

Ultralong C–C bonds in hexaphenylethane derivatives*

Takanori Suzuki^{1,‡}, Takashi Takeda¹, Hidetoshi Kawai^{1,2}, and Kenshu Fujiwara¹

¹*Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan;* ²*PRESTO, Japan Science and Technology Agency, Honcho, Kawaguchi, Saitama 332-0012, Japan*

Abstract: The longer C–C bond than the standard (1.54 Å) is so weakened that it is cleaved easily, as found in the parent hexaphenylethane (HPE). However, the compounds with an ultralong C–C bond (1.75 Å) can be isolated as stable solids when the bond-dissociated species does not undergo any reactions other than bond reformation. This is the central point in designing the highly strained HPEs, which were obtained by two-electron reduction of the corresponding dications. Steric repulsion of “front strain” is the major factor to expand the central C–C bond of HPEs. During the detailed examination of the ultralong C–C bond, the authors discovered the intriguing phenomenon of “expandability”: the C–C bond length can be altered over a wide range by applying only a small amount of energy (1 kcal mol⁻¹) supplied by crystal packing force. This observation indicates that the much longer C–C bond than the shortest nonbonded contact (1.80 Å) will be realized under the rational molecular design concept.

Keywords: covalent bonds; long bonds; X-ray structures; hexaphenylethanes; strained molecules; redox system.

INTRODUCTION

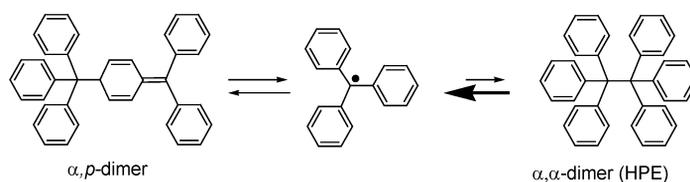
Hexaphenylethane

Hexaphenylethane (HPE) is a molecule with a lot of riddles [1]. Triphenylmethyl (Ph₃C•) dimerizes to form an unsymmetrical hydrocarbon (α , p -dimer) since the central C–C bond in HPE (α , α -dimer) is so weakened by steric factors that it is cleaved easily to regenerate two radicals (Scheme 1). The derivatives of α , α -dimers can be isolated by attaching large enough substituents on the phenyl groups that prevent α , p -dimer formation [2]. Another series of stable HPEs are obtained by switching the bonding process of the radicals from an intermolecular into an intramolecular one (Scheme 2) [3]. At the same time, proper “clumping” of phenyl groups reduces the steric repulsion in the HPEs formed by bonding.

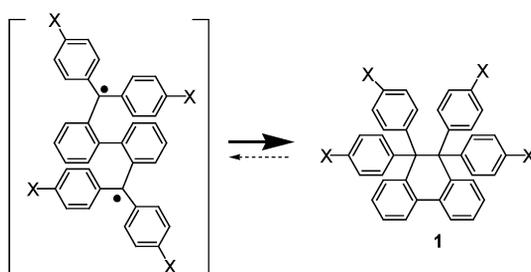
Thus, 9,9,10,10-tetraphenyl-9,10-dihydrophenanthrene (**1**, X = H) [4] has been known as a stable hydrocarbon for years. Very low reactivity of this hydrocarbon toward molecular oxygen suggests that steady-state concentration of the bond-dissociated diradical is negligible, although the central C–C bond length was calculated to be much longer (1.65 Å) [3] than the standard (1.54 Å). The steric repulsion between the phenyl groups facing each other (“front strain”) [5] is most probable as a major factor to account for the elongation. At any event, the outstanding stability of **1** (X = H) clearly shows that

*Paper based on a presentation at the 12th International Symposium on Novel Aromatic Compounds (ISNA-12), 22–27 July 2007, Awaji Island, Japan. Other presentations are published in this issue, pp. 411–667.

[‡]Corresponding author



Scheme 1 Divergent pathway for dimerization of triphenylmethyl.

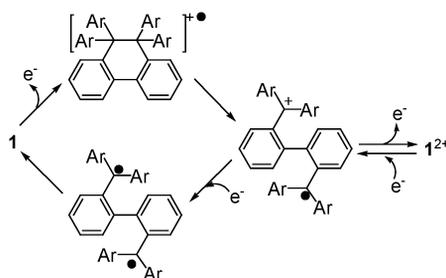


Scheme 2 Intramolecular C–C bond formation to dihydrophenanthrene-type HPEs **1**.

the intramolecular C–C bond formation is much more favored than other chemical processes even though the resulting C–C bond in **1** is long and weakened [6].

Electrochromic systems based on hexaphenylethane skeleton

In 1997, we reported short-step preparation [7] of bis(triarylmethyl) dyes $\mathbf{1}^{2+}$ with a biphenyl-2,2'-diyl skeleton, which afford colorless dihydrophenanthrene-type HPEs **1** ($X = \text{NMe}_2, \text{OMe}$) by C–C bond formation upon reduction. The latter are stable colorless crystals with electron-donating properties thanks to fourfold amino or methoxy substitution. No signs of weakened-bond dissociation were observed under ambient conditions. As studied by Maslak [8], mesolysis of polyarylated C–C bonds requires less energy than homolysis. Thus, one-electron oxidation of **1** ($X = \text{NMe}_2, \text{OMe}$) causes bond fission to give biphenylic cation radicals $\mathbf{1}^{\bullet+}$, which is more easily oxidized to the corresponding dication $\mathbf{1}^{2+}$ (Scheme 3) [9]. Electrochemical interconversion of **1** and $\mathbf{1}^{2+}$ exhibits vivid color change. Several isosbestic points were observed in the spectroelectrograms (Fig. 1), indicating that clean reaction occurs with negligible steady-state concentration of other chemical species such as $\mathbf{1}^{\bullet+}$ [7]. Reversible C–C bond formation/cleavage is the central point in designing “dynamic redox pairs” [10], which endows the electrochromic systems with high electrochemical bistability. Such behavior is closely related with the “intramolecular switching of single bonds”, shown by the pioneering works by Hünig [11].



Scheme 3 Mechanism for interconversion between HPEs **1** and dication $\mathbf{1}^{2+}$ upon two-electron transfer.

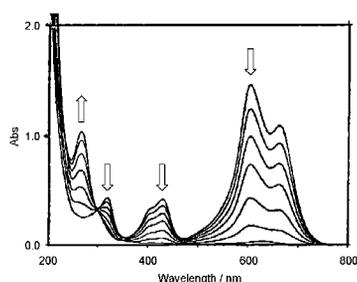


Fig. 1 Changes in UV-vis spectrum of 1^{2+} ($X = \text{NMe}_2$; $\log \varepsilon = 5.05$ at $\lambda = 604$ nm) salt upon constant-current electrochemical reduction in MeCN.

RESULTS AND DISCUSSION

Low-temperature X-ray analyses on dihydrophenanthrene-type HPEs

In the course of our studies on the advanced electrochromic systems with fluorescence and/or chiroptical properties as additional outputs [12], we have constructed a series of dihydrophenanthrene-type electrochromic donors, whose X-ray structures could be successfully determined with high accuracy by conducting the data collection at low temperature (Chart 1). We have found the values in the range of 1.61–1.65 Å for the central C–C bond, thus confirming that the C–C bond length is larger than the standard as predicted for the parent hydrocarbon (**1**, $X = \text{H}$). The experimental verification also indicates that the expansion is the common feature for the dihydrophenanthrene-type HPEs. It has been also revealed that the major factor to account for the elongation is the “front strain” because the flanking bonds are also longer than the standard, which connects the ethane carbon and one of the aryl groups. Although the “orbital-interaction-through-bond” [13] might also help bond elongation, its contribution seems only marginal since this effect should have shortened but not expanded the flanking bonds.

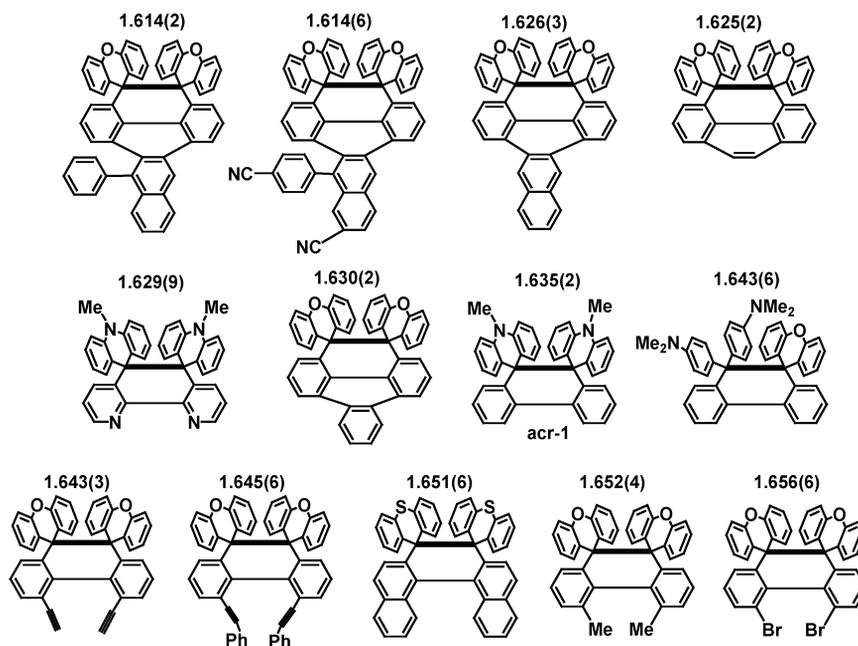
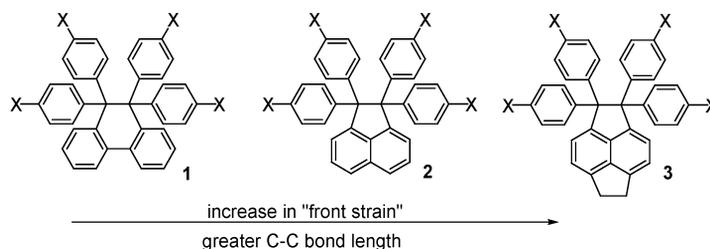


Chart 1 The C–C bond length in various dihydrophenanthrene-type HPEs determined by low-temperature X-ray analyses.

Longer C–C bond in HPEs with the acenaphthene skeleton

The “front strain” shown above is closely related with the torsional strain of ethanes in the sense that both strain energies increase as the torsion angle decreases from 60° to 0° . By adopting the rigid five-membered ring in place of the chair-like six-membered structure, HPEs **2** with the acenaphthene skeleton would suffer from the larger “front strain” to exhibit the longer C–C bond than the dihydrophenanthrene-type HPEs **1** (Scheme 4). This is the case: the central C–C bond length for **acr-1** is 1.635(2) Å with the inner-torsion angle of $47.1(1)^\circ$ [12a], whereas those values in **acr-2** are 1.696(3) Å and $18.1(3)^\circ$ [14a] (Fig. 2).



Scheme 4 Structural variation of HPEs with different degree of “front strain”.

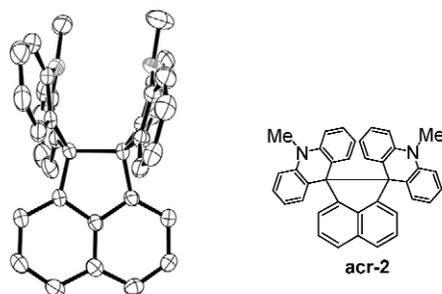


Fig. 2 Low-temperature X-ray analysis of **acr-2**. The length for the central C–C bond is 1.696(3) Å.

Thus, the acenaphthene scaffold in HPEs **2** is one of the ideal skeletons to seek for exploiting compounds with an extremely long C–C bond. Although the estimated bond-dissociation energy (BDE) for the long C–C bond of 1.70 Å is only 20 kcal mol^{-1} [6], a series of 1,1,2,2-tetraarylacenaphthenes **2** could be isolated as stable solids with no signs of decomposition under ambient conditions. They were prepared independently by us [14] and by Gabbaï [15] from the corresponding naphthalene-1,8-diyl dications upon reduction. Remarkable stability of **2** can be rationalized by considering the non-Kekulé structure for the bond-dissociated species (naphthalene-1,8-diyl diradicals). So that, if formed, they only undergo bond reformation to give **2**. The drawback is, however, that the five-membered ring of the acenaphthene skeleton is not so rigid as we had expected. The severe “front strain” induces skewing deformation of the acenaphthene skeleton of **2** in some cases.

Thus, the experimentally determined lengths of the long C–C bond in acenaphthene-type HPEs **2** exhibit considerable variation. The central C–C bond is not so long {1.633(3) Å for X = Cl [15a] and 1.670(3) Å for X = MeO [15b]} when the five-membered ring adopts the skewed conformation with the larger torsion angle for $C_{8a}-C_1-C_2-C_{2a}$ [$27.9(3)^\circ$ for X = Cl and $20.6(2)^\circ$ for X = MeO, respectively]. In contrast, other derivatives of HPEs **2** with the eclipsed conformation {X = H: $0.0(2)^\circ$ [15b] and X = tBu: $7.2(2)^\circ$ [14b]} suffer from the larger “front strain”, which expands the polyarylated C–C bond [X = H: 1.701(3) Å and X = tBu: 1.708(4) Å, respectively]. It is less probable that the elec-

tronic effects of the substituents on the aryl groups determine the preference for the eclipsed/skewed conformation, so that, the torsion angle would be affected by a small energy difference provided by crystal packing force.

By modifying the acenaphthene skeleton to increase its rigidity, skewing deformation would become more costly than expanding the long C–C bond. Thus, the pyracene-type HPEs **3** with the extra five-membered ring are the better candidates to exhibit ultralong C–C bond more promisingly. This is also the heart of the authors' molecular design to realize the C–C bond length beyond 1.75 Å.

Ultralong C–C bond in HPEs with the pyracene skeleton

By starting with 5,6-dibromoacenaphthene and various diaryl ketones, a series of acenaphthene-5,6-diyl bis(diarylmethyl)iums were obtained, from which HPEs **3** with the pyracene framework were generated upon reduction [16]. The X-ray analyses have shown that all of them adopt the eclipsed conformation with the torsion angle of C_{8a}-C₁-C₂-C_{2a} less than 3°, and consequently, all of the central C–C bonds are longer than 1.7 Å. Extremely long bonds are found in **3** (X = H) [1.754(2) Å] and **3** (X = F) [1.761(4) Å]. The polyarylated C–C bond in a highly strained caged compound had been known as the longest [1.713(2) Å] among the pure hydrocarbons as studied by Herges [17]. In the case of halogenated aromatics, Toda's dihalonaphthocyclobutenes [18] were the world-record holders [diiodide, 1.734(5) Å]. Our approach by using the pyracene skeleton could make it possible to generate the compounds having the longer C–C bond than these excellent precedents.

Though largely separated, there must be an ordinary covalent bond between C₁-C₂ in **3**. The two carbons are hybridized in an sp³ manner, as judged by the tetrahedral coordination determined by X-ray analyses (Fig. 3) and by ¹³C NMR spectroscopy [78.73 ppm for **3** (X = H) in CDCl₃]. In this way, the authors have succeeded in establishing the general scheme to design the HPE derivatives with an ultralong C–C bond: (1) increase in "front strain" by torsional fixation and skeletal rigidity; (2) non-Kekulé structure for the bond-dissociated species that can only undergo bond-reforming without giving any by-products. The latter condition is essential to isolate and characterize the HPE containing a weakened central C–C bond.

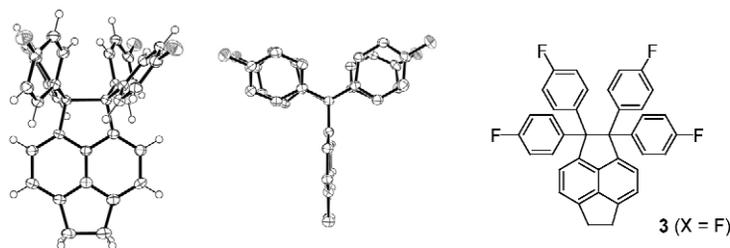


Fig. 3 Low-temperature X-ray analysis of **3** (X = F). The length for the central C–C bond is 1.761(4) Å.

Based on the proposal for linear relationship between bond lengths and BDEs [6], the C₁-C₂ bond in **3** (X = H, F) shown above should have been assumed to have the negative BDE values of -2.5 and -5.5 kcal mol⁻¹, respectively, which is meaningless. Thus, there should be a nonlinear relationship or some special effects in the region of the ultralong and the extremely long C–C bond. In any event, the BDEs are very small for the central bond of pyracenes **3**. During further examination of extremely long C–C bond in the pyracene-type HPEs, the authors have encountered the special occasion in related to the "expandability" of the C–C bond, that is, exceptionally large difference in bond length among conformational isomorphs [19].

“Expandability” of the ultralong C–C bond

Compared with the conformational polymorphs where different conformers crystallize separately in the different crystal forms, the conformational isomorphs have been seldom observed, by which the different conformers are packed orderly in the same crystal [20]. The latter is the case for the pyracene-type HPE **acr-3** attached with two spiro(10-methylacridane) units. According to the X-ray analysis at $-180\text{ }^{\circ}\text{C}$, there are four crystallographically independent molecules in the unsolvated crystal. Two adopt the eclipsed conformation [inner torsion angle: $3.4(2)$, $9.4(2)^{\circ}$], and the other two are skewed-shaped [$23.4(1)$, $24.7(1)^{\circ}$] (Fig. 4). As expected, the eclipsed conformers possess much longer central C–C bond [$1.771(3)$ and $1.758(3)$ Å] than the skewed molecules [$1.712(2)$ and $1.707(2)$ Å] [19]. By measuring the diffraction data at several different temperatures, it was shown that the bond lengths are marginally temperature-dependent and exhibit continuous elongation upon elevating temperature. The longest bond length is as large as $1.781(6)$ Å at $-40\text{ }^{\circ}\text{C}$ and $1.791(3)$ at $140\text{ }^{\circ}\text{C}$, respectively. The latter value is one of the largest ever reported for the C–C bond length found in the uncharged organic molecules [21].

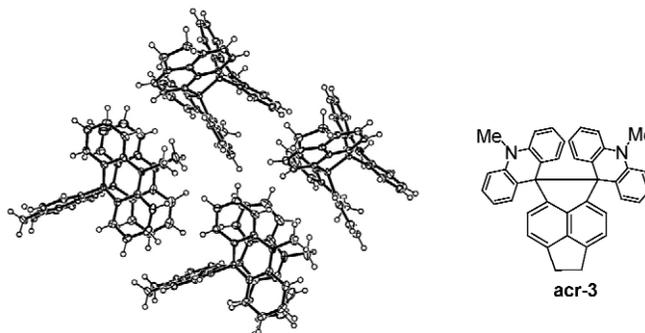


Fig. 4 Four crystallographically independent molecules in the crystal of **acr-3**. The lengths for the central C–C bond are $1.707(2)$, $1.712(2)$, $1.758(3)$, and $1.771(3)$ Å at $-180\text{ }^{\circ}\text{C}$.

More importantly, the above results indicate that the central C–C bond in HPE **acr-3** changes its bond length from $1.707(2)$ to $1.771(3)$ Å at $-180\text{ }^{\circ}\text{C}$ by switching strain-relieving modes from skewing the rigid skeleton to expanding the C–C bond. The difference of $0.064(3)$ Å is remarkable. Coexistence of two conformers in the same crystal shows that they have nearly the same heat of formation. Theoretical calculation at the B3LYP/6-31G* level indicated that **acr-3** has the two energy-minimized geometries, which differ less than 1 kcal mol^{-1} in energy. The eclipsed conformer (torsion angle: 0°) is predicted to possess the C–C bond longer than the skewed one (16.4° , global minimum), which corresponds well to the experimental observation of large difference of that bond.

CONCLUSION

This work has demonstrated that HPEs with an ultralong C–C bond (>1.75 Å) could be prepared and isolated as stable solids under the rational molecular design concept. These results show that the previously proposed linear correlation between bond length and BDEs [6] is not valid in the extreme cases shown here. The authors also encountered the intriguing phenomenon, “expandability” of the ultralong bond. Thus, there is a chance to find even longer C–C bonds. We admire Herges’ view published in 1997 [17], “Stable C–C bonds even longer than the smallest nonbonding distance of two carbon atoms, 1.80 Å [22], are conceivable”, and we are very close to it.

REFERENCES

1. (a) J. M. McBride. *Tetrahedron* **30**, 2009 (1974); (b) W. Schlenk, A. Herzenstein, T. Weickel. *Chem. Ber.* **43**, 1753 (1910).
2. M. Stein, W. Winter, A. Rieker. *Angew. Chem., Int. Ed. Engl.* **17**, 692 (1978).
3. (a) W. D. Hounshell, D. A. Dougherty, J. P. Hummel, K. Mislow. *J. Am. Chem. Soc.* **99**, 1916 (1977); (b) B. Kahr, D. V. Engen, K. Mislow. *J. Am. Chem. Soc.* **108**, 8305 (1986).
4. G. Wittig, H. Petri. *Justus Liebigs Ann.* **505**, 17 (1933).
5. H. C. Brown, H. Bartholomay Jr., M. D. Taylor. *J. Am. Chem. Soc.* **66**, 435 (1944).
6. A. A. Zavitsas. *J. Phys. Chem. A* **107**, 897 (2003).
7. T. Suzuki, J. Nishida, T. Tsuji. *Angew. Chem., Int. Ed. Engl.* **36**, 1329 (1997).
8. P. Maslak, J. N. Narvaez, T. M. Vallombroso Jr. *J. Am. Chem. Soc.* **117**, 12373 (1995).
9. T. Suzuki, J. Nishida, T. Tsuji. *Chem. Commun.* 2193 (1998).
10. T. Suzuki, E. Ohta, H. Kawai, K. Fujiwara, T. Fukushima. *Synlett (Account)* 851 (2007).
11. (a) M. Horner, S. Hünig. *J. Am. Chem. Soc.* **99**, 6122 (1977); (b) S. Hünig, C. A. Briehn, P. Bäuerle, A. Emge. *Chem.—Eur. J.* **7**, 2745 (2001).
12. (a) T. Suzuki, A. Migita, H. Higuchi, H. Kawai, K. Fujiwara, T. Tsuji. *Tetrahedron Lett.* **44**, 6837 (2003); (b) T. Suzuki, R. Yamamoto, H. Higuchi, E. Hirota, M. Ohkita, T. Tsuji. *J. Chem. Soc., Perkin Trans. 2* 1937 (2002); (c) T. Suzuki, S. Tanaka, H. Higuchi, H. Kawai, K. Fujiwara. *Tetrahedron Lett.* **45**, 8563 (2004); (d) T. Suzuki, S. Tanaka, H. Kawai, K. Fujiwara. *Chem. Asian J.* **2**, 171 (2007); (e) T. Suzuki, T. Iwai, E. Ohta, H. Kawai, K. Fujiwara. *Tetrahedron Lett.* **48**, 3599 (2007); (f) T. Suzuki, R. Tamaki, E. Ohta, T. Takeda, H. Kawai, K. Fujiwara, M. Kato. *Tetrahedron Lett.* **48**, 3823 (2007).
13. (a) R. Hoffmann. *Acc. Chem. Res.* **4**, 1 (1971); (b) R. Gleiter. *Angew. Chem., Int. Ed. Engl.* **13**, 696 (1974); (c) M. N. Paddon-Row. *Acc. Chem. Res.* **15**, 245 (1982); (d) K. D. Jordan, M. N. Paddon-Row. *Chem. Rev.* **92**, 395 (1992).
14. (a) H. Kawai, T. Takeda, K. Fujiwara, T. Suzuki. *Tetrahedron Lett.* **45**, 8289 (2004); (b) T. Takeda, H. Kawai, K. Fujiwara, T. Suzuki. Unpublished results.
15. (a) H. Wang, F. P. Gabbaï. *Angew. Chem., Int. Ed.* **43**, 184 (2004); (b) H. Wang, F. P. Gabbaï. *Org. Lett.* **7**, 283 (2005).
16. T. Takeda, H. Kawai, R. Herges, K. Fujiwara, T. Suzuki. Unpublished results.
17. S. Kammermeier, P. G. Jones, R. Herges. *Angew. Chem., Int. Ed. Engl.* **36**, 1757 (1997).
18. (a) F. Toda, K. Tanaka, Z. Stein, I. Goldberg. *Acta Crystallogr., Sect. C* **52**, 177 (1996); (b) K. K. Baldrige, Y. Kasahara, K. Ogawa, J. S. Siegel, K. Tanaka, F. Toda. *J. Am. Chem. Soc.* **120**, 6167 (1998); (c) F. Toda, K. Tanaka, M. Watanabe, K. Tamura, I. Miyahara, T. Nakai, K. Hirotsu. *J. Org. Chem.*, **64**, 3102 (1999); (d) F. Toda. *Eur. J. Org. Chem.* 1377 (2000); (e) K. Tanaka, N. Takamoto, Y. Tezuka, M. Kato, F. Toda. *Tetrahedron* **57**, 3761 (2001).
19. H. Kawai, T. Takeda, K. Fujiwara, T. Inabe, T. Suzuki. *Cryst. Growth Des.* **5**, 2256 (2005).
20. (a) T. Mori, H. Inokuchi. *Bull. Chem. Soc. Jpn.* **61**, 591 (1988); (b) P. Guionneau, C. J. Kepert, M. Rosseinsky, D. Chasseau, J. Gaultier, M. Kurmoo, M. B. Hursthouse, P. Day. *J. Mater. Chem.* **8**, 367 (1998); (c) S. S. Turner, P. Day, T. Gelbrich, M. B. Hursthouse. *J. Solid State Chem.* **159**, 385 (2001); (d) K. Ogawa, Y. Kasahara, Y. Ohtani, J. Harada. *J. Am. Chem. Soc.* **120**, 7107 (1998); (e) H. Nazir, M. Yildiz, H. Yilmaz, M. N. Tahir, D. Ülkü. *J. Mol. Struct.* **524**, 241 (2000); (f) M. Kurahashi. *Bull. Chem. Soc. Jpn.* **49**, 2927 (1976).
21. V. G. Fritz, S. Wartanessian, E. Matern, W. Hönle, H. G. v. Schnering. *Z. Anorg. Allg. Chem.* **475**, 87 (1981).
22. J. L. Adcock, A. A. Gakh, J. L. Pollitte, C. Woods. *J. Am. Chem. Soc.* **114**, 3980 (1992).