

## An azonia derivative of hexahelicene

Kiyoshi Sato,<sup>a\*</sup> Sadao Arai,<sup>b</sup> Takamichi Yamagishi<sup>a</sup> and Tomoaki Tanase<sup>c</sup>

<sup>a</sup>Department of Applied Chemistry, Graduate School of Engineering, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397, Japan, <sup>b</sup>Department of Chemistry, Tokyo Medical University, 6-1-1 Shinjuku, Shinjuku-ku, Tokyo 160-8402, Japan, and <sup>c</sup>Department of Chemistry, Faculty of Science, Nara Women's University, Nara-shi, Nara 630-8285, Japan  
Correspondence e-mail: sato-kiyoshi@c.metro-u.ac.jp

Received 26 November 2002

Accepted 24 December 2002

Online 28 February 2003

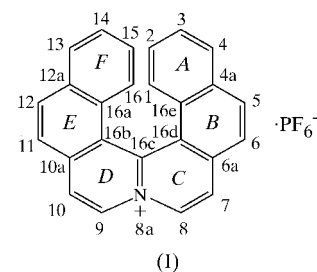
In 8a-azonia[6]helicene hexafluorophosphate or 8a-azonia-phenanthro[3,4-c]phenanthrene hexafluorophosphate, C<sub>25</sub>H<sub>16</sub>N<sup>+</sup>·PF<sub>6</sub><sup>-</sup>, replacement of an outer bridgehead carbon of hexahelicene by a quaternary Nsp<sup>2</sup> atom results in a geometrical change in the helical structure. The racemic heterohelicene forms homochiral columnar stacks through intermolecular π–π donor–acceptor interactions in the crystal-line state.

## Comment

Helicenes, well known non-planar polycyclic aromatic compounds, have fascinated chemists since the initial synthesis of [6]helicene (Newman *et al.*, 1955) because of their unique helical structure (Laarhoven & Prinsen, 1984). A number of carbohelicenes and heterohelicenes incorporating thiophene, pyrrole, furan and pyridine rings have been synthesized to date and some of their crystal structures have also been determined (Meurer & Vögtle, 1985). Recently, we succeeded in the first synthesis of cationic heterohexahelicenes, *viz.* azonia[6]helicenes, possessing a quaternary Nsp<sup>2</sup> atom at a bridgehead position of the outer or inner helix skeleton (Arai *et al.*, 1989, 1995). The present study is concerned with the structure of the 8a-azonia[6]helicene hexafluorophosphate salt, (I), which has a quaternary N atom at the outer bridge-head and can be compared with the structure of carbohelicene (de Rango *et al.*, 1973). Also, this cationic heterohelicene has both π-electron acceptor and donor parts in one molecule and is therefore expected to form a well defined stacked structure in the crystalline state.

Single-crystal X-ray analysis revealed that (I) crystallized as a racemate, with two enantiometric pairs of heterohelicene cations and four counter-anions in the unit cell. The molecular geometry of the azonia[6]helicene cation greatly resembles that of carbo[6]helicene and shows common features which are generally found in all other helicenes studied, *viz.* the aromatic rings deviate significantly from planarity, the inner

C–C bonds are lengthened and the outer bonds are shortened compared with a value of 1.39 Å for a typical aromatic C–C distance.



However, the most important structural difference between (I) and carbo[6]helicene is seen around the N atom. The three N–C bond lengths of (I) are significantly contracted (*ca* –0.03 Å) compared with those of the corresponding C–C bonds in carbo[6]helicene, and the bond angles C8–N8a–C9 and C16b–C16c–C16d for (I) are also slightly different from the corresponding angles of carbo[6]helicene (Table 1). When compared with the structural data of the quinolizinium cation (Sato *et al.*, 2001) and azoniafluoranthene (Boubekeur *et al.*, 1989), it is seen that these differences are a common feature in

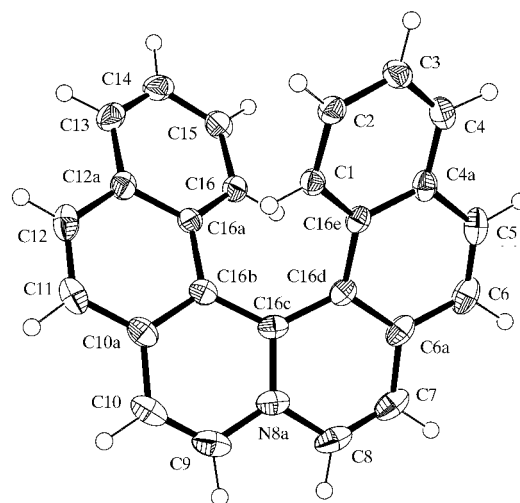
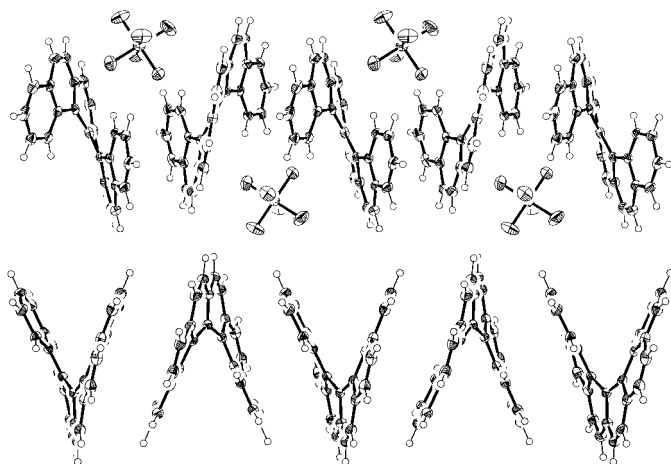


Figure 1

The molecular structure of the 8a-azonia[6]helicene cation in (I), shown with 50% probability displacement ellipsoids for non-H atoms.

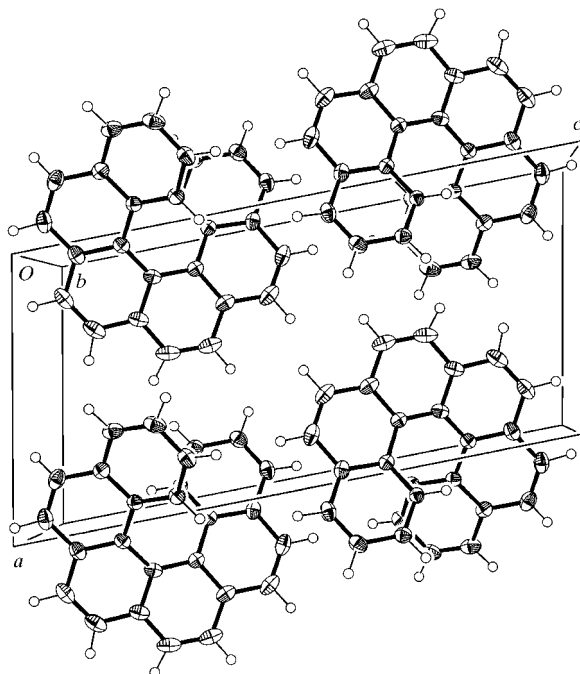
azonia aromatic compounds (Arai & Hida, 1992). The subtle changes at the central moiety alter the geometry of the helix of helicene. Table 1 summarizes the angles between the least-squares planes of the six-membered rings (defined in the *Scheme*) and the torsion angles of the inner bonds, and compares them with the corresponding values for carbo[6]helicene taken from the literature (de Rango *et al.*, 1973). These values indicate that 8a-azonia[6]helicene tends to be flattened compared with carbo[6]helicene; the angle between the least-squares planes of the two terminal benzene rings of (I) is 49.85 (6)° versus 58.5° in carbo[6]helicene.



**Figure 2**

Two views of one of the enantiomerically pure cylindrical column stacks extending along the *b* axis. The  $\text{PF}_6^-$  anions have been omitted for clarity in the bottom view.

On the other hand, inspection of the molecular packing of (I) reveals the formation of a well defined one-dimensional helical columnar structure extending along the *b* axis (Fig. 2). Each column consists of a single enantiomer and the interstitial regions of the column are occupied by  $\text{PF}_6^-$  anions (Fig. 2, top). The helicene molecules are stacked one above the other in an antiparallel arrangement (Fig. 2, bottom). The mean interplanar separation between the overlapping naphthalene rings is *ca* 3.5 Å, which suggests the presence of a face-to-face-type  $\pi$ - $\pi$  interaction. In addition, attractive electronic interactions between the central  $\pi$ -acceptor quinolizinium moiety and the terminal  $\pi$ -donor benzene rings facilitate the above geometrical arrangement and contribute to the stabilization of the columnar stacks. It has been reported that planar



**Figure 3**

The crystal packing in (I), viewed down the *b* axis. The  $\text{PF}_6^-$  anions have been omitted for clarity.

acridizinium (benzo[*b*]quinolizinium) cations in the crystalline state exist exclusively facing each other in an *anti*-head-to-tail arrangement (Ihmels *et al.*, 1999).

Fig. 3 shows the secondary packing diagram of the helical columns in the crystal, viewed in a projection along the *b* axis. There are homochiral arrays (of the columns) parallel to the *ab* plane with periodical inversion of the helicity along the *c* axis. The packing pattern of racemic (I) differs greatly from that of the carbo- and other heterohelicenes; most racemic helicenes form racemate crystals in which two antipodes stack either alternately or in an interpenetrative fashion. To the best of our knowledge, one reported crystalline form of carbo[5]-helicene is the only example where similar homochiral arrays are formed in the crystal structure (Kuroda, 1982).

## Experimental

Compound (I) was prepared by the photocyclization of 2-stylynaphtho[1,2-*a*]quinolizinium hexafluorophosphate in a manner similar to that reported previously by Arai *et al.* (1989). Single crystals of (I) were obtained by slow evaporation from an acetonitrile solution (m.p. 508–510 K).

### Crystal data

$\text{C}_{25}\text{H}_{16}\text{N}^+\cdot\text{PF}_6^-$	$D_x = 1.619 \text{ Mg m}^{-3}$
$M_r = 475.37$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4702 reflections
$a = 9.1026 (7) \text{ \AA}$	$\theta = 3.4\text{--}27.5^\circ$
$b = 12.1235 (9) \text{ \AA}$	$\mu = 0.21 \text{ mm}^{-1}$
$c = 18.019 (1) \text{ \AA}$	$T = 153.2 \text{ K}$
$\beta = 101.219 (3)^\circ$	Prism, yellow
$V = 1950.5 (2) \text{ \AA}^3$	$0.35 \times 0.30 \times 0.30 \text{ mm}$
$Z = 4$	

**Table 1**

Comparison of selected geometric parameters.

	Azonia[6] <sup>a</sup>	Carbo[6] <sup>b</sup>
Selected bond lengths (Å) and angles (°) around the N atom		
N8a(C8a)—C8	1.393 (2)	1.416 (6)
N8a(C8a)—C9	1.390 (2)	1.420 (6)
N8a(C8a)—C16c	1.391 (2)	1.420 (4)
C16b—C16c	1.436 (2)	1.444 (4)
C16c—C16d	1.437 (2)	1.449 (4)
C8—N8a(C8a)—C9	118.0 (1)	122.2 (4)
C8—N8a(C8a)—C16c	118.0 (1)	119.0 (3)
C9—N8a(C8a)—C16c	118.0 (1)	118.8 (3)
N8a(C8a)—C16c—C16b	116.4 (1)	116.9 (3)
N8a(C8a)—C16c—C16d	116.4 (1)	117.5 (3)
C16b—C16c—C16d	127.2 (1)	125.6 (3)
Angles (°) between two least-squares planes (see Scheme)		
A—B	12.26 (6)	9.8
B—C	12.80 (6)	15.2
C—D	14.07 (6)	14.4
D—E	12.71 (6)	15.2
E—F	11.87 (6)	11.5
A—F	49.85 (6)	58.5
Torsion angles (°) of the inner helix skelton		
C1—C16e—C16d—C16c	18.2 (2)	11.2
C16e—C16d—C16c—C16b	25.7 (2)	30.0
C16d—C16c—C16b—C16a	28.2 (2)	30.3
C16c—C16b—C16a—C16	19.1 (2)	15.2
Non-bonding distance (Å) between terminal rings		
C1...C16	3.191 (2)	3.03

Notes: (a) this work; (b) de Rango *et al.* (1973).

## Data collection

Rigaku/MSC Mercury CCD diffractometer	4412 independent reflections
$\omega$ scans	3690 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (Blessing, 1995)	$R_{\text{int}} = 0.022$
$T_{\text{min}} = 0.880$ , $T_{\text{max}} = 0.938$	$\theta_{\text{max}} = 27.5^\circ$
11 700 measured reflections	$h = -11 \rightarrow 11$
	$k = -15 \rightarrow 15$
	$l = -23 \rightarrow 22$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 0.1568P]$
$R(F) = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.126$	$(\Delta/\sigma)_{\text{max}} = 0.030$
$S = 0.92$	$\Delta\rho_{\text{max}} = 0.30 \text{ e } \text{\AA}^{-3}$
3690 reflections	$\Delta\rho_{\text{min}} = -0.29 \text{ e } \text{\AA}^{-3}$
362 parameters	
H-atom parameters not refined	

Data collection: *CrystalClear* (Rigaku Corporation, 2000); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994) and *DIRDIF94* (Beurskens *et al.*, 1994); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPIII* (Johnson & Burnett, 1996); software used to prepare material for publication: *TEXSAN*.

This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan under grant No. 14740352 and a Grant-in-Aid for Promoted Research by Young Researchers (TMU).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1095). Services for accessing these data are described at the back of the journal.

## References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Arai, S. & Hida, M. (1992). *Adv. Heterocycl. Chem.* **55**, 261–358.
- Arai, S., Ishikura, M., Sato, K. & Yamagishi, T. (1995). *J. Heterocycl. Chem.* **32**, 1081–1083.
- Arai, S., Yafune, T., Okubo, M. & Hida, M. (1989). *Tetrahedron Lett.* **30**, 7217–7218.
- Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., de Gelder, R., Israel, R. & Smits, J. M. M. (1994). *The DIRDIF94 Program System*. Technical Report, Crystallography Laboratory, University of Nijmegen, The Netherlands.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Boubekeur, K., Fourmigue, M. & Batail, P. (1989). *Acta Cryst.* **C45**, 1636–1637.
- Ihmels, H., Leusser, D., Pfeiffer, M. & Stalke, D. (1999). *J. Org. Chem.* **64**, 5715–5718.
- Johnson, C. K. & Burnett, M. N. (1996). *ORTEPIII*. Version 1.0.2. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Kuroda, R. (1982). *J. Chem. Soc. Perkin Trans. 2*, pp. 789–794.
- Laarhoven, W. H. & Prinsen, W. J. C. (1984). *Top. Curr. Chem.* **125**, 65–130.
- Meurer, K. P. & Vögtle, F. (1985). *Top. Curr. Chem.* **127**, 1–76.
- Molecular Structure Corporation (1999). *TEXSAN*. Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.
- Newman, M. S., Lutz, W. B. & Lednicer, D. (1955). *J. Am. Chem. Soc.* **77**, 3420–3421.
- Rango, C. de, Tsoucaris, G., Declercq, J. P., Germain, G. & Putzeys, J. P. (1973). *Cryst. Struct. Commun.* **2**, 189–190.
- Rigaku Corporation (2000). *CrystalClear*. Rigaku Corporation, 3-9-12 Aki-shima, Tokyo, Japan.
- Sato, K., Arai, S., Yamagishi, T. & Tanase, T. (2001). *Acta Cryst.* **C57**, 174–175.
- Sheldrick, G. M. (1993). *SHELXL93*. University of Göttingen, Germany.