11%), mp 227-229°; ir (potassium bromide): 3010, 2850, 1810 (C=O), 1460, 1400, 1270, 1220, 1060, 960, 940, 820, 730 $cm^{-1}$; pmr (deuteriochloroform): δ 6.48 (d, 1H),6.73 (d, 1H), 7.00-7.50 (m, 7H) (for aromatic ring protons); cmr (deuteriochloroform): δ 51.60 (C-3), 113.14, 116.54, 119.53, 120.46, 128.53, 129.90, 133.54, 134.06, 149.65, 175.10 (C=O); ms: m/z (relative intensity, %) 534 (25, $M^+$), 508 (76), 429 (10), 353 (5), 328 (30), 149 (13), 97 (26), 70 (37), 57 (98), 43 (100); tlc (chloroform): Rf 0.67.

*Anal*. Calcd. For $C_{20}H_9Br_3O_3$: C, 44.73; H, 1.69; Br, 44.64. Found: C, 44.65; H, 1.53; Br, 44.25.

**2',5,7'-Trichloro-3',6,6'-trimethylspiro[benzofuran-3(2*H*)-9'-[9*H*]xanthen]-2-one (2f).**

From 10 g of 4-chloro-3-methylphenol (0.07 mole) and 6.3 g of oxalic acid (0.07 mole) with 6.8 g of sulfuric acid (0.07 mole) there was obtained by the same procedure 14 g of 2f (45%), mp > 300°; ir (protassium bromide): 3500, 2950, 1800 (C=O), 1750, 1620, 1480, 1440, 1390, 1380, 1310, 1250, 1170, 1090, 1060, 940, 870, 780 $cm^{-1}$: pmr (deuteriochloroform): δ 2.35 (s, 6H), 2.49 (s, 3H), 6.63 (s, 2H), 7.05 (s, 1H), 7.11 (s, 1H), 7.20 (s, 1H), 7.25 (s, 1H); cmr (deuteriochloroform); δ 19.97, 20.85, 51.08 (C-3), 109.92 113.45, 117.88, 119.68, 119.80, 125.76, 126.68, 127.27, 129.36, 130.28, 131.26, 138.68, 138.82, 139.38, 149.16, 152.10, 174.99, (C=O); ms: m/z (relative intensity, %) 444 (37, $M^+$), 416 (95, $M^+$-CO), 381 (100), 317 (15), 229 (5), 182 (30), 165 (43), 119 (20), 69 (17); tlc (chloroform): $R_f$ 0.73.

*Anal*. Calcd. for $C_{23}H_{15}Cl_3O_3$: C, 61.98; H, 3.39; Cl, 23.86. Found: C, 61.69; H, 3.60; Cl, 23.61.

**2',3',5,6,6',7'-Hexamethylspiro[benzofuran-3(2*H*)-9'-[9*H*]xanthen]-2-one (2g).**

From 5 g of 3,4-dimethylphenol (0.041 mole) and 3.7 g of oxalic acid (0.041 mole) with 3 g of concentrated sulfuric acid (0.031 mole) there was obtained by the same procedure 11.8 g of 2 g (75%), mp 273-275°; ir (potassium bromide): 2910, 1800 (C=O), 1620, 1500, 1450, 1400, 1320, 1260, 1200, 1130, 1120, 1080, 1050, 1020, 950, 910, 880, 860, 800, 740 cm-1; pmr (deuteriochloroform): δ 2.06 (s, 6H), 2.15 (s, 3H), 2.21 (s, 6H), 2.25 (s, 3H), 6.41 (d, 1H), 6.78 (s, 1H), 6.98 (s, 2H), 7.06 (s, 1H), 7.23 (s, 1H); cmr (deuteriochloroform): δ 18.95, 19.51, 19.61, 20.36, 51.20 (C-3), 107.11, 111.55, 115.93, 117.05, 118.00, 125.93, 127.51, 128.02, 130.60, 130.89, 131.79, 133.67, 138.43, 148.94, 151.69, 176.23 (C=O); ms: m/z (relative intensity, %) 384 (10, $M^+$), 356 (27, $M^+$-CO), 341 (100, $M^+$-CO-OH+2); hr-ms: m/z 384.1696, Calcd. For $C_{26}H_{24}O_3$ 384.1723; tlc (chloroform): $R_f$ 0.59.

*Anal*. Calcd. for $C_{26}H_{24}O_3$: C, 81.22; H, 6.29. Found: C, 81.02; H, 6.10.

**1',3',4,6,6',8'-Hexamethylspiro[benzofuran-3(2*H*)-9'-[9*H*]-xanthen]-2-one (2h).**

From 5 g of 3,5-dimethylphenol (0.041 mole) and 3.7 g of oxalic acid (0.041 mole) with 4 g of concentrated sulfuric acid (0.041 mole) there was obtained by the same procedure 5.7 g of 2h (36%),

mp 294-296°; ir (potassium bromide): 2970, 2920, 1800 (C=O), 1790, 1620, 1610, 1600, 1560, 1480, 1440, 1400, 1330, 1190, 1150, 1120, 1080, 1030, 970, 900, 850, 700 $cm^{-1}$, pmr (deuteriochloroform): δ 1.69 (s, 3H), 1.91 (s, 6H), 2.25 (s, 6H), 2.33 (s, 3H), 6.5-6.7 (m, 3H), 6.82 (s, 2H), 7.24 (s, 1H); cmr (deuteriochloroform): δ 19.29, 20.68, 20.92, 21.28, 21.60, 49,72 (C-3) 108.12, 109.34, 109.49, 114.45, 115.25, 124.08, 125.35, 126.95, 127.78, 128.44, 135.51, 136.51, 136.17, 137.17, 139.09, 139.84, 141.33, 150.74, 153.20, 177.50 (C=O); ms: m/z (relative intensity, %) 384 (2.5, $M^+$), 342 (5.5), 306 (2), 226 (13), 122 (100), 90 (73), 77 (20); hr-ms: m/z 384.1734, Calcd. For $C_{26}H_{24}O_3$ 384.1724; tlc (chloroform): Rf 0.58.

*Anal*. Calcd. for $C_{26}H_{24}O_3$: C, 81.22; H, 6.29. Found: C, 81.05; H, 6.11.

## III. Reaction mechanism of the formation of the novel spirolactone (2d as an example)

As for the details of the mechanism of assembly of 2a-h including the structures 2a and 2d established by the X-ray analysis, some reasonable speculations are possible. As shown in Figure 2, it is surmised that the initial step probably involves a Friedel-Crafts type reaction between phenol 1d and oxalic acid to form the oxalophenol 3. Subsequently, nucleophilic attack of two other phenol molecules to the protonated carbonyl carbon atom of 3 forms the intermediates 5 with three phenol rings connected by the lactone moiety. Further, the intermediates 5 proceed by the intramolecular cyclization to the xanthene ring accompanying the loss of one molecule of water to yield the ultimate product 2d.

## IV. X-ray moleculer and crystal structure analysis of the novel spirolactones of dibenzo[c,h]xanthene

Preliminary crystallographic information was obtained on several of the novel spirolactones or their solvates with aromatic solvents used on crystallization. Comparison of the crystal data in Table 2 strongly suggests that crystals examined in this way appear to have a similar packing scheme in the unit cell between the nitrobenzene and *p*-xylene solvates of 2a, and between the *p*-xylene solvate of 2b and 2d. With respect to the unit cell, in the case of the *p*-xylene solvate of 2b and 2d, the values of a-axis is approximately 2 times those of the nitrobenzene and *p*-xylene solvates of 2a depending upon the z-values. In addition, the space groups are related to each other among the nitrobenzene and *p*-xylene solvates of 2a, or the *p*-xylene solvate of 2b and 2d. These facts suggest that crystals composed of spirolactone molecules have similar packing schemes, regardless of the occupied aromatic solvents in the unit cell. That is, it shows that the solvent molecules are inserted into the space composed of the spirolactones possessing the rigid and bulky molecular conformation. Crystals of the 1:1 nitrobenzene solvate of 2a chosen for detailed studies were obtained from nitrobenzene in the triclinic system (Table 2), because the *p*-xylene solvates were gradually decomposed by the X-ray.

A crystal with approximate dimensions of 0.2 x 0.3 x 0.35 mm was used for the X-ray experiment. The unit cell dimensions and other crystal data were obtained by a least-squares fit of 24 medium-angle reflections as in Table 2. Intensity data for $2\theta < 120°$ were collected on a Rigaku AFC-5 four-circle diffractometer equipped with rotating anode by the θ-2θ scan technique using a nickel-filtered Cu Kα radiation (λ= 1.54178 Å). The scan speed was 4°/minute in θ and the scan range in θ was varied by

1.2° + 0.15° tan θ. Backgrounds were counted for 5 s at both ends of a scan with an offset of 50% of the scan range from the calculated position of the Kα peak. Three periodically monitored reflections showed no significant crystal deterioration. Of the 4654 independent reflections measured, 3753 reflections had intensities greater than 3σ(I) where σ(I) was estimated from counting statistics. Lorentz and polarization corrections were applied, but no absorption correction was made. The structure (Figure 1) was solved by the direct method (MULTAN78)[3] and refined anisotropically by the block-diagonal least-squares procedure[4,5]. The function minimized was $\Sigma w(|Fo|-|Fc|)^2$ where $w=1/\sigma(Fo)^2$. Hydrogen atoms were located on a difference Fourier map, which were refined isotropically at the final stages of the refinement[5]. The final R value was 0.049 for 3753 observed reflections where $R = \Sigma \| Fo|-|Fc \| /\Sigma|Fo|$, and a weighted $Rw = (\Sigma w(|Fo|-|Fc|)^2 /w|Fo|^2)^{1/2}$ was 0.050 with a GOF of 0.612 (quality of fit = $[\Sigma w(|Fo|-|Fc|)^2/(Nobsd-N_{para})]^{1/2}$)[6]). All parameter shifts during the cycles were less than 0.1σ and a final difference Fourier map showed no peak larger than 0.24 e/Å$^3$.

**Molecular Structure (Figure 3 and 4).**

The molecular structure (ORTEP drawing)[7] of 2a with atom labeling is presented in Figure 3. The bond lengths and angles are schematically shown in Figure 4. Compound 2a possess a *ψ*-like shape composed of

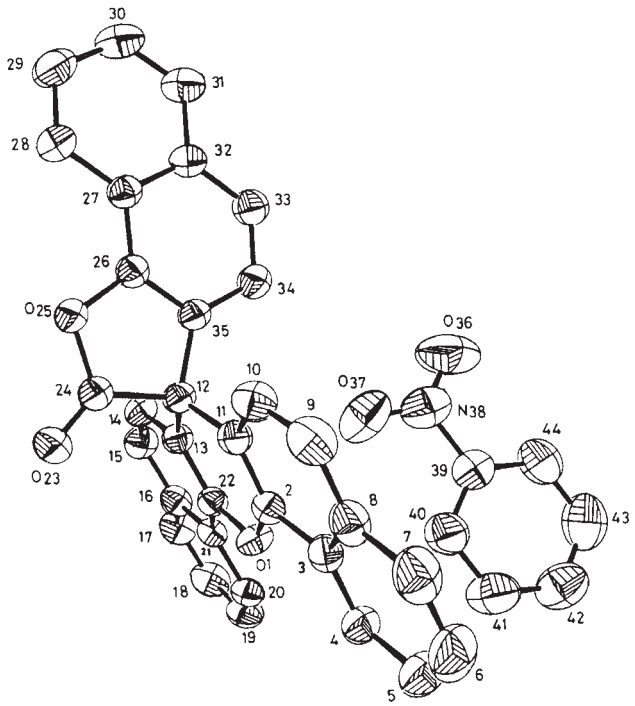


**Figure 3. Molecular structure (ORTEP [Ref.7] drawing) of the nitrobenzene solvate of 2a. Non-hydrogen atoms are drawn as thermal ellipsoids with 50% probability level.**

three naphthalene rings fused by the spirolactone, the most interesting point of which may be the dihedral angles of the planar naphthalene rings; 5.9° between rings A and B, 86.9° between rings A and C, and 81.4° between rings B and C, respectively. These dihedral angles may be compared with the corresponding values in the reported molecular structure of 2',5,7'-trichlorospiro[benzofuran-3(2*H*)-9'-(9*H*)xanthen]-2-one (2d)1); 22.8, 83.6, and 73.6° in order, respectively. The great difference in the butterfly angles of the benzoxanthene ring of 2a and 2d (5.9 and 22.8°) seems to be caused by electron-withdrawing effects of the chloride atoms and the lesser steric hindrance of the phenyl ring of 2d in comparison with the bulky naphthalene ring of 2a. The average C-C-C angle is 120.0° for each of rings A, B and C. The carbonyl group has the normal bond length (1.18 Å). The average C-C bond lengths in rings A, B, and C are normal, 1.398 and 1.397 Å, respectively. The C-O bonds in dibenzo[*c*,*h*]xanthene ring have the values of 1.373 and 1.382 Å, which are comparable to the same bond of the lactone moiety (1.407 Å).

**Crystal Structure (in Figure 5).**

The crystal structure is shown in Figure 5. Nitrobenzene molecules are packed by van der Waals contacts in the unit cell, whose intermolecular distances are more than 3.275 Å. That is, a specific cavities are

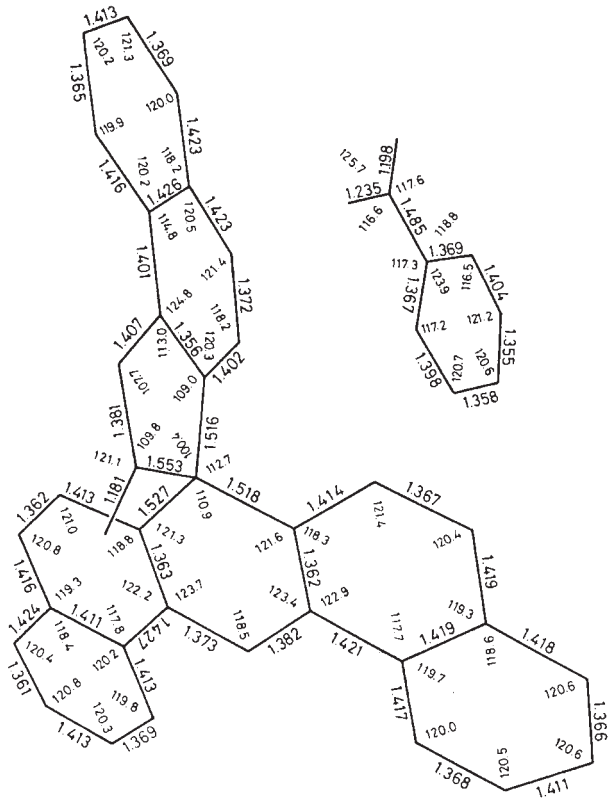

**Figure 4. Bond lengths (Å) and angles (°) for 2a. Estimated standard deviations ranged between 0.004 and 0.005 Å, and between 0.2 and 0.4°, respectively.**

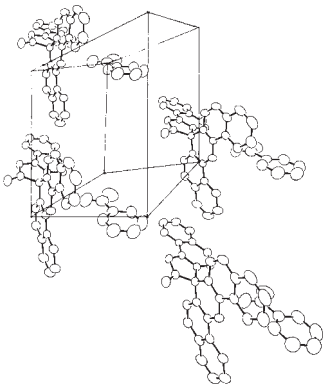

**Figure 5. Molecular packing arrangement for 2a(ORTEP drawing).**

composed in the unit cell of crystals. It's cavities are occupied aromatic molecules, such as nitrobenzene, xylene, and other substitute benzene molecules. The nitrobenzene ring exists in the space composed of two adjacent molecules of 2a in the unit cell. The nitrobenzene molecules are also stacked parallel to the lactone moiety of 2a and perpendicular to the dibenzo[*c*,*h*]xanthene plane. All other intermolecular contacts correspond to normal van der Waals interactions.

## V. X-ray moleculer and crystal structures analysis of the novel spirolactones of xanthene

***Collection and Reduction of Crystallographic Data.***

The crystal selected for the measurement of the lattice parameters and intensity data was a cleaved fragment which had approximate dimensions of 0.20×0.15×0.25 mm. A preliminary examination of the crystal carried out on a Rigaku AFC diffractometer showed it to be monoclinic. Systematic absences of $h+k=2n+1$ for *hkl* and $l=2n+1$ for *h*01 showed the space group to be C*c* or C*2/c*. The correct space group was later confirmed to be C*2/c* by the successful refinement of the structure. The unit cell parameters at room temperature were refined by the least-squares method using the Bragg angles (Cu *Kα* λ=1.54178 Å) of thirty reflections (20°<2θ<35°). The unit cell dimensions and other data are summarized in Table 4. Intensity data were collected at room temperature on the Rigaku AFC diffractometer utilizing nickel-filtered Cu *Kα* radiation. The 2θ-ω scan were employed with a scan speed of 4° $min^{-1}$ in 2θ and scan range which was varied by 1.2° + 0.15° tanθ. Background counts were taken at both ends of the scan with a displacement of 3.0° from the *Kα* peak; the time of each measurement was one-third of the scan time. A total of 2823 unique reflections was measured in the range of 0°<2θ<120°. The intensities of three standard reflections were measured after every 57 reflections; three intensities dropped by an average of a few percent over the period of data collection, but no correction factor was applied because the decrease was not considered significant. Lorentz and polarization corrections were applied to convert intensities to structure amplitudes, but no absorption corrections were applied. Standard deviations in the structure amplitudes, σ(*F*o), were derived from counting statistics.

**Table 3 Final Atomic Parameters of Non-hydrogen Atoms with Estimated Standard Deviations in Parentheses for 2d**

$$\text{Beq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}) \text{ (defined as } U_{11} \frac{B_{11}}{8\pi^2 a^{*2}}, \underline{\text{etc}}.)$$

| Atoms | x | y | z | Biso/Beq |
|---|---|---|---|---|
| O1 | 0.0144 (2) | 0.1413 (2) | 0.0764 (2) | 4.29 |
| C2 | 0.0527 (3) | 0.1768 (3) | −0.0205 (3) | 3.59 |
| C3 | 0.1854 (3) | 0.2058 (3) | −0.0169 (3) | 3.68 |
| C4 | 0.2696 (3) | 0.2000 (3) | 0.0789 (3) | 4.36 |
| C5 | 0.3971 (3) | 0.2325 (3) | 0.0801 (4) | 5.59 |
| C6 | 0.4458 (3) | 0.2712 (4) | −0.0140 (4) | 6.35 |
| C7 | 0.3663 (3) | 0.2755 (3) | −0.1088 (4) | 5.95 |
| C8 | 0.2336 (3) | 0.2430 (3) | −0.1130 (3) | 4.54 |
| C9 | 0.1485 (3) | 0.2487 (3) | −0.2083 (3) | 5.24 |
| C10 | 0.0222 (3) | 0.2224 (3) | −0.2049 (3) | 4.69 |
| C11 | −0.0280 (3) | 0.1855 (3) | −0.1098 (3) | 3.66 |
| C12 | −0.1687 (3) | 0.1572 (3) | −0.1085 (3) | 3.66 |
| C13 | −0.1987 (3) | 0.1309 (3) | 0.0101 (3) | 3.61 |
| C14 | −0.3225 (3) | 0.1115 (3) | 0.0354 (4) | 4.63 |
| C15 | −0.3529 (3) | 0.0841 (3) | 0.1380 (4) | 5.27 |
| C16 | −0.2608 (3) | 0.0747 (3) | 0.2223 (3) | 4.54 |
| C17 | −0.2895 (4) | 0.0485 (4) | 0.3300 (4) | 6.40 |
| C18 | −0.1975 (4) | 0.0403 (4) | 0.4106 (4) | 7.41 |
| C19 | −0.0719 (4) | 0.0642 (4) | 0.3900 (4) | 6.37 |
| C20 | −0.0416 (3) | 0.0902 (3) | 0.2859 (3) | 4.72 |
| C21 | −0.1357 (3) | 0.0963 (3) | 0.2009 (3) | 3.76 |
| C22 | −0.1089 (3) | 0.1232 (3) | 0.0912 (3) | 3.39 |
| O23 | −0.2516 (3) | −0.0541 (2) | −0.2830 (3) | 5.38 |
| C24 | −0.2513 (3) | 0.0449 (3) | −0.2399 (3) | 4.05 |
| O25 | −0.3321 (2) | 0.0746 (2) | −0.3080 (2) | 3.97 |
| C26 | −0.3060 (3) | 0.1982 (3) | −0.2351 (3) | 3.66 |
| C27 | −0.3649 (3) | 0.2592 (3) | −0.2825 (3) | 3.92 |
| C28 | −0.4561 (3) | 0.2056 (3) | −0.4049 (3) | 4.79 |
| C29 | −0.5025 (4) | 0.2751 (4) | −0.4443 (4) | 6.01 |
| C30 | −0.4611 (4) | 0.4000 (4) | −0.3624 (4) | 6.83 |
| C31 | −0.3755 (3) | 0.4542 (3) | −0.2418 (4) | 5.67 |
| C32 | −0.3240 (3) | 0.3850 (3) | −0.1982 (3) | 4.28 |
| C33 | −0.2311 (3) | 0.4396 (3) | −0.0757 (3) | 4.47 |
| C34 | −0.1767 (3) | 0.3742 (3) | −0.0364 (3) | 4.17 |
| C35 | −0.2157 (3) | 0.2507 (3) | −0.1197 (3) | 3.67 |
| C36 | 0.0701 (4) | 0.6083 (4) | 0.3463 (4) | 13.96 |
| O37 | 0.0414 (4) | 0.4230 (3) | 0.2186 (3) | 10.06 |
| N38 | 0.0802 (3) | 0.5145 (4) | 0.3267 (4) | 8.38 |
| C39 | 0.1460 (3) | 0.5069 (4) | 0.4415 (4) | 5.74 |
| C40 | 0.1601 (4) | 0.4006 (4) | 0.4176 (4) | 6.47 |
| C41 | 0.2195 (5) | 0.3928 (4) | 0.5265 (5) | 8.55 |
| C42 | 0.2603 (5) | 0.4875 (5) | 0.6504 (5) | 8.54 |
| C44 | 0.1868 (4) | 0.6047 (4) | 0.5645 (4) | 6.84 |
| HC4 | 0.236 (3) | 0.172 (3) | 0.147 (4) | 2.74 |
| HC5 | 0.457 (4) | 0.228 (3) | 0.153 (4) | 3.76 |

**Table 3 (continued)**

| Atoms | x | y | z | Biso/Beq |
|---|---|---|---|---|
| HC6 | 0.547 (4) | 0.298 (4) | −0.012 (4) | 3.96 |
| HC7 | 0.403 (4) | 0.304 (4) | −0.181 (4) | 4.40 |
| HC9 | 0.182 (4) | 0.273 (3) | −0.282 (4) | 3.25 |
| HC10 | −0.043 (4) | 0.228 (3) | −0.271 (4) | 3.42 |
| HC14 | −0.390 (3) | 0.120 (3) | −0.028 (4) | 2.76 |
| HC15 | −0.448 (4) | 0.070 (3) | 0.158 (4) | 3.59 |
| HC17 | −0.385 (4) | 0.029 (4) | 0.346 (4) | 3.85 |
| HC18 | −0.221 (4) | 0.018 (4) | 0.490 (4) | 4.16 |
| HC19 | 0.003 (4) | 0.066 (4) | 0.455 (4) | 4.03 |
| HC20 | 0.051 (4) | 0.104 (3) | 0.270 (4) | 3.26 |
| HC28 | −0.487 (4) | 0.115 (3) | −0.463 (4) | 3.36 |
| HC29 | −0.569 (4) | 0.233 (3) | −0.537 (4) | 3.74 |
| HC30 | −0.497 (4) | 0.454 (3) | −0.394 (4) | 3.70 |
| HC31 | −0.345 (4) | 0.551 (3) | −0.177 (4) | 3.55 |
| HC33 | −0.203 (4) | 0.535 (3) | −0.014 (4) | 3.31 |
| HC34 | −0.106 (4) | 0.413 (3) | 0.050 (4) | 2.98 |
| HC40 | 0.126 (4) | 0.325 (4) | 0.319 (4) | 4.42 |
| HC41 | 0.231 (4) | 0.311 (4) | 0.513 (4) | 4.39 |
| HC42 | 0.303 (4) | 0.482 (4) | 0.737 (4) | 5.08 |
| HC43 | 0.277 (4) | 0.669 (4) | 0.772 (4) | 5.80 |
| HC44 | 0.173 (4) | 0.688 (4) | 0.578 (4) | 5.59 |

**Table 4 Crystal data of 2d**

| | |
|---|---|
| Mol. Formula | $C_{20}H_9O_3Cl_3$ |
| Mol. wt. | 403.64 |
| Space group | *C*2/*c* |
| Cell dimensions | |
| *a*/Å | 21.316 (9) |
| *b*/Å | 17.267 (4) |
| *c*/Å | 9.158 (6) |
| *β*/ ° | 94.05 (5) |
| Unit cell volume/Å3 | 3362.2 |
| *Z*-value | 8 |
| Dc/g $cm^{-3}$ | 1.59 |
| $\mu/cm^{-1}$ (Cu *Kα*) | 51.96 |

***Solution and Refinement of the Structure.***

The structure was solved by the direct method using MULTAN[3)] to calculate phases for the 300 reflections with $|Eo|>1.60$. The E-map computed from the phases with the largest combined figure of merit (2.59) revealed all the non-hydrogen atoms. The 1993 observed reflections for which $|Fo|$ were greater than $3\sigma(Fo)$ were used for the block-diagonal least-squares refinement of the structure. The function minimized was $\Sigma w(|Fo|-|Fc|)^2$, where w is the unit weight for $0<|Fo|\leq 20$ and $w=(20/|Fo|)^{-2}$ for $|Fo|>20$. An initial

refinement using individual isotropic temperature factors for the non-hydrogen atoms led to a conventional $R=(\Sigma||Fo|-|Fc||)/\Sigma|Fo|$ of 0.143. After the successive refinement with the anisotropic temperature factors for all the non-hydrogens, all the hydrogen atoms were readily located from the difference Fourier map. In the further refinement positional and isotropic thermal parameters for the hydrogen atoms were included. The refinement, after 6 cycles of block-diagonal least-squares calculation, converged to an $R$ of 0.088 and a weighted $Rw=(\Sigma w|Fo|-|Fc|)^2/\Sigma w|Fo|^2)^{1/2}$ of 0.088. An extinction parameter was refined because extinction effects were considered significant. The refinement was completed when the largest shift in any parameters among the non-hydrogen atoms was less than 0.01% of standard deviations, while the largest shift for the hydrogen atoms was 0.09%. The final positional and thermal parameters are given in Table 5. The largest peak in the final difference map, 0.2 $eÅ^{-3}$, was located near the chlorine atoms. The atomic scattering factors for Cl, O, and C were those of Cromer and Weber[10] and for H, the scattering factors of Stewart, Davidson, and Simpson[11] were used. Computations were performed by the crystallographic program system UNICS[8].

The molecular structure and the labeling sequence of 2d is presented in the ORTEP drawing of Figure 6. The molecule of 2d has a T-like shape with the benzofuranone moiety nearly perpendicular to the xanthene plane. The gross molecular conformation and the configuration around the spiro-carbon atom (Cl) of 2d are similar to the corresponding part of 2a (Ref.1). The bond distances and angles of 2d are presented in Table 6. The average C-C bond lengths in the benzene rings A, C, and E are 1.376, 1.391, and 1.392 Å, ring D of 2d are comparable with 1.382 and 1.369 Å of 4-azaphenoxathiin,[12] 1.401 and 1.386 Å of phenoxathiin,[13] and 1.378 and 1.377 Å of fluorescein[9] within the experimental errors.

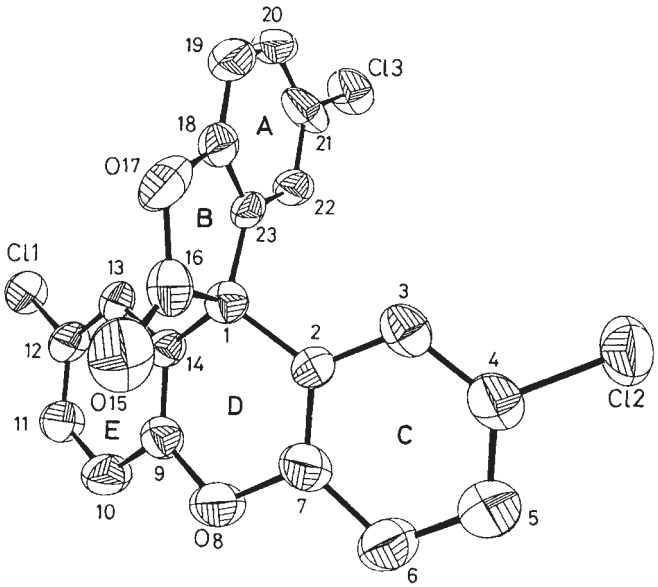


**Figure 6. ORTEP drawing of the compound 2d. Thermal ellipsoids are drawn at the 50% probability level.**

In Table 7 the best least-squares planes are given together with the displacement of the atoms from the best planes. The lactone ring B is coplanar with ring A, and its orientation is almost perpendicular to the xanthene ring, which is similar to that observed in 2a.[1] The dihedral angles between rings A-C, rings A-E, and rings C-E are 73.6°, 83.6°, and 22.81°, respectively, which may be compared with those of 2a (81.4°,

**Table 5 Final positional and thermal parameters of non-hydrogen and hydrogen atoms with estimated standard deviations for 2d**

$$B_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$$

| Atoms | x | y | z | Beq or B/Å$^2$ |
|---|---|---|---|---|
| CL1 | 0.2463 (2) | 0.1307 (2) | 0.5068 (2) | 6.71 |
| CL2 | −0.0900 (2) | 0.3244 (2) | −0.1451 (2) | 7.10 |
| CL3 | 0.0673 (2) | 0.4861 (2) | 0.3778 (2) | 7.93 |
| C1 | 0.1177 (5) | 0.2286 (6) | 0.0752 (5) | 4.09 |
| C2 | 0.0523 (5) | 0.2116 (6) | 0.0188 (5) | 3.91 |
| C3 | 0.0153 (5) | 0.2706 (6) | −0.0324 (6) | 4.78 |
| C4 | −0.0434 (5) | 0.2502 (6) | −0.0856 (6) | 5.05 |
| C5 | −0.0636 (5) | 0.1754 (7) | −0.0918 (6) | 5.33 |
| C6 | −0.0269 (6) | 0.1157 (7) | −0.0407 (6) | 6.01 |
| C7 | 0.0301 (6) | 0.1367 (6) | 0.0158 (6) | 5.10 |
| O8 | 0.0655 (4) | 0.0745 (4) | 0.0669 (5) | 6.62 |
| C9 | 0.1091 (5) | 0.0921 (6) | 0.1676 (6) | 5.09 |
| C10 | 0.1272 (6) | 0.0291 (6) | 0.2525 (7) | 6.30 |
| C11 | 0.1712 (6) | 0.0416 (6) | 0.3558 (6) | 5.81 |
| C12 | 0.1951 (5) | 0.1143 (6) | 0.3699 (6) | 5.15 |
| C13 | 0.1775 (5) | 0.1778 (6) | 0.2858 (6) | 4.51 |
| C14 | 0.1338 (5) | 0.1646 (6) | 0.1795 (5) | 4.02 |
| O15 | 0.1786 (4) | 0.1718 (5) | −0.1354 (4) | 6.77 |
| C16 | 0.1653 (5) | 0.2248 (6) | −0.0557 (6) | 4.88 |
| O17 | 0.1961 (4) | 0.2946 (5) | −0.0682 (4) | 5.73 |
| C18 | 0.1715 (5) | 0.3459 (6) | 0.0393 (6) | 4.57 |
| C19 | 0.1880 (6) | 0.4197 (7) | 0.0552 (7) | 6.32 |
| C20 | 0.1592 (6) | 0.4626 (6) | 0.1583 (7) | 6.45 |
| C21 | 0.1085 (7) | 0.4297 (6) | 0.2500 (7) | 7.83 |
| C22 | 0.0919 (6) | 0.3526 (6) | 0.2376 (6) | 5.22 |
| C23 | 0.1269 (5) | 0.3095 (6) | 0.1232 (5) | 3.80 |
| HC3 | 0.031 (5) | 0.330 (6) | −0.032 (5) | 2.5 |
| HC5 | −0.108 (8) | 0.162 (10) | −0.136 (9) | 3.9 |
| HC6 | −0.052 (5) | 0.058 (6) | −0.009 (6) | 3.5 |
| HC10 | 0.110 (5) | −0.026 (6) | 0.245 (6) | 2.3 |
| HC11 | 0.186 (7) | −0.005 (8) | 0.423 (8) | 3.5 |
| HC13 | 0.209 (5) | 0.232 (6) | 0.265 (6) | 2.5 |
| HC19 | 0.225 (6) | 0.444 (7) | −0.017 (7) | 3.4 |
| HC20 | 0.172 (5) | 0.552 (5) | 0.155 (5) | 1.5 |
| HC22 | 0.057 (5) | 0.328 (6) | 0.326 (6) | 2.7 |

† Tables of the final thermal parameters and the observed and the calculated structure factors are deposited as Document No. 8510 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

86.9°, and 5.9° in order).[1] The great difference in the butterfly angles of the xanthene rings in 2a and 3 (22.81° and 5.9°) seems to be caused by electron-withdrawing effects of the chlorine atoms and the lesser steric hindrance of the phenyl ring of 2d in comparison with the bulky naphthalene ring of 2a. On the other hand, the corresponding value of 9.4° for fluorescein is comparable with that of 2a (5.9°). The projection of the crystal structure along the b-axis is shown in Figure 8, and the shortest intermolecular distances are given in Table 8. There are no unusually close contacts of atoms in the unit cell, and all the intermolecular

**Table 6 Bond lengths (*l*/Å) and angles (φ/ °) in 2d**

| | | | | | | |
|---|---|---|---|---|---|---|
| (a) | Bond lengths for non-hydrogen atoms | | | | | |
| | CL1-C12 | 1.744 (6) | CL2-C4 | 1.732 (9) | CL3-C21 | 1.717 (8) |
| | C1-C2 | 1.549 (11) | C1-C14 | 1.516 (9) | C1-C16 | 1.517 (8) |
| | C1-C23 | 1.482 (11) | C2-C3 | 1.390 (11) | C2-C7 | 1.379 (13) |
| | C3-C4 | 1.420 (12) | C4-C5 | 1.364 (15) | C5-C6 | 1.395 (13) |
| | C6-C7 | 1.402 (13) | C7-O8 | 1.411 (11) | O8-C9 | 1.389 (8) |
| | C9-C10 | 1.408 (11) | C9-C14 | 1.365 (13) | C10-C11 | 1.396 (11) |
| | C11-C12 | 1.364 (14) | C12-C13 | 1.407 (10) | C13-C14 | 1.414 (8) |
| | O15-C16 | 1.193 (8) | C16-O17 | 1.375 (12) | O17-C18 | 1.398 (8) |
| | C18-C19 | 1.334 (14) | C18-C23 | 1.337 (9) | C19-C20 | 1.318 (10) |
| | C20-C21 | 1.438 (12) | C21-C22 | 1.385 (14) | C22-C23 | 1.448 (8) |
| (b) | Bond lengths involving hydrogen atoms | | | | | |
| | HC3-C3 | 1.08 (9) | HC5-C5 | 1.08 (13) | HC6-C6 | 1.16 (9) |
| | HC10-C10 | 1.02 (9) | HC11-C11 | 1.08 (9) | HC13-C13 | 1.16 (9) |
| | HC19-C19 | 1.08 (8) | HC20-C20 | 1.07 (9) | HC22-C22 | 1.15 (6) |
| (c) | Bond angles | | | | | |
| | C23-C1-C16 | 100.4 (6) | C23-C1-C14 | 117.4 (4) | | |
| | C23-C1-C2 | 114.7 (7) | C16-C1-C14 | 107.4 (7) | | |
| | C16-C1-C2 | 107.2 (4) | C14-C1-C2 | 108.8 (7) | | |
| | C7-C2-C3 | 118.5 (8) | C7-C2-C1 | 120.2 (7) | | |
| | C3-C2-C1 | 121.4 (8) | C4-C3-C2 | 118.0 (9) | | |
| | C5-C4-C3 | 122.6 (8) | C5-C4-CL2 | 119.8 (7) | | |
| | C3-C4-CL2 | 117.6 (7) | C6-C5-C4 | 119.9 (8) | | |
| | C7-C6-C5 | 117.1 (9) | O8-C7-C6 | 115.0 (8) | | |
| | O8-C7-C2 | 121.0 (8) | C6-C7-C2 | 123.9 (8) | | |
| | C9-O8-C7 | 116.9 (6) | C14-C9-C10 | 122.8 (7) | | |
| | C14-C9-O8 | 122.3 (6) | C10-C9-O8 | 114.9 (8) | | |
| | C11-C10-C9 | 118.6 (9) | C12-C11-C10 | 118.6 (7) | | |
| | C13-C12-C11 | 123.4 (6) | C13-C12-CL1 | 118.1 (7) | | |
| | C11-C12-CL1 | 118.3 (5) | C14-C13-C12 | 117.7 (8) | | |
| | C13-C14-C9 | 118.7 (6) | C13-C14-C1 | 120.4 (7) | | |
| | C9-C14-C1 | 120.8 (5) | O17-C16-O15 | 122.1 (6) | | |
| | C1-C16-O17 | 108.5 (6) | O15-C16-C1 | 129.3 (8) | | |
| | C18-O17-C16 | 110.0 (5) | C23-C18-C19 | 124.7 (6) | | |
| | C23-C18-O17 | 108.9 (7) | C19-C18-O17 | 126.4 (6) | | |
| | C20-C19-C18 | 120.2 (8) | C21-C20-C19 | 119.3 (9) | | |
| | C22-C21-C20 | 121.2 (7) | C22-C21-CL3 | 118.7 (6) | | |
| | C20-C21-CL3 | 120.1 (7) | C22-C23-C1 | 112.1 (5) | | |
| | C18-C23-C1 | 112.1 (5) | | | | |

van der Waals distances are larger than 3.26 Å.

As the molecular structure of 2d has been elucidated by the X-ray diffraction method, a plausible reaction mechanism leading to the formation of 2d could be infered as shown in Figure 2. The initial step probably involves a Friedel-Crafts type reaction between phenols (1d) and oxalic acid to form the oxalophenols (3). Subsequently, the nucleophilic attack of another phenols (1d) to the protonated carbonyl carbon atom of 4 forms the intermediates (5) with three phenol rings connected by the lactone moiety. Further, the intermediates (5) proceed by the intramolecular cyclization on the xanthene ring accompanying the loss of one molecule of water to reach 2d. Thus the reaction mechanism to form 2d seems to be based on the nucleophilic approach of the electron localized ortho-position of phenols to the carbonyl carbon atom, which results in the loss of four molecules of water.

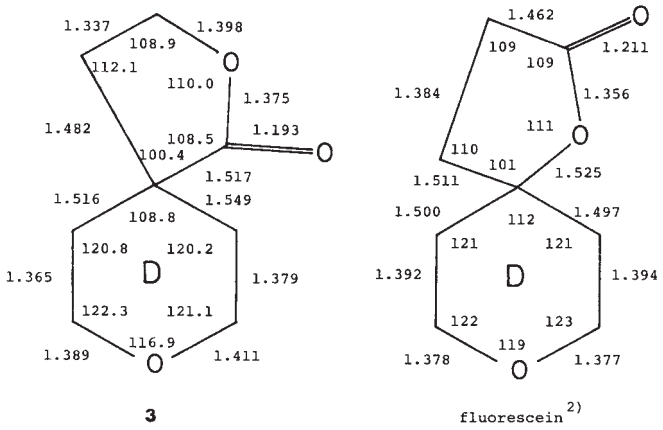


**Figure 7. The selected bond lengths and angles around the spiro carbon atom of 2d and fluorescein. The standard deviations are described in Table 6.**

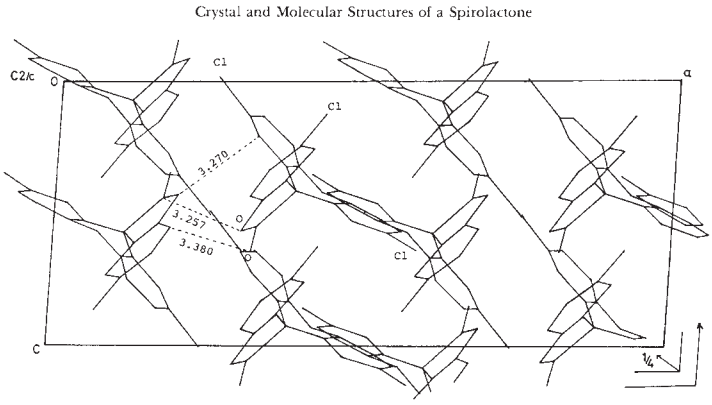


**Figure 8. Projection of the structure along the b-axis for 2d.**

**Table 7 Least-squares planes and deviations (*d*/Å) of atoms from the Planes in 2d**

| | | | | | |
|---|---|---|---|---|---|
| Plane A: Defined by the atoms C18-C23 | | | | | |
| $-0.7151X + 0.2669Y - 0.6461Z + 1.2829 = 0$[a]) | | | | | |
| C18 | 0.013; | C19 | 0.001; | C20 | -0.019 |
| C21 | 0.019; | C22 | -0.005; | C23 | -0.009 |
| Plane B: Defined by the atoms C1, C16, O17, C18, and C23 | | | | | |
| $-0.7323X + 0.3150Y - 0.6038Z + 1.0369 = 0$ | | | | | |
| C1 | -0.008; | C16 | 0.014; | O17 | -0.014 |
| C18 | 0.006; | C23 | 0.002; | O15 | -0.005 |
| Plane C: Defined by the atoms C2-C7 | | | | | |
| $0.3902X + 0.1095Y - 0.9142Z + 0.1252 = 0$ | | | | | |
| C2 | 0.008; | C3 | 0.004; | C4 | -0.016 |
| C5 | 0.008; | C6 | 0.012; | C7 | -0.011 |
| Plane E: Defined by the atoms C9-C14 | | | | | |
| $-0.6944X + 0.2179Y - 0.6859Z + 0.3037 = 0$ | | | | | |
| C9 | 0.011; | C10 | -0.000; | C11 | -0.004 |
| C12 | -0.002; | C13 | 0.007; | C14 | -0.013 |

a) Expressed in an orthogonal coordinate system in Å units.

**Table 8 Intermolecular distances less than 4Å in 2d**

| | |
|---|---|
| CL2···C3[a)] | 3.385 (5) |
| C6···O8[b)] | 3.400 (12) |
| C16···O17[c)] | 3.257 (10) |
| O17···C13[c)] | 3.270 (8) |
| C18···O15[c)] | 3.388 (11) |
| C19···O15[c)] | 3.380 (13) |
| Symmetry code | Symmetry operation |
| a | $-x, y, 1/2-z$ |
| b | $-x, -y, -z$ |
| c | $1/2-x, 1/2-y, -z$ |

## References and Notes


1) M. Kimura, *Bull. Chem. Soc. Japan*, 58, 905 (1985).
M. Kimura, *J. Heterocyclic Chem.*, 24, 283 (1987).
2) M. Kimura and I. Okabayashi, *Chem. Pharm. Bull.*, 31, 3357 (1983).
3) G. Germain, P. Main and M. M. Woolfson, *Acta Crystallogr.*, Sect A, 27, 368 (1971).
4) Atomic scattering factors for non-hydrogen atoms are those of "International Tables for X-ray Crystallography", Kynoch Press, Birmingham (1974), Vol IV, P 71, and for hydrogen atoms, p 108.
5) Computations were done on an ACOS 850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University, and an ACOS 900 computer at Niigata University Computation Center. Principal program system employed was UNICS [Ref. 8], whose parts are arranged by the present author for the ACOS 900 computer, and programs for the bond length and angle calculations, the atomic parameter table, and some brief calculations for publication by the ACOS 900 computer were made by the present author.
6) Supplementary materials; tables of the anisotropic thermal parameters, the observed and calculated structure factors

are available. They may be obtained from the authors.
7) C. K. Johnson, ORTEP II. Report ORNL-3794, 1970, Oak Ridge National Laboratory, Tennessee.
8) T. Ashida and N. Yasuoka, UNICS-Osaka, the Computation Center, Osaka University, 1979.
9) R. S. Osborn and D. Rogers, *Acta Crystallogr., Sect. B*, 31, 359 (1975).
10) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 24, 321 (1968).
11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).
12) C. H. Womack, J. C. Turley and G. E. Martin, and M. Kimura and S. H. Simonsen, *J. Heterocyclic Chem.*, 18, 1173 (1983).
13) S. Hosoya, *Acta Crystallogr., Sect. A*, 20, 429 (1966).

〔2009. 9. 28 受理〕