3048 © 1984 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 57, 3048—3051 (1984) [Vol. 57, No. 11

# The Crystal Structure of 13*H*-Dibenz[*a*,*de*]anthracen-13-one

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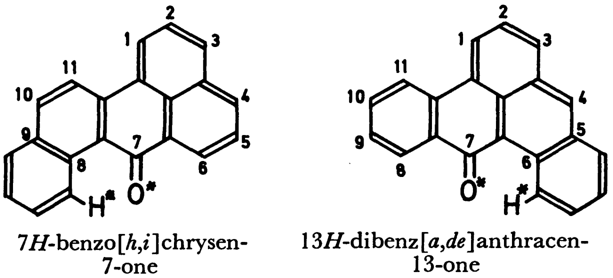
(Received February 27, 1984)

Crystals of the title compound, $C_{21}H_{12}O$, are orthorhombic, belong to the space group $Pn2_1a$, have lattice constants of $a$=14.227(3), $b$=15.551(4), $c$=12.436(3) Å, and also have $Z$=8. The structure was determined using the direct method and was refined by using a full-matrix least-squares method to an $R$ value of 0.106 on the basis of 1964 reflections with $|F_o|>3\sigma(|F_o|)$. The molecules is slightly distorted from the planar conformation owing to a steric repulsion between the O and H atoms. The molecules are stacked in pairs and two pairs with different overlapping modes are randomly arranged with different populations. It has been qualitatively explained that the populations of disordered molecules reflect the difference in their lattice energies.

It has been assumed that the glycerol condensation of benz[*a*]anthracene-9,10-dione results in the formation of two isomeric products: 7*H*-benzo[*h*,*i*]chrysen-7-one (8,9-BzBT)†† and 13*H*-dibenz[*a*,*de*]anthracen-13-one (5,6-BzBT)††. The crystal and molecular structure of 8,9-BzBT has been determined using the X-ray diffraction method.[1] The molecule is distorted from the planar conformation owing to a steric repulsion between the O* and H* atoms. Around an inversion center, the molecules are stacked in pairs. Two pairs with different overlapping mode are randomly arranged with different populations. The present work was undertaken to confirm the structure of another isomer, 5,6-BzBT, and to compare its crystal and molecular structure with that of 8,9-BzBT.



7*H*-benzo[*h*,*i*]chrysen-7-one (8,9-BzBT)††

13*H*-dibenz[*a*,*de*]anthracen-13-one (5,6-BzBT)††

Scheme

†† The names in common use.

## Experimental

The title compound was prepared by a method which has been reported previously.[1] The crystals used for X-ray work were grown by slow sublimation in a sealed glass tube with a nitrogen atmosphere (100 Pa). Crystal data are as follows: $C_{21}H_{12}O$; M.W. 280.1; orthorhombic; $a$=14.227(3), $b$=15.551(4), $c$=12.436(3) Å, and $U$=2751.4(9) Å$^3$; $D_x$=1.352 g cm$^{-3}$; $Z$=8; space group $Pn2_1a$; $\mu$(Cu $K\alpha$)=42.6 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°($2\theta$) min$^{-1}$. The dimensions of the crystal used for data collection were 0.4×0.35×0.3 mm. A total of 2569 independent reflections were measured (up to $2\theta$=125.0°) using graphite monochromated Cu $K\alpha$ radiation, of which 1694 reflections with $|F_o|>3\sigma(|F_o|)$ were used for the analysis. Corrections were made for Lorentz and polarization factors, but not for absorption.

## Structure Determination

Systematic absences of $0kl$, $k+l=2n+1$ and $hk0$, $h=2n+1$ indicated the space group to be Pnma or $Pn2_1a$. The packing consideration suggested a non-centrosymmetric arrangement and the structure was successfully refined on the basis of the space group $Pn2_1a$. There are two crystallographically independent molecules in an asymmetric unit, which are denoted as A and B. The structure was determined using the direct method, with the MULTAN 78 program.[2] This structure was refined using the block-diagonal least-squares method with isotropic thermal parameters. After 6 cycles of refinement ($R$=0.20), 20 small peaks due to the disordered B molecule were found on the difference map*. This molecule is denoted as C. Further refinement was performed using the full-matrix least-squares method with the SHELX 76 program.[3] The anisotropic thermal parameters were used for the non-hydrogen atoms of the A and B molecules and the isotropic thermal parameters were used for the atoms of the C molecules and H atoms. The C molecule was constrained to have the same structure as that of A. The final $R$ became 0.106. The population factors of the B and C molecules were refined to be 0.80(1) and 0.20(2), respectively. No peaks higher than 0.3 eÅ$^{-3}$ were found on the final difference map. The atomic scattering factors were taken from Ref. 4. The final atomic parameters with their standard deviations are listed in Table 1.**

## Results and Discussion

Figure 1 illustrates the crystal structure of 5,6-BzBT viewed along the b axis. One of the two crystallographically independent molecules takes a disordered structure, B and C, which are situated on nearly the same plane and have different orientations. The two

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* No diffuse scattering was observed on the Weissenberg photographs.

** Lists of the observed and calculated structure factors, anisotropic thermal parameters for non-H atoms and positional parameters for H atoms are deposited as Document No. 8444 at the office of the Chemical Society of Japan.

Table 1. Final atomic coordinates with their estimated standard deviations in parentheses, multiplied by $10^4$ for atoms of molecule A and B, and $10^3$ for atoms of molecule C

| Atom | $x$ | $y$ | $z$ | $B$ or $B_{eq}$/Å | Atom | $x$ | $y$ | $z$ | $B$ or $B_{eq}$/Å |
|---|---|---|---|---|---|---|---|---|---|
| C( 1A) | 3431( 8) | 3260( 8) | 7395(10) | 6.4 | C(12B) | 8978( 8) | −145( 9) | 4617(10) | 4.8 |
| C( 2A) | 3822( 9) | 2421( 6) | 7311( 8) | 5.3 | C(13B) | 8530( 9) | −982( 9) | 4659(10) | 4.9 |
| C( 3A) | 4626( 9) | 2267( 7) | 6787(10) | 6.1 | C(14B) | 7653( 8) | −1157( 7) | 5260( 8) | 3.2 |
| C( 4A) | 5911( 8) | 2885( 7) | 5754( 8) | 5.2 | C(15B) | 7282(10) | −1999( 9) | 5303(10) | 5.1 |
| C( 5A) | 6388( 9) | 3555( 8) | 5236( 8) | 5.7 | C(16B) | 7222( 8) | −452( 7) | 5838(10) | 3.7 |
| C( 6A) | 5989( 7) | 4422( 6) | 5203( 8) | 4.4 | C(17B) | 8460( 8) | 497( 8) | 5148( 9) | 3.9 |
| C( 7A) | 4721( 8) | 5427( 6) | 5925( 9) | 5.6 | C(18B) | 5218(10) | −1737(10) | 7013(11) | 6.0 |
| C( 8A) | 3426( 7) | 6324( 6) | 6630( 8) | 4.4 | C(19B) | 4717(10) | −1095(10) | 7594(10) | 6.1 |
| C( 9A) | 2606( 8) | 6465( 6) | 7200( 8) | 5.1 | C(20B) | 5105( 9) | −286(11) | 7587(11) | 5.9 |
| C(10A) | 2201( 7) | 5775( 8) | 7652( 9) | 6.1 | C(21B) | 5839(10) | −22(10) | 7056(10) | 5.4 |
| C(11A) | 2549( 9) | 4949( 7) | 7580( 9) | 5.9 | O( B) | 7205( 6) | 1026( 6) | 6175( 7) | 5.8 |
| C(12A) | 3389( 7) | 4819( 6) | 7007( 7) | 4.1 | C( 1C) | 711( 3) | −251( 3) | 535( 3) | 2.7( 8) |
| C(13A) | 3823( 7) | 3927( 7) | 6936( 8) | 4.8 | C( 2C) | 791( 5) | −286( 5) | 469( 5) | 7.4(17) |
| C(14A) | 4682( 7) | 3851( 7) | 6359( 8) | 4.6 | C( 3C) | 858( 4) | −229( 4) | 436( 5) | 5.9(14) |
| C(15A) | 5088( 8) | 3022( 7) | 6300( 8) | 4.9 | C( 4C) | 922( 3) | −90( 3) | 424( 4) | 3.6( 9) |
| C(16A) | 5118( 7) | 4579( 7) | 5827( 8) | 5.1 | C( 5C) | 929( 4) | −1( 4) | 451( 5) | 5.4(12) |
| C(17A) | 3815( 6) | 5524( 7) | 6540( 7) | 4.0 | C( 6C) | 857( 4) | 41( 4) | 509( 5) | 5.6(12) |
| C(18A) | 7247( 9) | 3422( 9) | 4706(10) | 7.1 | C( 7C) | 706( 3) | 17( 3) | 627( 4) | 3.8( 9) |
| C(19A) | 7662( 8) | 4078(12) | 4139(12) | 9.0 | C( 8C) | 564( 4) | −9( 3) | 737( 4) | 5.1(11) |
| C(20A) | 7231(11) | 4834( 8) | 4068(10) | 7.5 | C( 9C) | 493( 3) | −69( 3) | 779( 4) | 3.4( 9) |
| C(21A) | 6468( 7) | 5031( 7) | 4596( 9) | 4.8 | C(10C) | 501( 3) | −147( 3) | 743( 3) | 3.1( 8) |
| O( A) | 5113( 6) | 6046( 5) | 5559( 7) | 6.8 | C(11C) | 566( 3) | −187( 3) | 674( 4) | 4.0(10) |
| C( 1B) | 8892(11) | −1666( 9) | 4121(11) | 5.8 | C(12C) | 632( 3) | −125( 3) | 638( 4) | 4.3(10) |
| C( 2B) | 8497( 9) | −2528( 9) | 4139(12) | 5.6 | C(13C) | 709( 3) | −167( 3) | 560( 4) | 3.9(10) |
| C( 3B) | 7702(10) | −2710( 9) | 4708(12) | 5.8 | C(14C) | 781( 3) | −104( 3) | 530( 4) | 3.6( 9) |
| C( 4B) | 6511(10) | −2171( 9) | 5847(10) | 4.9 | C(15C) | 847( 3) | −146( 2) | 465( 3) | 2.3( 7) |
| C( 5B) | 6075( 7) | −1495( 8) | 6398( 9) | 3.8 | C(16C) | 781( 3) | −15( 3) | 547( 4) | 3.5( 9) |
| C( 6B) | 6354( 9) | −634( 9) | 6427(10) | 4.5 | C(17C) | 637( 3) | −39( 3) | 668( 3) | 2.9( 8) |
| C( 7B) | 7615( 8) | 408( 9) | 5764( 9) | 4.2 | C(18C) | 1009( 4) | 50( 4) | 407( 4) | 4.9(11) |
| C( 8B) | 8840(10) | 1335(10) | 5073(10) | 5.4 | C(19C) | 1004( 3) | 139( 3) | 431( 3) | 3.4( 9) |
| C( 9B) | 9596(10) | 1519(10) | 4571(12) | 6.3 | C(20C) | 918( 4) | 178( 4) | 485( 5) | 5.3(12) |
| C(10B) | 10118(10) | 928(11) | 4134(11) | 6.6 | C(21C) | 854( 4) | 123( 4) | 525( 5) | 5.9(13) |
| C(11B) | 9821(11) | 70(10) | 4133(11) | 5.9 | O( C) | 709( 2) | 88( 2) | 667( 3) | 4.8( 8) |

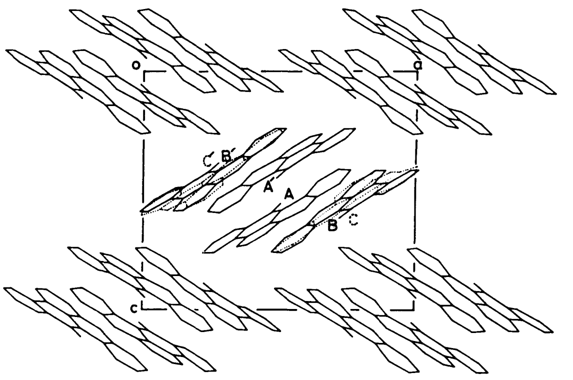

Fig. 1. Projection of the crystal structure along the b axis.
A and B′, and A and C′ form dimer pairs; A and A′ *etc.* are related to each other by the symmetry $2_1$.

crystallographically independent molecules are stacked on each other as shown in Fig. 2. The mean interplanar distances between A and B′, and A and C′, are 3.47(2) and 3.58(2) Å, respectively, which are similar to 3.47(1) and 3.52(3) Å observed in the 8,9-BzBT crystal.[1)] There is no unusually short contacts between the molecules.

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 significantly distorted from a planar conformation owing to the overcrowding around the O atom, which is also found in the 8,9-BzBT crystal. The steric repulsion between O and C(21)-H(21) is released mainly by the enlargement of the O-C(7)-C(16) angle and the twisting of the C(7)-O and C(6)-C(21) bonds. The angle of O-C(7)-C(16) and the twisting angle of O-C(7)···C(6)-C(21) are 126° and 8.2° in A, and 125° and 6.3° in B, respectively. They are comparable to 123° and 6° in 8,9-BzBT.

The interplanar distances between A and B′ or A and C′ seems to indicate that the interaction between the two molecules should be weak. This suggests that the difference in populations of the disordered molecules, B and C, is brought about by the crystalline field. A similar disordering is also found in the 8,9-BzBT crystal. In order to clarify the effect of the crystalline field, the lattice energies were calculated for the two ordered structures using the program PCK5;[5] one is composed of A and B, and the other of A and C. Only the nonbonded interatomic repulsive force was taken into account. The orientation and translation of the molecules were refined to obtain the minimum lattice energy, the molecular geometry being fixed. Several starting structures were constructed by rotating and translating the molecules to a small extent from the position determined by X-ray analysis. Figure 4 shows the structures with the minimum lattice energies and the structure studied by X-ray analysis. The structure

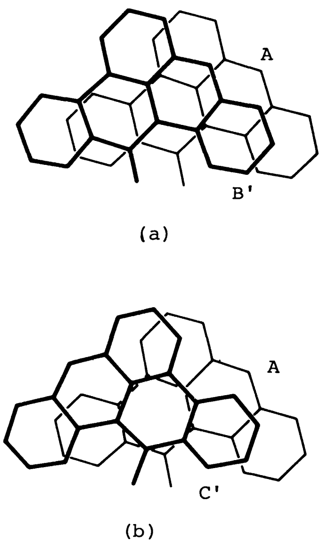

Fig. 2. Overlapping modes.
(a) Dimer pair of A and B′.
(b) Dimer pair of A and C′.

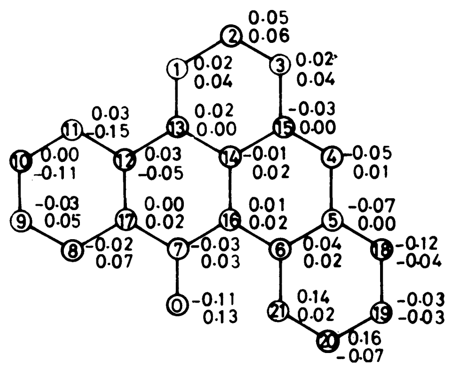

Fig. 3. Numbering scheme and atomic shifts ($l$/Å) from the mean planes of molecules ; the upper and lower values refer to the A and B molecules, respectively.

TABLE 2. BOND LENGTHS ($l$/Å)

| | A | B | | A | B |
|---|---|---|---|---|---|
| C (1)-C (2) | 1.42 | 1.45 | C (8)-C (9) | 1.38 | 1.28 |
| C (1)-C (13) | 1.31 | 1.36 | C (8)-C (17) | 1.37 | 1.41 |
| C (2)-C (3) | 1.34 | 1.36 | C (9)-C (10) | 1.34 | 1.30 |
| C (3)-C (15) | 1.48 | 1.46 | C (10)-C (11) | 1.38 | 1.40 |
| C (4)-C (5) | 1.40 | 1.40 | C (11)-C (12) | 1.41 | 1.38 |
| C (4)-C (15) | 1.37 | 1.32 | C (12)-C (13) | 1.52 | 1.45 |
| C (5)-C (6) | 1.46 | 1.40 | C (12)-C (17) | 1.38 | 1.41 |
| C (5)-C (18) | 1.40 | 1.49 | C (13)-C (14) | 1.42 | 1.48 |
| C (6)-C (16) | 1.48 | 1.46 | C (14)-C (15) | 1.42 | 1.41 |
| C (6)-C (21) | 1.39 | 1.43 | C (14)-C (16) | 1.45 | 1.45 |
| C (7)-C (16) | 1.44 | 1.45 | C (18)-C (19) | 1.37 | 1.42 |
| C (7)-C (17) | 1.51 | 1.43 | C (19)-C (20) | 1.33 | 1.37 |
| C (7)-O | 1.20 | 1.24 | C (20)-C (21) | 1.30 | 1.30 |

The values of e.s.d.'s are 0.01—0.02 in A and 0.02—0.03 in B.

TABLE 3. BOND ANGLES ($\phi$/°)

| | A | B | | A | B |
|---|---|---|---|---|---|
| C (2)-C (1)-C (13) | 122 | 125 | C (1)-C (13)-C (12) | 122 | 121 |
| C (1)-C (2)-C (3) | 122 | 121 | C (1)-C (13)-C (14) | 121 | 115 |
| C (2)-C (3)-C (15) | 116 | 117 | C (12)-C (13)-C (14) | 117 | 124 |
| C (5)-C (4)-C (15) | 122 | 118 | C (13)-C (14)-C (15) | 117 | 120 |
| C (4)-C (5)-C (6) | 121 | 127 | C (13)-C (14)-C (16) | 122 | 118 |
| C (4)-C (5)-C (18) | 122 | 115 | C (15)-C (14)-C (16) | 121 | 122 |
| C (6)-C (5)-C (18) | 117 | 118 | C (3)-C (15)-C (4) | 117 | 117 |
| C (5)-C (6)-C (16) | 118 | 114 | C (3)-C (15)-C (14) | 121 | 122 |
| C (5)-C (6)-C (21) | 117 | 120 | C (4)-C (15)-C (14) | 121 | 121 |
| C (16)-C (6)-C (21) | 126 | 125 | C (6)-C (16)-C (7) | 122 | 122 |
| C (16)-C (7)-O | 122 | 121 | C (6)-C (16)-C (14) | 118 | 117 |
| C (17)-C (7)-O | 121 | 123 | C (7)-C (16)-C (14) | 121 | 120 |
| C (16)-C (7)-C (17) | 118 | 117 | C (7)-C (17)-C (18) | 119 | 117 |
| C (9)-C (8)-C (17) | 122 | 124 | C (7)-C (17)-C (12) | 121 | 128 |
| C (8)-C (9)-C (10) | 117 | 122 | C (8)-C (17)-C (12) | 121 | 115 |
| C (9)-C (10)-C (11) | 124 | 120 | C (5)-C (18)-C (19) | 120 | 120 |
| C (10)-C (11)-C (12) | 118 | 119 | C (18)-C (19)-C (20) | 120 | 116 |
| C (11)-C (12)-C (13) | 120 | 128 | C (19)-C (20)-C (21) | 124 | 128 |
| C (11)-C (12)-C (17) | 118 | 119 | C (6)-C (21)-C (20) | 121 | 119 |
| C (13)-C (12)-C (17) | 121 | 113 | | | |

The values of e.s.d.'s are 1°.

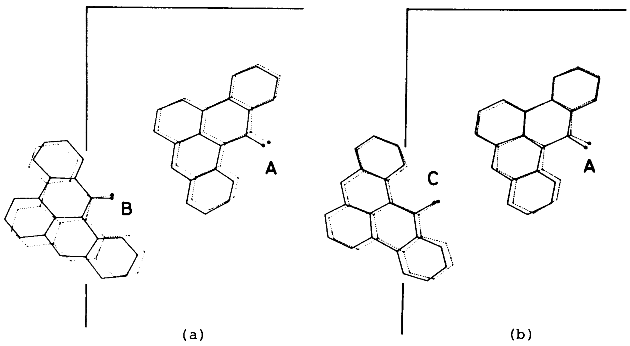

Fig. 4. Results of the packing analysis for 5,6-BzBT. The structures with minimum energies and the ones obtained by the X-ray analysis are dotted and solid lines, respectively.

calculated for B is considerably different from the X-ray structure. The lattice energies calculated are 25.1 and 31.8 KJ mol$^{-1}$ for (a) and (b), respectively. This result qualitatively explains the smaller population of the C molecule.

Similar calculations were also performed for the disordered structure of 8,9-BzBT. In this case, the asymmetric unit of the space group $P2_1/c$ contains one molecule, which is disordered with a ratio of about 4:1. Figure 5(a) shows the structure obtained by X-ray analysis and by the minimum-energy calculation for the molecule with the greater population, whereas Fig. 5(b) is the corresponding one for the molecule with the smaller population. The minimum lattice energies are 13.8 and 31.0 KJ mol$^{-1}$ for (a) and (b), respectively. These results suggest that several packing modes have energies similar to each other in the crystals of such condensed polycyclic aromatic compounds and the populations of the disordered molecules reflects the difference in their lattice energies.

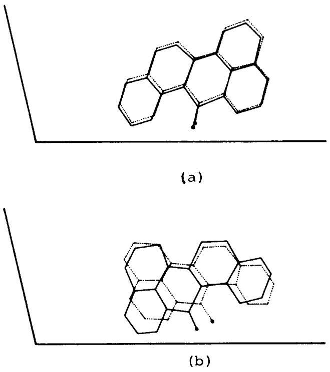

Fig. 5. Results of the packing analysis for 8,9-BzBT. (a) and (b) correspond to the molecules (I) and (II),[1] respectively.
The stuctures with minimum energies and the ones obtained by the X-ray analysis are dotted and solid lines, respectively.

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