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Detection of a diradical intermediate in the cis–trans isomerization of 5,5′-bis(4,5-diphenyl-2*H*-imidazol-2-ylidene)-5,5′-dihydro-$\Delta^{2,2'}$-bithiophene

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Abstract—5,5′-Bis(4,5-diphenyl-2*H*-imidazol-2-ylidene)-5,5′-dihydro-$\Delta^{2,2'}$-bithiophene provides a rare example of the detection of a diradical intermediate in the cis–trans isomerization. The reversibility and the energy profiles for both the cis–trans isomerization and the diradical formation indicate that the observed diradical is an intermediate in the cis–trans isomerization.
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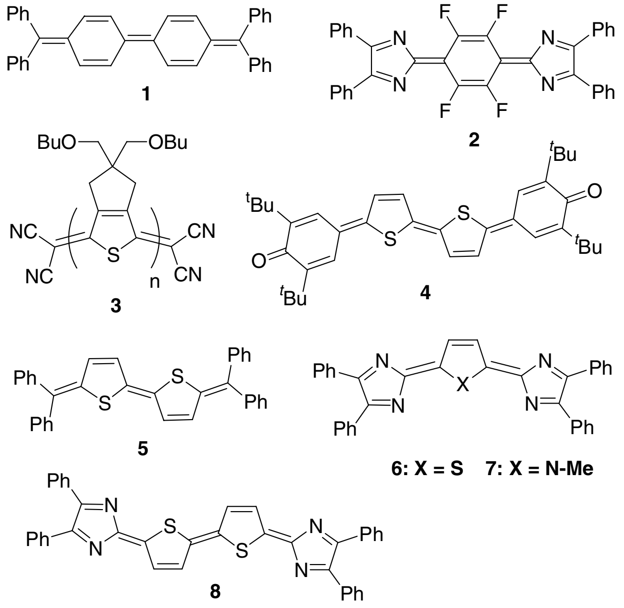
There has been considerable interest in diradical character of quinoid compounds.[1–5] Chichibabin's hydrocarbon **1** is a typical example and has a long history.[1] Recently, Abe and co-workers have reported an interesting thermal dimerization reaction of **2** in solution.[3b] They proposed a mechanism of dimerization through diradical $\mathbf{2}^{\cdot\cdot}$ in equilibrium with quinoid **2**, where a small energy gap ($\Delta E_{\mathrm{ST}} = $ ca. 2.4 kcal mol^{-1}) between the singlet quinoid ground state and the triplet diradical was theoretically estimated. More recently, Otsubo, Aso, and co-workers reported that extended quinoidal oligothiophenes **3** with dicyanomethylene terminals exist as equilibrium mixtures of the possible diradicals, whose fractions are surprisingly high, up to 28% for heptamer **3** ($n = 6$).[4]

Hitherto, several Chichibabin-type dithienoquinoid analogues **4** and **5** have also been synthesized. These compounds showed a facile cis–trans isomerization with no indication of diradical participation.[6] However, in principle, a facile cis–trans isomerization must be related to a weak C–C bond that can result from their diradical character. In the course of our studies of charged and spin systems,[7] we have been interested in the titled dithienoquinoid analogue **8** as an extension of thienoquinoids **6** and **7**. Compound **6** and **7** showed strong electron-accepting ability due to 5π-system of the imidazolylidene terminals with no diradical character.[8] We report diradical participation in the cis–trans isomerization of **8** (Scheme 1).

Compound **10** was synthesized from the corresponding dialdehyde **9**[9] in 45% yield according to the general procedure for the preparation of lophines (2,4,5-triphenylimidazole) (Scheme 2).[10] Oxidation of **10** using



Scheme 1. Chichibabin's hydrocarbon **1** and its analogues.

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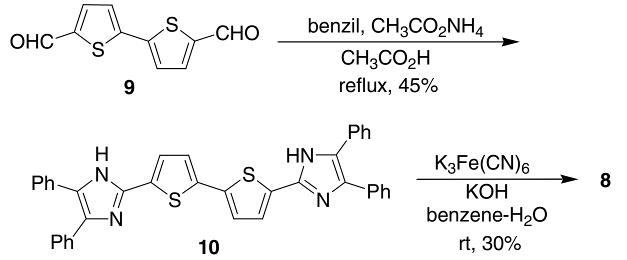


Scheme 2. Preparation of **8**.

$K_3Fe(CN)_6$ in benzene–aqueous KOH heterogeneous solution afforded compounds **8** in 30% yield as a deep green solid ($\lambda_{max} = 735$ ($\log \varepsilon = 4.51$) in CH_2Cl_2).

Temperature dependence of the ^1H NMR spectra (in $CDCl_3$) is shown in Figure 1. At −20 °C, two pairs of the doublet (H_a, H_b, and H_c, H_d) with 1.1:1 ratio are clearly seen, indicating the presence of both the trans- and cis-isomers.[11] Increasing the temperature broadens the signals. The line-shape analysis ($k_{ex} = k_{t-c} + k_{c-t}$) well fit the observed spectra in the temperature range between −20 and 20 °C, giving $\Delta H^{\neq} = 12.8 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\neq} = -3.05 \pm 0.95$ cal K^{-1} mol^{-1} for k_{c-t} and $\Delta H^{\neq} = 13.1 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\neq} = -2.21 \pm 0.95$ cal K^{-1} mol^{-1} for k_{t-c}.[12] The rate of isomerization is comparable to that for **4** ($\Delta G^{\neq} = 13.4$ kcal mol^{-1} at $T_c = 10$ °C)[6b] but faster than that for **5** ($\Delta G^{\neq} = 17.2$ kcal mol^{-1} at $T_c = 75$ °C).[6a] Interestingly, the line shape remained still broad at higher temperatures (20–50 °C), in which the estimated k_{ex} clearly deviates from the proton exchange process as shown in the Eyring plots (Fig. 2a). This indicates the presence of additional line-broadening process other than the proton exchange.

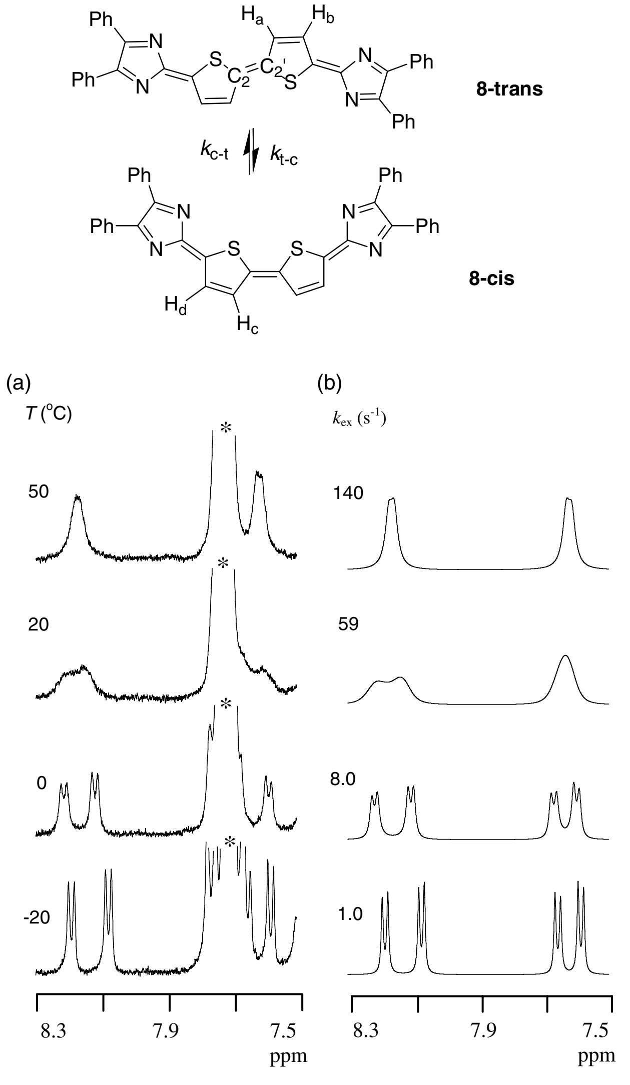


Figure 1. cis–trans Isomerization of **8** (top) and ^1H NMR spectra (300 MHz) of **8** (bottom) (a) measured in $CDCl_3$ at −20, 20, 0, and 50 °C, intense peaks of aromatic protons on terminal phenyl groups are marked by ∗. (b) simulation spectra with the rate constant k_{ex} of proton-exchange.

The line-broadening at higher temperature region (20–50 °C) was found to be derived from the presence of a radical species. The single broad featureless radical signal was found in the EPR spectrum in $CHCl_3$ or toluene (Supporting Information). Importantly, the signal intensity increases (decreases) as the temperature increases (decreases) and the process is reversible. Furthermore, no decomposition product was detected by TLC after heating. These results indicate that the observed radical

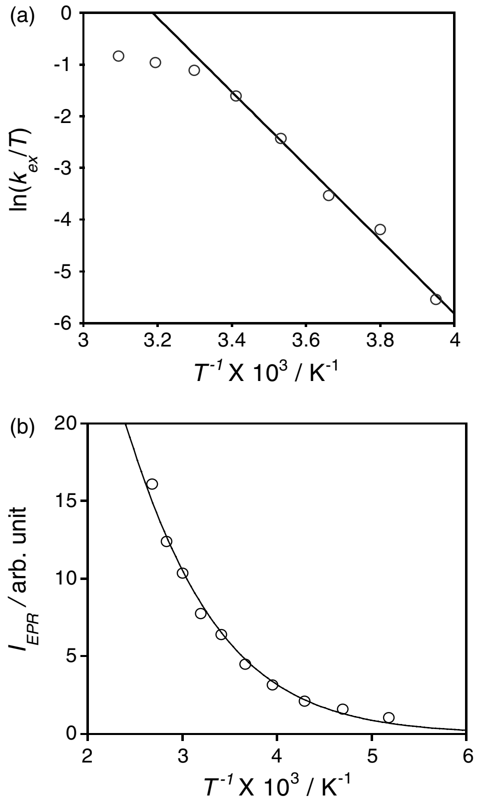


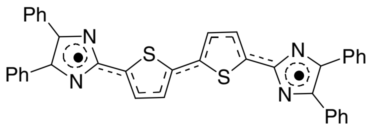
Figure 2. (a) Eyring plots of the rate constant k_{ex} in the cis–trans isomerization of **8** in $CDCl_3$. The solid line is obtained from the least-square fitting for the five data in lower temperature region. (b) The temperature dependence of EPR signal intensity in toluene. The solid line is theoretical curves obtained from the singlet–triplet model using a triplet excitation energy of 3.01 kcal mol^{-1}.

species is not involved in irreversible processes such as an impurity or decomposition products but as a species in thermal equilibrium with **8**. The signal intensity $I_{\rm EPR}$ was plotted as a function of T^{-1} (Fig. 2b). The plots can be well simulated by the singlet–triplet model Eq. 1,[13]

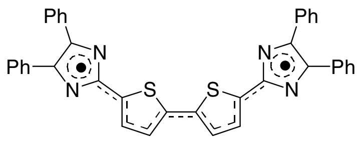
$$I_{\rm EPR} = {\rm C}\exp(-\Delta E_{\rm ST}/{\rm R}T)/\{1+3\exp(-\Delta E_{\rm ST}/{\rm R}T)\}1/T \qquad (1)$$

where a thermally excited triplet diradical is in equilibrium with the singlet state according to the Boltzmann distribution. We propose $\mathbf{8}^{\cdot\cdot}$ as a possible diradical. The energy gap $\Delta E_{\rm ST}$ between the quinoid **8** and the thermally excited triplet diradical $\mathbf{8}^{\cdot\cdot}$ was experimentally determined as 3.01 ± 0.01 kcal mol^{-1}, which is comparable to the reported value for **2** (2.37 kcal mol^{-1}) by Abe and co-workers.[3b] The EPR signals could be observed in a wide temperature range between −80 and 100 °C. The diradical quantity was roughly estimated to be ca. 0.2% at 20 °C by comparing the signal area to the known concentration of DPPH dissolved in a same volume of toluene at the same EPR conditions. The straight line observed in Eyring plots at lower temperatures (−20 to 20 °C) indicates that the line broadening due to the intermolecular spin exchange between **8** and $\mathbf{8}^{\cdot\cdot}$ has a negligible contribution because of low concentration of $\mathbf{8}^{\cdot\cdot}$. Obviously, the contribution of this intermolecular process increases at higher temperature because of the exponential increase of the concentration of $\mathbf{8}^{\cdot\cdot}$. Thus, these experiments are consistent with a proposal that the observed paramagnetic species is the triplet diradical $\mathbf{8}^{\cdot\cdot}$, although rigorous identification of the structure is rather difficult because of the structureless EPR spectrum in solution.[14] Recently reported extended quinoidal oligothiophenes **3** and an extended viologen also exhibited similar broad EPR signals in solution.[4,5]

In order to obtain an insight into the energy profile of $\mathbf{8}^{\cdot\cdot}$, we have carried out theoretical calculations (B3LYP/6-31G*) for the closed shell singlet quinoid **8** and the open shell triplet diradical form $\mathbf{8}^{\cdot\cdot}$ at their optimized geometries.[15] The calculated $\Delta E_{\rm ST}$ value ($\mathbf{8}^{\cdot\cdot}$-*trans*: 6.48 kcal mol^{-1}, $\mathbf{8}^{\cdot\cdot}$-*cis*: 7.16 kcal mol^{-1}) has a somewhat larger but same order value with the observed $\Delta E_{\rm ST}$ value (3.01 kcal mol^{-1}), supporting $\mathbf{8}^{\cdot\cdot}$ as the observed triplet diradical.



8$^{\cdot\cdot}$-trans



8$^{\cdot\cdot}$-cis

The diradical $\mathbf{8}^{\cdot\cdot}$ has a small torsion angle between the two thiophene rings and a bond length; C2–C2′ = 1.423 Å with a torsion angle between the two thiophene rings of 0.4° for $\mathbf{8}^{\cdot\cdot}$-*trans* and 1.423 Å with 0.2° for $\mathbf{8}^{\cdot\cdot}$-*cis*. The calculated bond length is considerably longer than the typical thienoquinoid double bonds (1.385 Å)[16] but shorter than that for the thiophene–thiophene single bond (1.448 Å),[17] suggesting the partial double bond character in the C2–C2′ bond in $\mathbf{8}^{\cdot\cdot}$.

It should be noted that the diradical $\mathbf{8}^{\cdot\cdot}$ ($\mathbf{8}^{\cdot\cdot}$-*trans* and $\mathbf{8}^{\cdot\cdot}$-*cis*) partially retains its quinoid-like planar structure and therefore does not directly lead to the cis–trans isomerization. The cis–trans isomerization would undergo via a largely twisted transition state that is brought by the rate-determining C2–C2′ bond-rotation of $\mathbf{8}^{\cdot\cdot}$. In order to estimate the rotational barrier in the diradical $\mathbf{8}^{\cdot\cdot}$, we have also calculated the energies of the singlet and triplet diradicals with the perpendicularly restricted geometry ($\mathbf{8}^{\cdot\cdot}$**-90**, dihedral angle ∠S–C2–C2′–S = 90°) by DFT calculations.[18] The singlet and triplet diradicals $\mathbf{8}^{\cdot\cdot}$**-90**s are almost degenerate in their energies within 2.79×10^{-2} kcal mol^{-1} (Supporting Information). The energy difference between **8**-*trans* (**8**-*cis*) and $\mathbf{8}^{\cdot\cdot}$**-90** is calculated to be 11.3 (11.0) kcal mol^{-1}. Thus, the mechanism of cis–trans isomerization involving $\mathbf{8}^{\cdot\cdot}$ and its C2–C2′ bond rotation can roughly reproduce the observed activation enthalpy $\Delta H^{\neq}$ value ($k_{\rm c-t}$: $\Delta H^{\neq} = 12.8 \pm 0.3$ kcal mol^{-1}, $k_{\rm c-t}$: $\Delta H^{\neq} = 13.1 \pm 0.3$ kcal mol^{-1}). The plausible reaction path with the energy profile is depicted in Figure 3.

In summary, 5,5′-bis(4,5-diphenyl-2*H*-imidazol-2-ylidene)-5,5′-dihydro-$\Delta^{2,2'}$-bithiophene **8** was found to provide a rare example of the detection of a diradical intermediate in the cis–trans isomerization. The proton-exchange dynamic NMR studies clarified that the cis–trans-isomerization proceeds with the activation parameters, $\Delta H^{\neq} = 12.8 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\neq} = -3.05 \pm 0.95$ cal K^{-1} mol^{-1} for $k_{\rm c-t}$ and $\Delta H^{\neq} = 13.1 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\neq} = -2.21 \pm 0.95$ cal K^{-1} mol^{-1} for $k_{\rm t-c}$. On the other hand, an additional line-broadening process due to the spin exchange was detected in DNMR and EPR studies. The EPR study showed the presence of thermally activated triplet diradical species in equilibrium with the quinoid ground state.

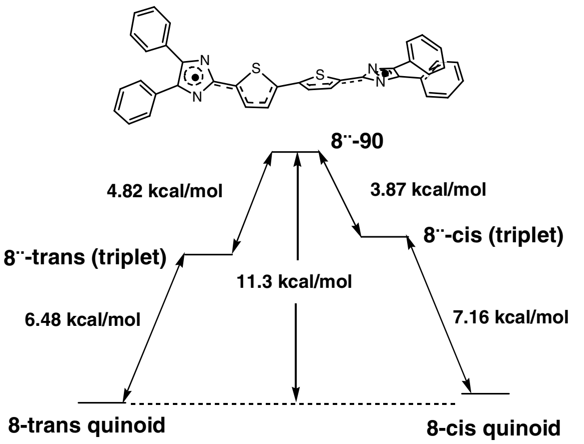


Figure 3. Energy profile of cis–trans Isomerization in **8** obtained by DFT calculations. The singlet and triplet diradicals $\mathbf{8}^{\cdot\cdot}$**-90**s are almost degenerate in their energies ($\Delta E_{\rm ST} = 2.79 \times 10^{-2}$ kcal mol^{-1}).

The energy gap between the singlet quinoid and the thermally activated triplet diradical was determined as $\Delta E_{ST} = 3.01 \pm 0.01$ kcal mol^{-1}. The triplet diradical **8**$^{\cdot\cdot}$ was proposed to be an EPR-detected species. The ΔE_{ST} value and the $\Delta H^{\neq}$ value in the cis–trans isomerization are roughly consistent with the calculated energy profile of **8**$^{\cdot\cdot}$ and the bond rotated highly twisted **8**$^{\cdot\cdot}$**-90**.

Acknowledgements

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Supplementary material

Supporting Information Available: Detail synthetic procedure for **8**, DNMR and EPR data, and results of DFT calculations. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.05.084.

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11. These protons are tentatively assigned by assuming 1) the major isomer (53:47 at −20 °C) is a trans-isomer in accordance with theoretical calculations and 2) the inner protons appear at a higher field than the outer proton.[4] H_a 7.58 ppm (d, $J = 5.2$ Hz), H_b 8.08 (d, $J = 5.2$ Hz) for **8**-*trans* isomer, and H_c 7.65 (d, $J = 5.2$ Hz), H_d 8.19 (d, $J = 5.2$ Hz) for **8**-*cis* isomer.
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18. The diradical **8**$^{\cdot\cdot}$**-90** has a hypothetical structure to estimate the rotational barrier of the C2–C2′ bond in **8**$^{\cdot\cdot}$. The full geometrical optimization of **8**$^{\cdot\cdot}$**-90** leads to the structure of planar diradicals.