Studies on the Conformation of Helical Poly(2,3-quinoxaline)s. Empirical Energy Calculation and Theoretical Circular Dichroism

Yoshihiko Ito,* Eiji Ihara, and Masahiro Murakami

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

Masahiko Sisido*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

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ABSTRACT: Empirical conformational energy calculations were performed on helical poly(2,3-quinoxaline)s to predict stable conformations. Two energy minimum conformations were found by varying the dihedral angle (ψ) between two adjacent quinoxaline units from 5 to 180°. Circular dichroism (CD) spectra were calculated for the two stable conformations (ψ = 45 and 135°) on the basis of exciton theory. The experimental CD spectrum of (+)-poly(2,3-quinoxaline) was in accord with the theoretical spectrum for a right-handed helical conformation with a dihedral angle of 135°.

Introduction

In the previous papers, we reported aromatizing polymerization of 1,2-diisocyanoarenes catalyzed by organopalladium complexes, giving poly(2,3-quinoxaline)s.[1,2] The X-ray crystal structure of the oligo(2,3-quinoxaline) thus prepared suggested that the main-chain structure of poly(2,3-quinoxaline) may be helical.[3] Actually, we succeeded in the synthesis of enantiomeric isomers of poly(2,3-quinoxaline)s which showed the same optical rotations with opposite signs and circular dichroism (CD) spectra of complete mirror images.[2] They may be atropisomers in terms of the helical sense, and the exciton splitting in their CD spectra can be ascribed to the helical arrangement of quinoxaline chromophores. In this paper, conformational energy calculations and theoretical CD calculations were carried out to predict the helical structure (e.g., the energetically stable conformation and the helical sense of each enantiomer) of chiral poly(2,3-quinoxaline)s.

Results and Discussion

The chiral poly(2,3-quinoxaline)s **3** were prepared by block copolymerization of 1,2-diisocyano-3,6-dimethyl-4,5-bis(propoxymethyl)benzene (**2**) with pentamer **1** (Scheme I).[2] The degree of polymerization of **2** was ca. 40. The empirical conformational energy calculations and theoretical CD calculations on the poly(2,3-quinoxaline) **3** may be adequately approximated by those on poly[2,3-(5,6,7,8-tetramethylquinoxaline)] **4** (Chart I). The approximation may be justified for the following reasons. Both UV absorption spectra of monomeric quinoxalines **5** and **6** showed the same profiles. The energy profile of poly[2,3-(5,8-dimethyl-6,7-bis(propoxymethyl)quinoxaline)] **3** would not be significantly changed from that of poly[2,3-(5,6,7,8-tetramethylquinoxaline)] **4**, even though the total energy may be increased by the propoxymethyl side chains, which spread out of the helical main chain of quinoxaline. Although polymer **3** contains the quinque(2,3-quinoxaline) part derived from the starting **1**, it was neglected in the CD calculation since the pentamer **7** did not show intense CD above 230 nm.

Conformational Calculations. The conformational energy calculations were carried out by using POLYGRAF. The structure parameters (bond lengths and angles) for the quinoxaline group were taken from the crystallographic data of a ter(2,3-quinoxalinyl)palladium complex.[4] The total energy of quinoxaline 20-mers was calculated by varying the dihedral angle ψ between two adjacent

Scheme I

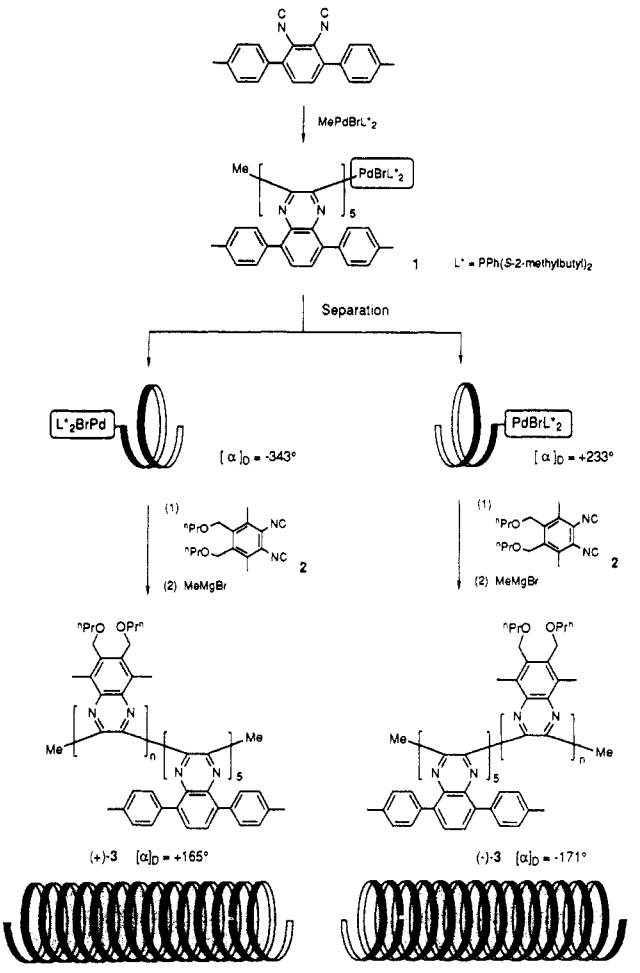
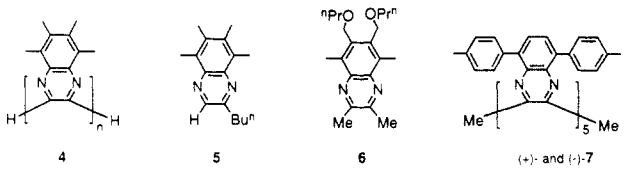


Chart I



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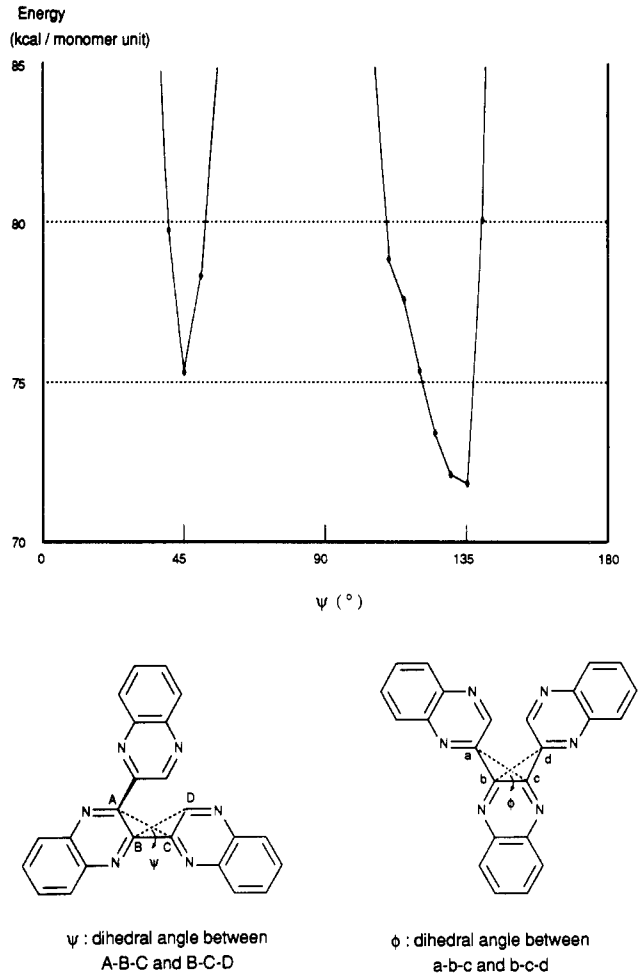


Figure 1. Energy profile of poly(2,3-quinoxaline) **4** (ϕ = 0°).

quinoxaline units from 5 to 180° with an interval of 5°. The dihedral angle ϕ shown in Figure 1 was assumed to be 0°. In some cases, however, the latter dihedral angle was also varied. In those cases, the dihedral angle between the plane a–b–c and the plane of the quinoxaline ring was set to $\phi/2$. All bond angles and bond lengths were fixed in this calculation.

As shown in the energy profile (Figure 1), two energy minima appeared at ψ = 45 and 135°. The minima are separated by a high energy barrier, indicating the existence of two stable conformers which are not interconvertible. The slight deviation of ϕ from 0° resulted in the rise of the total energy. The NAMOD ball-and-stick models[5] of the two conformers are shown in Figure 2. Of the two possible conformations, that with ψ = 135° is more likely, because of its lower energy (3.5 kcal/residue mol) and wider allowed region.

X-ray structural analysis of the propagating quater(2,3-quinoxalinyl)palladium(II) complex (Figure 3)[6] revealed that the four sequential quinoxaline units take a helical structure with ψ = 123–148°. The finding also suggests that the conformer with ψ = 135° is more likely for the poly(2,3-quinoxaline) **3**. The conclusion is supported by the results of CD calculation to be described below.

Theoretical Circular Dichroism. Theoretical CD was computed on the basis of the exciton theory developed by Woody.[7] The CNDO/S-CI MO calculation and experimental peak assignment for quinoxaline have been reported.[8] The absorption peak at 316 nm (ϵ 6.32 × 10^3, CH_2Cl_2) is polarized along a long axis. However, the MO calculation predicted two transitions in this region, one being long-axis polarized and the other being short-axis

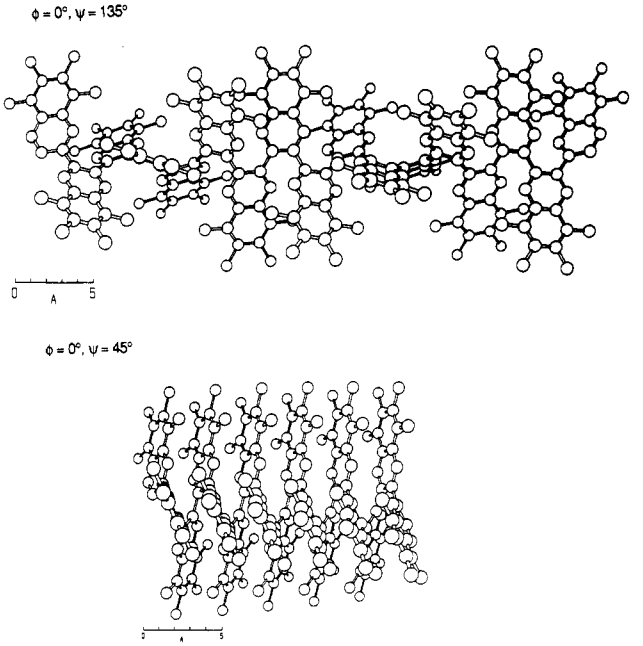


Figure 2. Ball-and-stick molecular models for two energy minimum conformations of poly(2,3-quinoxaline) **4**.

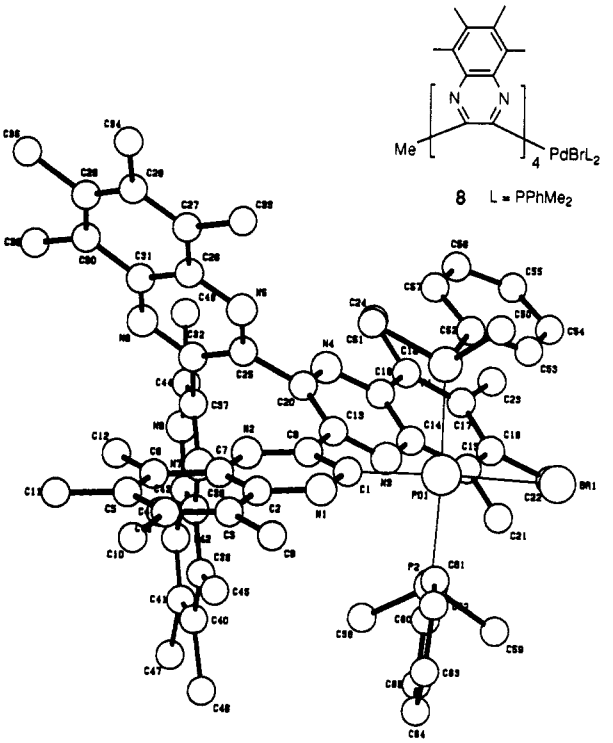
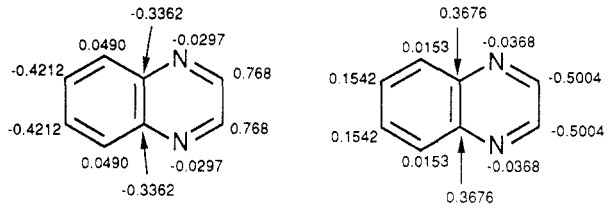


Figure 3. X-ray crystal structure of quater(2,3-quinoxalinyl)-palladium **8**.

polarized. The peak must have some contribution from the n–π^* transition. Therefore, the assignment of the peak at 316 nm is not clear. The intense peak at 233.5 nm (ϵ 2.92 × 10^4, CH_2Cl_2) is shown to be long-axis polarized, in accordance with the MO data. The other peak at shorter wavelengths is not assigned. In the CD calculation, the allowed π–π^* band at 233.5 nm and small band at 316 nm, both being long-axis polarized, were taken into consideration. Since the assignment of the 316-nm band is not clear, the comparison between theoretical and experimental spectra may be made only at the allowed band.

The transition moments and the monopole charges of two π–π^* bands were calculated from PPP–CI molecular orbitals. The magnitudes of the monopole charges were corrected to reproduce the experimental spectrum of the



Transition at 252 nm Transition at 329 nm

Figure 4. Monopole charges for the two π–π^* transitions of the quinoxaline chromophore.

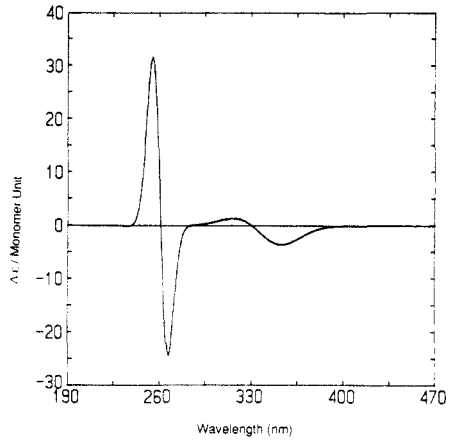


Figure 5. Theoretical CD curve for a right-handed poly(2,3-quinoxaline) of $\psi = 135°$.

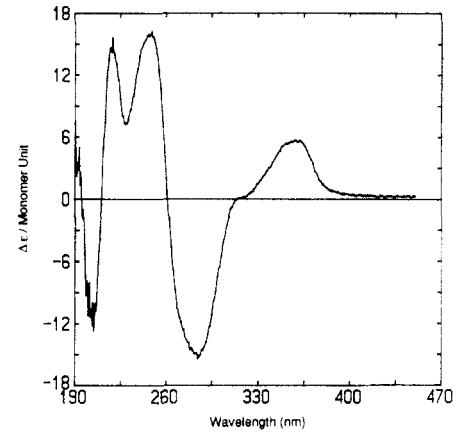


Figure 6. CD spectrum of (+)-poly(2,3-quinoxaline) 3.

model monomer **5**. As the energy of π–π^* transitions, the peak wavelengths of the experimental spectrum of **5** (252 and 329 nm) were used instead of the calculated ones (225 and 309 nm) for quinoxaline. The monopole charges for the two π–π^* transitions are listed in Figure 4.

CD spectra were calculated on the possible conformations of **4** predicted from the above energy calculations. The number of quinoxaline units, n, was 20 in the calculation. The calculated $\Delta\epsilon$ divided by n becomes flat when $n > 10$. Figure 5 shows the theoretical CD spectrum of a right-handed poly(2,3-quinoxaline) 20-mer with $\psi = 135°$. The spectrum exhibits a negative exciton couplet at 260 nm, and this pattern is the same as the observed spectrum of (+)-poly(2,3-quinoxaline) **3** in Figure 6. The observed spectrum also exhibits a positive couplet at 215 nm and a positive cotton effect at 360 nm. They may originate from higher energy transitions and n–π^* transitions of the quinoxaline chromophore, respectively, and both are not considered in this calculation.

A CD spectrum was also calculated on a helical structure with $\psi = 45°$ (Figure 7). The calculated spectrum is quite different from the experimental one either for the (+)-poly(2,3-quinoxaline) derivative or for the (–)-poly(2,3-quinoxaline) derivative. This result supports our assumption that the conformation with $\psi = 135°$ is more likely than that with $\psi = 45°$ for the poly(2,3-quinoxaline) derivative and that the (+)-poly(2,3-quinoxaline) exists in a right-handed helical conformation. Inversely, the (–)-poly(2,3-quinoxaline) derivative exists in a left-handed helix with $\psi = -135°$.

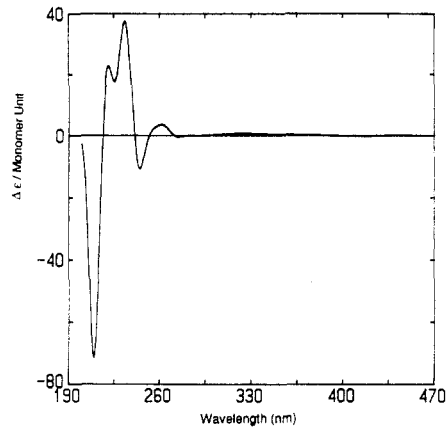


Figure 7. Theoretical CD curve for a right-handed poly(2,3-quinoxaline) of $\psi = 45°$.

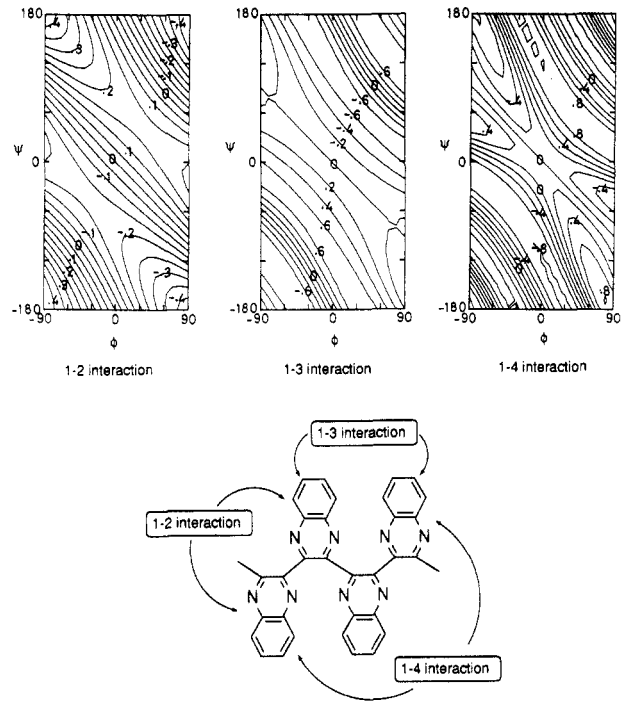


Figure 8. Contour maps of chirality parameters for three types of interactions.

To study the origin of the exciton splitting, the chirality parameter was calculated for 1–2, 1–3, and 1–4 pairs of quinoxaline units (Figure 8).[9] The chirality parameter is defined as $\zeta = \mathbf{r}_{12}(\mathbf{m}_1 \times \mathbf{m}_2)$ where $\mathbf{r}_{12}$ is a unit vector along the center-to-center interchromophore vector and $\mathbf{m}_1$ and $\mathbf{m}_2$ are the unit vectors along the long axis of the quinoxaline ring. Negative ζ-values indicate a positive (lower wavelength)–negative (higher wavelength) exciton couplet as shown in Figure 5. Contrary to the theoretical CD spectrum calculated taking all contributions (Figure 5), the 1–2 and 1–4 interaction showed positive chirality parameters. This indicates that the contributions of 1–2 and 1–4 interactions are small compared with that of the 1–3 interaction where strong ζ-value is obtained around the region of $\phi = 0°$ and $\psi = 135°$. Therefore, the negative exciton couplet at 260 nm is mainly ascribed to the right-

handed helical arrangement of a quinoxaline chromophore in a 1–3 interaction.

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles for compound 8 (7 pages). Ordering information is given on any current masthead page.

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(6) Crystal data (8): $C_{65}H_{73}BrN_8P_2Pd$, MW = 1214.6, monoclinic, space group $C2/c$; a = 31.567 (9), b = 16.095 (3), c = 32.466 (9) Å; β = 126.83°; U = 13202 (6) Å^3, Z = 8, D_c = 1.222 g/cm^3; Cu Kα radiation (λ = 1.541 78 Å), μ = 47.4 cm^{-1}. Intensity data were measured on a Rigaku AFC-5R diffractometer using an $\omega - 2\theta$ scan technique. A total of 9780 unique reflections within $2\theta \leq 120°$ was collected. The structure was solved by the heavy-atom method and refined anisotropically by the block-diagonal least-squares technique to R = 0.057, R_w = 0.085, and S = 1.13 for 8409 reflections with $F_o > 3\sigma(F_o)$. H atoms were not located.
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