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The Crystal Structure of Phenanthrene: Picric Acid Molecular Complex

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Synopsis. The crystal structure of phenanthrene: picric acid molecular complex was determined by X-ray crystal analysis. Phenanthrene and picric acid molecules are stacked alternately along the c-axis, making their molecular planes parallel to each other. The intramolecular hydrogen bonding exists in a picric acid.

Phenanthrene: picric acid is one of the π-molecular complexes. Three polymorphs at least have been known.[1] Herbstein and Kaftory reported cell dimensions,[2] but crystal structures have not been described. We have tried to elucidate the crystal structure and will report here the results obtained.

Experimental

The components in equimolar ratio were solved in an excess of methanol. Yellow needles were precipitated by evaporation of the solution at room temperature. The diffraction intensities were measured on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation at 23 °C. Crystallographic and other information is summarized in Table 1.

The ω-2θ scan mode with a scan rate of 8° min^{-1} was employed with the ω scan range $(1.1+0.5\tan\theta)°$. A total of 2807 reflections with $|F_o|>3\sigma(|F_o|)$ was collected up to 2θ of 140°. No absorption correction was applied [$\mu(\mathrm{Cu}\,K\alpha)=10.99\,\mathrm{cm}^{-1}$]. The structure was solved by a direct method using the program MULTAN[3] and refined by the block-diagonal least-squares method using initially B_{iso} and finally B_{ij} for non-hydrogen atoms. The difference Fourier synthesis showed two H atoms of phenanthrene and picric acid, and H atom of picric acid OH. The positions of other ten H atoms were calculated and refined. Final R was 0.076 (R_w= 0.083, S=1.045). The function minimized was $\sum w(|F_o|-|F_c|)^2$, where w of 1.0 was used. Atomic scattering factors were quoted from International Tables for X-Ray Crystallography (1974).[4]

Table 1. Crystallographic and Other Information for Phenanthrene: Picric Acid Complex

Molecular formula	$C_{14}H_{10}:C_6H_3N_3O_7$
Formula weight	407.33
Crystal dimensions/mm³	0.3X0.2X0.1
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell dimensions a /Å	8.812(2)
Cell dimensions b /Å	14.546(2)
Cell dimensions c /Å	7.052(1)
Cell dimensions α/°	95.18(2)
Cell dimensions β/°	92.07(2)
Cell dimensions γ/°	97.34(1)
Melting point/°C	146
Density D_m/g cm⁻³	1.50
Density D_x/g cm⁻³	1.517
Z	2
$\mu(\mathrm{Cu}\,K\alpha)/\mathrm{cm}^{-1}$	10.99

Results and Discussion

Cell dimensions are significantly different from those reported by Herbstein and Kaftory (a=8.99, b=14.81, c=7.12 Å, α=101.5, β=99.2, and γ=102.1°). The crystal used in this study is different from that used by Herbstein in morphology. The final atomic

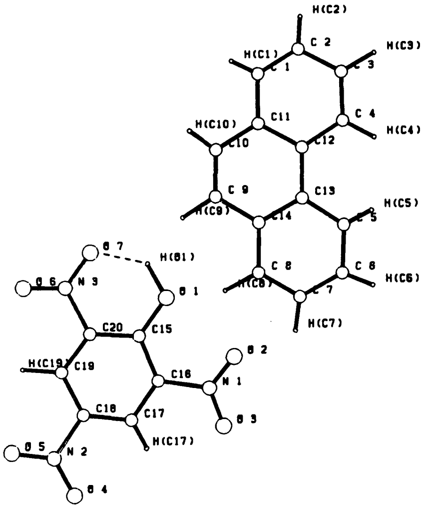

Fig. 1. Atomic numbering and a hydrogen bonding (dashed line).

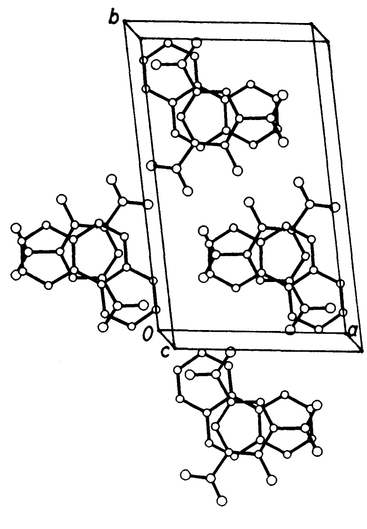

Fig. 2. Arrangement of molecules in the unit cell (some molecules along the edges have been removed for clarity).

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($/\text{Å}^2$) of Phenanthrene: Picric Acid Complex Standard Deviations are in Parentheses

Atom	x	y	z	B_{eq}[a)]	Atom	x	y	z	B_{eq}[a)]
O 1	5518(4)	4270(2)	1017(5)	4.4	C 6	2710(5)	2169(3)	5098(7)	3.8
O 2	8216(5)	5018(3)	2216(12)	10.9	C 7	2820(5)	3140(4)	5110(7)	4.3
O 3	9995(4)	4219(3)	2336(11)	9.9	C 8	4176(6)	3688(3)	5635(7)	3.8
O 4	9138(4)	977(3)	2647(6)	5.5	C 9	6941(5)	3838(3)	6668(6)	3.3
O 5	6898(5)	201(2)	1938(6)	5.7	C10	8173(5)	3448(3)	7155(7)	3.3
O 6	2702(4)	1777(3)	352(6)	5.8	C11	8118(4)	2467(3)	7208(6)	2.6
O 7	2969(4)	3273(3)	182(6)	5.4	C12	6721(4)	1874(3)	6725(6)	2.3
N 1	8676(4)	4296(3)	2150(7)	4.2	C13	5382(4)	2283(3)	6161(6)	2.3
N 2	7785(5)	922(2)	2177(6)	3.9	C14	5503(5)	3270(3)	6158(6)	2.8
N 3	3462(4)	2533(3)	471(6)	4.0	C15	6040(5)	3463(3)	1285(6)	2.9
C 1	9427(5)	2067(3)	7775(7)	3.6	C16	7581(4)	3435(3)	1843(6)	2.7
C 2	9379(5)	1131(4)	7828(7)	4.1	C17	8146(4)	2624(3)	2131(6)	2.9
C 3	8011(6)	541(3)	7358(7)	4.0	C18	7164(5)	1799(3)	1858(6)	2.8
C 4	6701(5)	914(3)	6829(7)	3.1	C19	5643(5)	1765(3)	1312(6)	2.9
C 5	3958(4)	1748(3)	5624(6)	3.0	C20	5119(4)	2591(3)	1032(6)	2.8

a)The equivalent isotropic temperature factors were computed using the following equation:

$$B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha).$$

Table 3. Bond Lengths($/\text{Å}$) and Bond Angles($/°$) of Phenanthrene: Picric Acid Complex Standard Deviations are in Parentheses

O1–C15	1.340(5)	C11–C12	1.421(4)	O2–N1–O3	123.0(4)	C4–C12–C13	122.8(3)
O2–N1	1.170(5)	C12–C13	1.446(5)	O2–N1–C16	119.4(3)	C11–C12–C13	118.9(3)
O3–N1	1.186(5)	C13–C14	1.425(5)	O3–N1–C16	117.6(3)	C5–C13–C12	122.8(3)
O4–N2	1.216(5)	C15–C16	1.407(5)	O4–N2–O5	125.2(4)	C5–C13–C14	118.5(3)
O5–N2	1.220(4)	C15–C20	1.409(5)	O4–N2–C18	117.6(3)	C12–C13–C14	118.7(3)
O6–N3	1.206(5)	C16–C17	1.367(6)	O5–N2–C18	117.3(3)	C8–C14–C9	120.4(3)
O7–N3	1.242(6)	C17–C18	1.381(5)	O6–N3–O7	125.1(3)	C8–C14–C13	119.4(3)
N1–C16	1.474(4)	C18–C19	1.374(5)	O6–N3–C20	117.9(4)	C9–C14–C13	120.2(3)
N2–C18	1.483(5)	C19–C20	1.370(6)	O7–N3–C20	117.0(3)	O1–C15–C16	121.3(3)
N3–C20	1.488(5)			C2–C1–C11	121.4(3)	O1–C15–C20	123.6(3)
C1–C2	1.362(7)			C1–C2–C3	120.1(4)	C16–C15–C20	115.1(3)
C1–C11	1.417(6)			C2–C3–C4	119.8(4)	N1–C16–C15	120.8(3)
C2–C3	1.398(6)			C3–C4–C12	121.4(3)	N1–C16–C17	116.5(3)
C3–C4	1.390(6)			C6–C5–C13	120.7(3)	C15–C16–C17	122.7(3)
C4–C12	1.404(5)			C5–C6–C7	120.9(3)	C16–C17–C18	118.6(3)
C5–C6	1.381(6)			C6–C7–C8	120.4(4)	N2–C18–C17	118.2(3)
C5–C13	1.410(5)			C7–C8–C14	120.0(4)	N2–C18–C19	119.3(3)
C6–C7	1.402(7)			C10–C9–C14	120.4(3)	C17–C18–C19	122.5(3)
C7–C8	1.369(6)			C9–C10–C11	122.0(3)	C18–C19–C20	117.3(3)
C8–C14	1.437(6)			C1–C11–C10	121.2(3)	N3–C20–C15	120.1(3)
C9–C10	1.336(6)			C1–C11–C12	118.9(3)	N3–C20–C19	116.0(3)
C9–C14	1.437(5)			C10–C11–C12	119.8(3)	C15–C20–C19	123.9(3)
C10–C11	1.426(6)			C4–C12–C11	118.3(3)		

parameters are listed in Table 2.[††]

Bond lengths and interbond angles are given in Table 3. The atomic numbering is shown in Fig. 1.[5]

The arrangement of the molecules in a unit cell is shown in Fig. 2. Phenanthrene and picric acid molecules are stacked along the c-axis, making their molecular planes parallel to each other. The distance between them is 3.4 Å. Those in opposite directions in a stack are also 3.4 Å. Thus there is no indication of 'pairing' of molecules within a stack.

The nitro group O2–N1–O3 (dihedral angle 11.8° to a plane of benzene ring) protrudes from the stacked column. Other two nitro groups are sandwiched in between two phenanthrene molecules (dihedral angles 0.53° for the nitro group O4–N2–O5 and 2.55° for O6–N3–O7).

In the crystal of picric acid the possibility of an intermolecular hydrogen bonding have been envisaged by Srikrishnan et al.[6] In the crystal of phenanthrene: picric acid complex, however, a difference Fourier map showed no clear evidence of an intermolecular hydrogen bonding. The H atom (H(O1)) of phenol OH is located at a reasonable position for intramolecular hydrogen bonding bet-

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[††] The complete tables of observed and calculated structure factors, isotropic thermal parameters and the atomic coordinates of hydrogen atoms, and anisotropic thermal parameters of non-hydrogen atoms are kept as Document No. 8779 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

ween O(1) and O(7), the distances from which are 1.13 and 1.67 Å respectively. Such an intramolecular hydrogen bonding may cause the difference between the two N–O distances of the nitro group O6–N3–O7.

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