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Reaction of 9-Diazofluorene with 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone: The Structure and the Behaviors of the Resulting Product

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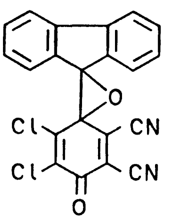
The title reaction gave 3′,4′-dichloro-1′,6′-dicyanospiro[fluorene-9,7′-[3′]norcarene]-2′,5′-dione (**2**) in a good yield. Recrystallizations of **2** from solvents such as benzene, dioxane, acetonitrile, and acetone gave each molecular complex consisting of a **2**/solvent molar ratio of 1 : 1. The structure of **2** was determined by the use of one complex, $\mathbf{2}\cdot CH_3COCH_3$, by an X-ray crystallographic analysis, which revealed that an interaction between **2** and acetone was not very strong. Such a host-guest interaction was shown also from ^1H NMR spectroscopy and a differential thermal analysis of the complex. Compound **2** afforded the corresponding spiroacetals of 9-fluorenone through reactions with ethylene glycol and 1,3-propanediol.

Diazoalkanes are best represented as resonance hybrids comprising linear structures with opposing dipoles.[1a,b] They react with electrophiles (largely at carbon) and with nucleophiles (at nitrogen).[1c] Furthermore, these diazo compounds behave as 1,3-dipoles[2] or carbene precursors.[3] On the other hand, quinones have conjugated two carbonyl groups and two carbon-carbon double bonds and can be considered as being dipolarophiles.[4] In particular, the quinones substituted by electronegative groups, such as halogen and/or cyano group(s),[5] become strong electron acceptors.[6] Thus, the reactions of diazoalkanes with quinones have aroused wide interest from mechanistic or synthetic points of view and have been described by various authors.[7]

Generally speaking, diazoalkanes achieve 1,3-dipolar cycloaddition to the carbon-carbon double bonds of *p*-benzoquinone and of incompletely blocked *p*-quinones to give pyrazoline derivatives,[8] while the diazo compounds attack the carbonyl group(s) of completely blocked *p*-quinones to afford oxiranes[8c,d,9] with the evolution of nitrogen. Needless to say, the oxirane formation from the former quinones[8e,9a] and the pyrazoline formation from the latter[8f,10] have also been reported.

In a previous paper,[11] we stated that we had obtained 2,3-dichloro-5,6-dicyanodispiro[2,5-cyclohexadiene-1,2′-oxirane-3′,9″-fluoren]-4-one (**1**) through a reaction of 9-diazofluorene (9-DF) with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). The instability of the 9-fluorenylidene-DDQ adduct in an acetone-d_6 solution precluded its characterization by ^{13}C NMR spectroscopy. However, chemical support of the structure (**1**) was deduced from the seemingly straightforward formation of acetals by reactions of the adduct with alcohols (as described hereinafter). We recently undertook an X-ray analysis of a crystal which included acetone used for recrystallization of the adduct, and determined its structure to be that of 3′,4′-dichloro-1′,6′-dicyanospiro[fluorene-9,7′-[3′]-norcarene]-2′,5′-dione (**2**) rather than that of **1**.



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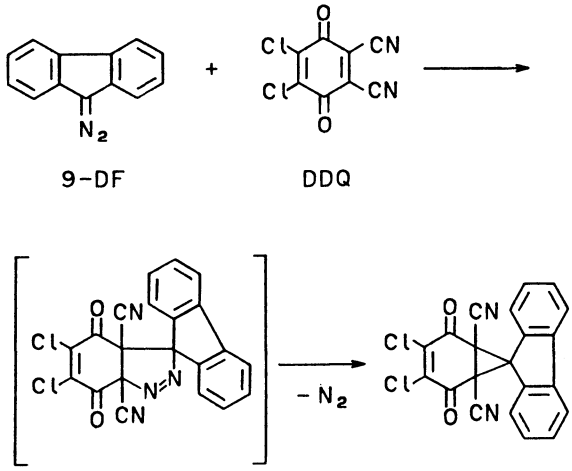
Results and Discussion

Reaction of 9-DF with DDQ. A solution of 9-DF in acetonitrile was added drop by drop with stirring into a solution of DDQ of acetonitrile at room temperature. The evolution of nitrogen was immediately observed and an orange substance was obtained, accompanied by 9,9′-bifluorenylidene (**3**). The substance, upon standing under vacuum for several hours, turned from orange to a yellow powder, **2**.

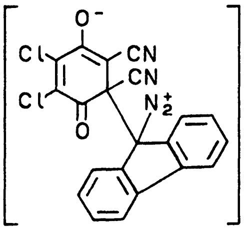
Regarding the formation of **2** from 9-DF and DDQ, the following routes can be suggested: (A) 1,3-Dipolar cycloaddition of the diazo compound to a quinone carbon-carbon double bond takes place to give substituted 3a,4,7,7a-tetrahydro-3*H*-indazole-4,7-dione (**4**), and then the loss of nitrogen gives **2**. In fact, such dipolar cycloadducts have been isolated in the many



9-DF DDQ

4 2

reactions of diazo compounds and quinones.[8] It has been reported that the reactions of 9-DF with *p*-benzoquinone and with 1,4-naphthoquinone give the dihydroxy-3*H*-indazole derivatives.[12] On the other hand, it has been noted that, upon sufficiently raising the temperature in these reactions (in refluxing benzene), a dipolar reaction and a loss of nitrogen occur to give cyclopropanes while the dienolization to form dihydroxy-3*H*-indazole derivatives can be effectively avoided.[13] In our reaction system of 9-DF with DDQ bearing electron-withdrawing groups, the 3*H*-indazole was not isolated because of its instability, even under the present reaction condition. Cycloaddition, however, was observed to occur in the double bond of the cyano group site in DDQ in preference to that of the chloro site. This finding can be explained according to a difference in electron-withdrawing ability between the chloro and the cyano groups. (B) A direct nucleophilic attack of the diazo carbon on the carbon atom adjacent to the cyano group in DDQ leads to the formation of a diazonium betain intermediate (**5**), which gives **2** through a loss of nitrogen and a ring closure. This route may be ruled out for the formations of indazole derivatives from diazo compounds and quinones. (C) A charge-transfer complex of DDQ and 9-DF may be formed as the first step, followed by the formation of a radical ion pair prior to the free radical ions,[14] which may combine to give the pyrazoline (**4**) as a precursor of **2**. The 1 : 1 charge-transfer complexes of DDQ with durene[15] and with *p*-phenylenediamine[16] have been isolated. The formations of a DDQ radical anion in a DDQ–diphenyldiazomethane system[17] and of a radical ion pair for DDQ and 9-DF[14] have been observed by means of their electron spin resonance and electronic absorption spectra. From the point of view of the one-electron redox potentials, $E_{1/2}$(+0.51[18] and +1.21[19] V vs. SCE in acetonitrile for DDQ and 9-DF, respectively), it seems unlikely to us that the above-mentioned pyrazoline formation proceeds through the radical ions.



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Inclusion of Some Solvents. Upon recrystallization from acetone, **2** slowly precipitated as big yellowish-orange columnar crystals, which exhibited the values of elementary analysis for a molecular compound consisting of one molecule of **2** and one molecule of acetone. The mass spectra of the molecular complex (**2**·CH_3COCH_3) revealed *m/z* 390 (M^+ −58 (C_3H_6O)) as the highest peak. The ^1H NMR spectra (in $CDCl_3$) of **2**·CH_3COCH_3 were all similar to superimposed spectra of the components; none of the peak shifts were observed. This finding shows that **2**·CH_3COCH_3 completely dissociates into the components in the solvent because of a week interaction between **2** and the ketone. When the big crystals of **2**·CH_3COCH_3 were stored in a dry-seal desiccator, their surfaces gradually changed to yellow powder. When crushed crystals of **2**·CH_3COCH_3 were kept in vacuo by use of a rotary oil pump for one hour or so, they completely changed to yellow powder, **2**. The recrystallization of **2** or **2**·CH_3COCH_3 from ethyl methyl ketone gave a new molecular complex (**2**·$C_2H_5COCH_3$) having a molar ratio of **2** to the ethyl methyl ketone of 1 : 1 in either case; the complex showed the same behavior as those of **2**·CH_3COCH_3 in its characterization by mass and ^1H NMR spectroscopy. In addition, **2** forms crystalline molecular complexes of 1 : 1 stoichiometry with a variety of guest molecules such as benzene, tetrahydrofuran, dioxane, and acetonitrile. Furthermore, these host-guest compounds make a change in the guests upon recrystallization from the other solvents,[11] as mentioned above regarding the conversion of **2**·CH_3COCH_3 into **2**·$C_2H_5COCH_3$. Differential thermal analyses (DTA) of each host-guest compound gave endothermic peaks at respective temperatures between 74 and 107 °C (for six kinds of samples), all of the compounds recorded the start of exothermic peaks at temperature 185—187 °C.[11] Although the host-guest compounds with polar additives (acetonitrile and ketones) have a tendency to indicate higher DTA endothermic peak points than the boiling points of these additives, the

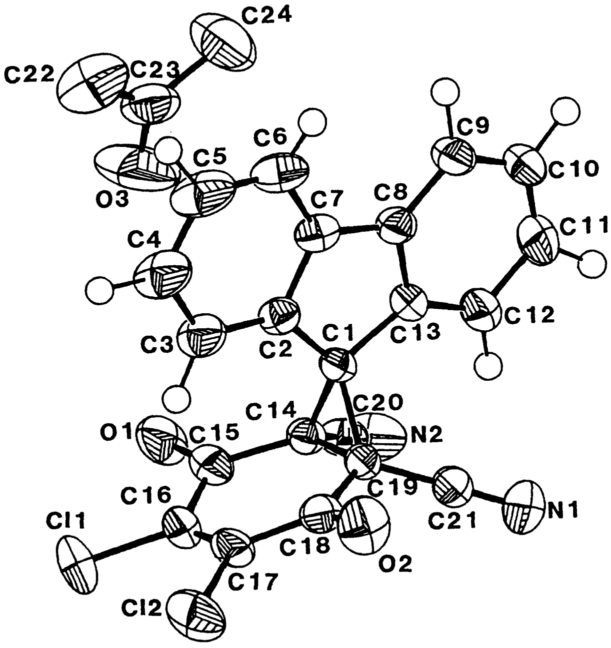


Fig. 1. ORTEP drawing of **2**·CH_3COCH_3.

relationship of the peak points to the natures of the additives is not clear.

X-Ray Crystal Structure. A perspective view of a complex, **2**·CH_3COCH_3, is shown in Fig. 1 by an ORTEP drawing[20] together with the atomic numberings. The bond distances and the bond angles are listed in Tables 1 and 2, respectively.

The cyclopropane ring of **2** is formed with a short bond, C14-C19 (1.505 Å), and two longer bonds, C1-C14 (1.542 Å) and C1-C19 (1.556 Å). The bond angles in the cyclopropane ring are 58.1° (C14-C1-C19), 61.4° (C1-C14-C19) and 60.5° (C1-C19-C14), respectively. These facts show a cyclopropane ring having a tendency to be an isosceles triangle.

Table 1. Bond Distances (in Å) of **2**·CH_3COCH_3 with Estimated Standard Deviations in Parentheses

Bond	Distance	Bond	Distance	Bond	Distance
C1-C2	1.518(4)	C2-C3	1.379(4)	C3-C4	1.390(5)
C4-C5	1.365(5)	C5-C6	1.377(5)	C6-C7	1.390(5)
C2-C7	1.404(4)	C7-C8	1.441(4)	C8-C9	1.393(4)
C8-C13	1.400(4)	C9-C10	1.375(5)	C10-C11	1.381(5)
C11-C12	1.380(5)	C12-C13	1.392(4)	C13-C1	1.507(4)
C1-C14	1.542(3)	C14-C15	1.515(4)	C15-O1	1.201(4)
C15-C16	1.485(4)	C16-CL1	1.698(3)	C16-C17	1.337(4)
C17-CL2	1.703(3)	C17-C18	1.477(4)	C18-O2	1.200(4)
C18-C19	1.516(4)	C19-C21	1.444(4)	C21-N1	1.138(4)
C19-C14	1.505(3)	C19-C1	1.556(3)	C14-C20	1.445(4)
C20-N2	1.138(5)	O3-C23	1.202(6)	C22-C23	1.483(6)
C23-C24	1.485(7)				

The projected view of the crystal structure of the complex, **2**·CH_3COCH_3, is represented in Fig. 2. The shortest distance between the acetone molecule and **2** is that of O2-C22 (*X*, 1+*Y*, *Z*) (3.286 Å). This distance reveals the existence of a hydrogen bond,[21] though it is very weak, judging from the sum (3.40 Å[21]) of the van der Waals radii of a methyl group and an oxygen atom.

Reaction of 2 with Diols. It was found that, in acetonitrile at room temperature, **2** reacted with diols to give spiroacetals (**6**). Besides **6**, an almost quantitative amount of 2,3-dichloro-5,6-dicyanohydroquinone ($DDQH_2$) was isolated along with 9-fluorenone (**7**). The formation of the by-product, **7**, can be ascribed to the action of residual water present in the used solvent and/or of the water used in the treatment of the reaction mixture.

Table 2. Bond Angles (in Degree) of **2**·CH_3COCH_3 with Estimated Standard Deviations in Parentheses

Bond	Angle	Bond	Angle	Bond	Angle
C2-C1-C13	104.8(2)	C14-C1-C19	58.1(2)	C1-C2-C7	107.2(3)
C3-C2-C7	119.5(3)	C2-C3-C4	119.2(3)	C3-C4-C5	121.1(3)
C4-C5-C6	120.7(3)	C5-C6-C7	119.0(3)	C2-C7-C6	120.4(3)
C2-C7-C8	110.3(3)	C7-C8-C13	109.5(3)	C9-C8-C13	120.2(3)
C8-C9-C10	119.2(3)	C9-C10-C11	120.6(3)	C10-C11-C12	121.1(3)
C11-C12-C13	119.0(2)	C8-C13-C12	119.8(3)	C1-C13-C8	108.1(3)
C1-C14-C15	120.3(2)	C1-C14-C20	117.8(2)	C1-C14-C19	61.4(2)
C14-C15-C16	118.5(2)	O1-C15-C14	119.7(3)	O1-C15-C16	121.8(3)
C15-C16-C17	122.9(3)	CL1-C16-C15	115.2(2)	CL1-C16-C17	121.8(2)
C16-C17-C18	122.8(3)	CL2-C17-C16	122.5(2)	CL2-C17-C18	114.6(2)
C17-C18-C19	118.0(2)	O2-C18-C17	122.7(2)	O2-C18-C19	119.3(2)
C14-C19-C18	118.9(3)	C18-C19-C21	110.7(3)	C14-C19-C21	120.3(3)
C1-C19-C14	60.5(2)	N2-C20-C14	179.6(3)	N1-C21-C19	178.5(3)
O3-C23-C22	120.8(4)	O3-C23-C24	118.9(4)	C22-C23-C24	120.3(4)

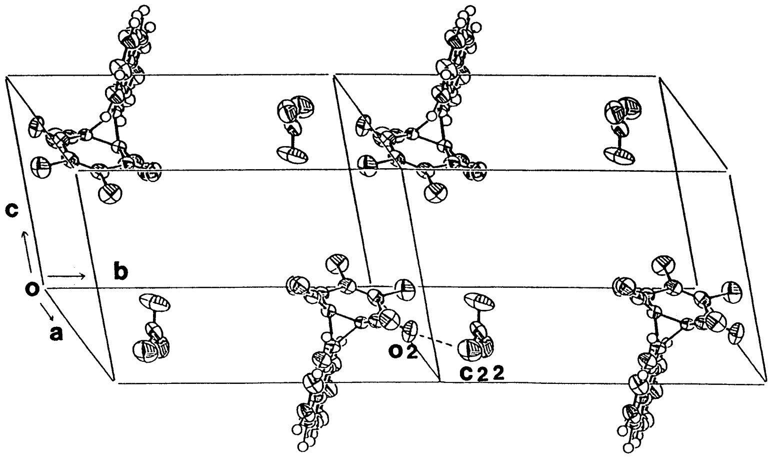
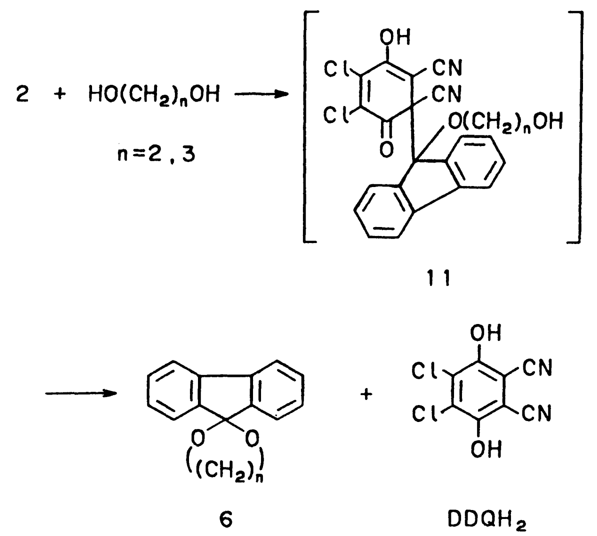
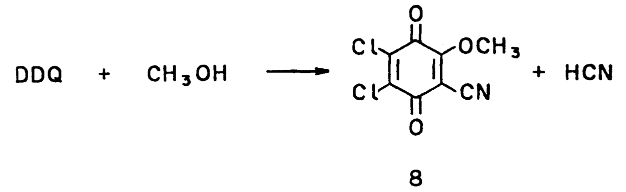
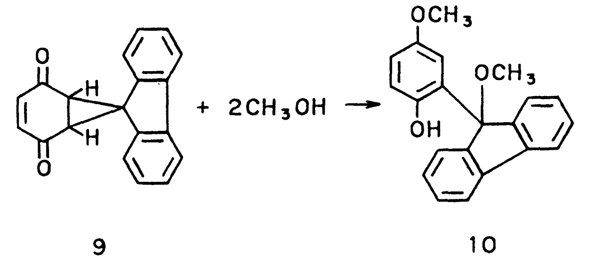


Fig. 2. The projected view of the crystal structure of **2**·CH_3COCH_3.







The nucleophilic displacement of the cyano group in DDQ by methanol proceeds to give 2,3-dichloro-5-cyano-6-methoxy-*p*-benzoquinone (**8**) at room temperature,[22] and the nucleophilic ring opening of the cyclopropane in spiro[fluorene-9,7′-[3′]norcarene]-2′,5′-dione (**9**) by methanol proceeds to afford 4-methoxy-2-(9-methoxy-9-fluorenyl)phenol (**10**).[13] In respect that the reaction of **2** with the diols has led to the production of the corresponding acetals and DDQH$_2$; the intermediate (**11**) represented above may be formed prior to the acetals. The cyclopropane ring of **2** provides electron-withdrawing cyano, carbonyl, and 9-fluorenylidene groups as well as strains inherent in a three-membered cyclic alkane. A nucleophilic attack of the diol takes place on the spiro carbon atom, leading to the ring opening; the follow-up proton migration occurs from the resulting oxonio hydrogen to the carbonyl oxygen to give **11**. In this intermediate, because of the strong electron-withdrawal of the DDQ moiety, the 9-fluorenylidene site is most likely subject to an internal nucleophilic attack by the other alcohol oxygen atom. Thus, an internal acetalization and an aromatization of the DDQ moiety provide **6** and DDQH$_2$. Here, it is left as a possibility that **11** undergoes an intermolecular nucleophilic attack with another molecule of the diol to give the corresponding noncyclic acetal. However, the noncyclic acetals could not be isolated also in the presence of more excess diols than those in the above-mentioned runs.

As mentioned above, a small amount of 9,9′-bifluorenylidene (**3**) was obtained in the reaction of 9-DF and DDQ. Whereas, from a stirred acetonitrile solution of **2** and 9-DF, **3** was not detected by means of high-performance liquid chromatography, both of the starting materials were recovered unchanged. Such a result was also shown by employing diphenyldiazomethane instead of 9-DF. Mechanistically, **3** could be derived from the diazonium betain intermediate, which had been provided by a nucleophilic attack of the diazo carbon on one carbonyl oxygen in DDQ, as described for the stilbene derivative formation in the reactions of aryldiazomethanes with chloranil.[9c,d]

Experimental

The melting points were determined on a Laboratory Devices Melt-Temp instrument and uncorrected. The infrared spectra were recorded on a Hitachi 260-10 spectrometer. The ^{1}H NMR spectra were taken on a Varian EM-390 spectrometer (90 MHz) and the ^{13}C NMR spectra were taken on a JEOL FX-200 spectrometer at 50.10 MHz (measured at NMR Application Laboratory, Nippon Denshi LTD., Tokyo, Japan) by the use of tetramethylsilane as an internal standard in acetone-d_6 or chloroform-d_3. Mass spectral data were obtained with a Hitachi RUM-6E mass spectrometer at an ionization potential of 70 eV. The DTA was accomplished with a Shimadzu DTA-system (thermal analysis instrument 30-series), all the samples being heated at a rate of 10 K min^{-1} from room temperature to 190 °C.

Materials. 9-Diazofluorene[23] and diphenyldiazomethane[24] were prepared by oxidation of the corresponding hydrazones with yellow mercury(II) oxide, the former; mp 99 °C[25] (from ether), the latter; mp 29—30 °C[26] (from light petroleum). Although 9-DF can be preserved for a long time in a refrigerator, the diazomethane must be prepared just before use. Benzene, acetone, ethyl methyl and diethyl ketones, acetonitrile, and dioxane were used after the commercial reagents had been purified according to the published directions.[27] DDQ was obtained from a commercial source and recrystallized from dichloromethane; mp 213—214 °C.[28] The diols were distilled under reduced pressure before use after the commercial materials were dried over Molecular Sieves 3A.

Reaction of 9-DF with DDQ. To a stirred solution of DDQ (3.63 g, 16 mmol) in acetonitrile (100 ml) was added dropwise over 40 min at 22—27 °C a solution of 9-DF (2.88 g, 15 mmol) in acetonitrile (50 ml); the evolution of nitrogen began immediately. Stirring was allowed to continue until the gas evolution was no longer observed after completing the addition. The evolved nitrogen was almost the theoretical amount, based on the diazo compound used. The orange-yellow flocculent precipitate formed under stirring was collected and washed with a small quantity of cold acetonitrile. A further crop was obtained by concentrating the mother liquor under reduced pressure. The combined products were crystallized from dichloromethane to give **2** (5.45 g, 93%) as a yellow powder. Evaporating the acetonitrile mother liquor, treating the residue with ether, and cooling yielded red crystals of **3** (0.10 g, 2%). Upon employing acetone, dichloromethane, and benzene as the reaction solvent, the yield of **2** (70—90%) decreased with an increase in the yield of **3**. 3′,4′-Dichloro-1′,6′-dicyanospiro[fluorene-9,7′-[3′]norcarene]-2′,5′-dione (**2**): Mp 183 °C (decomp). Found: C, 64.39; H, 2.12; N, 7.16%. Calcd for $C_{21}H_8N_2O_2Cl_2$: C, 64.47; H, 2.06; N, 7.16%. MS m/z 390 (M^+). IR (KBr) 2250 (C≡N), 1710 (C=C), 1450, 1280, and 730 cm^{-1}. ^{13}C NMR ($(CD_3)_2CO$) δ=40.97 (s, fluorenylidene 9-C), 53.93 (s, $\underline{C}$-CN), 112.60 (s, CN), 134.41 (s, CCl), 175.73 (s, CO), 136.43, 142,09, 144.27, 147.39 (each s), 122.37, 123.50, 123.83, 126.66, 129.37, 130.24 (each d), and 132.70 (d, 2C). 9,9′-Bifluorenylidene (**3**): Red needles (from ether); mp 189—190 °C. Found: C, 95.00; H, 4.88%. Calcd for $C_{26}H_{16}$: C, 95.09; H, 4.91%. MS m/z 328 (M^+). IR (KBr) 3050, 1600 (C=C), 1440, 1340, 760, and 720 cm^{-1}.

Host-Guest Compounds. A general method is exemplified in the adduct formation of **2** with ethyl methyl ketone as follows. The powder of **2** was dissolved in 10 ml of the ketone placed in a 30-ml Erlenmeyer flask at about 40 °C. The top of the flask was covered by a piece of powder paper which had been perforated with a pin; the saturated solution was left to stand at room temperature for crystallization, which gave big yellowish-orange columnar crystals. The adduct, **2**·$C_2H_5COCH_3$, was filtered off before use: Found: C, 64.81; H, 3.48; N, 6.05; Cl, 15.31%. Calcd for $C_{25}H_{16}N_2O_3Cl_2$: 64.79, H, 3.31; N, 5.90; Cl, 15.21%. MS m/z 390 (M^+-72). ^{1}H NMR ($CDCl_3$) δ=1.20 (t, $CH_2C\underline{H}_3$), 2.12 (s, CH_3), 2.44 (q, CH_2), and 7.0—8.2 (8H, aromatic H).

All of the following adducts made in this way revealed the mass spectra having the highest peak at m/z 390 and the ^{1}H NMR spectra (in $CDCl_3$) having peaks attributable to the fluorenylidene protons and the original peaks of their respective guests.

2·CH_3COCH_3: Found: C, 64.02; H, 3.13; N, 6.16%. Calcd for $C_{24}H_{14}N_2O_3Cl_2$: C, 64.16; H, 3.14; N, 6.24%.

2·CH_3CN: Found: C, 64.10; H, 2.42; N, 9.70%. Calcd for $C_{23}H_{11}N_3O_2Cl_2$: C, 63.90; H, 2.57; N, 9.72%.

2·Tetrahydrofuran: Found: C, 64.70; H, 3.46; N, 6.12%. Calcd for $C_{25}H_{16}N_2O_3Cl_2$: C, 64.81; H, 3.48; N, 6.05%.

2·1,4-Dioxane: C, 62.58; H, 3.38; N, 5.90%. Calcd for $C_{25}H_{16}N_2O_4Cl_2$: C, 62.64; H, 3.37; N, 5.85%.

2·Benzene: Found: C, 68.88; H, 3.00; N, 6.01%. Calcd for $C_{27}H_{14}N_2O_2Cl_2$: C, 69.09; H, 3.01; N, 5.97%.

2·Tetrahydropyran: Found: C, 65.22; H, 3.78; N, 5.80%. Calcd for $C_{26}H_{18}N_2O_3Cl_2$: C, 65.42; H, 3.80; N, 5.87%.

2·$C_2H_5COC_2H_5$: Found: C, 65.51; H, 3.90; N, 5.68%. Calcd for $C_{26}H_{18}N_2O_3Cl_2$: C, 65.42; H, 3.80; N, 5.87%.

As for a change of the guests, for example, **2**·$C_2H_5COCH_3$ was recrystallized from acetonitrile, by a manner similar to that described above, to give the **2**·CH_3CN adduct as orange columnar crystals.

Spiro Acetals. To a solution of 1.00 g (2.6 mmol) of **2** in acetonitrile (30 ml) was added 1.00 g (16 mmol) of ethylene glycol; the solution was then stirred for 4 h at room temperature. The removal of the solvent under reduced pressure gave a pale-yellow oil. To the residue was added benzene (30 ml or so), and insoluble $DDQH_2$ was filtered off and washed with benzene. The washing and filtrate parts were combined, washed with a 5% solution of sodium carbonate (15 ml×3), followed by rinsing with a saturated solution of sodium chloride (15 ml×3) and drying over anhydrous magnesium sulfate. The concentration of the benzene solution gave an oily substance, which was chromatographed on alumina (about 300 mesh). Careful successive elution gave **7** (0.12 g, 26%) with benzene-ether (5 : 1) and a spiro acetal, **6a**, (0.32 g, 56%) with benzene-ether (1 : 1). The reaction of **2** with 1,3-propanediol, by the same method as described above, gave **7** (0.17 g, 37%) and **6b** (0.31 g, 51%) besides $DDQH_2$. The structures of $DDQH_2$ and **7** were assigned

Table 3. Fractional Atomic Coordinates with e.s.d.'s in Parentheses and Equivalent Isotropic Thermal Parameters (in Å^2)

(H atoms refined isotropically)

Atom	X	Y	Z	B_{eq}[a)]	Atom	X	Y	Z	B_{eq}[a)]
CL1	0.50857(9)	0.82840(7)	0.33643(11)	7.7	C14	0.9334(3)	0.7085(2)	0.3108(3)	4.0
CL2	0.55325(9)	1.01443(6)	0.23356(11)	7.3	C15	0.7800(3)	0.7193(2)	0.3208(3)	4.9
O1	0.7539(3)	0.6473(2)	0.3461(3)	7.9	C16	0.6677(3)	0.8206(2)	0.3037(3)	5.0
O2	0.8275(3)	0.9612(1)	0.1671(3)	7.2	C17	0.6864(3)	0.8997(2)	0.2598(3)	4.7
O3	1.0173(4)	0.1625(3)	0.3877(3)	11.4	C18	0.8199(3)	0.8935(2)	0.2233(3)	4.5
N1	1.2240(3)	0.8428(2)	0.3995(3)	7.0	C19	0.9535(2)	0.7981(2)	0.2621(3)	3.8
N2	1.1717(3)	0.5963(2)	0.5337(3)	7.1	C20	1.0669(3)	0.6460(2)	0.4357(3)	4.9
C1	0.9345(3)	0.7025(2)	0.1426(3)	3.8	C21	1.1056(3)	0.8220(2)	0.3400(3)	4.7
C2	0.7920(3)	0.7007(2)	−0.0226(3)	4.1	C22	0.8476(5)	0.1800(3)	0.1082(5)	9.1
C3	0.6309(3)	0.7390(2)	−0.0740(3)	5.3	C23	1.0034(4)	0.1459(2)	0.2492(4)	7.1
C4	0.5288(3)	0.7250(2)	−0.2385(4)	6.4	C24	1.1446(6)	0.0891(4)	0.2210(6)	11.5
C5	0.5855(4)	0.6741(3)	−0.3492(4)	6.7	HC3	0.593(3)	0.774(2)	0.002(3)	2.7
C6	0.7457(4)	0.6334(2)	−0.3001(3)	6.0	HC4	0.420(3)	0.752(2)	−0.274(3)	3.9
C7	0.8497(3)	0.6459(2)	−0.1360(3)	4.4	HC5	0.512(4)	0.666(2)	−0.453(4)	4.6
C8	1.0199(3)	0.6103(2)	−0.0555(3)	4.5	HC6	0.782(3)	0.597(2)	−0.373(4)	3.9
C9	1.1264(4)	0.5532(2)	−0.1186(3)	6.1	HC9	1.084(4)	0.532(2)	−0.233(4)	4.2
C10	1.2856(4)	0.5273(2)	−0.0148(4)	6.9	HC10	1.368(4)	0.481(2)	−0.053(4)	5.2
C11	1.3398(3)	0.5568(2)	0.1503(4)	6.5	HC11	1.448(4)	0.535(3)	0.227(4)	5.1
C12	1.2364(3)	0.6130(2)	0.2155(3)	5.4	HC12	1.274(3)	0.632(2)	0.326(3)	3.7
C13	1.0748(3)	0.6399(2)	0.1120(3)	4.2					

a) $B_{eq}=4/3\sum_i\sum_j B_{ij}a_ia_j$.

upon comparisons with the authentic samples.

Spiro[1,3-dioxolane-2,9′-fluorene] (6a): Mp 133—134 °C (from ether). Found: C, 80.26; H, 5.41%. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39%. MS m/z 224 (M^+). IR (KBr) 2860, 1440, 1110, 1060, 980, 935, 760, and 725 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=4.35 (s, 4H) and 7.1—7.7 (m, 8H).

Spiro[1,3-dioxane-2,9′-fluorene] (6b): Mp 172—173 °C (form ether). Found: C, 80.44; H, 5.92%. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92%. MS m/z 238 (M^+). IR (KBr) 2880, 1450, 1082, 1010, 960, 930, 770, and 740 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.9—2.2 (m, 2H), 4.35 (t, 4H, J=5.4 Hz, OCH_2), and 7.1—7.8 (m, 8H).

Crystallographic Measurements. The crystal of $2\cdot CH_3COCH_3$ was sealed in a Lindemann glass capillary with the mother liquor, because it gradually lost acetone molecules. Three dimensional X-ray data were collected using a crystal (0.4×0.3×0.2 mm) by Ni-filtered Cu$K\alpha$ radiation on a Rigaku automated four-circle diffractometer. The ω–2θ scan mode was employed at a rate of 10 ° min^{-1} (in ω). The backgrounds were counted for 2 s before and after each scan. A total of 3751 reflections was collected up to 2θ=125° and 2989 ($|F_o|>3\sigma|F_o|$) reflections were used in the analyses. The structure was solved by the direct method (MULTAN 74)[29] and refined by a block-diagonal least squares method (HBLS-V).[30] Anisotropic temperature factors were used for nonhydrogen atoms. The positions of the hydrogen atoms were calculated based on the molecular geometry. The methyl hydrogen atoms of the acetone molecule were neglected. These hydrogen atoms with isotropic temperature factors were included in further refinement. The final R and R_w values were 0.057 and 0.076, respectively. The weighting scheme used was $w=1/(\sigma(F_o)^2+0.0015\,(F_o)+0.0001\,(F_o)^2)$. The atomic scattering factors for all atoms were taken from Ref. 31. The final atomic coordinates are listed in Table 3[†].

Crystal Data: $C_{24}H_{14}N_2O_3Cl_2$, F.W.=449.3, triclinic, space group $P\bar{1}$, a=9.848(1), b=13.972(1), c=9.222(1) Å, α=101.27 (1), β=117.78(1), γ=71.96(1), V=1065.5(2) Å^3, D_c=1.401 g·cm^{-3}, Z=2.

All the computations were carried out on an ACOS computer at the Computation Center, Osaka University, and on an ACOS S-850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

[†] Tables of anisotropic temperature factors, and of observed and calculated structure factors are deposited as Document No. 8848 at the office of Bull. Chem. Soc. Jpn.

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