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Crystal and Molecular Structures of the Adduct of Fluoreno[9,1-*bc*]pyrylium-3-olate with Methyl Cinnamate and the Dimer of Fluoreno-[9,1-*bc*]pyrylium-3-olate

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The molecular structures of the adduct of fluoreno[9,1-*bc*]pyrylium-3-olate with methyl cinnamate (**1**), $C_{25}H_{18}O_4$, and the dimerized product of fluoreno[9,1-*bc*]pyrylium-3-olate (**2**), $C_{30}H_{16}O_4$, have been determined by the X-ray diffraction method. In the adduct (**1**), the phenyl ring is situated above the fluorene ring with a dihedral angle of 64°. The product **2** has a dimeric structure with a head-to-head type *anti*-configuration, and a local two-fold symmetry. Both crystals belong to a triclinic system with a space group $P\bar{1}$. The cell constants for **1** are a=13.287(4), b=8.794(3), c=8.797(3) Å, α=109.78(3), β=82.17(3), γ=88.58(3)°, and those for **2** are a=10.401(2), b=12.425(3), c=8.564(2) Å, α=103.77(4), β=108.76(4), γ=95.06(4)°. The structure of **1** was refined to R=0.067 for 2141 reflections, and that of **2** to R=0.058 for 2301 reflections.

Pyrylium-3-olate(**5**), formed by an intramolecular carbene–carbonyl reaction of **4**, has a resonance contribution of carbonyl ylide. It has been known that **5** is an unstable and reactive species and that it undergoes a 1,3-dipolar cycloaddition reaction with acetylenic, olefinic and carbonyl compounds.[1-3] When **5** was reacted with methyl cinnamate, a 1:1 adduct(**1**) was obtained in a 66% yield.[2] The structure of **1** was assigned on the bases of an elementary analysis and NMR data.[3] $Cu(acac)_2$-catalysed decomposition of 1-diazoacetylfluorenone(**3**) in the absence of dipolarophile in absolute benzene at 80 °C yielded a crystalline compound(**2**) quantitatively (Scheme).[3] The elemental analysis and mass spectrum for **2** showed a dimeric structure. Among four possible configurations for the dimer(**2**), an NMR study rejected two *syn*-configurations. In order to confirm the structure of **1** as well as to determine either of the two *anti*-configurations, X-ray analyses of **1** and **2** were undertaken.

Results and Discussion

The molecular structures of **1** and **2** drawn by DCMS-3[4] are shown in Fig. 1. The selected bond lengths and angles are given in Table 1.[5] The present X-ray analyses have established the molecular structures of **1** and **2**. In contrast to the case of 2-benzothiopyrylium-4-olate, where it gave a head-to-tail type dimer with a *syn*-configuration,[6] fluoreno[9,1-*bc*]pyrylium-3-olate(**5**) gave a dimer (**2**) with a head-to-head type *anti*-configuration. Hence, the structural formula of **6** in Ref. 3 should be revised. The structure of **2** shows that the dimerization of **5** occurred through a bond formation between the equivalent atoms in **5**. As pyrylium-3-olate, with a carbonyl ylide resonance structure, behaves as 4π component in cycloaddition, a concerted thermal [π4s+π4s] process is not allowed for the facile dimerization of **5** according to the rule of the conservation of orbital symmetry.[7] We presume that the dimer was formed by a two-step mechanism. The transition state to *syn*-dimer, in which the carbonyl groups lie above each other, is unfavored over that of an *anti*-dimer in terms of the dipolar or electrostatic repulsion between the carbonyl groups. This electronic effect might result in the exclusive formation of an *anti*-dimer.

As seen from Fig. 1, molecule **2** has a local 2-fold symmetry. The lengths and angles of the equivalent bonds within a molecule are similar (Table 1). The six-membered ring, through which the 2-fold axis passes, has a chair form. The two six-membered rings comprizing C(7), C(8), C(9), C(14), C(15), and O(1) in **2** have envelope form; the former five atoms lie on a mean plane with an rms deviation of 0.05 Å and O(1) deviates from the plane by about 0.68 Å for each ring. The two fluorene rings of **2** are slightly bent; the dihedral angles between the two benzene rings in each fluorene ring are 16 and 15°, respectively. The proton signal exhibiting an up-field shift in the NMR spectrum of **2** might be that of the hydrogen atoms bonded to C(5A) and C(5B), which are located above the aromatic ring.

The structure of **1** shows features that are similar to those observed in **2**. The fluorene ring is bent to the same extent as in **2**; the dihedral angle between the two benzene rings is 13°. The dihedral angle between the fluorene and phenyl rings is 64°. The six-membered ring of C(7), C(8), C(9), C(14), C(15), and O(1) also takes an envelope form; the O(1) deviated by 0.79 Å from the mean plane through the former five atoms. The coupling constants of the

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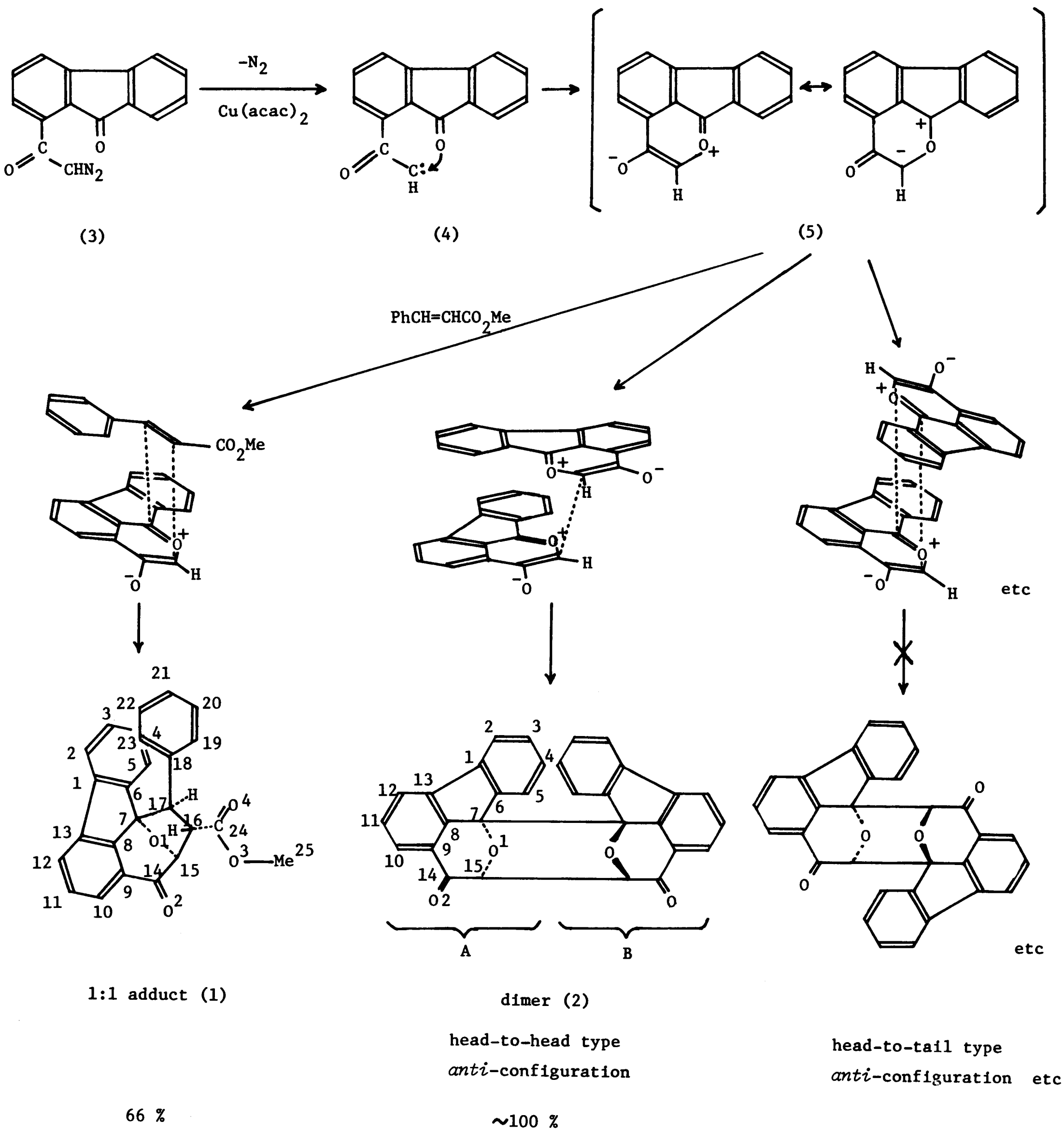
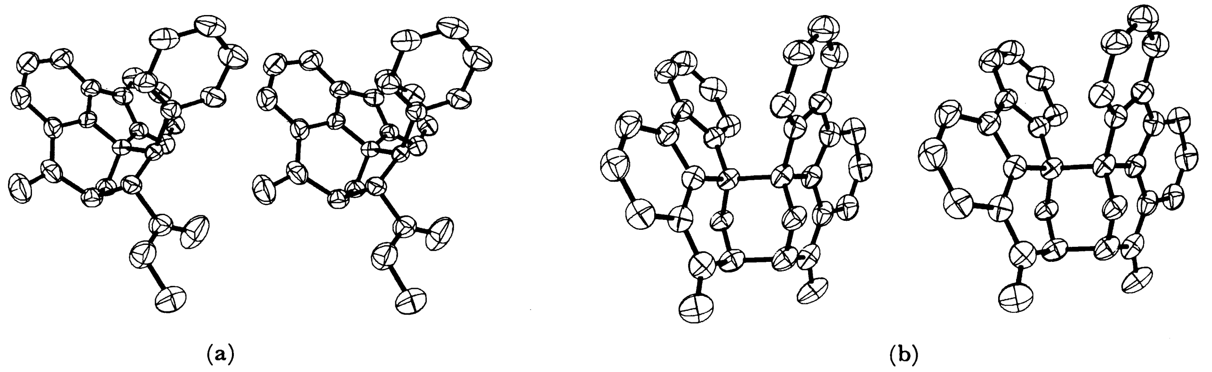


Scheme



(a) (b)

Fig. 1. Stereoscopic views of (a) the adduct **1** and (b) the dimer **2**.
The hydrogen atoms are omitted from the figures for the sake of clarity.

Table 1. Selected Bond Lengths and Angles with Estimated Standard Deviations in Parentheses

(a) Bond lengths (l/Å)	1	2	
		A[a]	B[a]
C (1)-C (2)	1.390(7)	1.396(5)	1.382(5)
C (1)-C (6)	1.405(6)	1.401(4)	1.400(4)
C (1)-C(13)	1.481(7)	1.475(4)	1.474(4)
C (2)-C (3)	1.388(8)	1.384(5)	1.382(5)
C (3)-C (4)	1.378(8)	1.386(5)	1.367(6)
C (4)-C (5)	1.398(8)	1.389(5)	1.401(5)
C (5)-C (6)	1.374(7)	1.391(4)	1.384(4)
C (6)-C (7)	1.508(6)	1.510(4)	1.521(4)
C (7)-C (8)	1.478(6)	1.494(4)	1.489(4)
C (7)-O (1)	1.447(5)	1.443(4)	1.433(3)
C (7)-C (7′)[c]	—	1.582(4)[b]	
C (8)-C (9)	1.386(6)	1.381(4)	1.386(4)
C (8)-C(13)	1.378(6)	1.398(4)	1.383(4)
C (9)-C(10)	1.408(8)	1.399(5)	1.391(5)
C (9)-C(14)	1.466(7)	1.476(5)	1.474(5)
C(10)-C(11)	1.365(8)	1.389(6)	1.381(5)
C(11)-C(12)	1.397(8)	1.392(5)	1.405(5)
C(12)-C(13)	1.399(7)	1.383(5)	1.393(5)
C(14)-C(15)	1.548(7)	1.542(5)	1.541(5)
C(14)-O (2)	1.217(7)	1.211(5)	1.216(4)
C(15)-O (1)	1.443(5)	1.437(4)	1.448(4)
C(15)-C(15′)[c]	—	1.523(5)[b]	
(b) Bond angles (ϕ/°)	1	2	
		A[a]	B[a]
C (2)-C (1)-C (6)	120.3(4)	120.5(3)	120.2(3)
C (2)-C (1)-C(13)	131.0(5)	130.3(3)	131.1(3)
C (6)-C (1)-C(13)	108.6(4)	109.1(3)	108.6(3)
C (1)-C (2)-C (3)	118.6(5)	118.2(3)	118.5(3)
C (2)-C (3)-C (4)	120.7(5)	121.1(4)	121.5(4)
C (3)-C (4)-C (5)	121.1(5)	121.3(3)	121.2(4)
C (4)-C (5)-C (6)	118.4(5)	117.9(3)	117.3(3)
C (1)-C (6)-C (5)	120.8(4)	120.9(3)	121.4(3)
C (1)-C (6)-C (7)	109.0(4)	109.3(3)	109.6(3)
C (5)-C (6)- C(7)	130.1(4)	129.7(3)	129.0(3)
C (6)-C (7)-C (8)	102.2(4)	101.7(2)	101.3(2)
C (6)-C (7)-O (1)	117.0(4)	114.7(2)	114.1(2)
C (6)-C (7)-C (7′)[c]	—	112.3(2)	111.8(2)
C (8)-C (7)-O (1)	108.3(3)	108.0(2)	108.3(2)
C (8)-C (7)-C (7′)[c]	—	112.0(2)	112.0(2)
O (1)-C (7)-C (7′)[c]	—	108.1(2)	109.1(2)
C (7)-C (8)-C (9)	123.9(4)	125.1(3)	124.4(3)
C (7)-C (8)-C(13)	112.2(4)	111.6(3)	112.2(3)
C (9)-C (8)-C(13)	123.6(4)	122.9(3)	122.7(3)
C (8)-C (9)-C(10)	117.5(5)	118.3(3)	118.3(3)
C (8)-C (9)-C(14)	114.9(4)	115.4(3)	115.3(3)
C(10)-C (9)-C(14)	127.4(5)	126.1(3)	125.8(3)
C (9)-C(10)-C(11)	118.8(5)	118.2(3)	119.1(3)
C(10)-C(11)-C(12)	123.5(6)	123.2(4)	122.4(4)
C(11)-C(12)-C(13)	117.8(5)	118.3(3)	117.9(3)
C (1)-C(13)-C (8)	106.7(4)	106.5(3)	107.2(3)
C (1)-C(13)-C(12)	134,6(5)	134.6(3)	133.4(3)
C (8)-C(13)-C(12)	118.4(4)	118.4(3)	119.0(3)
C (9)-C(14)-C(15)	114.9(4)	116.4(3)	117.2(3)
C (9)-C(14)-O (2)	125.6(5)	124.9(3)	124.6(3)
C(15)-C(14)-O (2)	119.6(5)	118.8(3)	118.3(3)
C(14)-C(15)-O (1)	112.1(4)	115.8(3)	114.6(3)
C(14)-C(15)-C(15′)[c]	—	108.2(3)	108.5(3)
O (1)-C(15)-C(15′)[c]	—	107.8(3)	106.7(3)
C (7)-O (1)-C(15)	101.5(3)	108.9(2)	109.2(2)

a) A and B represent halves of the **2** molecule. b) The value between the atoms related by the local two-fold axis within a molecule. c) Prime represents the atom of the other half within the molecule.

methine protons (J=1.7 Hz and J=6.9 Hz) seem to be consistent with ∠H-C(15)-C(16)-H=−99° and ∠H-C(16)-C(17)-H=146°, respectively.

Experimental

The formations and isolations of **1** and **2** have been reported.[3] ^{1}H NMR of **2** ($CDCl_3$) δ=4.42 (s, 2H), 6.32 (d, 2H), 6.8—8.0 (m, 12H).

Crystal Data. Adduct(**1**); $C_{25}H_{18}O_4$, M=382.4, triclinic, $P\bar{1}$, a=13.287(4), b=8.794(3), c=8.797(3) Å, α=109.78(3), β=82.17(3), γ=88.58(3)°, V=955.4 Å^3, Z=2, D_o=1.33 g/cm^3. D_c=1.33 g/cm^3. Dimer(**2**); $C_{30}H_{16}O_4$, M=440.5, triclinic, $P\bar{1}$, a=10.401(2), b=12.425(3), c=8.564(2) Å, α=103.77(4), β=108.76(4), γ=95.06(4)°, V=1001.4 Å^3, Z=2, D_o=1.46 g/cm^3, D_c=1.46 g/cm^3.

Crystallographic Measurements. The unit-cell constants and intensities of both crystals were measured with Ni-filterd Cu $K\alpha$ radiation on a Rigaku four-circle diffractometer. The intensities were measured with a θ-2θ scan technique up to 2θ=120° for **1** and 2θ=108° for **2**. The backgrounds for each reflection were measured for 5 s at both ends of the scan range. Reflections which were monitored every 100 reflections showed no significant variation in intensity during data collection. The intensities were corrected for the Lorentz and polarization factors.

Structure Determination of 1. The structure was solved by the vector-search method,[8] followed by a successive Fourier synthesis. Out of 2829 independent reflections, 2141 reflections whose intensities were greater than $3\sigma(I_o)$ were used for the refinement. The block-diagonal least-squares refinement[9] was made with anisotropic temperature factors for non-hydrogen atoms. The hydrogen atoms were located in the difference Fourier synthesis and included in a refinement with the isotropic temperature factors. Five of the strongest reflections were corrected for the extinction effect(g=3.7×10^{-6}). The weighting scheme used in the final cycle of the refinement was w=1.0 for $0<F_o\leqq20$ and $w=[1.0+0.2(F_o-20)]^{-1}$ for $F_o>20$. The final R value was 0.067 for 2141 reflections. The final atomic parameters are given in Table 2.[5]

Structure Determination of 2. The solution and refinement of the structure of **2** was done in the same way as that of **1**. The weighting scheme used in the final cycle of the refinement was w=0.4 for F_o=0, w=1.0 for $0<F_o\leqq7$, and $w=[1.0+0.36(F_o-7)]^{-1}$ for $F_o>7$. However, six of the

Table 2. Final Atomic Coordinates and Equivalent Temperature Factors of the Adduct (**1**)

$$B_{\text{eq}} = \frac{4}{3}\sum_i \sum_j \beta_{ij}\boldsymbol{a}_i\boldsymbol{a}_j$$

	x	y	z	B_{eq}/Å^2
C (1)	0.2376(3)	−0.1393(5)	0.2915(5)	3.7
C (2)	0.2800(4)	−0.2973(6)	0.2124(6)	5.1
C (3)	0.3679(4)	−0.3450(6)	0.2589(7)	5.3
C (4)	0.4113(4)	−0.2387(6)	0.3825(6)	4.8
C (5)	0.3701(3)	−0.0789(5)	0.4613(6)	3.9
C (6)	0.2829(3)	−0.0313(5)	0.4165(5)	3.3
C (7)	0.2243(3)	0.1323(5)	0.4746(5)	3.2
C (8)	0.1328(3)	0.0955(5)	0.3939(5)	3.1
C (9)	0.0441(3)	0.1967(5)	0.4402(6)	3.7
C(10)	−0.0371(4)	0.1451(7)	0.3522(7)	4.8
C(11)	−0.0245(4)	−0.0004(7)	0.2271(7)	5.4
C(12)	0.0628(5)	−0.1064(6)	0.1868(6)	4.8
C(13)	0.1425(3)	−0.0573(5)	0.2769(5)	3.8
C(14)	0.0434(3)	0.3404(6)	0.5864(6)	4.1
C(15)	0.1442(3)	0.3605(5)	0.6587(5)	3.6
C(16)	0.2240(3)	0.4234(5)	0.5504(5)	3.2
C(17)	0.2865(3)	0.2669(5)	0.4359(5)	2.8
C(18)	0.3098(3)	0.2502(5)	0.2582(5)	3.1
C(19)	0.4095(4)	0.2051(6)	0.1771(6)	4.2
C(20)	0.4341(4)	0.1936(6)	0.0141(6)	5.2
C(21)	0.3608(4)	0.2275(6)	−0.0674(5)	4.9
C(22)	0.2614(4)	0.2699(6)	0.0108(5)	4.5
C(23)	0.2357(3)	0.2821(5)	0.1724(5)	3.8
C(24)	0.2892(3)	0.5407(5)	0.6553(5)	3.9
C(25)	0.2917(4)	0.8118(6)	0.8351(6)	5.6
O (1)	0.1914(2)	0.2072(3)	0.6488(3)	3.5
O (2)	−0.0283(2)	0.4405(4)	0.6521(5)	5.6
O (3)	0.2379(2)	0.6828(4)	0.7345(4)	5.0
O (4)	0.3750(3)	0.5147(5)	0.6678(6)	7.5

Table 3. Final Atomic Coordinates and Equivalent Temperature Factors of the Dimer (**2**)

$$B_{\text{eq}} = \frac{4}{3}\sum_i \sum_j \beta_{ij}\boldsymbol{a}_i\boldsymbol{a}_j$$

	x	y	z	B_{eq}/Å^2
C (1A)	0.2181(3)	−0.1007(3)	0.5319(4)	3.6
C (2A)	0.1552(4)	−0.0605(3)	0.6503(4)	4.5
C (3A)	0.1520(4)	−0.1195(3)	0.7677(4)	5.0
C (4A)	0.2123(4)	−0.2144(3)	0.7707(4)	4.6
C (5A)	0.2735(3)	−0.2564(3)	0.6523(4)	3.8
C (6A)	0.2749(3)	−0.1989(2)	0.5318(3)	3.2
C (7A)	0.3259(3)	−0.2277(2)	0.3832(4)	3.1
C (8A)	0.3225(3)	−0.1218(2)	0.3293(4)	3.3
C (9A)	0.3961(3)	−0.0899(3)	0.2342(4)	3.9
C(10A)	0.3823(4)	0.0123(3)	0.1943(4)	4.6
C(11A)	0.2981(4)	0.0777(3)	0.2562(4)	4.9
C(12A)	0.2337(4)	0.0498(3)	0.3644(4)	4.4
C(13A)	0.2488(3)	−0.0507(2)	0.4051(4)	3.6
C(14A)	0.4915(3)	−0.1647(3)	0.1964(4)	4.1
C(15A)	0.5061(3)	−0.2620(3)	0.2806(4)	3.8
O (1A)	0.4659(2)	−0.2481(2)	0.4287(2)	3.4
O (2A)	0.5568(3)	−0.1553(2)	0.1046(3)	5.9
C (1B)	0.0106(3)	−0.4019(3)	0.2404(4)	3.5
C (2B)	−0.1277(3)	−0.4063(3)	0.2173(4)	4.5
C (3B)	−0.1964(3)	−0.3312(3)	0.1413(4)	4.8
C (4B)	−0.1305(3)	−0.2538(3)	0.0897(4)	4.9
C (5B)	0.0094(3)	−0.2481(3)	0.1105(4)	3.9
C (6B)	0.0782(3)	−0.3232(2)	0.1867(3)	3.2
C (7B)	0.2298(3)	−0.3330(2)	0.2333(3)	3.0
C (8B)	0.2311(3)	−0.4381(2)	0.2880(3)	3.2
C (9B)	0.3341(3)	−0.5024(2)	0.2967(4)	3.4
C(10B)	0.3203(4)	−0.6003(3)	0.3465(4)	4.2
C(11B)	0.2033(4)	−0.6315(3)	0.3798(4)	4.8
C(12B)	0.0932(4)	−0.5719(3)	0.3555(4)	4.4
C(13B)	0.1078(3)	−0.4744(2)	0.3047(4)	3.4
C(14B)	0.4383(3)	−0.4681(3)	0.2267(4)	3.9
C(15B)	0.4178(3)	−0.3694(3)	0.1464(4)	3.7
O (1B)	0.2775(2)	−0.3492(2)	0.0913(2)	3.3
O (2B)	0.5380(2)	−0.5125(2)	0.2276(3)	5.0

strongest reflections (which seemed to be affected by the extinction effect) were omitted from the refinement. The final R value was 0.058 for 2301 independent reflections. The final stomic parameters are given in Table 3.[5] The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[10]

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