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

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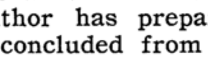
1, 2-Bis-(2-pyridyl)-ethylene (I) is expected to exhibit geometrical isomerism and to exist in a *cis*- and a *trans*-form. Hitherto, however, only one species has been known. It was first synthesized by Lénárt[1] and melted at 118∼119°C. But it has been unknown to which form it belongs. The present author has prepared the other form and concluded from physical properties that the former is the *trans*-isomer and the latter is the *cis*-isomer.



(I)

Experimental

Synthesis of 1, 2-Bis-(2-pyridyl)-ethylene. — It was prepared from 2-pyridylformaldehyde, α-picoline and anhydrous zinc chloride. 2-Pyridylformaldehyde, obtained from the Wako Co., was distilled under reduced pressure and the fraction boiling at 76∼77°C/17 mmHg was used. α-Picoline, obtained from the Eastman Kodak, was fractionated in an efficient column (b. p., 129.3°C).

A mixture of 2-pyridylformaldehyde (2 g.), α-picoline (3 g.) and anhydrous zinc chloride (2 g.) was heated in a sealed tube at 200°C for 24 hr. After being cooled, the dark brown viscid product was dissolved in aqueous hydrochloric acid. The acid solution was then basified with sodium hydroxide and steam-distilled to remove the unchanged α-picoline. The black oil, which separated on the surface of the solution, was extracted with chloroform and the chloroform extract was dried over anhydrous sodium sulfate and evaporated. The resinous residue was distilled under reduced pressure in a Claisen flask fitted with a wide saber-shaped side tube. A deeply yellow oil distilled out over the interval 150∼220°C /15 mmHg and condensed in the side tube. The distillate was extracted with boiling ether, and evaporation of the extract gave 1, 2-bis-(2-pyridyl)-ethylene as a brown sticky oil.

Separation of Two Isomers.—The isomers were

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[1] C. H. Lénárt, *Ann.*, 410, 95 (1915).

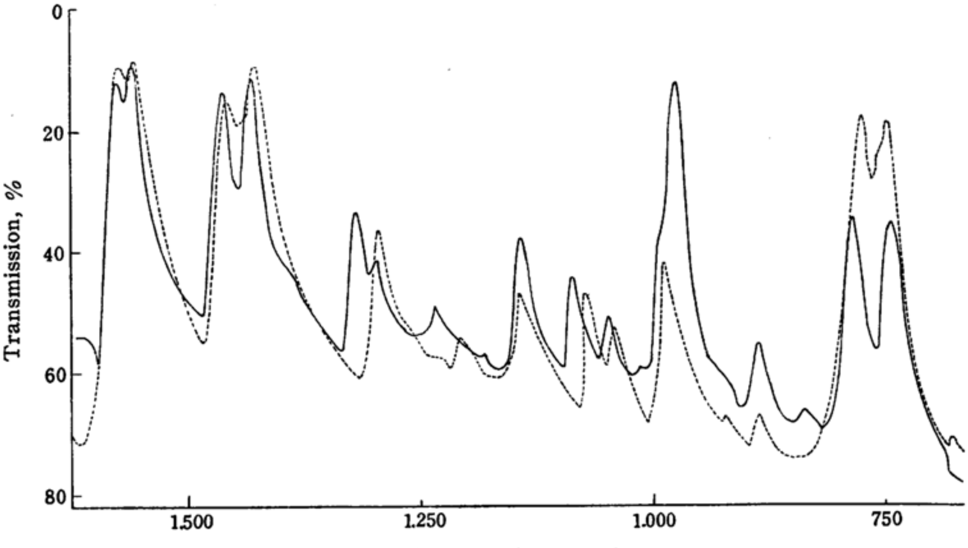

Fig. 1. Infrared spectra of 1,2-bis-(2-pyridyl)-ethylene.
—— compound II (*trans*), ------ compound III (*cis*)

separated by the elution chromatography. The oil was dissolved in chloroform, dried with calcium chloride, and chromatographed on a column (2×13 cm.) of alumina and the column was eluted with the same solvent to give pale brown crystals melting at 70~105°C. Two additional chromatographs on alumina column (2×41 cm.; chloroform) separated them into two parts. One (II), eluted first, forms colorless prisms, m. p. 120~121°C, and corresponds to the compound described by Lénárt. The other (III), contained in the next elute, forms colorless needles and melts sharply at 48.0~48.5°C.

Measurements of Physical Properties. — The boiling points at 15 mmHg pressure were measured by Garcia's method[2]. The pressure was kept constant with a mercury pressure controller fitted with a large buffer bottle (sensitivity, ±0.5 mmHg).

The ultraviolet absorption spectra in cyclohexane were measured with a Shimadzu spectrophotometer. The wavelength of the photometer was calibrated with the absorption band at 301 mμ of an aqueous potassium nitrate solution[3-5]. The infrared spectra in potassium bromide disks were obtained with a Hilger double beam spectrophotometer.

Results and Discussion

The results of the elementary analyses of the two species, II and III, are just the same and consistent with the formula, $C_{12}H_{10}N_2$ (Table I), thus showing that they are isomers.

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

	Compound II	Compound III
Elementary analysis		
Found	C: 78.97% H: 5.738 N: 15.42	C: 78.79% H: 5.729 N: 15.49
Calcd. for $C_{12}H_{10}N_2$	C: 79.09% H: 5.53 N: 15.38	
m. p.	120.0~121.0°C	48.0~ 48.5°C
b. p.	197.0°C	148.5°C
Configuration	*trans*	*cis*

The infrared spectra of the two isomers, II and III, are given in Fig. 1. All bands of II correspond to those of III, except two strong bands located at 968 and 1318 cm^{-1} as shown in Table II. The band at 986 cm^{-1} of III is not clearly noticed in the spectrum of II, but it seems to be hidden by the very strong band at 968 cm^{-1}, because a shoulder is found in this region. Lunde and Zechmeister[6] also found the absorption band at 980 cm^{-1} as a shoulder on the adjacent and intense band at 960 cm^{-1} in the spectra of many *trans*-diphenylpolyenes including *trans*-stilbene.

A number of the common absorption

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[2] C. R. Garcia, *Ind. Eng. Chem., Anal. Ed.*, **15**, 648 (1943).
[3] D. T. Ewing et al., ibid., **12**, 639 (1940).
[4] J. M. Vandenbelt et al., ibid., **17**, 235 (1945).
[5] H. Ley and F. Volbert, *Z. phisik. Chem.*, **130**, 308 (1927).

[6] K. Lunde and L. Zechmeister, *Acta Chem. Scand.*, **8**, 1421 (1954).

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

Compound II $\tilde{\nu}_{max}$ (cm^{-1})	Compound III $\tilde{\nu}_{max}$ (cm^{-1})	Assignment**
738 (vs)*	746 (vvs)*	Py-1
780 (vs)	778 (vvs)	Py-1
883 (m)	885 (w)	
968 (vvs)		E
(986 s)	986 (s)	Py-2
1045 (w)	1045 (w)	Py-2
1083 (m)	1073 (m)	Py-2
1138 (s)	1149 (m)	Py-2
1295 (w)	1299 (s)	
1318 (s)		
1428 (vvs)	1430 (vvs)	Py-2
1460 (vvs)	1460 (vs)	Py-3
1559 (vvs)	1561 (vvs)	Py-3
1574 (m)	1578 (s)	Py-3

* The letters shown in the brackets mean the relative intensities. v=very, s=strong, m=medium and w=weak.

** Py-1,2,3 mean the CH out-of-plane deformation, the CH in-plane deformation, and the ring stretching vibration of 2-substituted pyridine ring, respectively. E means the CH out-of-plane deformation of -CH=CH- (*trans*).

bands show that these two compounds have very similar structures. These bands are assigned to the vibrations arising from the 2-substituted pyridine ring as follows:

The infrared spectra of substituted pyridines are closely similar to those of substituted benzenes, although the effect of the electronegative nitrogen appears regularly. All substituted pyridines exhibit strong and characteristic absorptions in the regions 700∼850 cm^{-1} due to the out-of-plane bending vibrations of the ring CH. Shindo7) suggested that 2-substituted pyridines show intense absorptions in the regions 740∼780 cm^{-1}, while 3-derivatives do in the regions 770∼820 cm^{-1} (m–s) and 690∼730 cm^{-1} (vs), and 4-derivatives in the region 790∼850 cm^{-1} (s). The 738 cm^{-1} band of II and the 746 cm^{-1} of III suggest that these compounds are 2-derivatives.

Bellamy8) suggested that a series of weak absorptions in the regions 990∼1200 cm^{-1} shown by substituted benzenes are peculiar to the types of substitution. Randall et al.9) also found that the absorption near 1020 cm^{-1} in monosubstituted benzenes are independent of the nature of the substituent and assigned it to the in-plane bending vibration of CH. Shindo7) suggested that a series of weak but sharp absorptions in this region are also found in the case of monosubstituted pyridines and the positions are almost constant regardless of the nature of the substituent and that three absorption bands in the regions 988∼998 cm^{-1}, 1041∼1050 cm^{-1} and 1140∼1151 cm^{-1} are characteristic of 2-substituted pyridines. He also attributed them to the in-plane bending mode of the ring involving a considerable ring vibration. Of the four common bands in the spectra of the present compounds, three bands at 986, 1045 and 1138 cm^{-1} of II and those at 986, 1045 and 1149 cm^{-1} of III are respectively in good agreement with the above bands which are characteristic of 2-substituted pyridines. Now, according to Rasmussen10) the absorption band due to the bending frequencies of CH or the in-plane vibration of hydrogen in the aromatic ring appears in the vicinity of 1429 cm^{-1}. This band corresponds to the fourth, very strong band at 1428 cm^{-1} (II) and at 1430 cm^{-1} (III).

Aromatics have three highly characteristic absorption bands in the regions 1500∼1600 cm^{-1} and these bands are assigned to the C=C stretching vibration of the three double bonds round the ring. Of these bands, Randall et al.11) regarded a band in the regions 1575∼1587 cm^{-1} as a positive indication of conjugation of a double bond with the aromatic ring. Brownlie12) suggested that heterocyclic aromatics such as pyridine also give a similar pair of bands in the region from the C=C and the C=N links, although in this case the third skeletal vibration is usually at appreciably lower frequencies. According to Shindo7), 2-substituted pyridines have three bands in the regions 1450∼1600 cm^{-1} similar to those of substituted benzenes due to their ring double bond stretching vibrations. Compounds II and III show strong bands in this region. The bands at 1460(vvs), 1559(vvs) and 1574(m) cm^{-1} of compound II and 1460(vs), 1561 (vvs) and 1578 (s) cm^{-1} of compound III seem to arise from the 2-substituted pyridine rings, and especially the band at 1574 and 1578 cm^{-1} may be due to the pyridine ring conjugated with C=C double bond. Thus, it seems to be sure that both compounds II and III are 1,2-bis-(2-pyridyl)-ethylene.

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7) H. Shindo, *Pharm. Bull.* (*Japan*), **5**, 472 (1957).

8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen & Co., London (1954), p. 69.

9) R. R. Randall et al., *Trans. Faraday Soc.*, **52**, 9 (1956).

10) R. S. Rasmussen, *Forthscr. Chem. org. Naturstoffe*, **5**, 131 (1948).

11) Randall et al., "The Infrared Determination of Organic Structures", von Nostrand, New York (1949).

12) Brownlie, *J. Chem. Soc.*, **1950**, 3062.

Generally, *trans*-disubstituted ethylenes show intense absorptions near 965 cm^{-1}. Rasmussen and Brattain[13] showed that these absorption bands appear only with *trans* double bond. These absorptions are attributed to the out-of-plane bending vibrations of =CH of the *trans*-disubstituted ethylenes and the absence of these bands can be regarded as conclusive evidence of the absence of *trans* double bond. The strong band at 968 cm^{-1} of II and the lack of this band in the spectrum of III lead to the conclusion that II is the *trans*-form and III is the *cis*-form.

The other sharp band at 1318 cm^{-1} in the spectrum of II is also lacking in the curve of III. According to Lunde et al.[6] *trans*-stilbene gives two weak absorptions at 1312 and 1342 cm^{-1} and these bands are lacking in *cis*-stilbene. Probably, these phenomena have some stereochemical significance which, however, can not be interpreted at the present time.

The melting point of III is lower by about seventy degrees than that of II, as shown in Table I. As the *cis*-isomer always melts at a very much lower temperature than the *trans*-isomer does[14], II and III seem to be a *trans*- and a *cis*-isomer, respectively. Their boiling points at 15 mmHg pressure are also shown in Table I. But it is impossible to distinguish between geometrical isomers from their boiling points, because no general rule as in the case of the melting points holds here.

The ultraviolet spectra of compounds II and III also support the above results as follows: The ultraviolet spectra of geometrical isomers such as those of stilbene[15,16], cinamic acid[16], phenylbutadiene[17] and azobenzene[18] have been investigated. They are composed of the E- (ethylenic) and the K- (conjugated) bands. The absorption intensities of the E-bands of the geometrical isomers are almost equal, while the K-band of the *cis*-form is about half as intense as that of the *trans*-form and lies at somewhat shorter wavelengths. It is well interpreted from the spatial arrangement of groups in these molecules. One of the isomers which approaches more closely to coplanarity exhibits a higher degree of resonance and shows more intense absorption at somewhat longer wavelengths[19]. The ultraviolet absorption curves of II and III are given in Fig. 2. Both have three strong to medium absorption bands in the region of the K-band (Table III). Compound II shows more intense absorption than the compound III and the absorption is located at the longer wavelengths. These curves are typical of geometrical isomers and compound II is a *trans*-isomer and compound III is a *cis*-isomer.

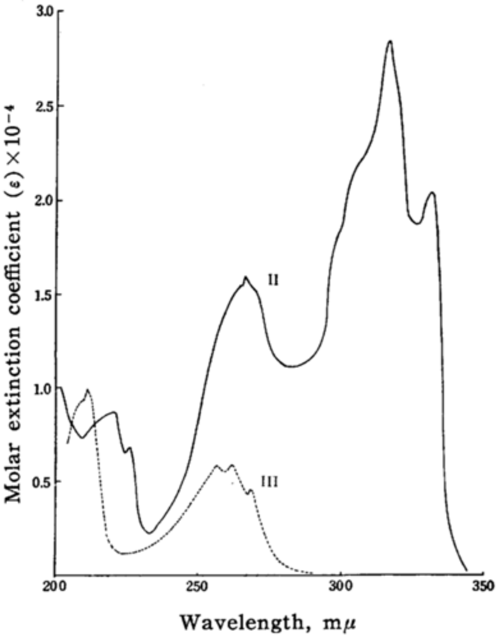

Fig. 2. Ultraviolet spectra of 1,2-bis-(2-pyridyl)-ethylene (II, *trans*; III, *cis*).

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

Compound II		Compound III	
λmμ	ε	λmμ	ε
220	8,770	211	9,920
226	6,830		
267	15,750	257	5,790
316	28,470	262	5,910
331	20,510	268	4,420
trans		*cis*	

λ, wavelength; ε, molar extinction coefficient.

The conclusion is that the 1,2-bis-(2-pyridyl)-ethylene described by Lénárt is a *trans*-isomer and the one separated by

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

[14] M. Murakami, "Stereo-organic Chemistry (*Kozo-Yuki Kagaku*)", Asakura Publishers, Tokyo (1956), p. 181.

[15] U. V. Solmssen, *J. Am. Chem. Soc.*, **65**, 2370 (1943).

[16] A. E. Gillam et al., "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold Publishers, London (1957), p. 269.

[17] O. Grummitt et al., *J. Am. Chem. Soc.*, **73**, 3479 (1951).

[18] R. N. Jones et al., *J. Chem. Soc.*, **1939**, 1315.

[19] R. S. Mullikan, *J. Chem. Phys.*, **7**, 364 (1939).

the present author is a *cis*-isomer. The *cis*-isomer(III) is very hygroscopic while the other is not. It may be presumed that the *cis*-structure is very unstable and that it becomes stable by coupling with a water molecule.

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