Extremely Long C−C Bond in (−)-*trans*-1,2-Di-*tert*-butyl-1,2-diphenyl- and 1,1-Di-*tert*-butyl-2,2-diphenyl-3,8-dichlorocyclobuta[*b*]naphthalenes

Fumio Toda,*,† Koichi Tanaka,† Masaki Watanabe,† Kenichi Tamura,† Ikuko Miyahara,‡
Tadashi Nakai,‡ and Ken Hirotsu*,‡

Department of Applied Chemistry, Faculty of Engineering, Ehime University,
Matsuyama 790-8577, Japan, and Department of Chemistry, Faculty of Science, Osaka City University,
Sugimoto-cho, Sumiyoshi-ku, Osaka 950, Japan

Received October 6, 1998

The sterically bulky *t*-Bu-substituted derivatives of 1,1,2,2-tetraphenyl-3,8-dichlorobuta[*b*]naphthalene (**5**), *trans*-1,2-*tert*-butyl-1,2-diphenyl- (**8**) and 1,1-di-*tert*-butyl-2,2-diphenyl-3,8-dichlorocyclobuta[*b*]naphthalene (**12**), were prepared. X-ray analysis of **8** and **12** at 150 K showed that C−C bonds of **8** and **12** are 1.686 and 1.729 Å, respectively. The latter bond length is longer than that of 1.720 Å in **5** and is the longest one reliably determined to date.

Introduction

An extremely long C−C bond length 1.720 Å[1] has been reported for the Csp^3-Csp^3 linkage in 1,1,2,2-tetraphenyl-3,8-dichlorobuta[*b*]naphthalene (**5**) prepared according to a new cyclobutaarene synthetic method (Scheme 1).[2] This was the longest C−C single bond,[3] although a comparable value 1.713 Å was recently reported for a similar compound (**6**) by Herges and his co-workers.[4] These extremely lengthened bonds were proven to be reasonable by theoretical calculations by Herges et al.,[4] Kertesz et al.,[5] Schleyer et al.,[6] and Siegel et al.[7] for **5** and by Herges et al. for **6**.[4] However, for the origin of the long bond in **5**, Herges[4] and Siegel[7] estimated a steric repulsion among phenyl groups on the cyclobutene ring, and Schleyer[6] estimated a through-bond interaction between the two phenyl groups located at the transpositions. In order to clarify the inconsistency, we prepared two di-*tert*-butyl-substituted derivatives **8** and **12**, and their molecular structures were studied by X-ray analysis.

Results and Discussion

Treatment of **1** with optically pure (−)-1-*tert*-butyl-1-phenyl-2-propyn-1-ol (**7**)[8] in the presence of Pd catalyst[9] gave the diacetylene diol corresponding to **3**, which upon treatment with $SOCl_2$ followed by heating gave (−)-trans-1,2-di-*tert*-butyl-1,2-diphenyl-3,8-dichlorocyclobuta[b]naphthalene (**8**). However, the optical purity of **8** is not determined. When *rac*-**7** was used instead of (+)-**7**, synthesis of **8** failed, although the reason is not clear. Similar treatment of **1** with a 1:1 mixture of **2** and 1,1-di(*tert*-butyl)-2-propyn-1-ol **9** gave a mixture of **3** (51%), **10** (5%), and the unsymmetrically substituted **11** (24% yield), and these were separated by column chromatography on silica gel using toluene as an eluent. Treatment of **11** with $SOCl_2$ followed by heating gave 1,1-di-*tert*-butyl-2,2-diphenyl-3,8-dichlorocyclobuta[*b*]naphthalene **12**. It has been reported that the treatment of **10** with $SOCl_2$ gives thermally stable diallene corresponding to **4**.[2] This suggests that the tetra-*tert*-butyl substituted cyclobuta[*b*]naphthalene is too unstable to exist due to a serious steric repulsion between the tert-butyl groups.

The crystal structures of **8** and **12** were determined by the X-ray diffraction method at 150 K, with no detectable crystal damage observed during data collection, and molecular structures of **8** and **12** are shown in Figures 1 and 2. The accuracy of the molecular dimension of **12** is pretty good, with an esd of ∼0.002 Å for bond lengths, while the crystal **8** contained 1 equiv of disordered *n*-hexane at 293 K, resulting in relatively low accuracy of observed geometrical parameters of **8**, although *n*-hexane is ordered at 150 K.

The molecule **8** has a 2-fold symmetry axis that goes through the midpoints of the C2−C3 and C8−C9 bonds. Both sides of the cyclobutene ring are very crowded with the ring almost completely covered by 1,2-diphenyl-1,2-di-*tert*-butyl groups from above and below. The naphthalene ring of **8** is planar within 0.056(4) Å, and C2 and C3 deviate by 0.22 and −0.24 Å from this plane, respectively, indicating that the cyclobutene ring is not planar but twisted. The bond lengths of the cyclobutene ring in **8** are C2−C3 = 1.686(5) Å, C1−C2 = 1.542(5) Å, C3−C4 = 1.536(5) Å, and C1−C4 = 1.419(5) Å.

The naphthalene ring of **12** is planar within 0.046(1) Å, and C2 and C3 deviate from this plane by 0.24 and −0.13 Å, respectively, showing that the similar twist of the cyclobutene ring is observed compared with that of **8**. The cyclobutene ring is completely shielded from the surroundings by 1,1-diphenyl-2,2-di-*tert*-butyl groups.

The bond lengths of the cyclobutene ring in **12** are C2−

---

† Ehime University.

‡ Osaka City University.

[1] Toda, F.; Tanaka, K.; Stein, Z.; Goldberg, I. *Acta Crystallogr., Sect. C* **1996**, *52*, 177.

[2] Toda, F.; Tanaka, K.; Sano, I.; Isozaki, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1757.

[3] Kaupp, G.; Boy, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 48.

[4] Kammermeier, S.; Jones, P. G.; Herges, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1757.

[5] Choi, C.-H.; Kertesz, M. *J. Chem. Soc., Chem. Commun.* **1997**, 2199.

[6] Bettinger, H. F.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Chem. Soc., Chem. Commun.* **1998**, 769.

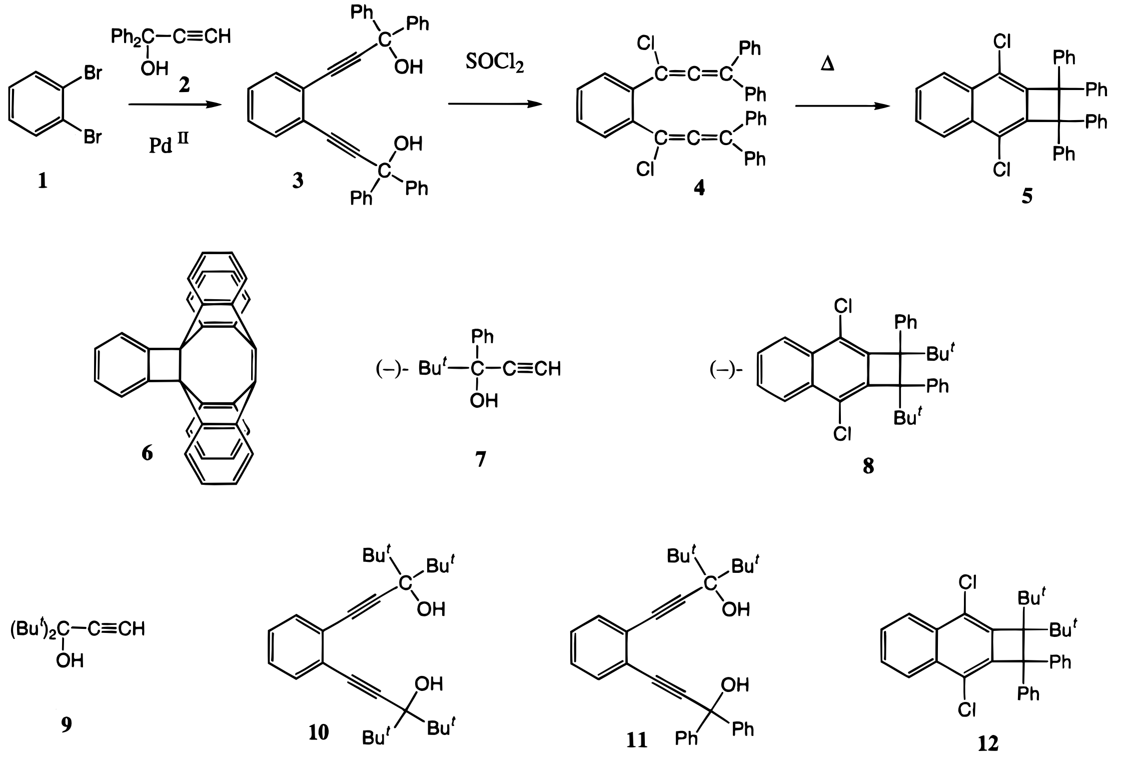
[7] Baldrige, K. K.; Kasahara Y.; Ogawa, K.; Siegel, J. S.; Tanaka, K.; Toda, F. *J. Am. Chem. Soc.* **1998**, *120*, 6167.

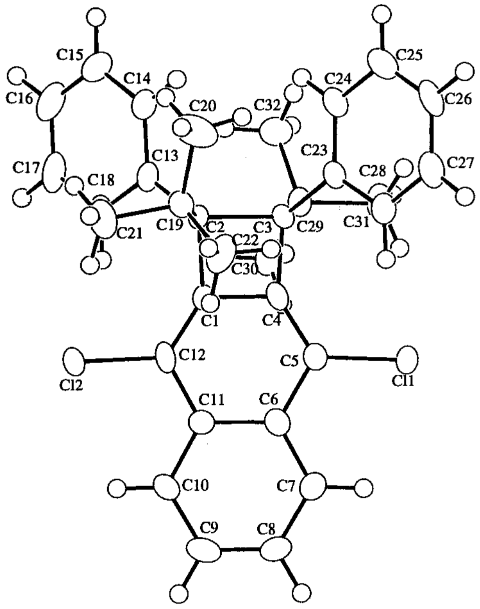
[8] Toda, F.; Tanaka, K.; Ueda, H. *Tetrahedron Lett.* **1981**, *22*, 4669.

[9] Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

10.1021/jo982010c CCC: $18.00

Scheme 1





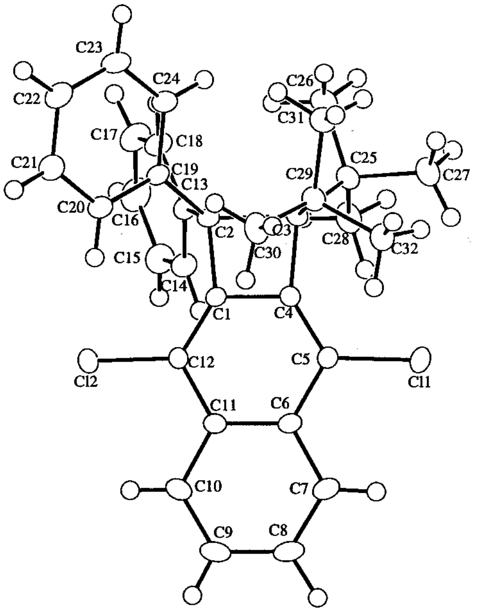


Figure 1. Compound **8** with atomic labeling. Selected distances (Å) and angles (deg) determined at 150 K (standard deviations 0.005 Å and 0.3°) and 293 K (0.008 Å and 0.6°) are as follows: C2−C3 = 1.686 (1.696 at 293 K), C1−C2 = 1.542 (1.540), C3−C4 = 1.536 (1.538), C1−C4 = 1.419 (1.416), C4−C5 = 1.365 (1.367), C1−C12 = 1.351 (1.340); C1−C2−C3 = 85.1 (84.5), C2−C3−C4 = 83.7(84.0), C2−C1−C4 = 93.1(94.1), C1−C4−C3 = 95.3(94.9). Selected nonbonded contacts (Å) are as follows: C13−C30 = 3.489, C13−C32 = 3.134, C14−C32 = 3.154, C20−C23 = 3.287, C20−C24 = 3.228, C22−C28 = 3.430.

Figure 2. Compound **12** with atomic labeling. Selected distances (Å) and angles (deg) determined at 150 K (standard deviations 0.002 Å and 0.1°) and 293 K (0.002 Å and 0.1°) are as follows: C2−C3 = 1.729 (1.734 at 293 K), C1−C2 = 1.529 (1.530), C3-C4 = 1.539 (1.535), C1−C4 = 1.409 (1.409), C4−C5 = 1.365 (1.370), C1−C12 = 1.367 (1.365); C1−C2−C3 = 83.8 (83.6), C2−C3−C4 = 83.2(83.3), C2−C1−C4 = 95.4(95.5), C1−C4−C3 = 95.3(95.5). Selected nonbonded contacts (Å) are as follows: C13−C26 = 3.354, C13−C28 = 3.156, C14−C28 = 3.261, C18−C26 = 3.388, C19−C30 = 2.964, C20−C30 = 3.314, C24−C31 = 3.296.

C3 = 1.729(2) Å, C1−C2 = 1.529(1) Å, C3−C4 = 1.539(2) Å, and C1−C4 = 1.409(2) Å.

Both structures of **8** and **12** have been solved also at 293 K. The bond distances and angles determined at 150 and 293 K are consistent within experimental errors. The Csp^3−Csp^3 single bonds of the cyclobutene ring in **8** and **12** are unusually long when compared with the typical Csp^3−Csp^3 bond, 1.51−1.59 Å.[4] The Csp^3−Csp^3 bond in **12** is even longer than the corresponding distance of

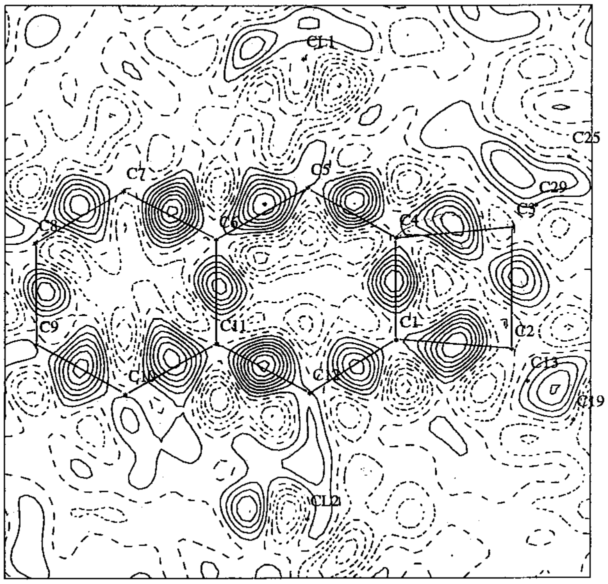


Figure 3. X−X deformation electron densities of **12** in the plane of the C1, C4, C5, C6, C11, and C12 rings. Contour interval 0.04 e/Å^3, negative electron densities dashed.

1.720(4) Å in **5**[1] and is the longest one reliably determined to date.

The X−X deformation electron density of **12** clearly shows bonding electrons of the cyclobutarene ring (Figure 3).[10] The bonding electron densities of cyclobutene are placed outside the ring to reduce the ring strain, which is essentially the same as that found in cyclobutarene compounds.[11] The unusual elongation of the Csp^3−Csp^3 bond in the cyclobutene ring may be mainly attributed to the steric repulsion among bulky substituents at C2 and C3. The larger steric congestion of **12** than that of **8** is consistent with the longer Csp^3−Csp^3 distance of **12** than that of **8**. On the contrary, through-bond interaction between two phenyls is not expected in **12**, although the interaction is expected in **8**.

Experimental Section

Preparation of 8. A mixture of **1** (2 g, 8.5 mmol), **7**[8] (8 g, 16.3 mmol), CuI (0.1 g), [(Ph$_3$P)$_2$PdCl$_2$] (0.3 g), PPh$_3$ (0.4 g), and NEt$_3$ (100 mL) was heated under reflux for 12 h. After filtration, the organic layer was evaporated and the residue chromatographed on silicagel to give (+)-1,2-bis(3-hydroxy-3-*tert*-butyl-3-phenyl-1-propynyl)benzene as colorless prisms (1.4 g, 37% yield, mp 95−97 °C, [α]$_D$ +42° (*c* 0.2, THF)). IR (Nujol): 3536, 3503 cm^{-1}. ^{1}H NMR: δ 0.95 (Me, 18H), 2.24 (OH, 2H), 7.27−7.57 (Ar, 14H). Anal. Calcd for $C_{32}H_{34}O_2$: C, 85.29; H, 7.60. Found: C, 85.02; H, 7.90. A solution of (+)-1,2-bis(3-hydroxy-3-*tert*-butyl-3-phenyl-1-propynyl)benzene (1.2 g), pyridine (3.5 mL), and SOCl$_2$ (3 mL) in THF (50 mL) was stirred at room temperature for 4 h. The reaction mixture was worked up by the usual method to give **8** as colorless prisms (0.31 g, 10% yield) Mp: 173−176 °C. [α]$_D$: −12° (*c* 0.05, CHCl$_3$)). ^{1}H NMR: δ 0.69 (Me, 18H), 7.29−8.52 (Ar, 14H). UV (CHCl$_3$): λ_{max} (ϵ) = 247 (11 100), 263 (2900), 274 (3600), 285 (5000), 296 (5900), 307 nm (4300). Anal. Calcd for $C_{32}H_{32}Cl_2$: C, 78.84; H, 6.62. Found: C, 78.59; H, 6.53.

Preparation of 12. A mixture of **1** (2.1 g, 8.9 mmol), **2** (3.41 g, 16.4 mmol), **9** (2.76 g, 16.4 mmol), CuI (0.04 g), [(Ph$_3$P)$_2$PdCl$_2$] (0.31 g), PPh$_3$ (0.24 g), and NEt$_3$ (100 mL) was heated under reflux for 24 h. After filtration, the organic layer was evaporated and the residue chromatographed on silica gel using toluene as an eluent to give **3** (2.23 g, 51% yield), **10** (0.18 g, 5% yield), and **11** (0.97 g, 24% yield). **3**. Colorless prisms. Mp: 162−164 °C. IR (Nujol): 3280, 2227 cm^{-1}. ^{1}H NMR: δ 2.9 (OH, 2H), 7.3−7.5 (Ar, 24H). Anal. Calcd for $C_{36}H_{26}O_2$: C, 88.14; H, 5.34. Found: C, 88.30; H, 5.20. **10**. Colorless prisms. Mp: 160−163 °C. IR (Nujol): 3588, 2229 cm^{-1}. ^{1}H NMR: δ 1.24 (Me, 36H), 2.35 (OH, 2H), 7.22−7.26 (Ar, 2H), 7.40−7.43 (Ar, 2H). Anal. Calcd for $C_{28}H_{42}O_2$: C, 81.90; H, 10.31. Found: C, 81.81; H, 10.36. **11**. Colorless prisms. Mp: 97−99 °C. IR (Nujol): 3494, 2216 cm^{-1}. ^{1}H NMR: δ 1.15 (Me, 18H), 2.35 (OH, 2H), 7.16−7.70 (Ar, 14H). Anal. Calcd for $C_{32}H_{34}O_2$: C, 85.29; H, 7.60. Found: C, 85.22; H, 7.23. A solution of **11** (0.92 g), pyridine (1.32 mL), and SOCl$_2$ (1.16 mL) in THF (50 mL) was stirred at 0 °C for 4 h. The reaction mixture was worked up by the usual method to give **12** as colorless prisms (0.22 g, 22% yield, mp 197−199 °C). ^{1}H NMR: δ 1.14 (Me, 18H), 7.19−7.26 (Ph, 10H), 7.72 (Ar, 2H), 8.49 (Ar, 2H). UV (CHCl$_3$): λ_{max} (ϵ) = 243 (26 000), 275 (4100), 286 (4800), 297 (5400), 309 nm (4200). Anal. Calcd for $C_{32}H_{32}Cl_2$: C, 78.84; H, 6.62. Found: C, 78.94; H, 6.60.

Crystallographic Studies. The X-ray data were collected on a Rigaku AFC7R four-circle diffractometer using $\omega/2\theta$ scan mode. All calculations were performed with the crystallographic software package teXsan (Molecular Structure Corp., 1985, 1992).

Crystal data for 8 (from n-hexane): $C_{32}H_{32}Cl_2{\cdot}C_6H_{14}$, orthorhombic, space group $P2_12_12_1$, Cu Kα radiation, $2\theta_{max}$ = 120°. The structure was solved by direct methods (SIR92)[12] and subsequent Fourier recycling (DIRDIF94)[13] and refined by full-matrix least-squares refinement against $|F|$, with all hydrogen atoms fixed at the calculated positions. Empirical absorption corrections were applied. (a) $T = 293$ K, $a = 18.114(1)$ Å, $b = 20.916(2)$ Å, $c = 8.585(1)$ Å, $U = 3252.5(4)$ Å^3. $D_c = 1.171$ g cm^{-3}, $\mu = 19.59$ cm^{-1}, 2794 independent intensities, 2515 observed ($I > 2.00\sigma(I)$). Weighting scheme = $1/[\sigma^2(F_o)^2 + (0.025)^2F_o{}^2]^{-1}$, $R = 0.072$, $R_w = 0.111$, GOF = 3.46, maximum residual electron density 0.44 e Å^{-3}. (b) $T = 150$ K, $a = 18.059(8)$ Å, $b = 20.540(9)$ Å, $c = 8.479(5)$ Å, $U = 3145(2)$ Å^3, $D_c = 1.211$ g cm^{-3}, $\mu = 20.26$ cm^{-1}, 2711 independent intensities, 2646 observed ($I > 2.00\sigma(I)$, weighting scheme = $1/[\sigma^2(F_o)^2 + (0.035)^2F_o{}^2]^{-1}$, $R = 0.055$, $R_w = 0.084$, GOF = 2.37, maximum residual electron density 0.37 e Å^{-3}.

Crystal data for 12 (from toluene): $C_{32}H_{32}Cl_2$, triclinic, space group P-1, Mo Kα radiation. The structure was solved by direct methods (SHELX86)[14] and subsequent Fourier recycling (DIRDIF94) and refined by full-matrix least-squares refinement against $|F|$ with isotropic hydrogens. Empirical absorption corrections were applied. (a) $T = 293$ K: $a = 9.935(1)$ Å, $b = 15.092(4)$ Å, $c = 9.293(1)$ Å, $\alpha = 105.10(1)°$, $\beta = 109.15(1)°$ $\gamma = 89.40(1)°$, $U = 1266.6(4)$ Å^3, $D_c = 1.278$ g cm^{-3}, $\mu = 2.75$ cm^{-1}, $2\theta_{max} = 50°$, 4443 independent intensities, 3955 observed ($I > 2.00\sigma(I)$), weighting scheme = $1/[\sigma^2(F_o)^2 + (0.035)^2F_o{}^2]^{-1}$, $R = 0.037$, $R_w = 0.058$, GOF = 1.65, maximum residual electron density 0.39 e Å^{-3}. (b) $T = 150$ K: $a = 9.861(5)$ Å, $b = 1\ 4.983(8)$ Å, $c = 9.253(5)$ Å, $\alpha = 105.37(7)°$, $\beta = 109.22(4)°$, $\gamma = 89.50(6)°$, $U = 1239(1)$ Å^3, $D_c = 1.306$ g cm^{-3}, $\mu = 2.81$ cm^{-1}, $2\theta_{max} = 60°$, 6530 independent intensities, 5837 observed ($I > 2.00\sigma\ (I)$), weighting scheme = $1/[\sigma^2(F_o)^2 + (0.035)^2F_o{}^2]^{-1}$, $R = 0.037$, $R_w = 0.066$, GOF = 1.68, maximum residual electron density 0.48 e Å^{-3}.

---

(10) Dunitz, J. D. *X-Ray Analysis and The Structure of Organic Molecules*; Verlag: New York, 1995; pp 391−417.

(11) Boese, R.; Blaeser, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 304.

(12) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(13) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-94 program system*; Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1944.

(14) Sheldrick, G. M. *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, 1985; pp 175−189.

Acknowledgment. This work was partly supported by the Grant-in-Aid for scientific research from the Ministry of Education, Science, Sports and Culture, Japan.

Supporting Information Available: X-ray crystallographic details for **8** and **12**. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 114661−114664. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk). (50 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

JO982010C