Supplementary Material of B204515J

Electrochiroptical response of a hexaarylethane derivative with the helical \( \pi \)-skeleton: Drastic UV-Vis and CD spectral changes upon electrolysis of \textit{dispiro[4,5-dibromo-9,10-dihydrophenanthrene-9,9\prime:10,9\prime\prime-bi[9H]xanthene]}

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Crystallographic Details

\textit{rac-1a}: \( \text{C}_{38}\text{H}_{22}\text{Br}_{2}\text{O}_{2}, M \ 670.40 \), colorless rod from CHCl3, 0.4 x 0.15 x 0.15 mm, monoclinic \( \text{P}2_1/c, a = 12.462(6), b = 15.613(7), c = 15.042(7) \ \bcirc, \beta = 111.35(1) \bcirc, U = 2725(2) \ bcirc^3, D_c (Z = 4) = 1.633 \text{ g cm}^{-1}. \) A total of 6174 unique data points (2\( \theta_{\text{max}} = 55.0 \bcirc \)) were measured at \( T = 153 \text{ K} \) on a Rigaku Mercury CCD camera apparatus (Mo-K\( \alpha \) radiation, \( \lambda = 0.71069 \bcirc \)).

Numerical absorption correction was applied (\( \mu = 30.19 \text{ cm}^{-1} \)). The structure was solved by the direct method and refined by the full-matrix least-squares method on \( F \) with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at the calculated positions. The final \( R \) and \( R_w \) values are 0.036 and 0.043 for 3567 reflections with \( I > 3\sigma I \) and 379 parameters. The maximum residual electron density is 0.46 e \( \bcirc^{-3} \). Atom numbering system is shown in Figure S1.

\textit{rac-1b}: \( \text{C}_{40}\text{H}_{28}\text{O}_{2}, M \ 540.66 \), colorless plate from CHCl3, 0.4 x 0.2 x 0.05 mm, monoclinic \( \text{P}2_1/n, a = 10.059(5), b = 14.309(7), c = 19.109(10) \ \bcirc, \beta = 97.049(7) \bcirc, U = 2729(2) \ bcirc^3, D_c (Z = 4) = 1.315 \text{ g cm}^{-1}. \) A total of 6033 unique data points (2\( \theta_{\text{max}} = 55.0 \bcirc \)) were measured at \( T = 153 \text{ K} \) on a Rigaku Mercury CCD camera apparatus (Mo-K\( \alpha \) radiation, \( \lambda = 0.71069 \bcirc \)).

Numerical absorption correction was applied (\( \mu = 0.79 \text{ cm}^{-1} \)). The structure was solved by the direct method and refined by the full-matrix least-squares method on \( F \) with anisotropic temperature
factors for non-hydrogen atoms. Hydrogen atoms were located at the calculated positions. The final $R$ value is 0.057 for 2925 independent reflections with $I > 3\sigma I$ and 379 parameters. The maximum residual electron density is 0.33 e Å$^{-3}$. Atom numbering system is shown in Figure S2.

(*R*-6): C$_{46}$H$_{40}$Br$_2$O$_6$, $M$ 848.63, colorless platelet from CHCl$_3$-EtOH, 0.1 x 0.1 x 0.03 mm, monoclinic, $C2$, a = 21.614(2), b = 9.8916(8), c = 9.6740(4) Å, $\beta$ = 113.459(2) $\degree$, $U$ = 1897.3(2) Å$^3$, $D_c$ (Z = 2) = 1.485 g cm$^{-1}$. A total of 2261 unique data points ($2\theta_{\text{max}} = 55.0 \degree$) were measured at $T = 123$ K on a Rigaku Mercury CCD camera apparatus (Mo-K$\alpha$ radiation, $\lambda$ = 0.71069 Å). Numerical absorption correction was applied ($\mu = 21.39$ cm$^{-1}$). The structure was solved by the Patterson method and refined by the full-matrix least-squares method on $F$ with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at the calculated positions. The final $R$ value is 0.032 for 1777 independent reflections with $I > 3\sigma I$ and 245 parameters. The maximum residual electron density is 0.37 e Å$^{-3}$. The axial chirality of this diasteromer was determined to be (*$R$*) based on the relative stereochemistry to the two asymmetric carbons derived from (*$R$*-1,3-butanediol). This molecule is located on the crystallographic 2-fold axis. Atom numbering system is shown in Figure S3b.
Figure S1. Ortep drawing of rac-1a showing the atom numbering system. The intramolecular contact between two Br groups is 3.423(1) Å, and the twisting angle around the biphenyl axis is 41.4(1) º.
Figure S2. Ortep drawing of *rac-1b* showing the atom numbering system. The intramolecular contact between two Me groups is $3.017(7)$ Å, and the twisting angle around the biphenyl axis is $40.2(1)$ °.
Figure S3a. Ortep drawing of (R)-6. The twisting angle around the biphenyl axis is 89.8°.

Figure S3b. Ortep drawing of (R)-6 (half unit) showing the atom numbering system.