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3,4-Benzopyrene (A New Refinement)

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Abstract. C₂₀H₁₂, monoclinic, *P*2₁/*c*, *a*=4.535 (5), *b*=20.40 (2), *c*=13.49 (1) Å, β=97.0°, *D*_m=1.351, *Z*=4, *D*_x=1.351 g cm⁻³. The structure determined by Iball & Young (1956) has been refined to an *R* of 0.069 for 1165 observed reflexions. The molecule is almost planar (deviations less than ±0.04 Å) and, as expected,

has two short bonds (1.342 and 1.352 Å) in the 'K regions' of the two phenanthrene nuclei.

Introduction. The structure of the monoclinic form of 3,4-benzopyrene was described by Iball & Young (1956) but since the coordinates were based mainly on

Table 1. *Final atomic coordinates* (×10⁴) *and temperature factors* (×10⁴) (*e.s.d.'s in parentheses*)

$$T = \exp [-(h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + hkb_{12} + klb_{23} + hlb_{13})].$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> ₁₁	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₂	<i>b</i> ₂₃	<i>b</i> ₃₃
C(1)	1172 (20)	-747 (4)	962 (6)	601 (51)	31 (19)	11 (28)	24 (2)	0 (6)	49 (5)
C(2)	-823 (19)	-1231 (4)	719 (6)	553 (50)	46 (20)	17 (28)	28 (3)	-1 (6)	46 (5)
C(3)	-1597 (18)	-1691 (4)	1456 (6)	461 (44)	35 (18)	44 (26)	23 (2)	-18 (6)	58 (5)
C(4)	-3687 (20)	-2198 (5)	1223 (7)	533 (51)	26 (21)	26 (31)	30 (3)	-35 (7)	75 (6)
C(5)	-4338 (22)	-2622 (5)	1959 (7)	729 (60)	-59 (23)	111 (34)	30 (3)	-11 (8)	77 (7)
C(6)	-2939 (21)	-2577 (4)	2922 (7)	629 (53)	-4 (21)	135 (31)	24 (2)	-6 (7)	83 (6)
C(7)	-857 (19)	-2078 (4)	3172 (6)	534 (46)	33 (19)	111 (26)	24 (2)	3 (6)	60 (5)
C(8)	619 (21)	-2013 (5)	4169 (7)	688 (56)	54 (22)	102 (31)	28 (3)	12 (7)	64 (6)
C(9)	2603 (20)	-1535 (5)	4419 (6)	666 (54)	61 (21)	38 (29)	29 (3)	12 (7)	49 (5)
C(10)	3357 (19)	-1063 (4)	3690 (6)	462 (45)	48 (18)	26 (26)	26 (2)	-1 (6)	48 (5)
C(11)	5359 (19)	-575 (4)	3936 (6)	518 (49)	44 (20)	-24 (29)	28 (3)	-8 (7)	56 (5)
C(12)	6078 (19)	-113 (4)	3217 (7)	512 (48)	27 (19)	54 (29)	21 (2)	-7 (6)	67 (6)
C(13)	8156 (21)	398 (5)	3496 (7)	550 (51)	39 (21)	36 (32)	28 (3)	-19 (7)	78 (6)
C(14)	8876 (22)	853 (5)	2814 (8)	649 (55)	-10 (23)	114 (34)	28 (3)	-19 (8)	95 (7)
C(15)	7478 (22)	817 (5)	1834 (7)	733 (57)	-9 (22)	181 (33)	23 (2)	-5 (8)	92 (7)
C(16)	5460 (21)	337 (4)	1548 (7)	666 (53)	52 (21)	147 (29)	26 (2)	1 (7)	65 (6)
C(17)	4686 (19)	-148 (4)	2225 (6)	529 (46)	47 (18)	73 (26)	23 (2)	0 (6)	51 (5)
C(18)	2603 (18)	-666 (4)	1953 (6)	484 (45)	38 (18)	23 (25)	23 (2)	0 (6)	48 (5)
C(19)	1930 (18)	-1112 (4)	2676 (6)	448 (43)	53 (16)	19 (24)	24 (2)	-1 (6)	38 (4)
C(20)	-157 (18)	-1624 (4)	2444 (6)	445 (39)	47 (17)	66 (23)	22 (2)	2 (6)	48 (4)

two-dimensional Fourier maps the molecular dimensions were not very accurate. New diffraction data have been collected from equi-inclination Weissenberg photographs (Cu $K\alpha$ radiation). The crystals tend to be twinned, but by splitting the crystals parallel to the needle axis it is possible to obtain small fragments which are not twinned. No corrections have been made for absorption ($\mu = 5.95 \text{ cm}^{-1}$). The unit cells of both the monoclinic and orthorhombic forms were first described by Iball (1936) but the structure of the orthorhombic form has not been determined.

The atomic parameters of Iball & Young (1956) for the C atoms were refined anisotropically by block-diagonal least-squares calculations. Calculated positions for the H atoms were included in the structure factor calculations but were not refined. The weighting scheme was $1/w = 1/\{1 + [(|F_o| - F^*)/G^*]^2\}^{1/2}$ with values of 20 and 15 for F^* and G^* respectively. The scattering factors were taken from *International Tables for X-ray Crystallography* (1974) and the final R was 0.069 for 1165 observed reflexions.* Atomic parameters are

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31373 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Atomic coordinates for hydrogen atoms ($\times 10^3$) and isotropic temperature factors

	x	y	z	$B(\text{\AA})^2$
H(1)	189	-43	43	4.49
H(2)	-176	-129	3	4.50
H(4)	-462	-225	46	5.50
H(5)	-599	-296	188	5.50
H(6)	-366	-288	349	5.00
H(8)	-33	-231	469	5.00
H(9)	373	-148	509	4.50
H(11)	649	-57	464	4.50
H(13)	913	39	425	5.00
H(14)	29	121	303	5.50
H(15)	831	115	140	5.50
H(16)	468	33	79	5.00

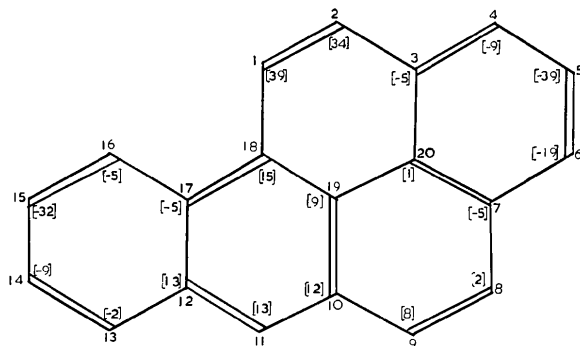


Fig. 1. 3,4-Benzopyrene: the numbering system and deviations ($\text{\AA} \times 10^3$) of the C atoms from the mean plane.

given in Tables 1 and 2. Bond lengths and angles are given in Table 3 and intermolecular contacts in Table 4. The numbering system and deviations from the mean plane are shown in Fig. 1.

Table 3. Bond lengths (\AA) and bond angles ($^\circ$) (*e.s.d.'s* in parentheses)

C(1)-C(2)	1.352 (12)	C(10)-C(11)	1.361 (12)
C(1)-C(18)	1.423 (11)	C(10)-C(19)	1.444 (11)
C(2)-C(3)	1.441 (12)	C(11)-C(12)	1.418 (12)
C(3)-C(4)	1.412 (12)	C(12)-C(13)	1.425 (12)
C(3)-C(20)	1.417 (11)	C(12)-C(17)	1.410 (11)
C(4)-C(5)	1.375 (14)	C(13)-C(14)	1.374 (14)
C(5)-C(6)	1.378 (13)	C(14)-C(15)	1.397 (14)
C(6)-C(7)	1.402 (12)	C(15)-C(16)	1.364 (13)
C(7)-C(8)	1.433 (12)	C(16)-C(17)	1.418 (12)
C(7)-C(20)	1.415 (12)	C(17)-C(18)	1.436 (12)
C(8)-C(9)	1.342 (13)	C(18)-C(19)	1.393 (11)
C(9)-C(10)	1.446 (12)	C(19)-C(20)	1.419 (11)
C(2)-C(1)-C(18)	121.8 (8)	C(11)-C(12)-C(17)	120.1 (8)
C(1)-C(2)-C(3)	121.4 (7)	C(13)-C(12)-C(17)	119.5 (8)
C(2)-C(3)-C(4)	122.5 (7)	C(12)-C(13)-C(14)	121.4 (8)
C(2)-C(3)-C(20)	117.6 (7)	C(13)-C(14)-C(15)	118.8 (9)
C(4)-C(3)-C(20)	119.9 (8)	C(14)-C(15)-C(16)	121.1 (9)
C(3)-C(4)-C(5)	119.8 (8)	C(15)-C(16)-C(17)	121.9 (8)
C(4)-C(5)-C(6)	121.6 (9)	C(12)-C(17)-C(16)	117.3 (8)
C(5)-C(6)-C(7)	119.6 (9)	C(12)-C(17)-C(18)	118.9 (8)
C(6)-C(7)-C(8)	121.1 (8)	C(16)-C(17)-C(18)	123.8 (7)
C(6)-C(7)-C(20)	120.7 (8)	C(1)-C(18)-C(17)	122.4 (7)
C(8)-C(7)-C(20)	118.2 (8)	C(1)-C(18)-C(19)	118.0 (7)
C(7)-C(8)-C(9)	121.7 (9)	C(17)-C(18)-C(19)	119.7 (7)
C(8)-C(9)-C(10)	121.3 (8)	C(10)-C(19)-C(18)	120.5 (7)
C(9)-C(10)-C(11)	121.8 (7)	C(10)-C(19)-C(20)	118.0 (7)
C(9)-C(10)-C(19)	118.9 (7)	C(18)-C(19)-C(20)	121.6 (7)
C(11)-C(10)-C(19)	119.3 (8)	C(3)-C(20)-C(7)	118.2 (7)
C(10)-C(11)-C(12)	121.5 (8)	C(3)-C(20)-C(19)	119.8 (7)
C(11)-C(12)-C(13)	120.4 (8)	C(7)-C(20)-C(19)	121.9 (7)

Table 4. Intermolecular distances $\leq 3.5 \text{\AA}$ (*e.s.d.'s* in parentheses)

(I)	x, y, z	
(II)	$1+x, y, z$	
C(10) ^I -C(7) ^{II}		3.480 (12) \AA
C(12) ^I -C(19) ^{II}		3.493 (12)
C(14) ^I -C(17) ^{II}		3.500 (13)
C(18) ^I -C(3) ^{II}		3.489 (12)
C(20) ^I -C(17) ^{II}		3.458 (13)

The equation of the mean plane of the C atoms is $0.7704X - 0.59537Y - 0.22693Z - 0.8638 = 0$ (X is parallel to \mathbf{a} , Y parallel to \mathbf{b} and Z perpendicular to \mathbf{a} and \mathbf{b}).

Discussion. 3,4-Benzopyrene is a very potent cancer producing compound and was first isolated from coal tar by Cook, Hewett & Heiger (1933) who synthesized it. The crystals used in the present investigation were prepared from this original sample. The structure of the molecule is now in agreement with expectation. There are two so-called 'K regions' of phenanthrene

in the molecule (bonds 1–2 and 8–9) and both are short, 1.352 and 1.342 Å respectively.

Although the molecule is approximately planar it is not as planar as some other aromatic condensed ring hydrocarbons; for example chrysene has a maximum deviation of 0.02 Å (Burns & Iball, 1960). There is overcrowding due to the H atoms attached to atoms 1 and 16 and this is relieved mainly by the slight twisting of the molecule so that atoms 1 and 16 are on opposite sides of the mean plane (separation normal to the plane, 0.044 Å) and there is no undue lengthening of the bond 17–18. In many similar compounds this kind of bond is greater than 1.46 Å.

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Copper(II) Formate–Urea–Water (1/2/2)

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Abstract. $\text{Cu}(\text{HCO}_2)_2 \cdot 2(\text{NH}_2)_2\text{CO} \cdot 2\text{H}_2\text{O}$, monoclinic, $P2_1/c$, $a = 8.275$ (4), $b = 8.346$ (3), $c = 8.018$ (3) Å, $\beta = 96.36$ (5)°, $Z = 2$, $D_m = 1.862$ (3), $D_x = 1.869$ g cm⁻³. The crystal consists of the same kind of copper formate layers, $[\text{Cu}(\text{HCO}_2)_2]_\infty$, as in $\text{Cu}(\text{HCO}_2)_2 \cdot 4\text{H}_2\text{O}$, between which urea and water molecules are held together by unique hydrogen bonds.

Introduction. Crystals suitable for X-ray studies were prepared from an aqueous solution of copper formate and a large excess of urea, at room temperature. The (100) plane is a pronounced cleavage plane and corresponds to (001) in copper formate tetrahydrate (hereafter abbreviated as CFTH).

Weissenberg and precession photographs showed the symmetry of monoclinic $P2_1/c$ (systematic absences: $h0l$ with l odd and $0k0$ with k odd). A blue 0.1 mm cubed crystal was mounted on a Rigaku automatic

four-circle diffractometer. The lattice parameters were determined from setting angles of the diffractometer with Mo $K\alpha_1$ radiation ($\lambda = 0.7093$ Å). Intensity data were collected on the same diffractometer by use of Mo $K\alpha$ radiation and of the ω - 2θ scan technique. The scan speed was 1°/min in 2θ and background intensities were measured for 10 s at both ends of each scan. A total of 1701 reflexions were observed in a region of $(\sin \theta)/\lambda < 0.72$ Å⁻¹. Corrections were made for Lorentz and polarization factors, but not for absorption ($\mu = 21.05$ cm⁻¹) and extinction.

The positions of all the non-hydrogen atoms were determined by the combined use of Patterson and Fourier syntheses. After four cycles of least-squares refinement the R value dropped to 0.063 ($R = \sum |F_o| - |F_c| / \sum |F_o|$). A difference Fourier map computed at this stage showed the positions of all H atoms. Further refinements with anisotropic temperature factors for

Table 1. *Final positional parameters* ($\times 10^4$) *and thermal parameters* (Å² $\times 10^2$)

Estimated standard deviations are given in parentheses. The anisotropic thermal factors are of the form $T = \exp[-\frac{1}{3}(h^2 a^{*2} B_{11} + \dots + 2k lb^* c^* B_{23})]$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
Cu	0	0	0	216 (1)	78 (1)	73 (1)	19 (1)	-5 (1)	2 (1)
C(F)	-161 (2)	2680 (2)	2342 (2)	215 (8)	138 (8)	117 (7)	40 (6)	-32 (6)	-12 (6)
C(U)	6307 (2)	468 (2)	3620 (2)	163 (7)	208 (8)	179 (7)	-15 (6)	19 (6)	-8 (6)
O(1F)	-644 (2)	2050 (1)	972 (1)	254 (6)	123 (5)	116 (5)	36 (5)	-31 (4)	-38 (4)
O(2F)	-531 (2)	4057 (1)	2758 (1)	263 (6)	95 (5)	102 (5)	18 (4)	-10 (4)	-18 (4)
O(U)	5426 (2)	-190 (2)	2430 (2)	275 (6)	227 (7)	213 (5)	-28 (6)	-76 (5)	-36 (5)
O(W)	2795 (2)	950 (2)	246 (2)	197 (6)	245 (6)	224 (6)	7 (5)	4 (5)	5 (5)
N(1)	6303 (2)	2030 (2)	3868 (2)	302 (8)	173 (7)	374 (9)	2 (7)	-121 (7)	9 (7)
N(2)	7307 (2)	-411 (2)	4662 (2)	342 (9)	172 (7)	316 (8)	24 (6)	-123 (6)	-30 (6)