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The Structure of 7*H*-Benzo[*hi*]chrysen-7-one (α Form)

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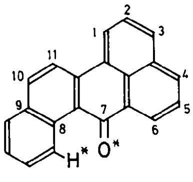
Abstract

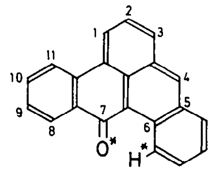
Crystals of the title compound, $C_{21}H_{12}O$, are monoclinic, space group $P2_1/c$, with the lattice constants a = 7·663 (1), b = 8·299 (1), c = 21·865 (2) Å, β = 102·61 (1)° and Z = 4. The structure was solved by the direct method and refined by a full-matrix least-squares program to an R value of 0·059 on the basis of 1301 reflections collected on an automated four-circle diffractometer. The molecules are slighly distorted from a planar structure owing to the overcrowding around the O atom. The structure consists of pairs of molecules and it is disordered. There are two pairs with different overlapping modes and they are arranged randomly with different populations. The interplanar distances in the dimer pairs are 3·47 (1) and 3·52 (3) Å respectively.

Introduction

The glycerol condensation of benz[*a*]anthraquinone affords two isomeric products. One is assigned as 7*H*-benzo[*hi*]chrysen-7-one (8,9-benzbenzanthrone, 8,9-BzBT), since the same compound can be obtained by the ring-closure of di-1-naphthyl ketone (Scholl & Seer, 1912). Accordingly, the other isomer is considered to be 13*H*-dibenzo[*b,mn*]phenanthren-13-one (5,6-benzbenzanthrone, 5,6-BzBT).



8.9-BzBT



5.6-BzBT

The crystals of 8,9-BzBT were subjected to X-ray crystal structure analysis in order to confirm the above assignments. It is also of interest to see how much the overcrowding around the O atom affects the molecular geometry. Such a molecular distortion due to a non-bonded O···H interaction has been reported for dibenz[*a,h*]anthraquinone (Entwistle, Iball, Motherwell & Thompson, 1969).

Experimental

The compound was prepared by the glycerol condensation method modified by one of the authors (SF). The resulting product was purified by column chromatography on activated alumina, followed by recrystallization from monochlorobenzene and sublimation in vacuum. The crystals used for X-ray work were grown as follows. The compound was sealed in an evacuated glass tube; this was placed vertically and its top and bottom were kept at 333 ± 5 and 443 ± 5 K respectively. The compound is dimorphous. The sublimate consisted mostly of pale-yellow needle-like crystals (α form). Orange-yellow rhomboidal crystals deposited at the bottom of the tube (β form). Preliminary unit-cell dimensions and the space groups of the two modifications were obtained from Weissenberg photographs. The cell dimensions of the α form were later refined by the least-squares method on the basis of the 2θ values on a four-circle diffractometer. The crystal data are listed in Table 1.

The intensity data were collected for the monoclinic modification (α form) in view of the smaller number of independent parameters to be determined. The dimensions of the crystal used for data collection were 0·4 × 0·35 × 0·2 mm. In total, 2388 independent reflections were measured on the automated four-circle diffractometer up to $2\theta \leq 50°$, using graphite-monochromated Mo $K\alpha$ radiation (λ = 0·7107 Å), the ω–2θ scan technique being employed. Among these, 1301 reflections with $|F| > 3\sigma(|F|)$ were selected and

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Table 1. *Crystal data*

7*H*-Benzo[*hi*]chrysen-7-one, $C_{21}H_{12}O$, $M_r = 280{\cdot}3$

	α Form	β Form
Crystal class	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*Bbmb* or *Bb2b*
Lattice constants	$a = 7{\cdot}663$ (1) Å	$a = 7{\cdot}70$ (5) Å
	$b = 8{\cdot}299$ (1)	$b = 67{\cdot}7$ (2)
	$c = 21{\cdot}865$ (2)	$c = 63{\cdot}5$ (2)
	$\beta = 102{\cdot}61$ (1)°	
	$V = 1357{\cdot}1$ (1) Å^3	$V = 33100$ (100) Å^3
	$Z = 4$	$Z = 96$
Density	$D_m = 1{\cdot}380$ Mg m^{-3}	
	$D_x = 1{\cdot}372$	$D_x = 1{\cdot}35$ Mg m^{-3}
Melting point	462 K	
Linear absorption coefficient	μ(Mo $K\alpha$) = 0·090 mm^{-1}	

used for subsequent calculations. Three standard reflections were monitored after every 50 measurements. The intensities of the standard reflections decreased gradually during the course of the measurements. Reflection intensities were corrected for this effect as well as for the usual Lorentz and polarization factors.

Structure analysis

The structure was solved using *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The E map with the highest figure of merit based on 205 reflections with $|E| \geq 1{\cdot}20$ revealed the positions of 22 non-hydrogen atoms. The atomic parameters thus obtained were refined by the least squares method, using isotropic thermal parameters for all the atoms. After six cycles the R value reduced to 0·26; however, most of the thermal parameters ranged between 6·0 and 8·0 Å^2, being unusually large for this type of crystal. On closer examination of the difference maps at this stage, a number of small peaks were found which could not be assigned to H atoms. The maps could be interpreted reasonably only if it was assumed that the structure is disordered; *i.e.* the molecules have two different orientations with different populations of about 4:1. When this type of disorder was taken into account the structure converged rapidly and all the atoms except H came out clearly on the Fourier maps. The H coordinates were evaluated at idealized positions with trigonal disposition and with C—H = 1·08 Å. Further refinement cycles with anisotropic thermal parameters for non-hydrogen atoms were carried out by using the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970), where the population parameter was also refined. The final R (= $\sum||F_o| - |F_c||/\sum|F_o|$) was 0·059 and R_w {= $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = [\sigma^2(|F_o|) + (0{\cdot}02|F_o|)^2]^{-1}$} was 0·077 for 1301 observed reflections. Neutral-atom scattering factors were used (*International Tables for X-ray Crystallography*, 1974). For H the values given by Stewart, Davidson & Simpson (1965) were employed. Table 2 lists the final atomic parameters.* At

Table 2. *Atomic parameters with e.s.d.'s in parentheses*

(i) The molecule forming dimer pair (I) [population: 0·77 (2); fractional parameters × 10^4, thermal × 10^3]

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

	x	y	z	U_{eq} (Å^2)
C(1)	8092 (9)	3190 (8)	5197 (4)	71 (5)
C(2)	8648 (6)	2480 (7)	5783 (3)	87 (2)
C(3)	7499 (10)	1679 (7)	6075 (2)	77 (2)
C(4)	4379 (11)	701 (7)	6013 (3)	66 (3)
C(5)	2609 (10)	584 (8)	5682 (3)	74 (3)
C(6)	2103 (7)	1320 (6)	5088 (3)	63 (2)
C(7)	2705 (9)	2899 (10)	4205 (4)	62 (3)
C(8)	3427 (11)	4659 (7)	3342 (3)	59 (2)
C(9)	4661 (10)	5546 (8)	3086 (4)	78 (3)
C(10)	6543 (11)	5498 (7)	3429 (3)	75 (3)
C(11)	6974 (7)	4706 (6)	3981 (3)	76 (2)
C(12)	5836 (32)	3806 (20)	4295 (13)	53 (4)
C(13)	6369 (5)	3110 (5)	4872 (2)	59 (2)
C(14)	5144 (9)	2276 (6)	5165 (3)	51 (2)
C(15)	5656 (8)	1546 (7)	5760 (3)	65 (2)
C(16)	3312 (8)	2144 (5)	4834 (2)	54 (2)
C(17)	3964 (6)	3798 (5)	3931 (2)	57 (2)
C(18)	1612 (10)	4670 (8)	2978 (3)	81 (3)
C(19)	1148 (19)	5573 (12)	2427 (4)	94 (5)
C(20)	2448 (21)	6425 (15)	2227 (5)	99 (4)
C(21)	4231 (15)	6447 (8)	2534 (4)	97 (4)
O	1120 (10)	2619 (18)	3949 (6)	106 (3)

(ii) The molecule forming dimer pair (II) (population: 0·23; fractional and thermal parameters × 10^3)

	x	y	z	U_{iso} (Å^2)
C(1′)	734 (4)	533 (5)	363 (2)	120 (15)
C(2′)	697 (2)	626 (2)	299 (1)	69 (5)
C(3′)	560 (3)	649 (2)	264 (1)	84 (6)
C(4′)	212 (7)	597 (6)	234 (2)	95 (19)
C(5′)	69 (6)	537 (5)	256 (2)	85 (11)
C(6′)	82 (3)	448 (3)	308 (1)	76 (7)
C(7′)	257 (6)	324 (5)	399 (2)	104 (19)
C(8′)	446 (3)	224 (2)	502 (1)	32 (4)
C(9′)	612 (3)	213 (2)	545 (1)	63 (5)
C(10′)	763 (4)	280 (3)	530 (1)	63 (9)
C(11′)	756 (2)	374 (2)	470 (1)	72 (5)
C(12′)	552 (12)	392 (9)	420 (5)	55 (23)
C(13′)	569 (2)	472 (2)	369 (1)	54 (4)
C(14′)	408 (4)	500 (3)	326 (1)	48 (6)
C(15′)	376 (3)	590 (3)	269 (1)	63 (7)
C(16′)	254 (2)	425 (2)	344 (1)	50 (5)
C(17′)	429 (2)	308 (2)	445 (1)	45 (3)
C(18′)	299 (3)	141 (3)	523 (1)	70 (6)
C(19′)	338 (3)	69 (4)	582 (1)	55 (7)
C(20′)	516 (3)	68 (3)	619 (1)	75 (9)
C(21′)	648 (4)	136 (3)	604 (1)	80 (8)
O′	116 (7)	291 (8)	406 (3)	144 (19)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36128 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the final stage of the refinement, all the atomic shifts for the molecule with population 0·77 were less than 40% of the corresponding standard deviations.

Description of the structure and discussion

The present study has indeed verified the chemical assignment of the condensation product of benz[*a*]anthraquinone. Fig. 1 illustrates the structure viewed along **a**. The molecules are grouped in pairs around the center of symmetry. There are two dimer pairs with different overlapping modes and the structure is disordered. Fig. 2 gives the two different overlapping modes in the pairs; they are designated (I) and (II). The pairs (I) and (II) are packed randomly with a population ratio of 0·77 (1) to 0·23. The tilt angles of the molecular planes with respect to **b** are broadly similar, being 56·0 (1)° for (I) and 57·4 (3)° for (II).

Owing to parameter interactions among the disordered atoms, some of the atomic coordinates have much larger standard deviations than others: for example, C(12), C(19), C(20) and C(21) (see Table 2). Thus, the bond lengths and angles involving these atoms may be meaningless. The bond lengths and angles for the molecule in (I) are listed in Tables 3 and 4 respectively. The standard deviations may still be underestimated. The observed molecular geometry is not accurate enough to warrant a detailed discussion. However, by drawing four resonance structures for the compound, with a double bond at the C–O position, one can easily see that C(7)–C(16), C(7)–C(17) and C(8)–C(18) are single bonds in all these structures and that C(2)–C(3) has more double-bond character than C(1)–C(2) or C(13)–C(14). In fact, the C–O distance of 1·24 (1) Å is normal for a double bond. Though not very significant, these and other bond characters expected from such a simple argument are reasonably reflected in the observed bond lengths (Table 3).

The molecule is distorted owing to the overcrowding around the O atom. Fig. 3 shows atomic shifts from the mean plane of the molecule in (I): $0{\cdot}308x - 0{\cdot}829y - 0{\cdot}467z + 6{\cdot}244 = 0$, where x, y and z are coordinates in Å referred to a, b and c^* respectively. The O atom has the largest shift of 0·19 (2) Å. The shifts of the C atoms from the mean plane indicate that the 8,9-benzo moiety has a good planar structure and is inclined at an angle of 3·6 (1)° with respect to the mean molecular plane on the opposite side of the O atom. Likewise, the naphthalene moiety, C(1),C(2)···C(6)···C(14),C(13), is also planar and is inclined by 2·4 (2)° in the same manner. Such buckling of the molecular framework relieves the short contacts between O···H(C18) and

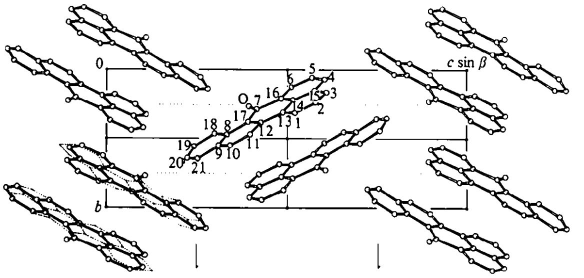

Fig. 1. The structure viewed along **a**. Molecules drawn with broken lines indicate the dimer pair (II).

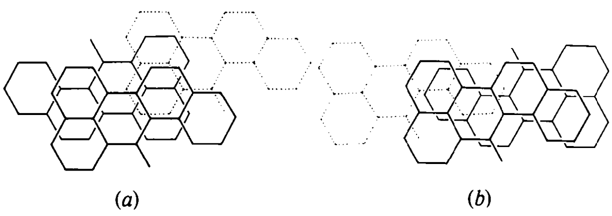
(*a*) (*b*)

Fig. 2. Overlapping mode (*a*) (I) and (*b*) (II). Molecules drawn with broken lines belong to the adjacent pair.

Table 3. *Bond lengths* (Å) *within the molecule in* (I) *with standard deviations in parentheses*

C(1)–C(2)	1·39 (1)	C(8)–C(18)	1·44 (1)
C(1)–C(13)	1·36 (1)	C(9)–C(10)	1·47 (1)
C(2)–C(3)	1·37 (1)	C(9)–C(21)	1·40 (1)
C(3)–C(15)	1·43 (1)	C(10)–C(11)	1·35 (1)
C(4)–C(5)	1·39 (1)	C(11)–C(12)	1·43 (3)
C(4)–C(15)	1·41 (1)	C(12)–C(13)	1·37 (3)
C(5)–C(6)	1·41 (1)	C(12)–C(17)	1·48 (2)
C(6)–C(16)	1·36 (1)	C(13)–C(14)	1·43 (1)
C(7)–C(16)	1·49 (1)	C(14)–C(15)	1·41 (1)
C(7)–C(17)	1·45 (1)	C(14)–C(16)	1·44 (1)
C(7)–O	1·24 (1)	C(18)–C(19)	1·40 (1)
C(8)–C(9)	1·41 (1)	C(19)–C(20)	1·37 (2)
C(8)–C(17)	1·45 (1)	C(20)–C(21)	1·39 (2)

Table 4. *Bond angles* (°) *within the molecule in* (I) *with standard deviations in parentheses*

C(2)–C(1)–C(13)	122 (1)	C(1)–C(13)–C(12)	122 (1)
C(1)–C(2)–C(3)	123 (1)	C(1)–C(13)–C(14)	117 (1)
C(2)–C(3)–C(15)	119 (1)	C(12)–C(13)–C(14)	122 (1)
C(5)–C(4)–C(15)	121 (1)	C(13)–C(14)–C(15)	123 (1)
C(4)–C(5)–C(6)	119 (1)	C(13)–C(14)–C(16)	119 (1)
C(5)–C(6)–C(16)	121 (1)	C(15)–C(14)–C(16)	118 (1)
C(16)–C(7)–C(17)	120 (1)	C(3)–C(15)–C(4)	123 (1)
C(16)–C(7)–O	115 (1)	C(3)–C(15)–C(14)	117 (1)
C(17)–C(7)–O	126 (1)	C(4)–C(15)–C(14)	120 (1)
C(9)–C(8)–C(17)	122 (1)	C(6)–C(16)–C(7)	119 (1)
C(9)–C(8)–C(18)	115 (1)	C(6)–C(16)–C(14)	121 (1)
C(17)–C(8)–C(18)	123 (1)	C(7)–C(16)–C(14)	120 (1)
C(8)–C(9)–C(10)	117 (1)	C(7)–C(17)–C(8)	122 (1)
C(8)–C(9)–C(21)	125 (1)	C(7)–C(17)–C(12)	116 (1)
C(10)–C(9)–C(21)	118 (1)	C(8)–C(17)–C(12)	122 (1)
C(9)–C(10)–C(11)	119 (1)	C(8)–C(18)–C(19)	121 (1)
C(10)–C(11)–C(12)	129 (1)	C(18)–C(19)–C(20)	119 (1)
C(11)–C(12)–C(13)	125 (2)	C(19)–C(20)–C(21)	124 (1)
C(11)–C(12)–C(17)	111 (2)	C(9)–C(21)–C(20)	116 (1)
C(13)–C(12)–C(17)	124 (2)		

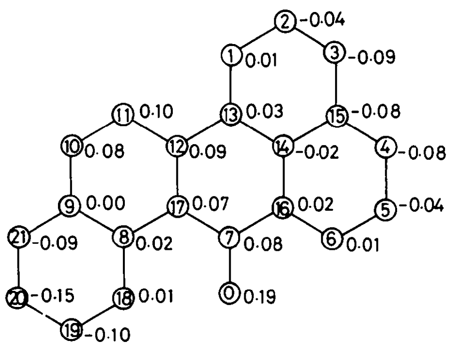

Fig. 3. Atomic displacements (Å) from the mean plane of the molecule (I). The estimated standard deviation is less than 0·02 Å.

O···H(C6); these are 2·08 (2) and 2·32 (2) Å respectively. This type of deformation is similar to that observed in dibenz[*a*,*h*]anthraquinone (Entwistle *et al.*, 1969), but the buckling of the molecular framework is much less than that reported for tetrabenzo[*a*,*cd*,*j*,*lm*]perylene (Kohno, Konno, Saito & Inokuchi, 1975).

As mentioned earlier, the molecules form dimer pairs, like pyrene (Robertson & White, 1947), perylene (Donaldson, Robertson & White, 1953) and benzo[*pqr*]perylene (White, 1948). In contrast, naphth[7,8,1,2-*defg*]anthrone (Fujisawa, Oonishi, Aoki & Iwashima, 1976) does not exhibit such a dimeric structure.

The interplanar spacing in the dimer pairs is 3·47 (1) Å in (I) and 3·52 (3) Å in (II), whereas the spacing between the pairs is 3·40 (1) Å [(I)···(I)] and 3·47 (3) Å [(II)···(II)]. The shortest C···C distance between dimer pairs (I) and (II) is 3·46 (3) Å. The interplanar spacing of 3·50 Å in naphth[7,8,1,2-*defg*]anthrone (Fujisawa *et al.*, 1976) lies between the observed values for (I) and (II).

References

Coppens, P. & Hamilton, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

Donaldson, D. M., Robertson, J. M. & White, J. G. (1953). *Proc. R. Soc. London Ser. A*, **220**, 311–321.

Entwistle, R. F., Iball, J., Motherwell, W. D. S. & Thompson, B. P. (1969). *Acta Cryst.* B**25**, 770–775.

Fujisawa, S., Oonishi, I., Aoki, J. & Iwashima, S. (1976). *Bull. Chem. Soc. Jpn*, **49**, 3454–3456.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Kohno, Y., Konno, M., Saito, Y. & Inokuchi, H. (1975). *Acta Cryst.* B**31**, 2076–2080.

Main, P., Woolfson, M. M., Lessinger, L., Germain, G. & Declercq, J. P. (1974). *MULTAN 74. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Robertson, J. M. & White, J. G. (1947). *J. Chem. Soc.* pp. 358–368.

Scholl, R. & Seer, C. (1912). *Justus Liebigs Ann. Chem.* **394**, 111–177.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

White, J. G. (1948). *J. Chem. Soc.* pp. 1398–1408.

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The Crystal Structure of 13-*cis*-Retinal. The Molecular Structures of its 6-*s*-*cis* and 6-*s*-*trans* Conformers

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Abstract

The crystal and molecular structure of 13-*cis*-retinal, $C_{20}H_{28}O$, has been determined by single-crystal X-ray diffraction techniques using counter methods. The structure was refined by full-matrix least-squares procedures using 2762 unique and significant (at the 2σ level) reflections to a final weighted R index of 0·062. Triclinic crystals form in the space group $P\bar{1}$ with unit-cell dimensions of a = 12·494 (6), b = 18·279 (8), c = 7·992 (5) Å, α = 100·26 (4), β = 90·26 (5), γ = 94·35 (4)°, with V = 1790 (2) Å^3, Z = 4, D_c = 1·055 Mg m^{-3}, M_r = 284·4, $F(000)$ = 624. The crystal structure discloses the presence of two conformers. In the 6-*s*-*trans* conformer, the double bond in the

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