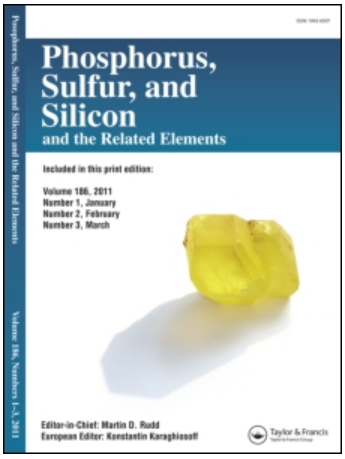


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis, Structure and Properties of Bridged and Unbridged Heterohelicenes

Kazuhiko Tanaka; Yoshinori Kitahara

To cite this Article Tanaka, Kazuhiko and Kitahara, Yoshinori(1999) 'Synthesis, Structure and Properties of Bridged and Unbridged Heterohelicenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 153: 1, 399 — 400
To link to this Article: DOI: 10.1080/10426509908546490
URL: http://dx.doi.org/10.1080/10426509908546490

Phosphorus, Sulfur and Silicon, 1999, Vol. 153-154, pp. 399-400
Reprints available directly from the publisher
Photocopying permitted by license only

Synthesis, Structure and Properties of Bridged and Unbridged Heterohelicenes

KAZUHIKO TANAKA and YOSHINORI KITAHARA

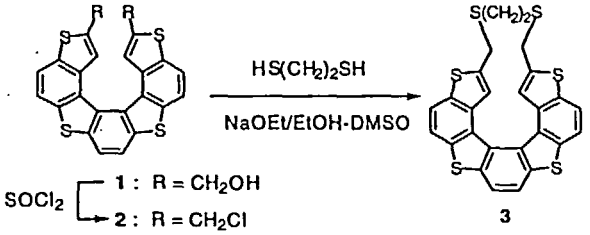
Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606–8502, Japan

The structure of a bridged thiaheterohelicene has been determined by X-ray crystallographic method, showing that the helicene framework exhibits significant elasticity and acts as a molecular spring.

Keywords: thiaheterohelicene; interplanar angle; molecular spring

Recently we have reported the first example of construction of a four-leaf clover motif from optically active (*P*)-2,13-bis(hydroxymethyl)-dithieno[3,2-e:3',2'-e']benzo[1,2-b:4,3-b']bis[1]-benzothiophene ((*P*)-**1**).[1] X-ray crystal analysis showed that the interplanar angle between the terminal thiophene rings of (*P*)-**1** is 33.83°. When racemic heterohelicenediol ((*PM*)-**1**) forms an inclusion complex with ethanol through a helical hydrogen-bonding, the interplanar angle increases to 37.96°.[2] These results clearly indicate that the helicene framework in the solid state exhibits significant elasticity by changing its interplanar angle, and thence the pitch of the helix. Since solvent effects and intramolecular hydrogen bonding play a role in solution, the interplanar angle observed in the crystal state is not necessarily that in solution. In order to investigate the relationship between the conformation in the solid state and that in solution, we designed and synthesized a bridged heterohelicene (**3**) starting from **1** and 1,2-ethanedithiol.

X-ray crystal analysis of **3** indicates that the interplanar angle between two terminal rings is 53.46°, which is very close to 54.51° of the clathrate (*PM*-**1**)(1,2-dichloroethane)$_{0.5}$.[3] The two sulfur atoms (S(28) and S(31)) of the bridge are in an *anti* orientation and thus the torsion angle of S(28)-C(29)-C(30)-S(31) is 176.2°. The bridge of one enantiomer of racemic thiaheterohelicene **3** locates above the helical framework of the same helicity as shown in Fig. 1b and the two columns of same helicity run parallel along the crystallographic *b* axis. We can conclude that thiaheterohelicenediol **1** functions as a molecular spring in the solid state due to the pattern of hydrogen bonds.



SCHEME 1 Synthesis of bridged [7]thiaheterohelicene (3).

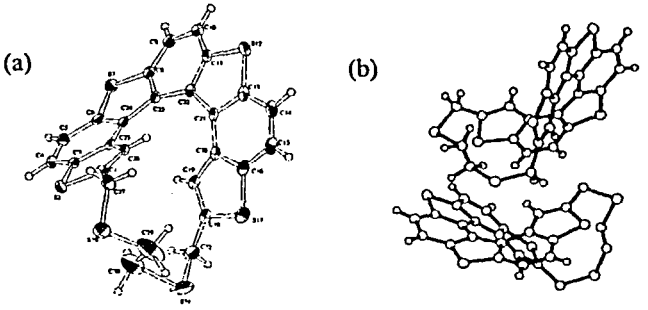


FIGURE 1 (a) ORTEP drawing of **3** and (b) molecular packing of **3**.

References

[1] K. Tanaka and Y. Kitahara, *J. Chem. Soc., Chem. Commun.*, 1141 (1998).
[2] K. Tanaka, Y. Shogase, H. Osuga, H. Suzuki, W. Nakanishi, N. Nakamura, and Y. Kawai, *J. Chem. Soc., Chem. Commun.*, 1873 (1995).
[3] K. Tanaka and Y. Kitahara, Manuscript in preparation.