Crystal Structure Refinement of 1,4,5,8-Tetrabromonaphthalene: A Twisted Chiral Naphthalene Induced by Steric Repulsion

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The peri-positions of an aromatic hydrocarbon, such as the 1- and 8-positions of naphthalene, are unique because of their closeness. The distance of hydrogens at the peri-positions of naphthalene is 2.446 Å,1 which is comparable to the sum of the van der Waals (vdW) radii of two hydrogen atoms 2.40 Å.2 Therefore, all of the elements and/or groups introduced on these positions induce short atomic contact that is smaller than the sum of vdW radii of two hydrogen atoms. Such peri-disubstituted compounds as 1,8-disubstituted naphthalene are important models of this overcrowded space. Two representative examples are known. One is a non-covalent interaction, such as the short atomic contacts of chalcogens for 1,8-dichalcogeno-naphthalene in the context of research on two-center four-electron σ- and π-bonds.3 Another example is a incorporation of a proton in 1,8-bis(dimethylamino)naphthalene, which is known as proton sponge.4 Such halogen derivatives as 1,8-dihalogenonaphthalenes have also attracted much attention. The molecules have been used as precursors for the above-mentioned chemistry, and their distorted structures are interesting for elucidating the relationship between the electronic structure and the distortion of the molecule.5 Among them, we focused on 1,4,5,8-tetrabromonaphthalene 1 (Fig. 1) because of its simple preparation and wide applications. Its single-crystal diffraction study was carried out in 1968.6 Unfortunately, the resolution of that experiment is not sufficient for contemporary science. Here we report the refinement of the molecular structure of 1 and discuss the twisted distorted structure.

The synthesis of the title compound 1 was performed according to a revised method reported in 2015.7 A single crystal suitable for a diffraction study was harvested from acetic acid.6 X-ray diffraction data for the crystal were collected using a Rigaku XtaLAB P200 diffractometer with graphite monochromated Mo-Kα radiation. The crystal information is given in Table 1 and the details are described in Supporting Information #1, SM#1. Theoretical studies carried out with a Gaussian program (Ver. 16, Revision A.03) and the details are shown in SM#2.

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The title molecule should have several conformational isomers that originate from the atomic repulsion manner of peri-bromines, such as 1a (point group: D_2h), 1b (C_2), 1c (D_2), and 1d (C_2h) shown in Fig. 1. The molecular structure obtained by a diffraction study is shown in Fig. 2. The most significant structural feature of 1 would be the extremely short Br–Br contacts, 3.2129(8)Å for Br1–Br4 and 3.2056(8)Å for Br2–Br3, which are much shorter than the sum of the vdW radii of two

Fig. 1 Four plausible stereoisomers of 1,4,5,8-tetrabromonaphthalene along with their point groups.

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Table 1 Crystal and experimental data

| Chemical formula: C_{10}H_{4}Br_{4} | Formula weight: 443.77 | T = 93(2)K |
|-----------------------------------|------------------------|-------------|
| Crystal system: monoclinic        | Space group: P2\textsubscript{1}/c |
| a = 9.470(3)\text{"A}            |            |            |
| b = 15.530(4)\text{"A}           |            |            |
| c = 7.340(2)\text{"A}            |            |            |
| V = 1078.75(5)\text{"A}^3        |            |            |
| D\textsubscript{c} = 2.732 g/cm\textsuperscript{3} | | |
| Radiation: Mo K\textalpha (\lambda = 0.71075 \text{"A}) | | |
| \mu(Mo K\textalpha) = 149.205 cm\textsuperscript{-1} | | |
| Crystal size = 0.270 \times 0.040 \times 0.040 mm\textsuperscript{3} | | |
| No. of reflections collected = 16427 | | |
| No. of independent reflections = 2389 | | |
| \(I > 2\sigma(I)\) = 0.0249 | | |
| Goodness-of-fit on F\textsuperscript{2} = 0.715 | | |
| (\Delta F)\textsubscript{max} = 0.85 e\text{"A}\textsuperscript{-1} | | |
| Measurement: Rigaku XtaLAB P200 diffractometer | | |
| Data collection & cell refinement program: CrystalClear | | |
| Data reduction program: CrystalStructure 4.2.5 | | |
| Structure determination: intrinsic phasing (SHELXT-2014/410) | | |
| Structure refinement program: SHELXL 2014/7 | | |
| CCDC: 1999102 | | |

Table 2 Bond distances (\text{"A}) and selected angles (°) of 1 (Mean bond distances for bond-\alpha, -\beta, -\gamma, -\delta, -\epsilon, and -\zeta and mean angles for \psi and \omega are also shown, assuming 1 takes perfect D\textsubscript{2} symmetry (the definitions for \alpha, \beta, \gamma, \delta, \epsilon, \zeta, \psi, and \omega are shown in Fig. 1c))

|        | \alpha = 1.912(3) | \beta = 1.433(4) | \gamma = 1.370(5) | \delta = 1.394(5) | \epsilon = 1.470(4) | \psi = 112.3(2) | \omega = 125.5(2) |
|--------|------------------|-----------------|------------------|-----------------|------------------|--------------|--------------|
| Br1-C1 | 1.909(3)         |                 |                  |                 |                  |              |              |
| Br3-C6 | 1.908(3)         |                 |                  |                 |                  |              |              |
| Br2-C4 | 1.918(3)         |                 |                  |                 |                  |              |              |
| Br4-C9 | 1.914(3)         |                 |                  |                 |                  |              |              |
| C1-C10 | 1.430(4)         |                 |                  |                 |                  |              |              |
| C5-C6  | 1.433(4)         |                 |                  |                 |                  |              |              |
| C3-C4  | 1.373(5)         |                 |                  |                 |                  |              |              |
| C9-C10 | 1.430(4)         |                 |                  |                 |                  |              |              |
| C6-C7  | 1.377(4)         |                 |                  |                 |                  |              |              |
| C8-C9  | 1.369(4)         |                 |                  |                 |                  |              |              |
| C2-C3  | 1.396(5)         |                 |                  |                 |                  |              |              |
| C5-C10 | 1.470(4)         |                 |                  |                 |                  |              |              |
| \angle Br1-C1-C2 | 112.3(2) | \angle Br2-C4-C3 | 112.4(2) | \angle Br4-C9-C8 | 112.5(2) | \angle Br1-C1-C10 | 125.4(2) |
| \angle Br3-C6-C7 | 112.0(2) | \angle Br2-C4-C5 | 125.0(2) | \angle Br3-C6-C7 | 126.0(2) | \angle Br4-C9-C10 | 125.5(2) |

Fig. 2 ORTEP drawing of 1 showing the thermal ellipsoid at 50% probability. (a) Top view, (b) side view from white arrow-b shown in (a), (c) bottom view from white arrow-c shown in (a), and (d) out-of-plane displacements (in units of 0.01 \text{"A}) of each atom from the least-squares naphthalene mean plane defined by ten carbon atoms.

It is known that naphthalene exhibits a unique bond alternation. The mean bond distances for bond-\beta, -\gamma, -\delta, and -\epsilon of 1 (for definitions, see Fig. 1) are 1.433(4), 1.370(5), 1.394(5), and 1.470(4)\text{"A}, respectively (Table 2). These distances are significantly longer (for bond-\beta and -\epsilon) than the corresponding bonds of naphthalene, considering the standard deviations 3\sigma of the experiments. Theoretical calculations (vide infra) for 1c and naphthalene also support this tendency (see SM#2).

To consider the details of the conformational isomerism of 1, theoretical studies were carried out under a vacuum condition, and it was found that 1c is the most stable one. The energies of 1a, 1b, and 1d are 1.2, 0.8, and 1.0 kcal mol\textsuperscript{-1} higher than that of 1c. Normal coordination analyses were also carried out for 1a - 1d. 1a has two (i = -24.18 and -19.85 cm\textsuperscript{-1}) imaginary frequencies, whereas 1b and 1d have one (i = -15.36 cm\textsuperscript{-1} and i = -12.44 cm\textsuperscript{-1}, respectively) imaginary frequency. Based on these results, we conclude that 1c racemizes at room temperature quickly through 1b as the transition state.

The packing motif of 1c is shown in Fig. 3. As mentioned above, the observed 1c is chiral and the stereochemistry shown in Fig. 2 is (M,M) using helicene terminology. The corresponding enantiomer, (P,P) isomer, is generated by an inversion operation. In the \beta-axis direction, (M,M) and (P,P) isomers are stacked alternately to produce a one-dimensional (1D) column. The interplanar interactions are nonuniform, i.e., the interplanar distances are 3.654 and 3.667 \text{"A} (Fig. 3b). It is worth

bromines, 3.70 \text{"A}. These contacts induce a large steric repulsion, and the atoms are located above and below the naphthalene mean plane. The deviations of the individual atoms from the least-squares naphthalene mean plane, defined by ten carbon atoms, are given in Fig. 2(d). The root-mean-square out-of-plane displacement, \Delta, of the naphthalenic ten atoms from the least-squares plane is 0.096 \text{"A}. The corresponding chloride, 1,4,5,8-tetrachloronaphthalene, also takes a similar conformation, as expected, and the \Delta value is smaller, 0.036 \text{"A}. This twisted form is chiral, as seen in the structures of 1,8-bis(1-adamantyl)-naphthalene derivatives, i.e., equatorenes. The crystal of 1 belongs to the P2\textsubscript{1}/c space group; therefore, the corresponding enantiomer is generated by a symmetry operation of this space group (vide infra).

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emphasizing that there is no significant intermolecular short Br–Br contact that is smaller than the sum of the vdW radii of two bromines (3.70 Å). The shortest distance was found between the 1D columns, 3.5992(8) Å, which produced another 1D ladder sheet structure in the (1.1.0) and (–1.–1.0) directions (Fig. 3(c)). This aggregation motif was found in a STM study. The lack of a short intermolecular atomic interaction might be the reason for the relatively low melting point of 1, 145 °C. The molecular structure of 1 was characterized. The characteristic features of this molecule could contribute to advanced materials chemistry, including surface science.

Acknowledgements

This work was supported in part by the Cooperative Research Program of “Network Joint Research Center for Materials and Devices: Dynamic Alliance for Open Innovation Bridging Human, Environment and Materials” Grant Number 20201317, and the Priority Research Program sponsored by the Asian Human Resources Fund of Tokyo Metropolitan Government (TMG).

Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/xraystruct/.

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\Delta = \sqrt{\frac{\sum_{i=1}^{n} \delta_i^2}{10}}
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