Improved Synthesis and Crystal Structure of 7*H*-Dibenz[*a,kl*]anthracen-7-one

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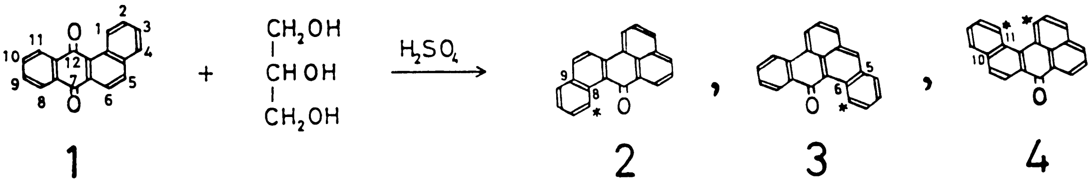
An improved synthetic method gives pure 7*H*-dibenz[*a,kl*]anthracen-7-one, $C_{21}H_{12}O$, in a higher yield than those reported so far. The crystal structure has been determined by X-ray analysis. The space group is $Pn2_1a$, with unit cell dimensions of a=23.325(5), b=14.149(3), c=3.986(1) Å, and Z=4. The structure was solved by the direct method and refined by the block-diagonal least-squares method to an R value of 0.044. The molecule is greatly distorted from the planar conformation because of an intramolecular steric repulsion between the hydrogen atoms.

Bradley *et al.* reported[1)] that the condensation of benz[*a*]anthracene-7,12-dione (**1**) with glycerol and concentrated sulfuric acid gave two products; 7*H*-benzo[*hi*]chrysen-7-one (8,9-BzBT, **2**) and 13*H*-dibenz[*a,de*]anthracen-13-one (5,6-BzBT, **3**). In this case, the cyclization in the 11 and 12 positions of **1** should occur to produce 7*H*-dibenz[*a,kl*]anthracen-7-one (10,11-BzBT, **4**), although they did not mention it. Clar *et al.* reported[2)] that 10,11-BzBT was prepared by decarboxylating its 13-carboxylic acid, which had itself been produced by the partial cyclization of 1,1′-binaphthyl-8,8′-dicarboxylic acid. However, this method requires many steps and gives only a poor yield. We reexamined the method reported by Bradley *et al.* and obtained 10,11-BzBT in a satisfactory yield.

Previously, we determined the crystal structures of 8,9-BzBT[3)] and 5,6-BzBT.[4)] These compounds are distorted from the planar conformation because of a steric repulsion between O and H, which are indicated by *. In 10,11-BzBT, the distortion from the planar structure is expected to be caused by the repulsion between the hydrogen atoms with *. The present paper deals with the crystal structure of **4** in comparison of the distortion modes with those of 8,9-BzBT and 5,6-BzBT.



Experimental

Synthesis of o-(1-Naphthoyl)benzoic Acid. A mixture containing naphthalene (25.0 g) and finely powdered anhydrous aluminum chloride (50.0 g) was dissolved in 120 ml of 1,1,2,2-tetrachloroethane, into which phthalic anhydride (25.0 g) was added with stirring, the temperature being kept below 10 °C for 2 h. Then the mixture was kept at 20 °C for 8 h. The contents were poured into water (300 ml) containing a small amount of hydrochloric acid, and the whole was steam-distilled. The cold residue was extracted with a small amount of 4% aqueous sodium hydroxide, and then concentrated hydrochloric acid was added until the solution was made acidic. After the solution had stood overnight, the precipitated *o*-(1-naphthoyl)benzoic acid was collected and washed with water. Recrystallization from glacial acetic acid gave the *o*-(1-naphthoyl)benzoic acid as white plates; mp 175—176 °C (uncorrected). Yield, 42.7 g.

Synthesis of Benz[a]anthracene-7,12-dione. *o*-(1-Naphthoyl)benzoic acid (21.0 g) was mixed with concentrated sulfuric acid (210 ml), and the mixture was heated to 65 °C for 4 h. After cooling, the contents were poured into water (1 l). The precipitate was collected and washed thoroughly with water. The crude product (7.2 g) was then boiled for 2 h with glacial acetic acid. Yield, 6.0 g; green yellow needles; mp 167—168 °C.

*Glycerol Condensation of Benz[*a*]anthracene-7,12-dione.* To a mixture of benz[*a*]anthracene-7,12-dione (5.0 g), aniline (5.0 g), and 80% sulfuric acid (140 g), glycerol (14.0 g) was added, drop by drop, at 50 °C. The mixture was then heated at 100 °C for 8 h. After cooling, the contents were poured into a large amount of water, collected, and washed with hot water. The crude product (3.2 g), a brown mass with a mp of 123—153 °C, was extracted with acetone (50 ml). The extraction was carried

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out by means of hot filtration. The filtrate, on evaporation to dryness, gave a dark brown mass (1.4 g). A chlorobenzene solution of this product was passed through a column of silica-gel (300 mesh) and eluted with chlorobenzene. The products was developed into three bands. The red band was separated and concentrated, giving red needles. Yield 0.2 g; mp 197—198 °C. The intense yellow band, overlapping with a pale yellow band, was eluted with chlorobenzene and concentrated to give a yellow mass (1.1 g); mp 162—168 °C. This product was dissolved in a large amount of ethanol, and the solution was put into a column of alumina. The absorbed layer was developed into two bands; the lower layer, an intense yellow band, was separated and concentrated to give intense yellow needles. Yield, 0.3 g; mp 183—184 °C. The upper layer, a pale yellow band, gave pale yellow needles. Yield 0.7 g; mp 188—189 °C. The red needles (mp 197—8 °C) and the intense yellow needles (mp 183—4 °C) were proved to be 5,6-BzBT[4] and 8,9-BzBT[3], respectively. Thus, the pale yellow needles (mp 188—9 °C) were assumed to be 10,11-BzBT.

X-Ray Data Collection of 10,11-BzBT. The crystals (mp 188—9 °C) were grown from an ethanol solution. Crystals; $C_{21}H_{12}O$, M.W. 280.3, orthorhombic, a=23.325(5), b=14.149(3), c=3.986(1) Å, and U=1315.4(5) Å^3, D_x=1.415 g cm^{-3}; Z=4; space group, Pn2$_1$a; μ(Mo $K\alpha$)=0.90 cm^{-1}. The intensity data were collected on a Rigaku automated four-circle diffractometer, using the $\omega/2\theta$ scan technique with a scanning rate of 4° (2θ) min^{-1}. The crystal size was 0.5×0.3×0.1 mm. A total of 1220 independent reflections were measured (up to 2θ=55°) using graphite monochromated Mo $K\alpha$ radiation, of which 656 reflections with $|F_o|>3\sigma$ ($|F_o|$) were used for the analysis. Correction was made for the Lorentz and polarization factors, but not for absorption.

Structure Determination

The systematic absences of $0kl$ ($k+l=2n+1$) and $hk0$ ($h=2n+1$) indicated the space group to be Pnma or Pn2$_1$a. The packing consideration suggested a non-centrosymmetric arrangement, and the structure was successfully refined on the basis of the space group Pn2$_1$a. The structure was determined by the direct method, with the MULTAN78 program[5], and was refined by the block-diagonal least-squares method. The coordinates of the hydrogen atoms were derived from an idealized geometry and refined with the isotropic temperature factor. The final R became 0.044. No peaks higher than 0.3 eÅ^{-3} were found on the final difference map. The atomic-scattering factors were taken from Ref. 6. The final atomic parameters, with their standard deviations, are listed in Table 1. Lists of the observed and calculated structure factors, the anisotropic thermal parameters for the non-H atoms, and the positional parameters for the H atoms are deposited as Document No. 8547 at the office of the Chemical Society of Japan.

TABLE 1. FINAL ATOMIC COORDINATES, WITH THEIR ESTIMATED STANDARD DEVIATIONS, MULTIPLIED BY 10^4 AND 10 FOR B_{eq}

Atom	x	y	z	B_{eq}/Å^2 a)
C (1)	1086 (2)	5879 (4)	4212 (17)	37 (2)
C (2)	1481 (3)	5202 (4)	5337 (18)	43 (2)
C (3)	1963 (3)	5473 (4)	7027 (18)	41 (2)
C (4)	2590 (2)	6736 (5)	9007 (18)	45 (2)
C (5)	2726 (3)	7682 (5)	9267 (18)	44 (2)
C (6)	2353 (2)	8362 (4)	7914 (17)	37 (2)
C (7)	1482 (2)	8788 (4)	4724 (18)	37 (2)
C (8)	601 (3)	9190 (4)	1755 (16)	39 (2)
C (9)	67 (3)	8970 (4)	609 (18)	40 (2)
C (10)	−178 (3)	8071 (4)	1283 (16)	36 (2)
C (11)	155 (2)	7373 (4)	2888 (15)	33 (2)
C (12)	749 (2)	7556 (4)	3670 (15)	30 (1)
C (13)	1152 (2)	6840 (4)	4789 (15)	31 (1)
C (14)	1682 (2)	7119 (4)	6283 (15)	31 (1)
C (15)	2077 (2)	6446 (4)	7445 (15)	34 (2)
C (16)	1848 (2)	8090 (4)	6382 (15)	32 (1)
C (17)	933 (2)	8486 (4)	3349 (15)	34 (2)
C (18)	−749 (3)	7866 (5)	332 (16)	43 (2)
C (19)	−999 (2)	7024 (5)	1102 (17)	43 (2)
C (20)	−698 (3)	6376 (4)	3043 (17)	42 (2)
C (21)	−134 (2)	6531 (4)	3911 (15)	36 (2)
O	1641 (2)	9613 (3)	4482 (14)	53 (1)

a) The equivalent isotropic temperature factors were computed using the following expression: $B_{eq}=1/3\sum_{ij}a_ia_ja_i^*a_j^*$.

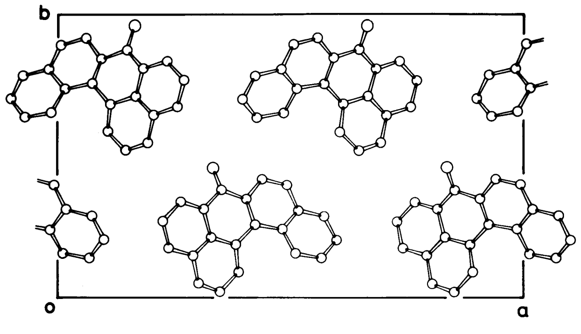

Fig. 1. Projection of the crystal structure along the c axis.

Results and Discussion

The present study has established the structure of **4**. This method is convenient for preparing not only 5,6-BzBT and 8,9-BzBT, but also 10,11-BzBT, since it gives pure 10,11-BzBT more easily and in a higher yield than the method described in Ref. 2.

Figure 1 illustrates the crystal structure of 10,11-BzBT viewed along the c axis. Molecules are stacked face-to-face along the c axis. The overlapping mode is shown in Fig. 2. The stacking disorder found in the crystals of 8,9-BzBT and 5,6-BzBT is not observed here. There are two dimer pairs of molecules with different populations in the crystals of 8,9-BzBT and 5,6-BzBT. The mean interplanar distance is 3.582 Å, which is larger than that of 3.47 Å between the molecules with larger populations in 8,9-BzBT and 5,6-BzBT. There are no unusually short contacts between the molecules.

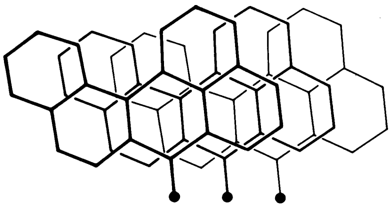

Fig. 2. Overlapping mode.

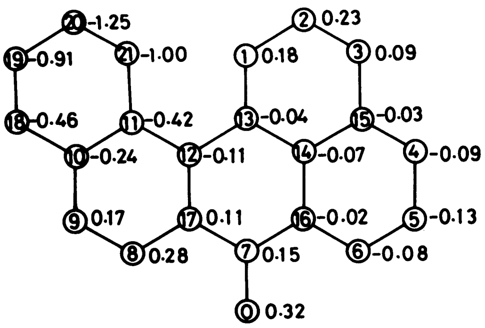

Fig. 3. Deviations of the atoms (l/Å) from the mean molecular plane.

The deviations of the atoms from the mean molecular plane are shown in Fig. 3. The bond distances and angles are listed in Tables 2 and 3 respectively. The molecules are greatly distorted from a planar conformation because of the steric repulsion, which is known as 1,7 interaction. The repulsion is released mainly by the enlargement of the C(1)–C(13)–C(12), C(11)–C(12)–C(13), and C(12)–C(11)–C(21) angles and the distortion from the planar conformation. The degree of the distortion was defined as the twisting angle around the pseudo bond of C(11)···C(13).[7] The angle of C(1)–C(13)···C(11)–C(21) is 33.4°. The corresponding angles (O–C···C–C) in 8,9-BzBT and 5,6-BzBT are 8.2° (Molecule A) and 6.3° (Molecule B) in the former, and 6.0° in the latter. These values are considerably smaller than that of

Table 2. Bond lengths (l/Å), with their estimated standard deviations

C (1)-C (2)	1.403(10)	C (9) -C (10)	1.420(10)
C (1)-C (13)	1.387(9)	C (10)-C (11)	1.409(9)
C (2)-C (3)	1.366(10)	C (10)-C (18)	1.415(9)
C (3)-C (15)	1.412(9)	C (11)-C (12)	1.445(8)
C (4)-C (5)	1.379(10)	C (11)-C (21)	1.428(9)
C (4)-C (15)	1.411(9)	C (12)-C (13)	1.453(9)
C (5)-C (6)	1.406(10)	C (12)-C (17)	1.389(8)
C (6)-C (16)	1.383(9)	C (13)-C (14)	1.427(9)
C (7)-C (16)	1.463(9)	C (14)-C (15)	1.404(9)
C (7)-C (17)	1.456(9)	C (14)-C (16)	1.427(9)
C (7)-O	1.228(9)	C (18)-C (19)	1.362(9)
C (8)-C (9)	1.363(10)	C (19)-C (20)	1.390(9)
C (8)-C (17)	1.414(9)	C (20)-C (21)	1.377(9)

Table 3. Bond angles (ϕ/°) with their estimated standard deviations

C (2)-C (1)-C (13)	122.8(7)	C (1)-C (13)-C (12)	124.0(6)
C (1)-C (2)-C (3)	120.5(7)	C (1)-C (13)-C (14)	116.0(6)
C (2)-C (3)-C (15)	119.1(7)	C (12)-C (13)-C (14)	119.7(6)
C (5)-C (4)-C (15)	120.7(7)	C (13)-C (14)-C (15)	121.2(6)
C (4)-C (5)-C (16)	119.6(7)	C (13)-C (14)-C (16)	120.8(6)
C (5)-C (6)-C (16)	120.5(7)	C (15)-C (14)-C (16)	117.8(6)
C (16)-C (7)-C (17)	118.9(6)	C (3)-C (15)-C (4)	119.7(6)
C (16)-C (7)-O	120.1(7)	C (3)-C (15)-C (14)	120.0(6)
C (17)-C (7)-O	121.0(7)	C (4)-C (15)-C (14)	120.3(6)
C (9)-C (8)-C (17)	119.4(6)	C (6)-C (16)-C (7)	120.6(6)
C (8)-C (9)-C (10)	120.6(6)	C (6)-C (16)-C (14)	120.7(6)
C (9)-C (10)-C (11)	119.5(6)	C (7)-C (16)-C (14)	118.7(6)
C (9)-C (10)-C (18)	120.7(6)	C (7)-C (17)-C (8)	116.3(6)
C (11)-C (10)-C (18)	119.8(6)	C (7)-C (17)-C (12)	121.0(6)
C (10)-C (11)-C (12)	120.1(6)	C (8)-C (17)-C (12)	122.6(6)
C (10)-C (11)-C (21)	117.1(6)	C (10)-C (18)-C (19)	121.5(7)
C (12)-C (11)-C (21)	122.7(6)	C (18)-C (19)-C (20)	119.0(7)
C (11)-C (12)-C (13)	124.3(6)	C (19)-C (20)-C (21)	121.2(7)
C (11)-C (12)-C (17)	116.5(6)	C (11)-C (21)-C (20)	120.7(6)
C (13)-C (12)-C (17)	119.2(6)		

TABLE 4. COMPARISON OF STERIC HINDRANCE

Molecule	ϕ/°	d(C···C)/Å
1	41.0	2.971
	41.5	2.944
2a) A	39	3.01
B	30	2.87
3a) A	30.1	2.94
B	37.6	2.96
4	31.4	3.03
5	33.4	2.993

1): Tetrabenzo[*a*,*cd*,*j*,*lm*]perylene,8) 2): Diphenanthro-[5,4,3-*abcd*: 5′,4′,3′-*jklm*]perylene,9) 3): Anthra[2,1,9,8-*hijkl*]benzo[*de*]naphtho[2,1,8,7-*stuv*]pentacene,7) 4): Benzo[*c*]phenanthrene,10) 5): This molecule.

a) A and B indicate the crystallographically independent molecules.

10,11-BzBT. On the other hand, similar distortion modes are observed in several related molecules, whose twisting angles are listed in Table 4 together with the C···C distances. The 1,7 interaction appears to play an important role in the distortion of such overcrowded molecules.

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