The Crystal and Molecular Structure of Naphthanthrone

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The crystals of naphthanthrone($C_{19}H_{10}O$) are orthorhombic, with the $P2_12_12_1$ space group and these lattice constants: $a=17.345(17)$, $b=3.973(13)$, $c=17.392(14)$ Å, and $Z=4$. The structure was solved by the Patterson method and refined by a block-diagonal least-squares program to give an R-value of 0.085 on the basis of the 897 observed reflections collected by Weissenberg photographs. The molecule is planar within the limits of experimental error and has an approximate symmetry of mm. The molecules are stacked face-to-face by van der Waals forces along the b-axis. The interplanar spacing is 3.50 Å.

The bimolecular condensation of benzanthrone (7*H*-benz[*de*]anthracen-7-one) affords condensation products with nine benzene rings. Similarly, naphthanthrone (6*H*-benzo[*cd*]pyren-6-one) gives products with eleven benzene rings. They are useful and interesting materials in the field of organic semiconductors. It is, therefore, desirable to know the crystal structures of these products and also those of the starting materials in order to study the intrinsic behavior of their electrical conduction. It may be suggested that symmetric naphthanthrone molecules are probably more closely packed in the crystal, since its melting point is 252 °C and far higher than that of benzanthrone (169 °C), in spite of the fact that the former molecule is larger than the latter one by only one additional benzene ring. From these points of view, the present investigation was carried out.

Experimental

The naphthanthrone was prepared by the condensation of pyrene and glycerol in sulfuric acid.[1] The crude product was dissolved in toluene and passed through a column of alumina to obtain the purified crystals. The crystals thus obtained were recrystallized from toluene. After several repetitions of this purification process, crystals suitable for X-ray work were selected.

The unit-cell dimensions were determined from the higher-order reflections on Weissenberg photographs calibrated by reflections from a Cu wire. The systematic absences were: $h00$ for h odd, $0k0$ for k odd and $00l$ for l odd.

Crystal data

$C_{19}H_{10}O$, $M=254.29$, mp 252 °C, Space Group: $P2_12_12_1$, $Z=4$; $a=17.345(17)$, $b=3.973(13)$, $c=17.392(14)$ Å, $U=1199$ Å^3; $D_x=1.409$, $D_m=1.42$ g cm^{-3}, $F(000)=528$, $\mu(\mathrm{Cu}\,K\alpha)=7.1$ cm^{-1}

The crystal used for X-ray work had dimensions of approximately $0.1\times0.1\times0.8$ mm. Sets of multiple-film equi-inclination Weissenberg photographs were taken about the b-axis (0th to 3rd layers) and about the c-axis (0th to 3rd layers). Cu $K\alpha$ radiation was employed throughout. The intensities were estimated by means of a Rigaku photometer MP3. Weak intensities were visually estimated with standard film strip. They were corrected for Lorentz and polarization factors, but no absorption correction was applied. The range of relative intensities was from 1 to 50000. 897 independent reflections fell within this range, whereas 429 others were too weak to be observed.

Structure Determination and Refinement

The orientation of the molecule was easily deduced from the three-dimensional Patterson maps, but the position of the center of gravity could not be fixed. Therefore, some two-dimensional models were assumed. One of them gave an R_{h0l}-value of 0.45. After two cycles of calculations of the structure factors and the electron densities $\rho(xz)$, the R_{h0l}-value dropped to 0.20. At this stage, the y coordinates of the molecule were calculated, taking the tilt and the packing into account. Structure factor calculations gave the R-value of 0.25.

The structure was refined by a block-diagonal least-squares method with a HBLS4 program written by Dr. Tamaichi Ashida. After six cycles of refinements, the R-value dropped to 0.15. Three more cycles of refinements with anisotropic temperature factors gave the R-value of 0.12. At this stage, the difference synthesis revealed all the hydrogen atoms. Further refinement cycles with isotropic temperature factors for hydrogen atoms reduced R to 0.085. The following weighting scheme was employed: $w=0.4$ if $F_0<F_{\min}(=4.0)$, otherwise $w=1.0$. The atomic scattering factors were taken from "*International Table for X-Ray Crystallography*" (1962).[2] The observed and calculated structure factors are listed in Table 1.** The final atomic parameters and their estimated standard deviations are summarized in Table 2.

Description of the Structure and Discussion

Figure 1 illustrates the structure projected along the b-axis. The molecules are stacked face-to-face by van der Waals forces along the b-axis. The interplanar spacing is 3.50 Å. It is slightly greater than the 3.44 and 3.45 Å of violanthrone[3] and the 3.42 Å of isoviolanthrone.[4] Figure 2 shows the superposition of the molecules.

The closest approach between the molecules occurs between O and C(11)($1-x$, $1/2+y$, $1/2-z$), the distance being 3.355 Å. Such short contacts between an oxygen atom and a carbon atom have been found in the crystals of the quinones observed hitherto.[3,5-7]

The bond lengths and angles in the molecule are shown in Figs. 3 and 4, together with estimated standard deviations. The average C–C bond length, 1.408 Å, is comparable to the value, 1.409 Å, of tetrabenzo-[*a*, *cd*, *j*, *lm*]perylene.[8] The bond lengths of C(17)–

** Table 1 has been deposited with the office of the Chemical Socity of Japan, 1-5 Kanda-Surugadai, Chiyoda-ku, Tokyo 113 (Document No. 7634).

TABLE 2. ATOMIC PARAMETERS

(a) Positional and thermal parameters for non-hydrogen atoms ($\times 10^4$), with e. s. d.'s in parentheses. The β_{ij}'s are defined by $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	1198(5)	1860(26)	4791(5)	54(4)	950(93)	53(4)	83(19)	25(4)	49(18)
C(2)	827(5)	3570(29)	4200(5)	45(4)	1066(97)	64(4)	−47(20)	3(4)	−24(22)
C(3)	1226(5)	4274(24)	3511(5)	45(4)	574(72)	49(4)	−35(15)	1(3)	−14(15)
C(4)	848(5)	5966(28)	2901(5)	46(4)	1060(97)	63(4)	23(21)	−2(4)	−23(21)
C(5)	1253(5)	7754(27)	2242(5)	62(5)	867(93)	57(4)	15(20)	−18(4)	−36(19)
C(6)	2032(5)	5757(25)	2153(4)	51(4)	807(82)	41(3)	6(17)	−7(3)	−58(16)
C(7)	2393(4)	4104(23)	2751(4)	40(3)	733(77)	31(3)	8(15)	−2(3)	−38(14)
C(8)	3194(5)	3181(24)	2646(4)	49(4)	813(82)	31(3)	−48(16)	1(3)	−31(14)
C(9)	3584(4)	1342(24)	3301(4)	33(3)	774(73)	33(3)	−37(15)	−2(3)	−25(14)
C(10)	4343(5)	430(24)	3226(5)	43(4)	813(83)	44(3)	−6(16)	−2(3)	−14(16)
C(11)	4720(5)	−1170(26)	3831(5)	40(4)	789(80)	55(4)	15(17)	−4(3)	−67(17)
C(12)	4323(5)	−1944(25)	4501(5)	45(4)	862(86)	49(4)	20(17)	−10(3)	−34(17)
C(13)	3545(5)	−936(25)	4591(4)	52(4)	921(81)	31(3)	−51(18)	−5(3)	−37(15)
C(14)	3175(4)	728(22)	3979(4)	38(3)	557(65)	30(3)	−23(14)	0(3)	−46(12)
C(15)	2388(4)	1649(22)	4055(4)	42(3)	643(73)	35(3)	−20(14)	4(3)	−31(14)
C(16)	2001(4)	3343(23)	3429(4)	49(3)	813(71)	31(3)	−48(13)	1(3)	−31(14)
C(17)	3117(5)	−1567(26)	5272(5)	64(5)	816(85)	41(3)	−43(18)	−6(4)	−33(16)
C(18)	2380(5)	−678(26)	5342(4)	59(4)	955(88)	34(3)	−40(18)	4(3)	23(16)
C(19)	1979(5)	926(25)	4733(4)	47(4)	777(77)	41(3)	−39(17)	6(3)	−22(16)
O	3553(3)	3753(19)	2036(3)	56(3)	1172(66)	43(2)	17(14)	7(3)	−9(13)

(b) Positional parameters for the hydrogen atoms ($\times 10^3$).
The mean isotropic temperature factor for the hydrogen atoms is 4.7(2.3) Å^2.

	x	y	z		x	y	z
H(C1)	85(5)	95(25)	526(4)	H(C10)	470(4)	95(22)	271(4)
H(C2)	19(4)	365(26)	421(4)	H(C11)	530(4)	−206(25)	381(4)
H(C4)	25(4)	644(22)	300(4)	H(C12)	467(5)	−344(26)	497(5)
H(C5)	101(4)	788(23)	179(4)	H(C17)	345(5)	−249(26)	564(5)
H(C6)	243(4)	609(20)	164(4)	H(C18)	198(4)	−131(24)	576(4)

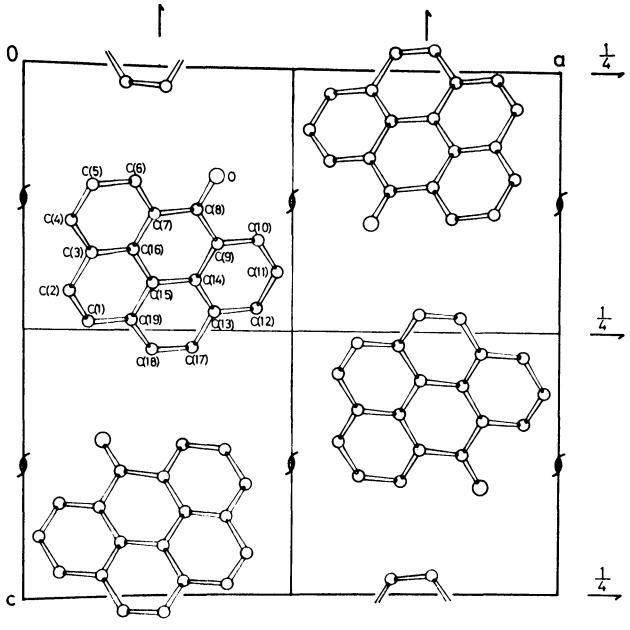

Fig. 1. A projection of the structure along the b-axis.

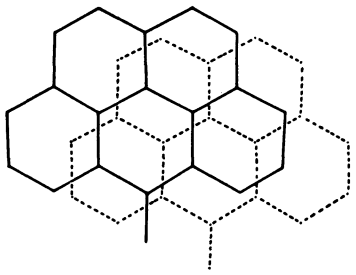

Fig. 2 Superposition of the naphthanthrone molecules.

C(18), C(14)–C(15), and C(8)–C(7) increase in that order (1.333→1.419→1.448 Å). The C(1)–C(2), C-(15)–C(16), and C(8)–C(9) bonds also show a similar tendency, their bond lengths are 1.390, 1.445, and 1.513 Å respectively. Similarly, such tendencies have been observed in dinaphthperopyrene (1.387→1.423→1.472 Å)[9] and tetrabenzo[*a*, *cd*, *j*, *lm*]perylene (1.348→1.418→1.474 Å).[8] The C–C–C angles range from 117.2° to 122.5°, and the three bonds around each carbon are coplanar within the limits of experimental error. Figure 5 shows the deviation of each atom from the mean plane of the molecule. The equation of the mean molecular plane is: $-0.2831x-$

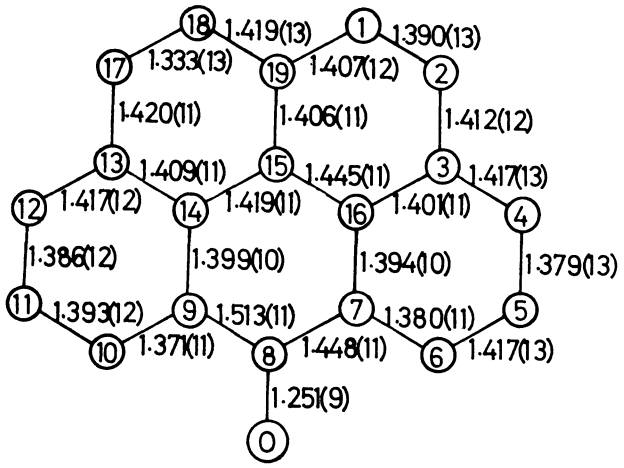

Fig. 3. Bond lengths (l/Å) with their estimated standard deviations.

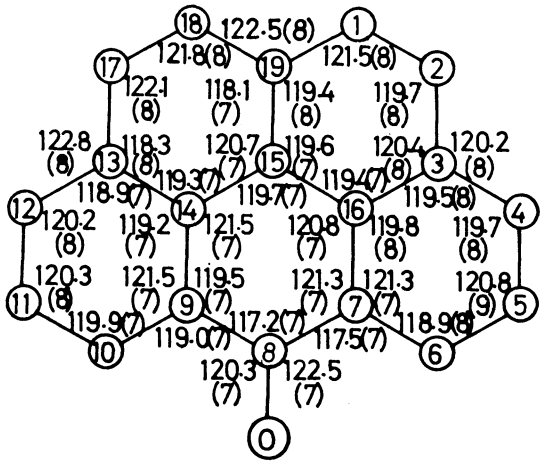

Fig. 4. Bond angles (φ/°) with their estimated standard deviations.

$0.8813y-0.3783z+4.421=0.0$, where x, y, and z are coordinates in Å units referred to the crystal axes, a, b, and c respectively.

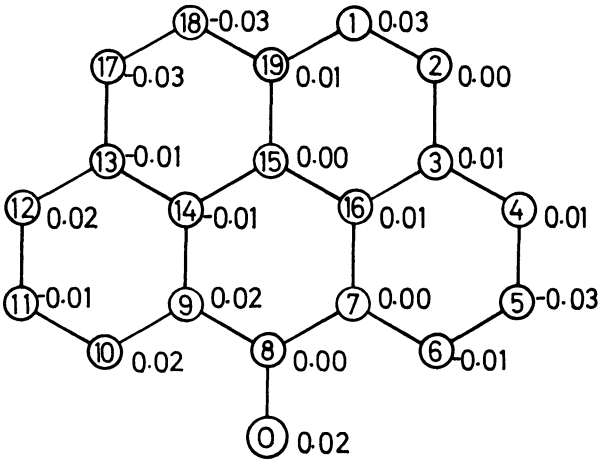

Fig. 5. Distances (l/Å) of atoms from the mean molecular plane.

All the calculations were carried out on a HITAC 8700/8800 at the Computer Center of University of Tokyo with a local version of the Universal Crystallographic Computation Program System, UNICS (1967).

References

1) W. Bradley and F. K. Sutcliffe, *J. Chem. Soc.*, **1951**, 2118.
2) "International Tables for X-Ray Crystallography," Vol. III, Birmingham, Kynoch Press (1962).
3) W. Bolten and H. P. Stadler, *Acta Crystallogr.*, **17**, 1015 (1964).
4) W. Bolten, *Acta Crystallogr.*, **17**, 1020 (1964).
5) I. A. S. Edwards and H. P. Stadler, *Acta Crystallogr.*, **B27**, 946 (1971).
6) H. P. Stadler, Solid State Physics, *Bussei*, **5**, 659 (1964).
7) H. P. Stadler, *Acta Crystallogr.*, **6**, 540 (1953).
8) Y. Kohno, M. Konno, Y. Saito, and H. Inokuchi, *Acta Crystallogr.*, **B31**, 2076 (1975).
9) J. M. Robertson and J. Trotter, *J. Chem. Soc.*, **1959**, 2614.