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Factors Affecting Photoisomerization of 4-Styrylpyridine

L. G. Gafiyatullin, L. I. Savostina, O. I. Gnezdilov, O. A. Turanova, I. V. Ovchinnikov, and A. N. Turanov

Zavoiskii Kazan Physical Technical Institute, Kazan Research Center, Russian Academy of Sciences, Sibirskii trakt 10/7, Kazan, Tatarstan, 420029 Russia
e-mail: sasha_turanov@rambler.ru

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Abstract—Photoisomerization of 4-styrylpyridine at different irradiation wavelengths (λ 365 and 254 nm) and in different solvents was studied by UV and ^{1}H NMR spectroscopy. A procedure for recording the UV spectra of 4-styrylpyridine dissolved in liquid crystalline films freely suspended within a frame. The results of quantum-chemical calculations of the geometry and UV spectra of 4-styrylpyridine isomers are presented.

Keywords: photoisomerization, 4-styrylpyridine, UV spectroscopy, NMR, isomerism

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Styrylpyridines are of particular interest as photoisomerized ligands in coordination compounds. Complexes of metal ions capable of spin crossover with photoisomerized ligands provide a new photoactive channel to control magnetic properties of coordination compounds [1]. Such ligands are promising candidates for opto- and magnetoelectronics applications, and by studying them in solution and in the solid or liquid crystalline (LC) state one can gain information important in terms of basic science. Moreover, the development of LC cells with electrocontrolled optical and photocontrolled magnetic properties will serve the progress of new technologies. How the results of photoisomerization of 4-styrylpyridine depend on irradiation wavelength and solvent is interesting to study by two reasons: for photo control of the state of metal ions in spin-crossover complexes of 4-styrylpyridine [2] and for elucidation of the features of the photochemical synthesis of benzo[*h*]isoquinoline, which is important for cancer chemotherapy and schizophrenia therapy [3], because benzo[*h*]isoquinoline is formed by dehydrogenation of a cyclic photoisomer [4] whose derivatives are 5-HT3 receptor antagonists.

We previously studied the kinetics of photoisomerization of 4-styrylpyridine and its 4-alkoxy derivatives under irradiation (λ 365 nm, solvents $CHCl_3$, CH_3CN) [5]. Under these conditions, unsubstituted *trans*-4-styrylpyridine **A** transforms into *cis* isomer **B** and then cyclizes to form compounds **C**. No further dehydration, i.e. transformation into benzo[*h*]-isoquinoline (**D**) occurs.

In the present work we describe for the first time the results of photoisomerization of 4-styrylpyridine at different irradiation wavelengths (λ 365 and 254 nm) in different solvents, consider the procedure of recording the UV spectra of 4-styrylpyridine in liquid crystalline films freely suspended within frames, and present the results of DFT quantum-chemical calculations of the molecular geometry of 4-styrylpyridine, as well as photoisomerization products of this compound and their UV spectra.

The UV spectra of azobenzenes, stylbenes, and other compounds in supported LC films were studied previously [6–10]. However, these compounds are poor complex-forming agents and, therefore, are unsuitable for fabrication of materials combining photoactive and spin-crossover properties.

UV spectroscopy. First we checked the response of pure solvents (CH_3CN, C_6H_{14}, and $CHCl_3$) on irradiation with light with λ 365 and 254 nm. All the three solvents are insensitive to irradiation at λ 365 nm. The spectrum of unirradiated CH_3CN contains a strong C≡N absorption band (λ_{max} 225 nm) which transforms into a band with three maxima (λ_{max} 247, 256, and 266 nm) on irradiation at λ 254 nm. Therefore, CH_3CN has limited application for measuring spectra at λ <

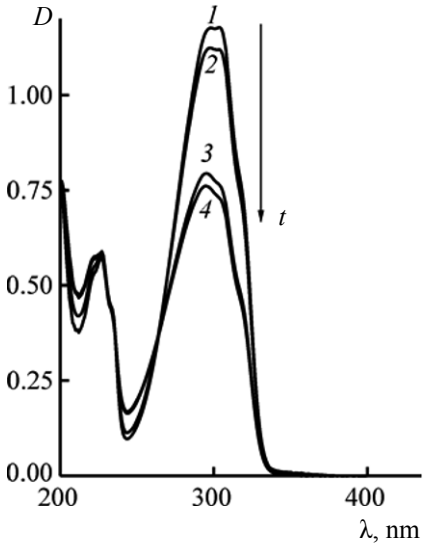


Fig. 1. Absorption spectra of 4-styrylpyridine in acetonitrile (*1*) before irradiation and after irradiation at λ 365 nm for (*2*) 10, (*3*) 30, and (*4*) 120 s and longer.

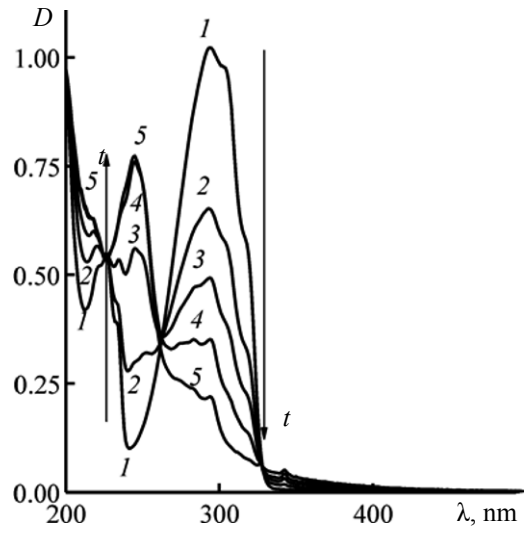


Fig. 2. Absorption spectra of 4-styrylpyridine in hexane (*1*) before irradiation and after irradiation at λ 254 nm for (*2*) 3, (*3*) 9, (*4*) 18, and (*5*) 30 min.

270 nm. In the UV spectra of hexane, only weak band λ_{max} 233 nm appears on irradiation (λ 254 nm).

The UV spectrum of irradiated $CHCl_3$ acquires an appreciable absorption band in the range 240–260 nm. The photochemistry of alkyl halides is well understood [11]. Primary dissociative processes form free chlorine atoms and free radicals which affect absorption at 240–260 nm.

The UV spectra of 4-styrylpyridine in acetonitrile on irradiation at λ 365 nm and in hexane and chloroform on irradiation at λ 254 nm are shown in Figs. 1–3.

The fact that the intensity of the band at $\lambda_{max} \approx 305$ nm in the spectra of 4-styrylpyridine in all the three solvents decreases on irradiation (λ 365 nm, Fig. 1) was explained by the isomerization *trans*- (**A**) → *cis*- (**B**) → cycle (**C**) [12, 13]. Evidence for this explanation comes from the NMR study in [5].

The result of irradiation of the 4-styrylpyridine solution with light with λ 254 nm depends on the solvent. In hexane, not only the band at λ_{max} 305 nm gets weaker, but also the band at λ_{max} 245 nm gets stronger, and also three isosbestic points appear in the spectra (Fig. 2); this result suggests that the solution contains predominantly two isomers which interconvert due to photoisomerization. This process gives rise to the dehydrogenation product **D** (benzo[*h*]isoquinoline). The band at λ_{max} 245 nm belongs to the latter compound, as evidenced by the results of ^{1}H NMR spectroscopy and DFT calculations. As mentioned above, the weak band at λ_{max} 233 nm is assignable to the irradiated solvent (C_6H_{14}).

UV irradiation (λ 254 nm) of a chloroform solution of 4-styrylpyridine, too, decreases the intensity of the band at λ_{max} 305 nm and simultaneously increases the intensity of the band at λ_{max} 345 nm with an isosbestic point (Fig. 3), and also increases the intensity of the chloroform absorption band in the range at 240–260 nm. Under these conditions (when the exposure to light is shorter than 15 s), the atomic chlorine formed by the decomposition of the solvent adds across the ethylene double bond in 4-styrylpyridine to form a CHCl–CHCl group, which is quite possible in dilute chloroform solutions. The light-induced formation of compounds with such groups is not ruled out both by DFT calculations and ^{1}H NMR spectroscopy (vide infra). When irradiation is longer than 15 s, all bands in the UV spectra decrease in intensity (not shown in the figure), which implies complete destruction of 4-styrylpyridine.

On alternating, i.e. cyclic short-time (a few second) irradiation of a chloroform solution of 4-styrylpyridine, the intensity of the band at λ_{max} 345 nm decreases by half on irradiation at λ 365 nm and recovers its intensity on irradiation at λ 254 nm. The possibility of formation of several conformers with different positions of chlorine and hydrogen atoms

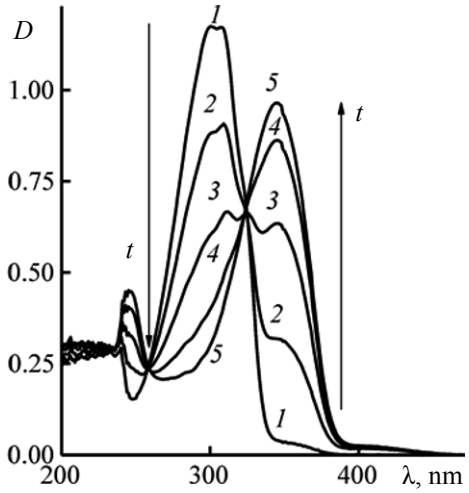


Fig. 3. Absorption spectra of 4-styrylpyridine in chloroform (*1*) before irradiation and after irradiation at λ 254 nm for (*2*) 3, (*3*) 6, (*4*) 9, and (*5*) 12 s.

agrees with the results of TZVP DFT calculations (the energy of the *cis* conformer is –1476.3427 au and the energy of the *trans* conformer is –1476.3803 au) and ^{1}H NMR data. However, in view of the importance for practical applications, the very fact that the state of the system can be controlled by short-time exposure to UV light deserves mentioning. The involved processes call for special research.

NMR spectroscopy. To identify the isomers of 4-styrylpyridine, formed in different conditions, we measured ^{1}H NMR spectra before and after irradiation. The most part (> 90%) of 4-styrylpyridine molecules in solutions before irradiation are present as *trans* isomers **A**, and the remaining part are *cis* isomer **B**. After 20–30-min irradiation (λ 365 nm) of a ~10^{-3} M solution, 4-styrylpyridine almost completely cyclizes into isomer **C** via intermediate isomerization to the *cis* form. The result of 30-min irradiation (λ 254 nm) depends on the solvent. In hexane cyclic isomer **C** undergoes dehydrogenation to form compound **D**, whereas in acetonitrile cyclic isomer **C** is the only reaction product.

The ^{1}H NMR spectra of chloroform solutions after irradiation (λ 254 nm) could not be assigned, because the destruction of the solvent is likely to produce several photoisomers of dichlorinated 4-styrylpyridine. It was only shown that the most part of chlorinated 4-styrylpyridines contain a CHCl–CHCl group.

Quantum-chemical calculations. To obtain evidence for the experimental results, we made use of the DFT quantum-chemical method to optimize the geometry of the isomers in study and calculate their UV. The resulting optimal geometries are shown in Fig. 4. According to the calculations, *trans* isomer **A** and dehydrogenation product **D** have a planar structure, unlike *cis* isomer **B** and cyclization product **C**.

The optimal geometries of structures **A–D** were calculated with different basis sets (see table). As seen from the table, as the basis set is extended from 6-311G(d,p) to cc-pCVTZ, the energy regularly decreases. Note that in going from the TZVP to cc-pCVTZ basis set the energy and steric structure changed inconsiderably, but the computing time with the cc-pCVTZ basis set was 3–4 times longer. Therefore, for further calculations we chose the TZVP basis set. According to the calculations, *trans* isomer **A** is preferred.

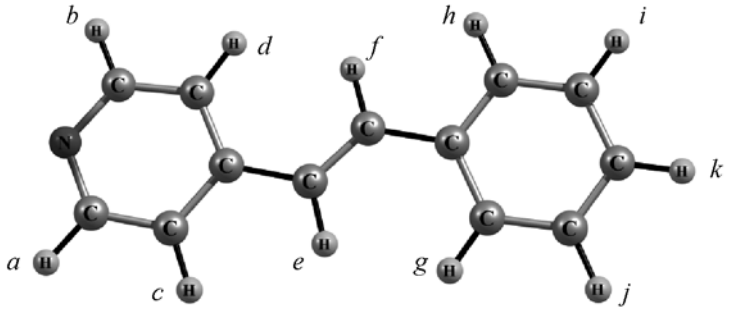
The table lists the calculated electron densities on the nitrogen atom in structures **A–D**. This information will be useful in planning the synthesis of photo-controlled spin-crossover Fe(III) complexes with the 4-styrylpyridine ligand.

For convenience in comparison to experiment, we calculated absorption spectra in the range 200–500 nm for structures **A–D** in corresponding solvents (Fig. 5). The calculated dependences agree well with the experimental data (Figs. 1–3), say, with the change in band intensity with structure (the *trans* isomer has a stronger absorption band than the *cis* isomer), as well as the change in λ_{max}.

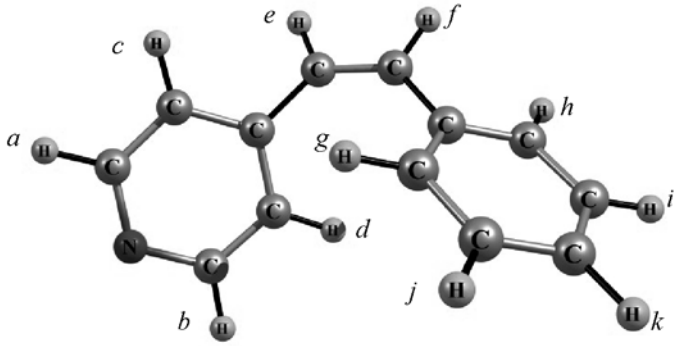
Photoisomerization in a LC matrix. To study the photoisomerization of styrylpyridines in a mesogenic environment, we chose as the LC matrix a commercial thermal indicator which meets all requirements for solving this task: (1) room temperature falls in the nematic temperature range 18–23°C; (2) sufficiently well dissolves styrylpyridines; (3) optically transparent in the absorption range of styrylpyridines (250–400 nm); and (4) insensitive to UV light.

For the most concentrated solution of 4-styryl-pyridine in the thermal indicator, the mesophase range is broader and shifts to higher temperatures (25–40°C).

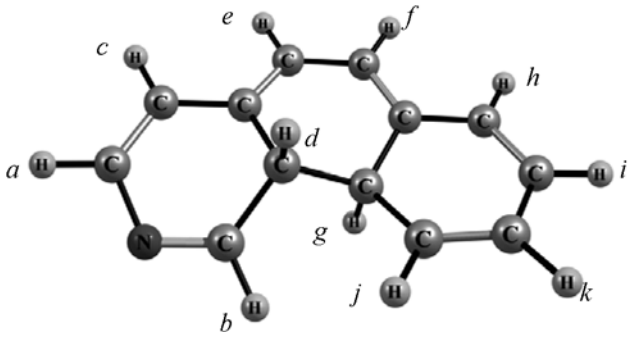
Liquid crystal domains efficiently scatter incident light. Therefore, the UV spectra of LC samples can only be obtained for very thin films. In LC films fixed a solid surface (the correlation length reaches 1 mm [14]), molecular interactions may much affect the kinetics of *cis–trans* transitions or even terminate



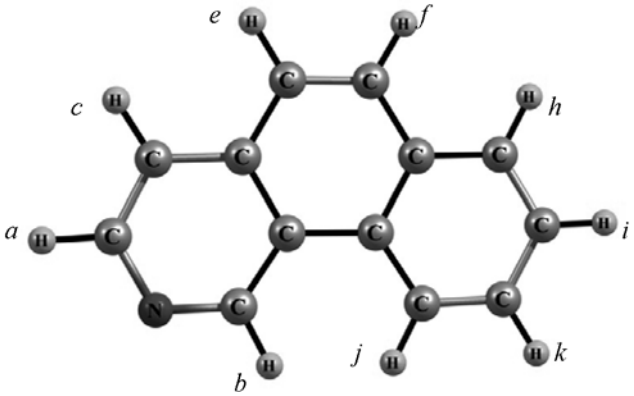
trans Isomer **A**



cis Isomer **B**



Cycle **C**



Dehydrogenated cycle **D**

Fig. 4. Optimized structures of 4-styrylpyridine and its photoirradiation products with proton denotation.

Energies of the *trans* (**A**) and *cis* (**B**) isomers of 4-styrylpyridine and its cyclization (**C**) and dehydrogenation (**D**) products, calculated with the basis sets 6-311G(d,p), TZVP, and cc-pCVTZ (PBE0 functional, ORCA software) and charges of the nitrogen atom

Compound	Energy, au			Nitrogen charge (charge au)
	6-311G**	TZVP	cc-pCVTZ	
A	–556.2039	–556.2480	–556.2721	–0.329
B	–556.0401	–556.2409	–556.2646	–0.374
C	–556.1439	–556.1877	–556.2106	–0.316
D	–555.0391	–555.0831	–555.1074	–0.349

isomerization. Therefore, in our study we suspended LC film within a frame with free side walls.

The UV spectra of the thin film of the thermal indicator with 4-styrylpyridine dissolved in it. The band at λ_{max} 305 nm belongs to 4-styrylpyridine, and the band at λ_{max} 230 nm was assigned to the thermal indicator. The intensity of the bands decreases with the time when the film is kept in a vertical position. The film thickness decreases, because the mixture flows down the cell bottom. Within about 40 min, the film gets very thin and destroys. As the film gets thinner, the relative intensity of the absorption bands of the indicator and 4-styrylpyridine ($A_{\lambda\ 305}/A_{\lambda\ 230}$ = 0.95) remains invariable within experimental error.

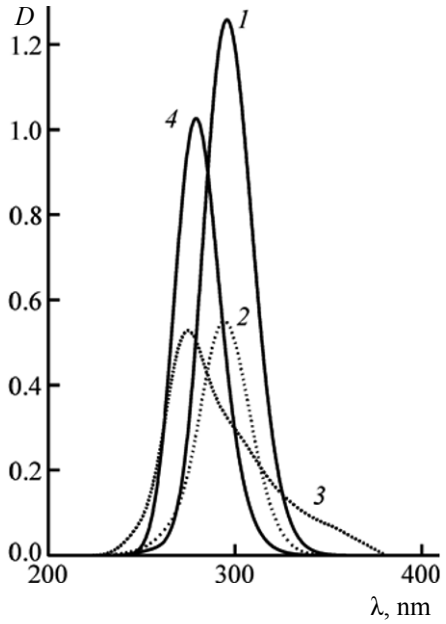


Fig. 5. Calculated UV spectra of 4-styrylpyridine isomers: (*1*) *trans* isomer **A** in acetonitrile, (*2*) *cis* isomer **B** in acetonitrole, (*3*) cyclic isomer **C** in acetonitrile, and (*4*) dehydrogenation product **D** in hexane.

UV irradiation (λ 365 nm) of such system leads to a considerable decrease of the 4-styrylpyridine band compared with the intensity of the indicator band ($A_{\lambda\ 305}/A_{\lambda\ 230}$ = 0.74). It should be noted that this effect is observed only after 3-min irradiation, whereas the same effect in an isotropic solution is already observed in 3 s [5]. The most obvious reason for this phenomenon is a much higher viscosity of the thermal indicator compared to isotropic liquids and strong intermolecular interactions the LC system. The photoirradiation product (**B** or **C**) could not be identified. A more detailed research on the irradiation of styrylpyridine in a LC matrix is in progress, and its results will be reported later.

EXPERIMENTAL

The UV spectra were recorded at room temperature on a Varian Cary 100 spectrophotometer in a 10-mm cell in the range 200–800 nm at a rate of 600 nm/min, slit width 1.5 nm. The samples were dissolved in CH_3CN, $CHCl_3$, and C_6H_{14} to a concentration of 1–2 × 10^{-5} M. The solutions were irradiated by Vilber Lourmat 6-W ultraviolet lamp at λ 365 or 254 nm.

In the experiments with thin films, the photoactive styrylpyridine was dissolved in the LC thermal indicator (~1 : 10) at 50°C. A frame (oval shape, dimensions 8 × 4 mm, made of stainless steel 0.15 mm in diameter, washed in acetone and dried before each experiment) was immersed into the solution and then taken out and let the film to cool down to room temperature; as this took place, excess solution ran off. Irradiation (λ 365 nm) and measuring the UV spectra were performed not taking the sample out of the instrument cell, and the reference cell was empty.

The textures and temperatures of phase transitions were determined using a Boetius micro hot-stage microscope (VEB NAGEMA). The error in the temperatures was ±0.1°C.

The ^{1}H NMR spectra were measured for 1.2×10^{-3} M solutions of 4-styrylpyridine at room temperature (20°C) on a Bruker Avance 400 spectrometer (400 MHz).

***trans* Isomer A.** The denotation of protons is shown in Fig. 4. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.04 d (1H^f, *J* 16.4), 7.35 d (1H^e, *J* 16.4), 7.40 d (2H$^{g,\,h}$, *J* 7.6), 7.43 t (1H^k, *J* 1.6), 7.44 d (2H$^{c,\,d}$, *J* 6.4), 7.56 dt (2H^{i,j}, *J* 7.2, 1.6), 8.59 d (2H$^{a,\,b}$, *J* 6.0).

***cis* Isomer B.** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.52 d (1H^f, *J* 16.0), 7.40 d (2H$^{g,\,h}$, *J* 7.6), 7.43 t (1H^k, *J* 1.6), 7.44 d (2H$^{c,\,d}$, *J* 6.4 Hz), 7.56 dt (2H^{i,j}, *J* 7.2, 1.6), 7.71 d (1H^e, *J* 16.0), 8.59 d (2H$^{a,\,b}$, *J* 6.0 Hz).

10*a*,10*b*-Dihydrobenzo[*h*]isoquinoline (cyclization product **C**). ^{1}H NMR spectrum (CD_3CN), δ, ppm (*J*, Hz): 6.51 d (1H^f, *J* 16.4), 6.84 d (1H^e, *J* 16.4), 7.23 t (1H^k, *J* 1.6), 7.24 d (2H$^{g,\,h}$, *J* 7.6), 7.25 d (2H$^{c,\,d}$, *J* 6.4), 7.26 dt (2H^{i,j}, *J* 7.2, 1.6), 8.48 d (2H$^{a,\,b}$, *J* 6.0).

Benzo[*h*]isoquinoline (dehydrogenation product **D**). ^{1}H NMR spectrum (C_6D_{14}), δ, ppm (*J*, Hz): 7.39 d (2H$^{c,\,e}$, *J* 8.5), 7.64 d (1H^h, *J* 7.6), 7.76 t (1H^i, *J* 7.6), 7.87 t (1H^k, *J* 7.2), 8.02 d (1H^f, *J* 8.5), 8.55 d (1H^a, *J* 5.1 Hz), 8.75 d (1H^j, *J* 7.6), 9.47 c (1H^b).

4-(1,2-Dichloro-2-phenylethyl)pyridine. The denotation of protons is the same as in *trans* isomer **A**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.31 d (1H^f, *J* 7.2), 6.50 d (1H^e, *J* 7.2), 7.17 t (2H$^{i,\,j}$, *J* 7.4), 7.35 d (2H$^{c,\,d}$, *J* 5.5), 7.43 t (1H^k, *J* 7.8), 7.45 d (2H$^{g,\,h}$, *J* 7.4), 8.46 d (2H$^{a,\,b}$, *J* 6.6).

Quantum-chemical calculations were performed by the DFT method using the ORCA software [15]. The UV spectra were calculated by the TD-DFT method [16] with fitting the absorption bandwidth at half height 30 nm. The density functional PBE [17] and the basis sets 6-311G(d,p), TZVP [18], and cc-pCVTZ [19] were used. The calculations involved full geometry optimization. Solvent effects on the UV spectra were included in the framework of the COSMO method [20] realized in the ORCA software for acetonitrile (ε 36.6, α 1.344) and hexane (ε 1.89, α 1.375).

4-Styrylpyridine was prepared by the procedure in [21].

Commercial thermal indicator, liquid crystalline, enantiotropic, brand 18-23, nomenclature number 181256, Technical Specifications 6-09-06-724-76, mesophase range 18–23°C, was used as received.

Commercial solvents CH_3CN, $CHCl_3$, and C_6H_{14} (Sigma–Aldrich) were purified by standard procedures; CD_3CN, $CDCl_3$, and C_6D_{14} were used as received.

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