Geometrical Isomers of α-Stilbazole

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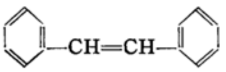
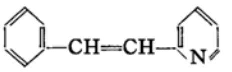
There is a series of stilbene derivatives which are substituted by one or two α-pyridyl groups for the phenyl groups of the stilbene. They are stilbene (I), α-stilbazole (II) and α-pyridostilbene, i.e. 1-2-bis-(α-pyridyl)-ethylene (III).


(I)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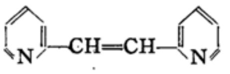
(III)

They are expected to exist in *cis*- and *trans*-structures as they are all 1,2-disubstituted ethylenes. Among the six isomers, *cis*- and *trans*-stilbene (I) are well known and recently the author reported two geometrical isomers of α-pyridostilbene (III)¹⁾. However, regarding α-stilbazole hitherto only one species which melts at 91°C has been known to us.

The author presumed that in the course of the preparation of the known species of α-stilbazole, the other isomer would be prepared as one of the by-products and then removed in some processes. The course was re-examined and it was found that the last recrystallization process removed completely the other isomer from the main product. Now, he has recovered the other isomer from the the filtrate, and then determined that the known species of α-stilbazole is a *trans*-isomer and the other is a *cis*-isomer on the basis of the data of the elementary analyses, the melting points, the ultraviolet and the infrared spectra.

Experimental

Syntheses of *cis*- & *trans*-α-Stilbazole.—A mixture of freshly purified benzaldehyde (b.p. 179~180°C), α-picoline (b.p. 129.3°C) and anhydrous zinc chloride in the ratio 3 : 2 : 1 was heated in in an autoclave at 200°C for 24 hr.²⁾ After being cooled, the dark brown and viscid product was dissolved in aqueous hydrochloric acid, steam distilled to remove benzaldehyde and basified with sodium hydroxide, followed by steam distillation to remove the residual α-picoline. The solution separated raw and purplish red stilbazole, which was extracted with chloroform. The chloroform extract was dried over anhydrous sodium sulfate. After the chloroform was evaporated, the residue was distilled under 10 mmHg pressure. Pale yellow liquid passed over the interval 170~180°C and condensed in a receiver. No α-stilbazole could be found in the fore-run which was collected separately in three traps kept at 0, −20 and −80°C, respectively. The main distillate in the receiver was recrystallized from boiling ethanol. The precipitate (**A**) melts at 91°C and corresponds to the known species of α-stilbazole. The yield was 60% theoretical. After ethanol was evaporated from the filtrate, there remained the brown oil. It was purified repeatedly by the elution chromatography (alumina, 2×40 cm., chloroform) until it showed the constant ultraviolet absorption spectrum. The purified oil (**B**) is colorless and melts at −50.0°C. The yield was nearly 3% theoretical.

Other Materials.—*cis- & trans-Stilbene.*—*cis*-Stilbene³⁾ was prepared from *cis*-α-phenylcinnamic

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1) T. Katsumoto, This Bulletin, **32**, 1019 (1959).
2) G. H. Lénárt, *Ann.*, **410**, 95 (1915).
3) C. C. Price, "Organic Syntheses", Vol. 33, John Wiley & Sons, Inc., New York (1953), p. 88.

acid and *trans*-stilbene[4] from benzoin, according to the methods of "Organic Syntheses". They were purified by the same method as the above. Their melting and boiling points are shown in Table II.

cis- & trans-α-Pyridostilbene.—The same samples that were synthesized in the preceding experiment[1] were used.

Analyses and Measurements.—Analytical data of the elementary analyses were determined by the Elementary Analyses Center of Kyoto University.

Melting points below the room temperature were measured in the following method, because the samples were so transparent even in the solid state as in the liquid state that the appearances did not change at the melting points. A liquid sample was packed as usual in a capillary tube which was then attached to a thermometer centered in a methanol bath. Dry air was sent into the bath to stir the methanol. A very thin and long glass wire was inserted in the capillary tube. As the bath was cooled in a dry ice-acetone mixture to −70°C, the sample solidified and the glass wire was fixed in it. Then, the methanol bath was transferred to an acetone bath that had been cooled near −40°C. The melting point was clearly observed as the glass wire could not be pulled out until the sample began to melt. *cis*-Stilbene and *cis*-stilbazole were viscid near the melting point.

Boiling points under reduced pressure were measured by Garcia's method[5] as described in the preceding paper[1].

The ultraviolet absorption spectra (in cyclohexane) were made with a Shimadzu QB-50 quartz spectrophotometer. The wavelengths of this photometer were calibrated with the absorption band at 301 mμ of an aqueous potassium nitrate solution. The infrared absorption spectra were obtained with a Hilger or a Leitz spectrophotometer equipped with a rock-salt prism. Readings were taken in the region of 1700∼670 cm^{-1} and always calibrated with the absorption bands of polystyrene.

Results and Discussion

As described above, the colorless liquid (**B**) was recovered from the filtrate of the recrystallization of the known species of α-stilbazole (A). The analytical data of the elementary analyses of the liquid (**B**) are shown in Table I and are in good

TABLE I. RESULTS OF THE ELEMENTARY ANALYSES OF **B**

	C	H	N
Found:	85.95%	6.32%	7.93%
Calcd. for $C_{13}H_{11}N$:	86.16	6.12	7.73

TABLE II. THE m.p.'s. AND b.p.'s. OF THE GEOMETRICAL ISOMERS

	Stilbene (I)		α-Stilbazole (II)		α-Pyridostilbene (III)	
	cis	*trans*	**B**(*cis*)	**A**(*trans*)	*cis*	*trans*
m.p.	−54.0°C	125.0°C	−50.0°C	91.0°C	48.5°C	121.0°C
b.p.	142°C/ 10 mmHg		141°C/ 10 mmHg	171°C/ 10 mmHg	149°C/ 15 mmHg	197°C/ 15 mmHg

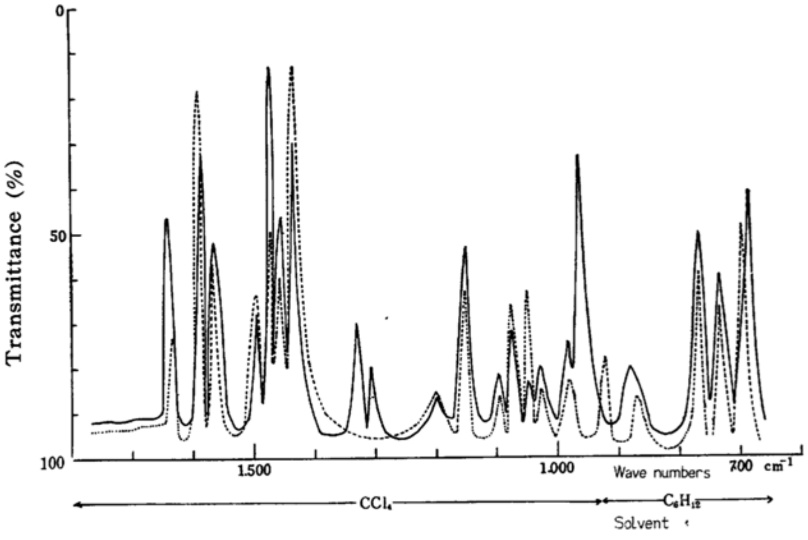

Fig. 1. Infrared absorption spectra of α-stilbazole.
—— **A** (*trans*) - - - - **B** (*cis*)

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[4] L. I. Smith, ibid., Vol. 23 (1943), p. 86.

[5] C. Garcia, *Ind.* Eng. *Chem., Anal. Ed.*, **15**, 648 (1943).

agreement with the calculated values for stilbazole $C_{13}H_{11}N$. It seems that **B** is also a species of α-stilbazole. **B** melts at −50.0°C, which is much lower as compared with the melting point of **A** (91°C). As a *cis*-isomer always melts at much lower temperature than a *trans*-isomer does (Table II and Ref. 6), **A** is a *trans*-isomer and **B** is a *cis*-isomer.

Fig. 1 shows the infrared absorption spectra of **A** and **B** in carbon tetrachloride or in cyclohexane. Each band of **A** is in good agreement with corresponding band of **B**, except two bands at 1330 and 965 cm^{-1} which will be discussed later. The good agreement indicates that **B** is the other isomer of **A**. Furthermore, this determination is made sure by the assignments of these absorption comparing their absorptions with those of the related compounds, stilbene (I) and α-pyridostilbene (III) as shown in Table III.

The fundamental studies$^{7-9)}$ on benzene vibrations have shown that the characteristic skeletal stretching modes of the semi-unsaturated carbon-carbon bonds lead to the appearance of a group of four bands between 1650～1450 cm^{-1}. Four absorptions corresponding to them are also expected theoretically in the case of pyridine and have been found in the similar range of the spectra of many pyridine derivatives$^{10,11)}$, although the vibrations are mostly found to shift to somewhat lower frequencies on passing from benzene to pyridine. In these ranges each of **A** and **B** shows seven absorptions due to BR-1, 3, 4 and PR-1, 2, 3, 4 vibration modes (Table III). The letters B and P in the table denote the vibrations arising from a benzene and a pyridine ring, respectively. These spectra show that **A** and **B** each consist of a benzene and a pyridine ring. Randall et al.$^{12)}$ regarded a bond in the range 1587～1575 cm^{-1}, namely, BR-2 in Table III, as an indication of the conjugation of an ethylenic double bond with an aromatic ring. In the spectra of α-stilbazole the BR-2 vibration is obscure, because the absorption range is very similar to that of the PR-1 vibration and they overlap one another, but the PR-2 vibration corresponding to the BR-2 vibration in the sense of the conjugation, is clearly seen. This shows that a pyridine ring in the α-stilbazole is conjugated with an ethylenic double bond.

In the range 1225～950 cm^{-1}, aromatic compounds all show a series of relatively weak but sharp bands, the positions of which vary with the type of substitution and are independent of the nature of substituents$^{11)}$. Randle and Whiffen$^{13,14)}$ have shown that they arise from the CH in-plane bending modes. Generally, mono-substituted benzenes show three absorptions in the ranges 1175～1125, 1110～1070 and 1070～1000 cm^{-1} $^{11,14,15)}$. In the case of α-substituted pyridines the similar absorptions also appear in the ranges 1151～1140, 1050～1040 and 998～986 cm^{-1} $^{10)}$. Five absorptions at **A** and **B** are located in the above absorption ranges of the mono-substituted benzenes and the α-substituted pyridines, and correspond to the BHI-2, 3 and the PHI-1, 2, 3 vibration modes. The absorptions due to the BHI-1 seem to be masked with those due to the PHI-1 mode (Table III). These absorptions show that the benzene and the pyridine ring of **A** and **B** are a mono-substituted benzene and an α-substituted pyridine ring.

Mono-substituted benzenes show two strong absorptions in the ranges of 770～730 cm^{-1} $^{11,12)}$ and 710～690 cm^{-1} $^{11,12,15)}$. They are assigned to the out-of-plane CH bending vibrations of five adjacent ring hydrogen atoms remaining on the benzene ring, and the absence of the latter band is a strong evidence of the latter band is a strong evidence of the absence of a mono-substituted benzene. On the other hand, α-substituted pyridines having four adjacent hydrogen atoms on the ring behave like an ortho-substituted benzene and absorb strongly in the range of 780～740 cm^{-1} $^{10,11)}$. The three strong bands corresponding to the above bands appear in the spectra of **A** and **B** (BHO-1, 2 and PHO in Table III).

Thus, **A** and **B** are both disubstituted ethylenes with a phenyl and an α-pyridyl radical, i.e. α-stilbazole.

Generally, *trans*-ethylenic double bonds give rise to two medium to strong bands in the ranges of 990～965 cm^{-1} $^{11,16)}$ and 1310

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6) M. Murakami, "Organic Stereochemistry (Kōzō Yūki-kagaku)", Asakura Publishers, Tokyo (1956), p. 181.

7) R. C. Lord et al., *J. Chem. Phys.*, **21**, 1170 (1953).

8) F. A. Andersen et al., ibid., **23**, 1047 (1955).

9) F. A. Miller et al., ibid., **24**, 996 (1956).

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

11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 2nd Ed., John Wiley & Sons, Inc., New York (1958).

12) H. M. Randall et al., "The Infrared Determination of Organic Structures", van Nostrand, New York (1949).

13) D. H. Whiffen, *J. Chem. Soc.*, **1956**, 1350.

14) D. H. Whiffen et al., *Trans. Faraday Soc.*, **52**, 9 (1956).

15) R. B. Barnes et al., "Infrared Spectroscopy", Reinhold Publishing Corp., New York (1944).

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

TABLE III. INFRARED ABSORPTIONS OF THE THREE PAIRS OF GEOMETRICAL ISOMERS (cm^{-1})

Stilbene (I)		α-Stilbazole (II)			α-Pyridostilbene (III)		Assignment*
cis[a,**]	*trans*[b]	**B** (*cis*)[c]	**A** (*trans*)[c]	**A** (*trans*)[b]	*cis*[b]	*trans*[b]	
		1632 m	1643 s	1636 s			
1607 m	1599 m			1598 sh			BR-1
		1590 vs	1586 vvs	1583 vvs	1585 vs	1582 s	PR-1
1578 w	1578 m						BR-2
		1570 s	1565 s	1566 sh	1569 vvs	1567 vs	PR-2
1496 s	1493 vs	1497 s	1497 m	1492 s			BR-3
		1471 s	1471 vvs	1466 vs	1467 vs	1468 vs	PR-3
1455 s	1453 vs	1453 m	1453 s	1453 vs			BR-4
		1435 vs	1433 vs	1428 vs	1438 vvs	1436 vs	PR-4
1412 m					1403 sh		*cis*-EHI
	1333 m		1331 vs	1330 s		1326 s	*trans*-EHI
	1302 m		1307 m	1305 s	1307 m	1303 m	
				1237 m		1234 w	
1183 w		1200 w	1198 w	1198 s			
1158 w	1157 m						BHI-1
		1147 s	1148 s	1147 s	1157 s	1146 s	PHI-1
		1093 w	1095 w	1095 m	1081 m	1090 m	PHI
1077 s	1073 s	1075 m	1074 m	1075 m			BHI-2
		1050 s	1049 w	1053 m	1053 m	1053 m	PHI-2
1033 m	1032 m	1030 w	1030 w	1033 w			BHI-3
		993 w	986 w		994 s	996 sh	PHI-3
	961 vvs		965 vvs	983 vvs		976 vvs	*trans*-EHO
924 s	912 m	923 m					
	880 w		880 w	893 m	893 w	880 m	
864 m	860 w	867 w		868 m			
					786 vs	788 s	
777 vvs	764 vvs	779 vs	772 vvs	779 vvs			BHO-1
		740 vs	735 vs	735 vvs	754 vvs	745 vs	PHO
694 vvs	685 vs	697 vs	688 vs	685 vs			BHO-2
				676 vs			

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

** The letters, a, b, c, denote the state of the samples in measurements: a, liquid condition without solvent; b, powder in a potassium bromide disk; c, carbon tetrachloride or cyclohexane solution.

TABLE IV. ULTRAVIOLET ABSORPTIONS OF THE THREE PAIRS OF THE GEOMETRICAL ISOMER (IN CYCLOHEXANE)

Compound	*cis*-Form				*trans*-Form			
	E-band		K-band		E-band		K-band	
	λ_{max}, mμ	ε	λ_{max}, mμ	ε	λ_{max}, mμ	ε	λ_{max}, mμ	ε
Stilbene (I)	207	19450	275	10730	228	15900	295	26600
	224	22600					306	24600
α-Stilbazole (II)	220	14860	285	9630	222	10570	275	15620
					228	11130	285	16470
					235	8570	314	24220
α-Pyridostilbene (III)	211	9920	257	5790	221	8770	267	15750
			262	5910	226	6620	316	28470
			268	4420			331	20510

~1290 cm^{-1} [11]. The former band was assigned by Kilpatrick and Pitzer to the out-of-plane bending vibration[11], while the latter was assigned by Sheppard and Sutherland[17] to the in-plane bending vibration, of the hydrogen atoms remaining on the *trans*-disubstituted ethylene. Especially the absence of the former band can be regarded as the conclusive evidence of the *trans*-ethylenic linkage. Not any absorptions corresponding to the above absorptions are found in the spectrum of **B**, while **A** gives rise to the two strong absorptions at 965 and 1330 cm^{-1} due to the *trans*-substituted ethylene (EHO, EHI in Table III). Thus, **B** is *cis*-α-stilbazole and **A** is *trans*-α-stibazole.

The ultraviolet spectra of **A** and **B** are compared with those of *cis*- and *trans*-isomers of stilbene (I) and α-pyridostilbene (III) in Table IV and Figs. 2–4. Each spectrum of stilbene and α-pyridostilbene consists of the E(ethylenic)-band and the K(conjugated)-band (Figs. 2 and 3). All the E-bands of both *cis*- and trans-isomers lie near 220 mμ. However, every K-band of the *trans*-isomer lies at a longer wavelength than that of the *cis*-isomer does. In addition, the intensity of the K-band is always much stronger in the *trans*-isomer than in the *cis*-isomer. The bathochromic displacements and much increase of the absorption intensities arise from the coplanarity of the molecular structure and then from the high degree of resonance on passing from the *cis*-structure to the

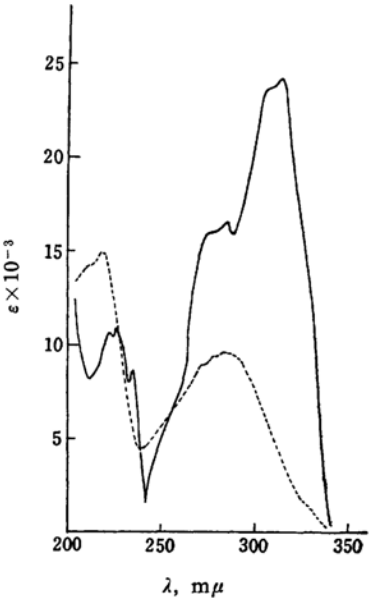

Fig. 3. Ultraviolet absorption spectra of α-stilbazole.
—— **A** (*trans*) ---- **B** (*cis*)

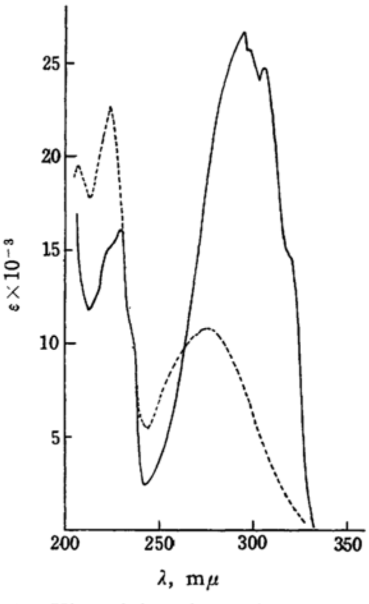

Fig. 2. Ultraviolet absorption spectra of stilbene.
—— *trans*-Fom ---- *cis*-Form

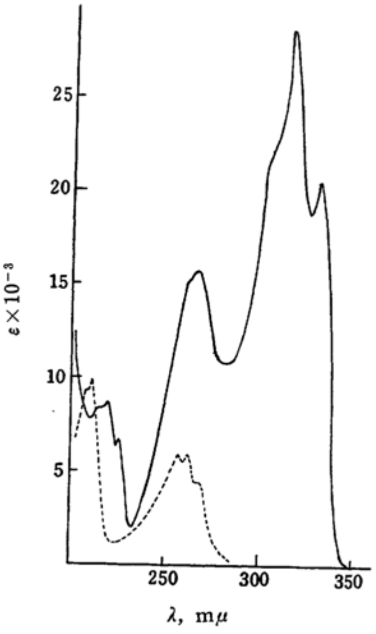

Fig. 4. Ultraviolet absorption spectra of α-pyridostilbene.
—— *trans*-Form ---- *cis*-Form

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

trans-structure[18]. Robertson and Woodward[19] indicated that, as the results of X-ray diffraction measurements, in *trans*-stilbene the bond joining the phenyl groups to the ethylenic group are 1.45 Å long. As the bond is considerably shorter than the usual saturated carbon-carbon bond (1.54Å), it is therefore a hybrid type, and two phenyl groups in *trans*-stilbene must exist almost in the plane in which ethylenic carbon and hydrogen atoms lie. Such configurations are expected in the cases of α-stilbazole (II) and α-pyridostilbene (III).

The spectra of **A** and **B** are typical of the *trans*- and the *cis*-structure (Fig. 3) and make sure of the above determination.

The conclusion is that a known species of α-stilbazole (**A**) is the *trans*-isomer and the other species (**B**) which was separated by the present author is the *cis*-isomer.

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[18] R. N. Jones, *J. Am. Chem. Soc.*, **65**, 1818 (1943).

[19] J. M. Robertson and I. Woodward, *Proc. Roy. Soc.*, **A162**, 568 (1937).