BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (5), 1547—1548 (1979)

The Crystal and Molecular Structure of an Isomer of Dibromoperylenes[1)]

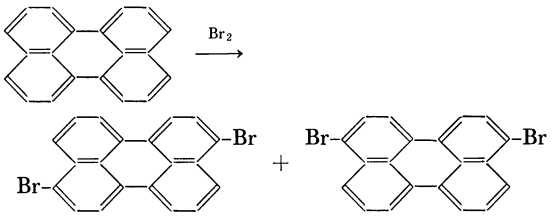
Tokiko UCHIDA,* Kozo KOZAWA, Yukinori NAGAO, and Takahisa MISONOO

Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo, Yamazaki, Noda, Chiba 278

(Received August 10, 1978)

Synopsis. Of two isomers of dibromoperylene, the one possessing the higher melting point has been determined to be 3,9-dibromoperylene from the X-ray diffractometer data. The crystals are monoclinic, with a space group of $P2_1/a$, $a=15.238$, $b=11.826$, $c=3.928$ Å, $\beta=95.53°$, $D_m=1.90$, $D_x=1.94$ g cm^{-3}, and $Z=2$. The structure was solved by the heavy-atom method. The final R value was 0.090 for 931 reflections.

As early as 1925, Zinke *et al.*[2)] obtained two kinds of dibromoperylene, **1** and **2**, by adding bromine to perylene. They presumed the one with the lower melting point, **2**, to be 3,10-dibromoperylene, since it was oxidized in sulfuric acid to produce 3,10-perylenequinone. However, the other dibromoperylene, **1**, has remained ambiguous as to the positions of its substituted bromine atoms. From the view point of our systematically synthetic study of perylene derivatives, the above-mentioned ambiguity is not permissible. Therefore, we have now determined the crystal and molecular structure of **1** from the three-dimensional X-ray data.



1 **2**

Experimental

Materials. Perylene (2.5 g) was dissolved in benzene (375 ml) at 80 °C; the solution was then cooled and the temperature kept at 35 °C with stirring. After adding bromine (7.5 g) to it in a drop-by-drop manner for about 10 min, the mixture was cooled and 3.9 g of solid products were separated. Then, the reaction products were fractionated into two parts, **1** and **2**, with aniline–nitrobenzene (1/1 v/v), the fractionation being done on the basis of the difference in their solubility.

The **1** portion was purified by repeated recrystallizations from aniline–nitrobenzene (1/1 v/v). Yield, 0.51 g; mp 289—293 °C. Found: C, 58.96; H, 2.28%. Calcd for $C_{20}H_{10}Br_2$: C, 58.57; H, 2.46%. **2** was obtained similarly by recrystallization from aniline–toluene (5/3 v/v). Yield, 0.71 g; mp 218—223 °C.[3)] Found: C, 58.16; H, 2.34%. Calcd for $C_{20}H_{10}Br_2$: C, 58.57; H, 2.46%.[4)]

Procedures. A c-elongated needle crystal of **1**, $0.05\times0.1\times0.5$ mm, was grown in a benzene solution. The reflection intensities and cell parameters were determined with a Rigaku four-circle diffractometer at the University of Tokyo with LiF-monochromatized Mo $K\alpha$ radiation ($\lambda=0.7107$ Å). The data were collected by the 2θ-ω scan method up to $2\theta\leqq55°$. Lorentz and polarization corrections were applied, but no absorption correction was made. The profiles of the reflection peaks showed that the crystal was rather poor in quality. Of the 1845 independent measured reflections, 931 (with $|F_o|>3\sigma(F)$) were used in the analysis.

Crystal Data. $C_{20}H_{10}Br_2$, $M_r=410.11$, monoclinic, space group $P2_1/a$, $a=15.238(3)$, $b=11.826(3)$, $c=3.928(3)$ Å, $\beta=95.53(2)°$, $U=704.5$ Å^3, $D_m=1.90$ (flotation), $D_x=1.94$ g cm^{-3}, $Z=2$, $\mu=59.8$ cm^{-1} (Mo $K\alpha$).

Structure Determination and Discussion

The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares procedure. The discrepancy index, R, was finally reduced to 0.090 with the anisotropic thermal parameters for non-hydrogen atoms, a constant isotropic thermal parameter (4.0 Å^2) for hydrogen atoms, and an anomalous dispersion correction for the bromine atom. The atomic scattering factors were adopted from the International Tables for X-Ray Crystallography, Vol. IV.[5)] All the computations were performed at the Computer Centre of the University of Tokyo, using the UNICS program system.[6)]

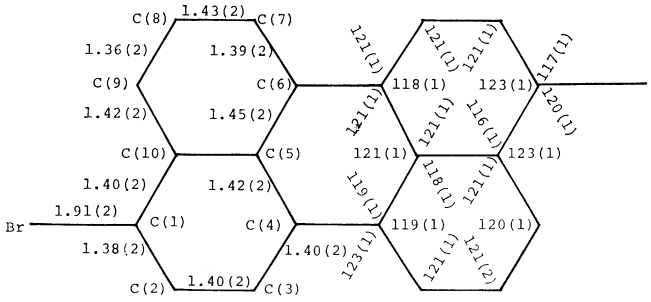


Fig. 1. Bond distances (Å) and angles(°). Estimated standard deviations are shown in parentheses.

The structure analysis indicates that the molecule has a center of symmetry and is 3,9-dibromoperylene. Table 1 gives the positional and thermal parameters,[7)] while the bond distances and angles are shown in Fig. 1. Though the relatively high value of the estimated standard deviations (esd's) prevents any precise discussion of the results, the structure of the perylene skeleton is not affected by the substituted bromine atoms.[8,9)] These large esd's might due to the poor crystallinity, as has been mentioned above.

The molecule makes the following least-squares plane:

$$0.3524X - 0.1280Y + 0.9270Z = 0$$

where X, Y, and Z are coordinates (in Å) referred to the a, b, and c* crystal axes respectively. The largest atomic deviation from this plane is 0.02 Å for C(7).

The dibromoperylene molecules stack to form a

TABLE 1. THE FINAL ATOMIC PARAMETERS ($\times 10^4$), WITH THEIR ESTIMATED STANDARD DEVIATIONS
The anisotropic thermal parameters are of the form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	−1350 (1)	4166 (1)	3826 (4)	58 (1)	62 (1)	697 (11)	43 (2)	52 (5)	−27 (6)
C(1)	−1087 (11)	2631 (11)	2813 (34)	50 (7)	41 (9)	378 (80)	19 (13)	−3 (38)	71 (45)
C(2)	−1711 (9)	1834 (13)	3469 (33)	29 (6)	79 (12)	343 (78)	40 (14)	−3 (34)	−3 (50)
C(3)	−1567 (9)	697 (12)	2731 (37)	29 (6)	67 (11)	502 (87)	11 (13)	74 (35)	71 (54)
C(4)	−799 (8)	348 (11)	1357 (33)	26 (6)	48 (9)	457 (85)	23 (12)	72 (34)	21 (46)
C(5)	−163 (8)	1176 (11)	734 (30)	19 (5)	53 (9)	346 (74)	22 (11)	−74 (30)	−35 (42)
C(6)	655 (8)	848 (12)	−628 (30)	22 (5)	73 (10)	308 (70)	3 (13)	−3 (31)	−46 (50)
C(7)	1271 (10)	1685 (14)	1161 (42)	35 (7)	83 (13)	630 (110)	22 (15)	94 (44)	119 (61)
C(8)	1103 (10)	2849 (14)	−454 (40)	31 (7)	76 (12)	601 (104)	14 (14)	66 (42)	15 (57)
C(9)	346 (9)	318 (13)	810 (39)	28 (6)	78 (12)	559 (100)	−9 (14)	−115 (40)	134 (58)
C(10)	−301 (8)	2358 (11)	1446 (33)	24 (6)	46 (9)	463 (83)	12 (11)	3 (34)	37 (46)
H(2)	−2211 (144)	1813 (164)	4842 (579)						
H(3)	−2020 (139)	238 (182)	3359 (530)						
H(7)	1609 (135)	1463 (177)	−2943 (529)						
H(8)	1695 (143)	3353 (173)	−996 (544)						
H(9)	332 (149)	4134 (151)	2245 (547)						

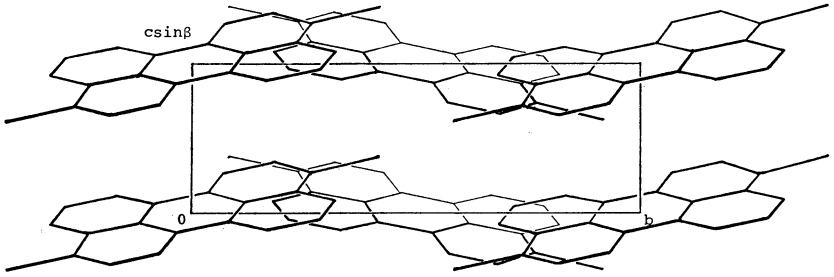


Fig. 2. The structure viewed along the a axis.

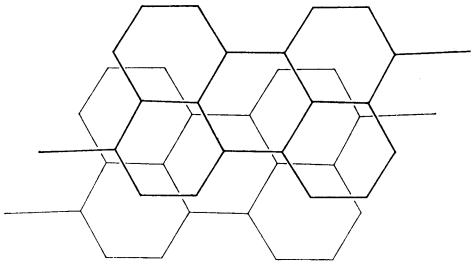


Fig. 3. Molecular overlap projected to the best plane.

column parallel to the c axis, as is shown in Fig. 2. Figure 3 gives the overlapping scheme of two adjacent molecules in a column projected on the molecular plane. The ovelapping manner of the perylene skeleton is very similar to that in the α-form crystal of perylene.[9] All the intermolecular Br···H distances exceed 3.0 Å. Since the sum of the van der Waals radii of Br and H is 3.12 Å, there might well not be any special interaction between intercolumnar atoms.

The authors wish to thank Dr. Maki Sato of the University of Tokyo for his help in the data collection.

References

1) Presented at the 37th National Meeting of the Chemical Society of Japan, Yokohama, April, 1978.
2) A. Zinke, F. Linner, and O. Wolfbauer, *Chem. Ber.*, **58**, 323 (1925).
3) Lit (Ref. 2) mp: **1**, 289.5—291.0 °C; **2**, about 190 °C.
4) The mass spectra of **1** and **2** showed identical patterns of ion peaks over the entire region examined, and gave the parent ion peaks at *m/e* 408, 410, and 412 corresponding to two bromine atoms. The IR spectra of both **1** and **2** also exhibited almost identical absorption patterns.
5) "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1974), pp. 72, 73, 80, and 149.
6) "Universal Crystallographic Computation Program System," ed by T. Sakurai, Crystallographic Society of Japan, Tokyo (1967).
7) The structure-factor table is kept in the office of the Chemical Society of Japan (Document No. 7919).
8) J. Tanaka, *Bull. Chem. Soc. Jpn.*, **36**, 1237 (1963).
9) A. Camerman and J. Trotter, *Proc. R. Soc. London, Ser. A*, **279**, 129 (1964).