Geometrical Isomers of 1,2-Bis-(4-pyridyl)-ethylene

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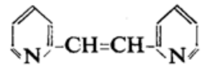
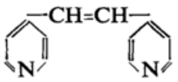
In the preceding paper[1] the author reported the geometrical isomers of 1, 2-bis-(2-pyridyl)-ethylene. Regarding 1,2-bis-(4-pyridyl)-ethylene, it is also expected that it will be able to exhibit geometrical isomerism and then to prove its existence in a cis and a trans form. Hitherto, however only one species[2,3] which melts at 151~152°C has been known. The author condensed 4-picoline and 4-pyridylaldehyde into 1,2-bis-(4-pyridyl)-ethylene and then separated two isomers from the ethylene, one corresponding to the known species and the other to the unknown one. The elementary analyses, molecular weight, melting points and ultraviolet and infrared absorptions, all prove that the former is a trans isomer and the latter a cis isomer of 1, 2-bis-(4-pyridyl)ethylene.



1, 2-Bis-(2-pyridyl)-
ethylene



1, 2-Bis-(4-pyridyl)-
ethylene

Experimental

Synthesis of 1, 2-Bis-(4-pyridyl)-ethylene.—The ethylene was synthesized from 4-pyridylaldehyde, 4-picoline and anhydrous zinc chloride according to Thayer and Corson's method[2]. 4-Pyridylaldehyde from the Aldrich Chemicals was distilled under 16 mmHg pressure and the fraction boiling at 85.5°C was used; the phenylhydrazone, m. p. 177.0~178.5°C (lit., 178~179°C[4]). 4-Picoline was separated from the "β-picoline", b. p. 140~148°C, according to the following method[5]. The "β-picoline" contains 3-picoline, 4-picoline and 2, 6-lutidine. 2, 6-Lutidine was first removed as the urea adduct[6], and then the mixture of the unchanged 3- and 4-picoline was converted into their oxalates[7]. 4-Picoline oxalate was separated by the fractional crystallization from the absolute alcohol solution, as it is less soluble in absolute ethanol than 3-picoline oxalate; 4-picoline oxalate, m. p. 138~139°C. 4-Picoline was recovered by the decomposition of the oxalate with sodium hydroxide and distilled; b. p. 145.0~146.0°C; picrate, m. p. 165.5~166.5C. The infrared absorption spectra of the 4-pyridylaldehyde and the 4-picoline showed the complete absence of the 2- and the 3-isomer, respectively in them. 4-Pyridylaldehyde (0.022 mol.), was heated with the equivaleat moles of 4-picoline and anhydrous zinc chloride in a sealed tube at 200~215°C for 16 hr. The reaction mixture was cooled, dissolved in 40 cc. of 3 N sulfuric acid, and basified with sodium hydroxide. The cooled alkaline solution was extracted twice with 30 cc. portion of ether and four times with 30 cc. portions of chloroform. The chloroform extract was dried over anhydrous potassium carbonate. After the greater part of the solvent was removed, the concentrated chloroform extract was chromatographed on a column (2×40 cm.) of alumina and the column was eluted with chloroform. The chromatograph afforded a satisfactory fractionation. One (**A**), eluted first, formed colorless, long needles, which melted at 151.5~152.5°C after three additional recrystallizations from water and corresponds to the known species of the ethylene. Yield, 17% theoretical. The other (**B**), contained in the next eluate, formed colorless, viscid oil and crystallized by being scratched with a sharp glass rod. The repeated recrystallizations of the crystals from cyclohexane-benzene (1 : 1) gave colorless, small needles, m. p. 110~111°C. Yield, 17.5% theoretical.

Measurements.—Molecular weight was determined by Rast's method. The ultraviolet absorption spectra (in absolute ethanol) were made with a Shimadzu QB-50 quartz spectrophotometer. The wavelengths of the photometer were calibrated with the absorption band at 301 mμ of an aqueous potassium nitrate solution. The infrared absorption spectra were obtained with a Shimadzu IR spectrophotometer equipped with a rock-salt prism. Readings were taken in the range 2000~670 cm^{-1} and calibrated with the absorption bands of polystyrene.

Results and Discussion

As described above, **A** is colorless, long needles and melts at 151.5~152.5°C, while **B** is colorless, small needles and melts at 110.0~111.0°C. **A** is identified with the known species of 1, 2-bis-(4-pyridyl)-ethylene, as the melting point is in good agreement with the published value of the ethylene (lit., 151~152°C[2]) and the result of the elementary analyses is consistent with the calculated value for the ethylene $C_{12}H_{10}N_2$ (Table I). Furthermore, the assignment of the infrared

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[1] T. Katsumoto, This Bulletin, **32**, 1019 (1948).

[2] H. I. Thayer and B. B. Corson, *J. Am. Chem. Soc.*, **70**, 2330 (1948).

[3] E. D. Bergmann et al., ibid., **74**, 5979 (1952).

[4] J. P. Wibaut et al., *Rec. trav. chim.* **64**, 30 (1945).

[5] T. Katsumoto et al., *Coaltar* (*Japan*), 3, 368 (1951).

[6] F. Othmer, *Ind. Eng. Chem.*, **40**, 168 (1948).

[7] A. G. Lidstone, *J. Chem. Soc.*, **1940**, 243.

TABLE I. COMPARISON OF THE TWO ISOMERS OF 1,2-BIS-(4-PYRIDYL)-ETHYLENE

Compound	A long needles	B small needles
M.p.	151.5∼152.5°C	110.0∼111.0°C
Elementary analyses		
Found	C: 78.9 % H: 5.75 N: 15.60	C: 79.0 % H: 5.83 N: 15.20
Calcd. for $C_{12}H_{10}N_2$	C: 79.1 % H: 5.53 N: 15.40	
Molecular weight		
Found	—	188
Calcd. for $C_{12}H_{10}N_2$		182

spectrum makes sure of the above determination, as is described later. The elementary analyses and molecular weight of B are also consistent with the calculated values for the ethylene (Table II); thus **B** is an isomer of A. Thayer et al. reported that 1,2-bis-(4-pyridyl)-ethane melted at 110∼111°C, which is the same temperature at which **B** melts. Although there is little possibility of producing the ethane in our experimentation, the author has proved that **B** is quite different from the ethane by the mixed examination and the infrared absorption spectra in carbon disulfide as follows; the ethane from the Aldrich Chemicals (m. p. 111∼112°C) depresses largely the melting point of **B** in the mixed examination and it shows no absorption in the range 830∼670 cm^{-1}, while **B** absorbs strongly at 763 cm^{-1}.

The infrared absorption spectra of the two isomers, **A** and **B**, are shown in Table II and Fig. 1. They resemble each other very closely except for a few absorptions. **A** and **B** give the following common absorptions; four absorptions in the range 1630∼1430 cm^{-1} due to the double bond stretching vibrations of the pyridine ring, three absorptions in the range 1250∼950 cm^{-1} due to the C–H in-plane bending vibrations of the 4-substituted pyridine ring and one strong absorption in the range 790∼830 cm^{-1} due to the C–H out-of-plane bending vibration of the 4-substituted pyridine ring, respectively[8,9,10]. These absorptions lie always in the range indicated by Shindo[8] and Katritzky[9] for the above vibration modes of the 4-substituted pyridine, as shown in the last column of Table II. A few absorptions that are not common to them arise from the disubstituted ethylene as will be discussed later. No other significant absorptions are found in the spectra. Thus, it is certain that **A** and **B** are the disubstituted ethylenes with 4-pyridyl radicals, i. e. 1,2-bis-(4-pyridyl)-ethylenes and the geometrical isomers with each other.

The geometrical arrangements of **A** and **B** are determined by the infrared and ultraviolet absorption spectra, the melting points, and the solubilities in organic solvents.

TABLE II. INFRARED ABSORPTION BANDS OF 1,2-BIS-(4-PYRIDYL)-ETHYLENE

A (trans)		B (cis)		Assignment*	Reference range
cm^{-1}	ε	cm^{-1}	ε		
1595	234	1603	206	PR-1	
1560	51	1567	57	PR-2	four bands in the range 1630∼1430 cm^{-1}
1504	24	1508	17	PR-3	
		1458	24		
1418	106	1420	111	PR-4	
1289	29			EHI (*trans*)	1310∼1290[13]
1242	51	1242	38	PHI-1	1232∼1211[8]
1070	24	1070	34	PHI-2	1070∼1053[8] 1072∼1055[9]
995	94	997	66	PHI-3	1003∼ 990[9] 997∼ 985[9]
966	145			EHO (*trans*)	990∼ 965[12]
951	61				
837	104				
821	182	819	103	PHO	790∼ 830[11]
		805	66		
		763	190	EHO (*cis*)	800∼ 650[11]

* PR means the stretching vibration of a pyridine ring; EHI and PHI mean the in-plane bending vibrations and EHO and PHO mean the out-of-plane bending vibrations of the hydrogen atoms remaining on an ethylene and a pyridine ring, respectively.

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[8] H. Shindo, *Pharm. Bull. (Japan)*, 5, 472 (1957).

[9] A. R. Katritzky and J. N. Gardner, *J. Chem. Soc.*, 1958, 2198.

[10] T. Katsumoto, This Bulletin, 33, 242 (1960).

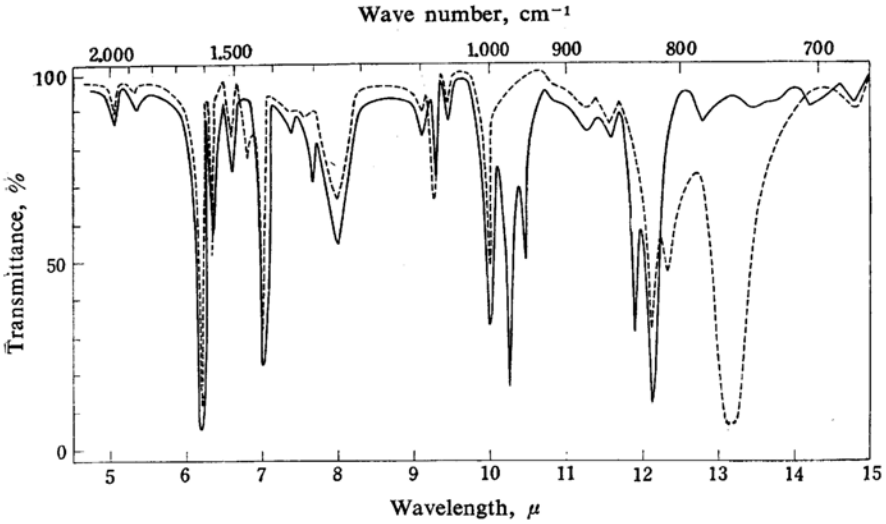

Fig. 1. Infrared absorption spectra of 1,2-bis-(4-pyridyl)-ethylene.
A 5 μ∼12.5 μ (chloroform), 12.5∼15 μ (acetone).
B 5 μ∼12.5 μ (chloroform), 12.5∼15 μ (carbon disulfide).
—— A (trans), ------ B (cis)

TABLE III. ULTRAVIOLET ABSORPTION BANDS OF 1,2-BIS-(4-PYRIDYL)-ETHYLENE (in absolute ethanol)

	E-band		K-band	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}
cis Form (**B**)	212 mμ	8,390	257 mμ	4,210
trans Form (**A**)	218 mμ	11,460	288 mμ	32,490
	223	11,990	299	33,380
			312	19,470

The infrared absorptions due to the cis- and the trans form are quite different[11]. trans isomers absorb strongly close to 965 cm^{-1} and weakly in the range 1310∼1290 cm^{-1}. Rasmussen and Brattain showed that the former absorptions appear only with the trans double bond[12]. This absorption is attributed to the =C–H out-of-plane bending vibration, and the latter to the in-plane bending vibration, of the *trans*-disubstituted ethylene[13]. Cis isomers give no absorptions in this range. **A** gives the two absorptions at 966 cm^{-1} and 1298 cm^{-1}, but the absorptions corresponding to them cannot be found in the spectrum of **B**. While, Zechmeister[14] suggested the *cis*-disubstituted ethylenes conjugated with double bonds on both sides give an absorption near 780 cm^{-1}. **B** absorbs strongly at 763 cm^{-1} as described above and **A** gives no absorptions in the regions. These absorptions suggest that **A** is a trans isomer and **B** is a cis isomer.

The melting point of **B** is lower by about forty degrees than that of **A**, as shown in

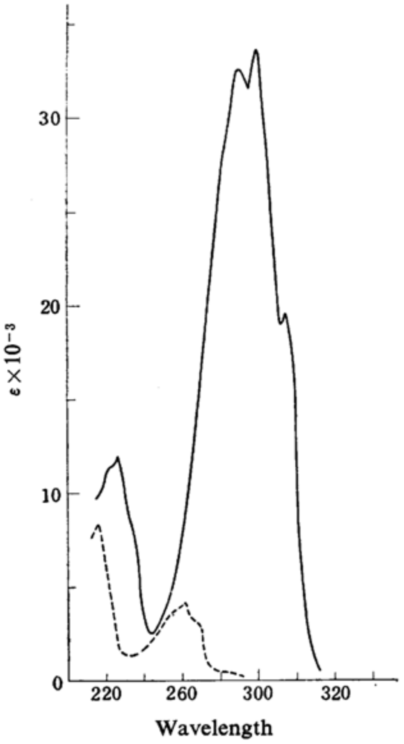

Fig. 2. Ultraviolet absorption spectra of 1,2-bis-(4-pyridyl)-ethylene.
—— A (trans), ---- B (cis)

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[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecule", 2nd Ed., Methuen, London (1958), p. 45.

[12] R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 131, 135 (1947).

[13] N. Sheppard and G. Sutherland, *Proc. Roy. Soc.* **A196**, 195 (1949).

[14] L. Zechmeister et al., *Acta Chem. Scand.*, **8**, 1421 (1954).

Table I. As the cis isomer always melts at a very much lower temperature than trans isomer does, **B** and **A** seem to be a cis and a trans isomer, respectively. The polar substance like a cis isomer is not easily dissolved in the non-polar solvents. **B** is insoluble in cyclohexane, while **A** is readily soluble in it. **B** seems to be a cis isomer.

Regarding the conjugation band of the ultraviolet absorption spectra, a cis isomer gives the spectrum similar to the sum of the spectrum of the component parts of the molecule on the either side of the double bond. The bathochromic displacement and much increase of the absorption intensity of the conjugation band always occur on passing from the cis structure to the trans structure. The ultraviolet absorption spectra of **A** and **B** are shown in Table III and Fig. 2. The conjugation band of 4-picoline has the intensity of some 2,000 at 255 mμ and that of **B** has about two times as much intensity of 4,210 as the former at 257 mμ. While **A** gives the band at 299 mμ with intensity 33,380. The ultraviolet absorption spectra of **A** and **B** are typical of the trans and the cis structure.

The conclusion is that the known species of 1, 2-bis-(4-pyridyl)-ethylene (**A**) is the trans isomer and another species (**B**) which was separated by the present author is the cis isomer.

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