# Synthesis and Charge Transfer Complexation of Chiral Polynitrohelicenes

Hitoshi Okubo, Daisuke Nakano, Masahiko Yamaguchi,* and Chizuko Kabuto†
*Department of Organic Chemistry, Graduate School of Pharmaceutical Sciences, Tohoku University, Aoba, Sendai 980-8578*
*†Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980-8578*

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1,12-Dimethylbenzo[*c*]phenanthrene-5,8-dinitrile is nitrated at symmetrical positions giving 2,11-dinitro-, 4,9-dinitro, and 2,4,9,11-tetranitrohelicenes depending on the reaction conditions. The electron-deficient helicenes form charge-transfer (CT) complexes with pyrene in the solution as well as in the solid state. Crystal of the CT complex obtained from either (*P*)- or (±)-tetranitrohelicene possesses columnar structure but with different helicity, diameter, and pitch.

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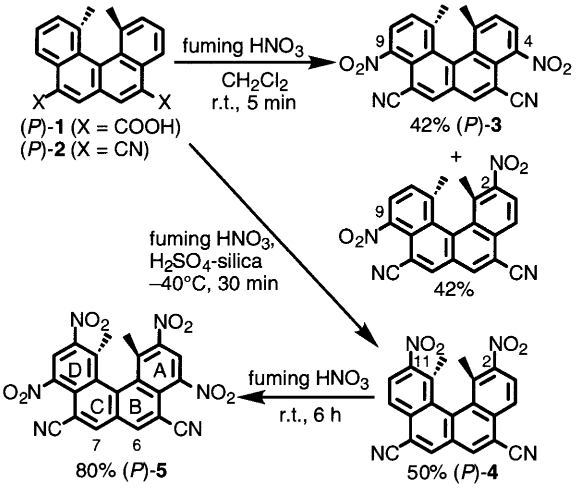
Helicenes are polycyclic aromatic compounds which can exhibit chirality based on the steric repulsions between the terminal aromatic rings.[1] Previously, we developed a multigram synthesis of an optically pure helicene, 1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarboxylic acid (**1**).[2] Since derivatives of **1** exhibit interesting behaviors in chiral recognition,[3] chiral LB film formation,[4] or chiral catalysis,[2] introduction of functional groups at the aromatic ring of **1** appears interesting. Described here are 1) polynitration reactions of **1** at symmetrical positions, and 2) charge-transfer (CT) complexation of the polynitrohelicenes and pyrene. The crystal structures of the CT complexes derived from the racemic and optically active helicene are compared.

Nitration of optically pure dinitrile (*P*)-**2**[5] obtained from (*P*)-**1** shows different regioselectivity depending on the conditions (Scheme 1). When (*P*)-**2** is reacted in fuming nitric acid at –40 °C for 30 min in the presence of sulfuric acid on silica gel,[6] 2,11-dinitrated (*P*)-**4** is obtained in 50% yield. In contrast, 4,9-dinitration of (*P*)-**2** takes place by the reaction with fuming nitric acid in dichloromethane at room temperature for 5 min giving (*P*)-**3** in 42% yield, which is accompanied by 2,9-dinitrated compound (42%). Nitration of (*P*)-**4** in fuming nitric acid under forcing reaction conditions (r.t., 6 h) gives 2,4,9,11-tetranitrohelicene (*P*)-**5** in 80% yield. No racemization is observed in the synthesis of (*P*)-**5**.[5] It should be noted that **2** can be nitrated regioselectively at symmetrical positions. Such optically active polynitrohelicenes have not been known before.

The electron-deficient helicenes form CT complexes with pyrene in organic solvents such as THF or acetone. CT absorption band appears at approximately 500 nm, when (*P*)-**5** and pyrene are mixed in acetone (Figure 1a). The complexation is also examined by NMR spectroscopy. The spectra of $7.0 \times 10^{-3}$ mol dm$^{-3}$ (*P*)-**4** in THF-$d_8$ and $2.0 \times 10^{-3}$ mol dm$^{-3}$ (*P*)-**5** in acetone-$d_6$ are measured as a function of pyrene concentration. The signals due to 6-*H* of (*P*)-**4** and (*P*)-**5** shift to higher magnetic field upon addition of pyrene (Figure 1b). The curve fitting of the data of NMR titration using non-linear least-square method provides the binding constants (*K*) for complexation in THF-$d_8$; (*P*)-**4**, 0.6 ± 0.2 mol$^{-1}$ dm$^3$; (*P*)-**5**, 2.0 ± 0.2 mol$^{-1}$ dm$^3$. In acetone-$d_6$; (*P*)-**5**, 5.0 ± 0.2 mol$^{-1}$ dm$^3$. The *K* values are in the range of those of the known achiral CT complexes.[7] The complex of tetranitrated (*P*)-**5** and pyrene is more stable than that of the dinitrated (*P*)-**4**. The *K* value of (±)-**5** and pyrene is identical to that of (*P*)-**5** and pyrene both in THF-$d_8$ and acetone-$d_6$.

**Scheme 1.**



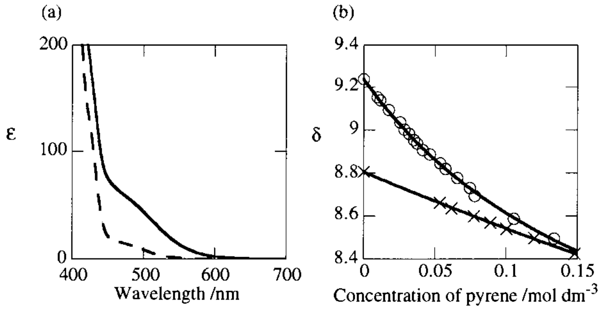


**Figure 1.** Complexation of polynitrohelicenes with pyrene. (a) UV-VIS spectra of (±)-**5** ($2.0\text{x}10^{-3}$ mol dm$^{-3}$) in the absence (- - -) and presence (—) of pyrene ($1.6\text{x}10^{-1}$ mol dm$^{-3}$) in THF at 20 °C. (b) Shifts in the NMR signals due to 6-*H* of (*P*)-**4** ($7.0\text{x}10^{-3}$ mol dm$^{-3}$ in THF-$d_8$) (O) and (*P*)-**5** ($2.0\text{x}10^{-3}$ mol dm$^{-3}$ in acetone-$d_6$) (X) upon addition of pyrene at 24 °C. Solid lines are the theoretical curves.

The dark red CT complexes of (*P*)-**5**•pyrene and (±)-**5**•pyrene precipitate by mixing **5** and pyrene in acetone. X-ray studies of the two complexes were carried out using crystals recrystallized from acetone.[8] In both crystals, **5** manifests a cylindrical helix, and is sandwiched by pyrene as shown in Figure 2. However, the structures are significantly different to each other as indicated by the crystallographic symmetries of trigonal and tetragonal lattice. In (*P*)-**5**•pyrene complex, the pyrene is stacked between the AB rings of the upper **5** and the CD rings of the lower **5**, and the helix consists of three com-

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plexes by $3_1$ axis symmetry along *c* cell axis. The molecules arrange straight into the slender cylinder with one-pitch length of 27.9 Å and ca. 12 Å diameter (Figure 2a and 2c). The helix is right-handed which probably is reflecting the helicity of (*P*)-**5**. On the other hand, pyrene in the racemic complex is stacked between the central BC rings of **5**, and the helix consists of four complexes by $4_1$ axis symmetry along *c* cell axis. The molecules arrange zigzag into the thick helix cylinder, having crystallographic $C_2$ symmetry, with one-pitch length of 24.5 Å and ca. 18 Å diameter (Figure 2b and 2d), and overlap slightly with the molecules in the adjacent inversion helix cylinder. It is worthwhile to note that the enamtiomers (*P*)-**5** and (*M*)-**5** form a separate helix, which is different from the usual pattern of the racemic mixed stack in helicene CT complexes,[9] and also that each helix possesses a reverse helicity to the chirality of **5**, i.e., left-handed for (*P*)-**5** and right-handed for (*M*)-**5**. To our knowledge, this is the first example to indicate clear differences in the crystal structures between optically active and racemic helicene CT complexes. Use of chiral helicene can be an interesting approach to control the crystal structures.

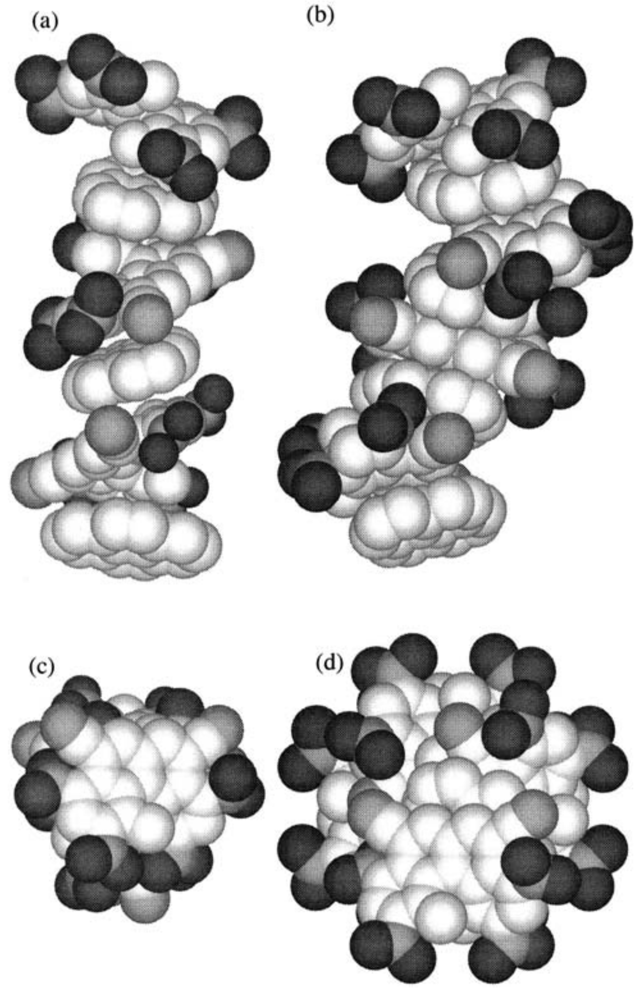

**Figure 2.** X-Ray structures of the (*P*)-**5**·pyrene complex (a and c) and the (±)-**5**·pyrene complex (b and d). Only a column containing (*P*)-**5**·pyrene complex is shown for the latter.

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**References and Notes**

1 Reviews. R. H. Martin, *Angew. Chem., Int. Ed. Engl.*, **13**, 649 (1974); H. Osuga and H. Suzuki, *J. Synth. Org. Chem. Jpn.*, **52**, 1020 (1994).

2 M. Yamaguchi, H. Okubo, and M. Hirama, *J. Chem. Soc., Chem. Commun.*, **1996**, 1771; H. Okubo, M. Yamaguchi, and C. Kabuto, *J. Org. Chem.*, **63**, 9500 (1998); H. Okubo and M. Yamaguchi, *Heterocycles*, **52**, 863 (2000).

3 K. Kano, S. Negi, R. Takaoka, H. Kamo, T. Kitae, M. Yamaguchi, H. Okubo, and M. Hirama, *Chem. Lett.*, **1997**, 715; K. Kano, S. Negi, H. Kamo, T. Kitae, M. Yamaguchi, H. Okubo, and M. Hirama, *Chem. Lett.*, **1998**, 151; K. Kano, H. Kamo, S. Negi, T. Kitae, R. Takaoka, M. Yamaguchi, H. Okubo, and M. Hirama, *J. Chem. Soc., Perkin Trans. 2*, **1999**, 15; K. Nakamura, H. Okubo, and M. Yamaguchi, submitted.

4 F. Feng, T. Miyashita, H. Okubo, and M. Yamaguchi, *J. Am. Chem. Soc.*, **120**, 10166 (1998); H. Okubo, F. Feng, D. Nakano, T. Hirata, M. Yamaguchi, and T. Miyashita, *Tetrahedron*, **55**, 14855 (1999).

5 H. Okubo, D. Nakano, S. Anzai, and M. Yamaguchi, submitted.

6 J. M. Riego, Z. Sedin, J. M. Zaldivar, N. C. Marziano, and C. Tortato, *Tetrahedron Lett.*, **37**, 513 (1996).

7 For example, M. W. Hanna and A. L. Ashbaugh, *J. Phys. Chem.*, **68**, 811 (1964); R. Foster and C. A. Fyfe, *Trans. Faraday Soc.*, **61**, 1626 (1965); R. Foster and J. W. Morris, *J. Chem. Soc. B*, **1970**, 703; H. J. M. Andriessen, W. H. Laarhoven, and R. J. F. Nivard, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 861.

8 X-ray data measurements were carried out using Rigaku/MSC Mercury CCD diffracrometer and structure refinements were made using SHELX93 program. Crystal data; (*P*)-**5**•pyrene, $C_{38}H_{20}N_6O_6$, MW = 688.61, $a = b = 9.7906(7)$, $c = 27.928(2)$Å, trigonal space group $P3_1$ (No. 144), $Z = 3$, $D_c = 1.480$ g/cm$^3$, $\mu$(Mo K$\alpha$) = 1.07 cm$^{-1}$, 12663 measured reflections (4856 unique). Final $R_1 = 0.058$, $R_w = 0.163$ for all reflections, $GOF = 0.91$. Crystal data; (±)-**5**•pyrene, $C_{38}H_{20}N_6O_6$, MW = 688.61, $a = b = 22.532(2)$, $c = 24.4668(6)$Å, tetragonal space group $I4_1$/acd (No. 142), $Z = 16$, $D_c = 1.473$ g/cm$^3$, $\mu$(Mo K$\alpha$) = 1.06 cm$^{-1}$, 44311 measured reflections (3785 unique). Final $R_1 = 0.048$, $R_w = 0.123$ for all reflections. $GOF = 1.21$.

9 X-ray structures of CT complexes containing helicenes. J. Bernstein, H. Regev, and F. H. Herbstein, *Acta Cryst.*, **B33**, 1716 (1977); M. Konno, Y. Saito, K. Yamada, and H. Kawazura, *Acta Crystallogr.*, **B36**, 1680 (1980); H. Nakagawa, K. Yamada, and H. Kawazura, *J. Chem. Soc., Chem. Commun.*, **1989**, 1378; N. Thorup, M. Hjorth, J. Larsen, and K. Bechgaard, *Acta Crystallogr.*, **C48**, 949 (1992); J. Larsen, A. Dolbecq, and K. Bechgaard, *Acta Chem. Scand.*, **50**, 83 (1996); K. Yamada, E. Oguma, H. Nakagawa, H. Kawazura, and H. Miyamae, *Acta Chem. Scand.*, **50**, 438 (1996).