

Crystal Structure Determination of 5,6-Dibromoacenaphthene from X-ray Powder Diffraction Data

Nongnuj Jaiboon*

Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand.

* Corresponding author, E-mail: nongnuj.j@chula.ac.th

Received 14 Feb 2001

Accepted 8 Jan 2002

ABSTRACT The new crystal structure of 5,6-dibromoacenaphthene has been successfully determined from X-ray powder diffraction data with monoclinic crystals, $P2_1/n$, $a = 7.88(1) \text{ \AA}$, $b = 11.64(1) \text{ \AA}$, $c = 11.62(1) \text{ \AA}$, $\beta = 107.09(9)^\circ$, $V = 1019.9(1) \text{ \AA}^3$ and $Z = 4$. Individual reflection intensities were extracted by means of *Le Bail's* method. The molecular structure of **1** was solved by direct methods and refined using the combination of least-squares and *Rietveld* methods. The final *Rietveld* refinement converged to the value of $R_p = 0.114$, $R_{wp} = 0.155$, $Bragg-R_f = 5.28$ for 8532 data points and 933 extracted reflections collected in the $2^\circ < 2\theta < 95^\circ$ range. The molecules have an interplanar π - π interaction between the acenaphthene planes with the average distance of $3.57(9) \text{ \AA}$. Moreover, the molecular dimer-pairwise packing diagram has an unexpected straight stacking, as opposed to the usual lateral stacking normally occurred in 5,6-dihaloacenaphthene.

KEYWORDS: Structure determination, X-ray powder diffraction, *Rietveld* Method, 5,6-dibromoacenaphthalene.

INTRODUCTION

X-ray single-crystal diffraction (XRSC) is the most powerful technique for determining crystal structures. Until recently, crystal structure determination from X-ray powder diffraction (XRPD) data was a challenging task.¹ Crystal structures of organic compounds determined from X-ray powder diffraction data are rare.² This paper reports a new crystal structure of 5,6-dibromoacenaphthene, which was determined from XRPD data using an *ab initio* method. The *ab initio* structure determination is the procedure of solving the phase problems without a preliminary model. This method is usually applied to classic inorganic compounds.³ In this technique, the powder diffraction data must be extracted into three-dimensional data in the same reciprocal lattice as the data collected from the XRSC technique using the full-pattern decomposed methods. After the data were extracted successfully, the phase problem was solved using the direct methods or the Patterson method. Finally, the model structure was refined using the least-squares and the full-pattern fitting methods (*Rietveld* method).

In this paper the crystal structure of the title compound was determined from X-ray powder

diffraction data. Its topology, crystal packing and intermolecular interactions, namely a π - π interaction, of the title compound were studied and were compared with the related compounds searched in the Cambridge Structural Database (CSD).⁴ In addition, the molecular dimer-pairwise packing diagram of the title compound has an unexpected straight stacking, as opposed to the usual lateral stacking diagrams, which normally occurred in 5,6-dihaloacenaphthene.

MATERIALS AND METHODS

X-ray data collection

The sample was gently ground in an agate mortar. The resulting powder was "side loaded" into a sample holder, and was smoothed with a glass slide to reduce preferred orientation. The step-scanned diffraction data were measured on a Rigaku diffractometer using graphite monochromatized Cu- K_α radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40kV and 30mA. The divergence slit size was 1 mm and the receiving slit was 0.1 mm. The pattern was collected in the $2^\circ < 2\theta < 100^\circ$ range with a step size of 0.01° and counting time of 10 seconds per step. The $K_{\alpha 2}$ contribution was mathematically removed from the data. The

pattern was indexed using TREOR90 programs⁵ on the basis set of the highest 20 observed lines. The best solution which indexed all the lines indicated a monoclinic unit cell with parameters $a = 7.88(1) \text{ \AA}$, $b = 11.64(1) \text{ \AA}$, $c = 11.62(1) \text{ \AA}$, $\beta = 107.09(9)^\circ$, $V = 1019.9(1) \text{ \AA}^3$. The systematic absences were consistent with the space group $P2_1/n$ ($h0l$; $h+l = 2n$, $h00$; $h = 2n$, $0k0$; $k = 2n$, $00l$; $l = 2n$).

Structure solution and refinement

Initially the powder pattern was refined by FULLPROF program⁶ using the following parameters; zero point error, background parameters (polynomial functions), peak shape profiles (*Pseudo-voigt coefficient*)⁷, FWHM parameters and lattice parameters. In this stage no structural model was used in the refinement cycles. Individual reflection intensities were extracted by means of *Le Bail's* decompositions⁸ of which 933 individual reflections were extracted. This extracted data was then used to solve the structure by direct methods using SHELXS-97 for PC⁹. The two bromine atomic positions were found from electron density maps; Br1 (0.1190, 0.9073, 0.3554), Br2 (0.4086, 0.9276,

0.2073), and were used as a starting structural model in the *Rietveld* refinement using FULLPROF. The individual intensities were re-extracted and a direct methods calculation was then recomputed until all non-hydrogen atoms were found. The model structure was refined using least squares method and difference Fourier maps. At the last step, all non-hydrogen atoms were found from difference Fourier maps, except for C6 and C12 which had to be calculated from idealized rigid planar positions using SHELXL-97¹². All non-hydrogen atoms, except Br1 and Br2, were refined with isotropic displacement parameters and Br1 and Br2 were refined with anisotropic displacement parameters. The atomic positions of C1, C6 and C11 were disordered and refined with fixed isotropic displacement parameters. All hydrogen atoms were placed in calculated positions and were refined with a riding model⁹ with U_{iso} being $1.5U_{eq}$ of the C-atoms to which they were attached. The final *Rietveld* refinement gave $R_p = 0.114$ and $R_{wp} = 0.155$. The final *Rietveld* plot is shown in Fig 1. Crystallographic data and details of the *Rietveld* refinement are given in Table 1.

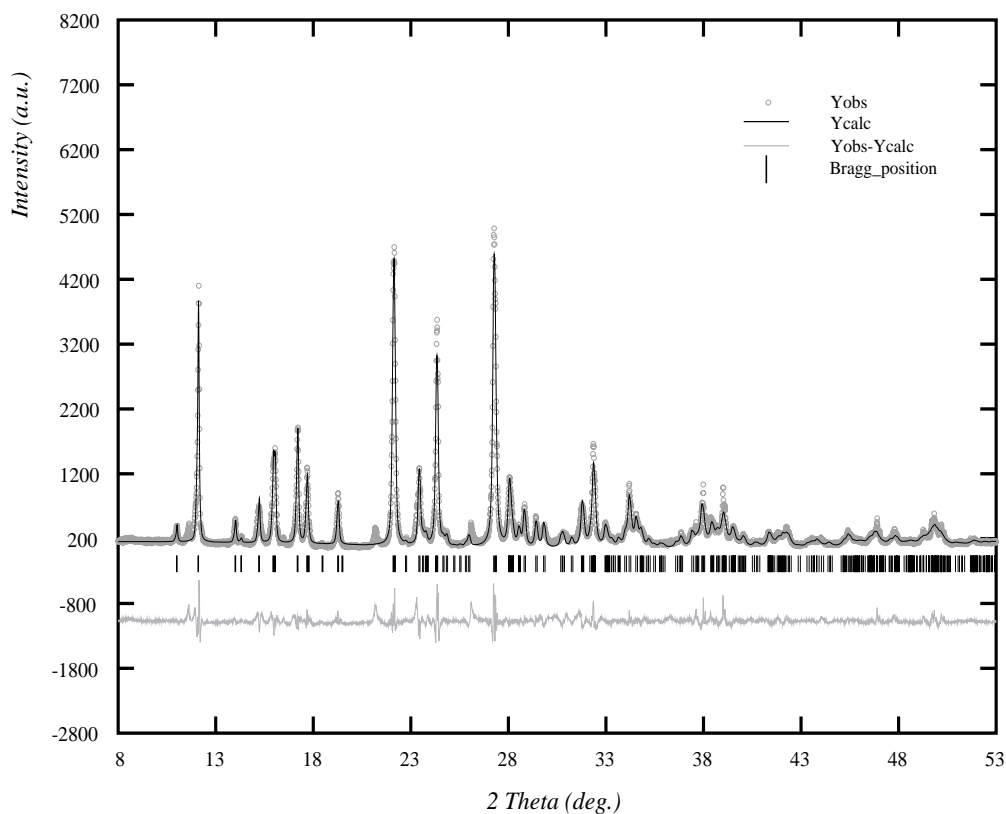


Fig 1. Experimental (o), calculated (solid line) and difference powder X-ray diffraction profiles for the *Rietveld* refinement of 5,6-dibromoacenaphthalene. Reflection positions are marked. The calculated powder diffraction profile is for the final refined crystal structure.

RESULTS AND DISCUSSION

The crystal structure of 5,6-dibromoacenaphthalene (**1**) was successfully determined from X-ray powder diffraction data. The drawing of this compound with atomic labeling is shown in Fig 2. Atomic positions for all non-hydrogen atoms, relevant bond distances and bond angles are given in Table 2 and Table 3, respectively. It should be noted that the structure determination of **1** from X-ray powder diffraction data was able to give only

Table 1. Crystallographic Data for 5,6-dibromoacenaphthalene (C₁₂H₈Br₂).

Formula weight	312.02
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (No.14)
<i>a</i>	7.88(1) Å
<i>b</i>	11.64(1) Å
<i>c</i>	11.62(1) Å
β	107.09(1)°
<i>V</i>	1019.9(1) Å ³
<i>Z</i>	4
<i>D</i> _{cal}	2.023 g cm ⁻³
λ (Cu K α ₁ , K α ₂)	1.54056, 1.54433 Å
Temperature (K)	298
Data range (°)	2 ≤ 2 θ ≤ 95
No. profile point	8532
No. parameters	111
Peak shape function	<i>Pseudo-voigt</i>
Background	Polynomial function
<i>R</i> _{exp}	0.066
<i>R</i> _p	0.114
<i>R</i> _{wp}	0.155

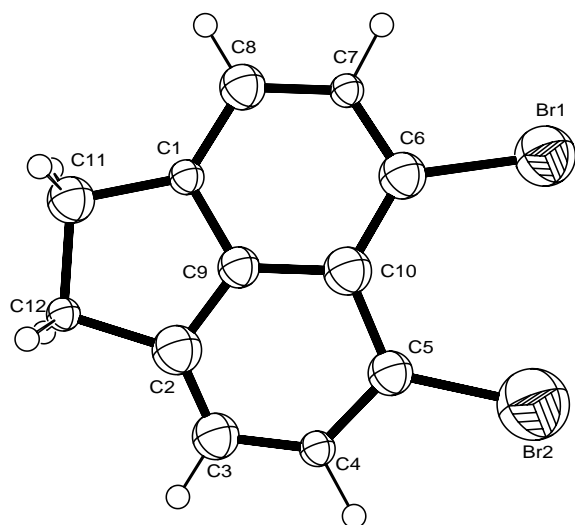


Fig 2. An ORTEP¹² view of 5,6-dibromo acenaphthalene.

average bond distances, overall topology, molecular conformations and crystal packing diagram.

Table 2. Atomic coordinates (x10⁴) and equivalent isotropic displacement parameters (Å² x 10³).

Atom	x	y	z	U(eq)
Br(1)	1091(5)	945(3)	3492(3)	67(2)
Br(2)	4169(6)	733(4)	2100(4)	94(2)
C(1)	-1570(40)	-2140(20)	920(30)	22(9)
C(2)	490(40)	-2220(30)	-120(30)	45(11)
C(3)	1810(40)	-1840(30)	-400(20)	40
C(4)	2890(30)	-1040(20)	310(30)	23(10)
C(5)	2570(40)	-430(20)	1250(20)	16(10)
C(6)	220(40)	-320(20)	2440(30)	40
C(7)	-1280(40)	-800(20)	2550(20)	21(10)
C(8)	-2190(40)	-1680(30)	1840(30)	38(11)
C(9)	0(40)	-1710(30)	800(30)	31(10)
C(10)	940(40)	-790(20)	1520(20)	12(9)
C(11)	-2170(40)	-3160(20)	50(20)	40
C(12)	-830(30)	-3220(20)	-650(20)	21(9)
CT01	367	-1308	1098	10

U(eq) is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Table 3. Bond lengths [Å] and angles [°] for 5,6-dibromoacenaphthalene.

Br(1)-C(6)	1.91(3)	C(3)-C(4)	1.36(3)
Br(2)-C(5)	1.92(2)	C(4)-C(5)	1.39(3)
C(1)-C(9)	1.38(4)	C(5)-C(10)	1.47(3)
C(1)-C(8)	1.40(3)	C(6)-C(7)	1.35(3)
C(1)-C(11)	1.55(3)	C(6)-C(10)	1.46(3)
C(2)-C(3)	1.26(4)	C(7)-C(8)	1.37(3)
C(2)-C(9)	1.37(3)	C(9)-C(10)	1.43(3)
C(2)-C(12)	1.57(3)	C(11)-C(12)	1.52(3)
CT01 - CT01'	3.91(2)		
C(9)-C(1)-C(8)	118(3)	C(7)-C(6)-Br(1)	115(3)
C(9)-C(1)-C(11)	108(3)	C(10)-C(6)-Br(1)	128(2)
C(8)-C(1)-C(11)	133(3)	C(6)-C(7)-C(8)	125(3)
C(3)-C(2)-C(9)	120(3)	C(7)-C(8)-C(1)	120(3)
C(3)-C(2)-C(12)	132(4)	C(2)-C(9)-C(1)	113(3)
C(9)-C(2)-C(12)	109(3)	C(2)-C(9)-C(10)	125(3)
C(2)-C(3)-C(4)	120(3)	C(1)-C(9)-C(10)	122(3)
C(3)-C(4)-C(5)	127(3)	C(9)-C(10)-C(6)	118(3)
C(4)-C(5)-C(10)	113(3)	C(9)-C(10)-C(5)	115(3)
C(4)-C(5)-Br(2)	122(2)	C(6)-C(10)-C(5)	127(3)
C(10)-C(5)-Br(2)	125(2)	C(12)-C(11)-C(1)	105(2)
C(7)-C(6)-C(10)	117(3)	C(11)-C(12)-C(2)	104(2)
C(4)-C(11)-C(12)-C(5)	1(3)		

Symmetry transformations used to generate equivalent atoms: *i*: -*x*, -*y*, -*z*.

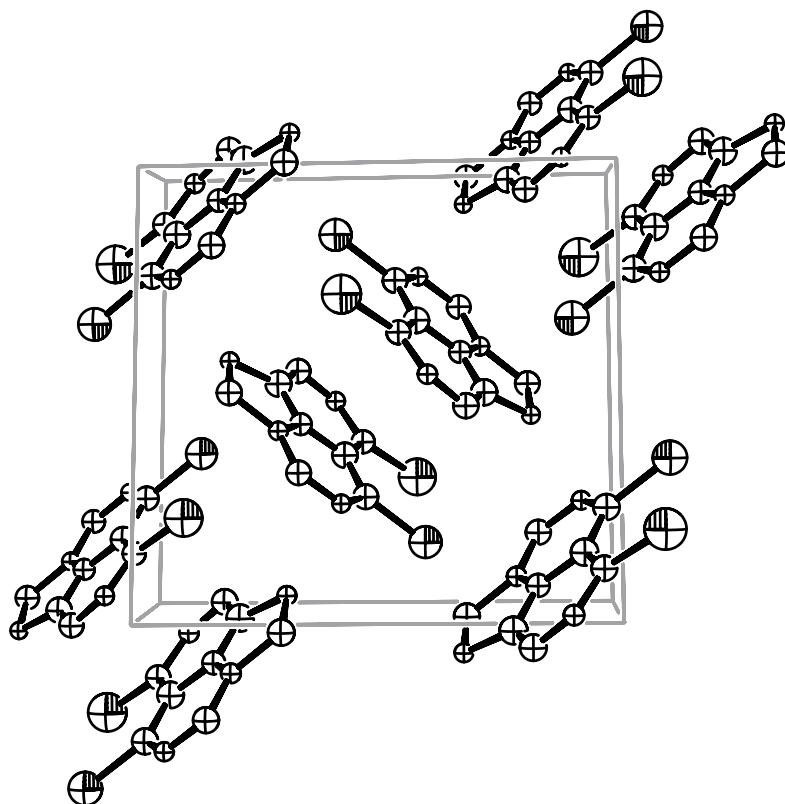


Fig 3. Molecular packing of 5,6-dibromoacenaphthalene along the *a*-axis, showing the π - π interaction between the acenaphthalene plans with the distance of 3.57(9) Å.

Comparison with 1,8-dibromonaphthene, in **1** the ethylene bridging the 1,2-positions has forced the 5,6-dibromoacenaphthene framework planar. Deviation of the acenaphthene carbon atoms from their least-squares planes (C1 to C10) are in the range of $-0.07(2)$ Å to $0.03(2)$ Å. The C-C bond distances in the acenaphthene ring showed considerable variation, falling in the range of $1.34(3)$ Å to $1.47(3)$ Å. These are corresponding to a search from the Cambridge Structural Database that the frameworks of dihaloacenaphthene were planar and the frameworks of dihalonaphthene were not planar. The bond distances of Br1-C1 ($1.91(3)$ Å) and Br2-C2 ($1.92(2)$ Å) were within the expected theoretical Br-C distance of 1.94 Å, but they were longer than that of 1.893 Å in 5-bromo, 6-chloroacenaphthene.¹⁰ The bridging ethano carbon atoms (C11 and C12) also lay in the naphthalene plane with the C11 and C12 deviations of $0.12(3)$ Å and $0.12(3)$ Å, respectively, and C4-C11-C12-C5 torsion angle of $1(3)^\circ$.

Using the latest version 5.12 of Cambridge Structural Database (CSD)⁴, a survey of crystal structures of 5,6-dihaloacenaphthene revealed that

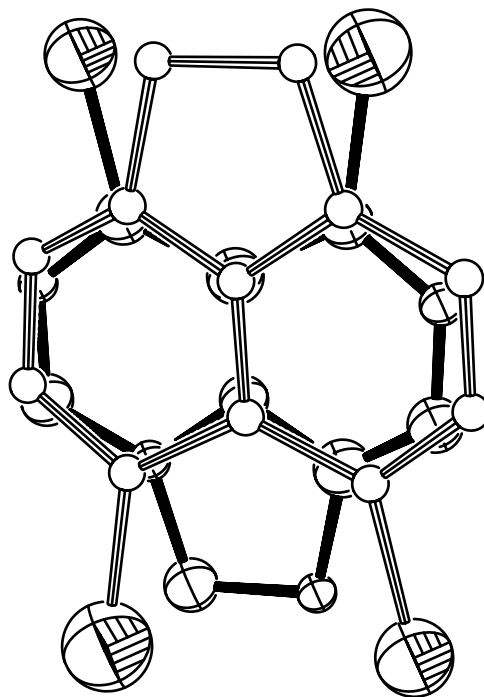


Fig 4. A p-p stacked pair of 5,6-dibromoacenaphthene.

the molecules prefer to stack laterally in a dimer-pairwise mode. This is probably due to the minimization of the repulsive force between the halogen atoms and between the ethylene bridges. When comparing between **1** and 5,6-dichloroacenaphthene¹², it can be seen that even though **1** is overcrowded with the bromine atoms, the acenaphthalene frameworks are packed in an unexpected straight dimer-pairwise of a herringbone type (Fig 3). The acenaphthalene planes are found in centrosymmetrically related pairs and parallel to one another by π - π interactions (Fig 4) with the interplanar distance of 3.57(9) Å, and the distance between their centroids [*CT01*...*CT01*(-x, -y, -z) = 3.91(2) Å].

ACKNOWLEDGEMENT

I am grateful to Dr M Watkinson and Dr RG Prichard for providing the 5,6-dibromoacenaphthalene. The financial support for this research was provided by the National Science and Technology Development Agency (NSTDA) to Nongnuj Jaiboon (CO-B-06-33-09-201). I wish to thank Dr Veera Muangsin and Dr Thawatchai Tuntulani for kind suggestions and reading of the manuscript.

REFERENCES

1. Harris KDM and Tremayne M (1996) Crystal structure determination from powder diffraction data. *Chem Mater* **8**, 2554-70.
2. Wessels T, Baerlocher C and McCusker LB (2000) Single-crystal-like diffraction data from polycrystalline materials. *Science* **284**, 5413, 477-9.
3. Reviews in Mineralogy (1989), The Mineralogical Society of America, Washington DC, Vol 20.
4. The Cambridge Structural Database (CSD) (2000), Cambridge Crystallographic Data Centre, Cambridge, UK.
5. Werner PE, Erikson L and Westdahl M (1985) TREOR, a semi-exhaustive trial-and-error powder indexing program for all symmetries. *J Appl Cryst* **48**, 367.
6. Rodriguez-Carvaj J, "FULLPROF program", In: *Collected Abstracts of Powder Diffraction Meeting*: Toulouse, France, July, 1990, 127.
7. Thompson P, Cox DE, Hastings JB, (1987). *Rietveld* refinement of Debye-Scherrer synchrotron X-ray data from Al₂O₃. *J Appl Cryst* **20**, 79.
8. Le Bail A, Duroy H, Forquet JL (1988) Ab initio structure determination of LiSbWO₆ by X-ray powder diffraction. *Mater Res Bull* **23**, 447.
9. Sheldrick GM (1997) SHELX-97, University of Gottingen, Germany.
10. Avoyan RL, Struchkov YT (1961) *Zh Strukt Khim* **5**, 407, 1964.
11. Avoyan RL, Struchkov YT (1961) *Zh Strukt Khim* **2**, 719.
12. Johnson CK and Bennett MN (1996) ORTEP-3 for Windows, University of Glasgow, UK.