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Substituted Stilbenes. I. Absorption Spectra*

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The absorption spectra of five pairs of *cis-trans* isomers of substituted stilbenes have been measured. The spectra of the geometrical isomers of *p*-amino *p*′-nitro stilbene hydrochloride are compared with those obtained by previous work.

IN the course of other work,[1] a number of pairs of *cis-trans* isomers of para-substituted stilbenes were prepared and their absorption spectra measured. The compounds studied were *p*-methoxy stilbene, *p*-methoxy *p*′-nitro stilbene, and *p*-amino *p*′-nitro stilbene. In addition, the spectra of stilbene and *p*-nitro stilbene were redetermined for pusposes of comparison. Previous work[2–6] on stilbene spectra has, with a few exceptions, been confined to the *trans* isomers.

EXPERIMENTAL

Materials

Trans-Stilbene

A pure sample of this compound (mp 124°) was recrystallized twice from chloroform and the crystals vacuum dried, mp 124.5–124.8°.

Trans-p-Methoxy Stilbene

A sample of this compound prepared by Mr. C. E. Kitto was given two crystallizations from absolute ethanol, mp 134.9–135.2°.

Trans-p-Nitro Stilbene

This compound was prepared by the method of Pfeiffer and Sergiewskaja.[7] Purification was accomplished by means of chromatography on alumina using 2:1 petroleum ether:benzene as developer, following the procedure of Zechmeister and McNeely.[8] The band was eluted with chloroform and the product recrystallized from cold eluate, mp 158°.

Trans-p-Methoxy p′-Nitro Stilbene

P-nitro phenyl acetic acid and anisaldehyde were condensed in the presence of piperidine. The product recrystallized from ethanol gave orange crystals, mp 133.0–133.5°. When crystallized from benzene:petroleum ether, the isomorphic form, greenish-yellow needles, was obtained. This modification showed the characteristic transition to the orange form at 100°, as described by Pfeiffer.[9]

Trans-p-Amino p′-Nitro Stilbene

A sample of this compound prepared by Buckles was further purified by chromatography on magnesium oxide with benzene developer and chloroform as eluant. Red crystals were obtained, mp 250.0–250.5°.

Cis-Stilbene

Ten grams of *trans*-stilbene were dissolved in 50 ml of benzene in a Pyrex flask and irradiated with a quartz mercury arc for 23 hours. *Trans*-stilbene was then precipitated from solution by evaporation and addition of petroleum ether. The recovered *trans* isomer was redissolved in fresh benzene, again irradiated, and similarly separated from solution. The combined solutions containing the *cis* isomer were evaporated down to an oil which was placed on an activated alumina chromatographic column (2×15 cm) and developed with 100 ml petroleum ether. The bulk of the remaining *trans* and all the decomposition products were left on the column while the *cis* passed through. The solution containing the *cis* was evaporated to yield a colorless oil which was repeatedly molecularly distilled at 70° until the absorption spectrum remained constant. The product was a colorless liquid, $n_D^{20}=1.6200$, weighing 1.6 g *Anal.* Calc. for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.21; H, 6.65.

Cis-p-Methoxy Stilbene

P-methoxy 1′-carboxy stilbene was catalytically decarboxylated by the procedure described by Ruggli and Staub.[10] The crude oil was repeatedly molecularly distilled until the ultraviolet absorption spectrum showed no further change. *Anal.* Calc. for $C_{15}H_{14}O$: C, 85.7; H, 6.67. Found: C, 85.97, 86.25; H, 7.08, 7.12.

Cis-p-Nitro Stilbene

The method used was similar to that of Calvin and Buckles[2] except that benzene was used for the solvent

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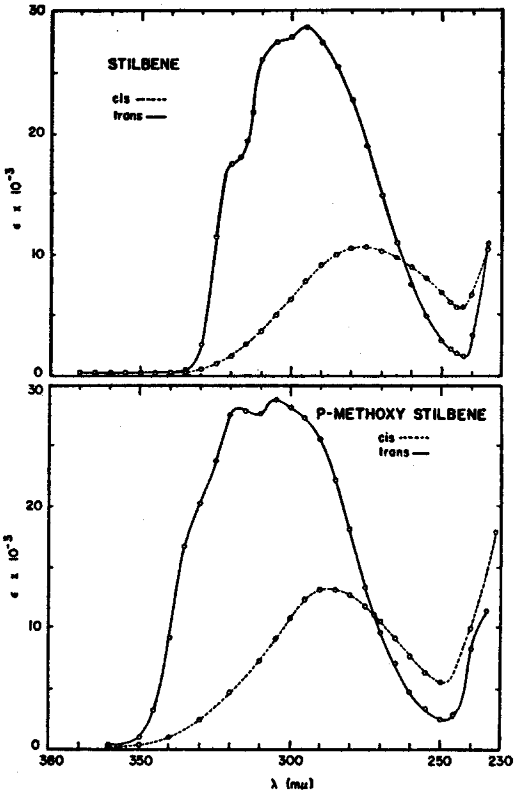

FIG. 1. Absorption spectra of stilbene (top) and *p*-methoxy stilbene (bottom).

during irradiation of the *trans* isomer and petroleum ether was added after irradiation to precipitate the bulk of the *trans* from solution. The supernate was chromatogrammed on alumina with 2:1 petroleum ether:benzene. A clean separation was made between decomposition products, *trans* and *cis*. The *cis* band was eluted with chloroform and the product molecularly distilled to give yellow crystals, mp 62.0–62.5°.

Cis-p-Methoxy p'Nitro Stilbene

Synthesis and purification were accomplished in the same manner as for *cis p*-nitro stilbene, mp 70.2–71.2°, *Anal.* Calc. for $C_{15}H_{13}O_3N$: C, 70.7; H, 5.13; N, 5.49. Found: C, 71.06; H, 5.24; N, 5.52.

Cis-p-Amino p'-Nitro Stilbene

Twenty-five ml benzene saturated with *trans-p*-amino *p'*-nitro stilbene were irradiated with a quartz mercury arc for one hour. The solution was put on a 3×20-cm magnesium oxide column and developed with benzene. The pale yellow *cis* band passed through the column, while the bright orange fluorescing *trans* band and decomposition products were completely retained. The *trans* was removed and re-irradiated and the separation process repeated. The total *cis* obtained was 25.7-mg red crystals, mp 99.5–100.5°. *Anal.* Calc. for $C_{14}H_{12}O_2N_2$: C, 70.00; H, 5.03. Found: C, 70.00; H, 5.00.

Spectra

All spectra were taken with a Beckman Model DU Quartz Spectrophometer with the exception of those for *p*-amino *p'*-nitro stilbene for which a Cary Recording Spectrophotometer was used. Unless otherwise indicated, the solvent was absolute ethanol.

RESULTS

The spectra of the free stilbenes in ethanol are given in Figs. 1–4 and show both the usual relations of *cis* and *trans* spectra and the familiar effects of the substituents on the spectra. As the interaction between the two ends of the molecule increases, there is a shift to longer wavelengths of the main absorption bands. The nitro group apparently washes out the evidences of vibrational structure found in both *trans*-stilbene and *trans-p*-methoxy stilbene.

The effect of polarity of solvent on the spectrum of a highly polar molecule is illustrated in Fig. 3 which gives the spectra of *p*-amino *p'*-nitro stilbene in ethanol and benzene. Traces of ethanol also suffice to quench completely the normally strong yellow-green fluorescence of *trans-p*-amino *p'*-nitro stilbene in benzene. The *cis* isomer does not fluoresce.

Of special interest is the case previously studied[2] in which the interaction of the substituent groups in

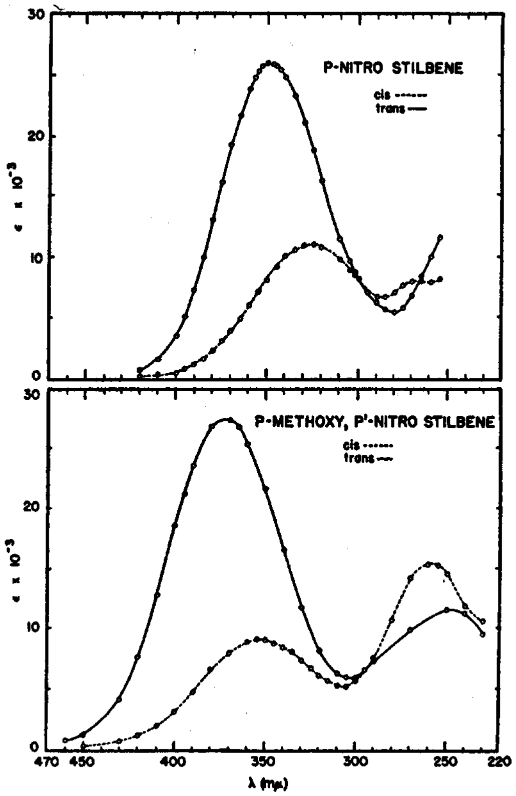

FIG. 2. Absorption spectra of *p*-nitro stilbene (top) and *p*-methoxy *p'*-nitro stilbene (bottom).

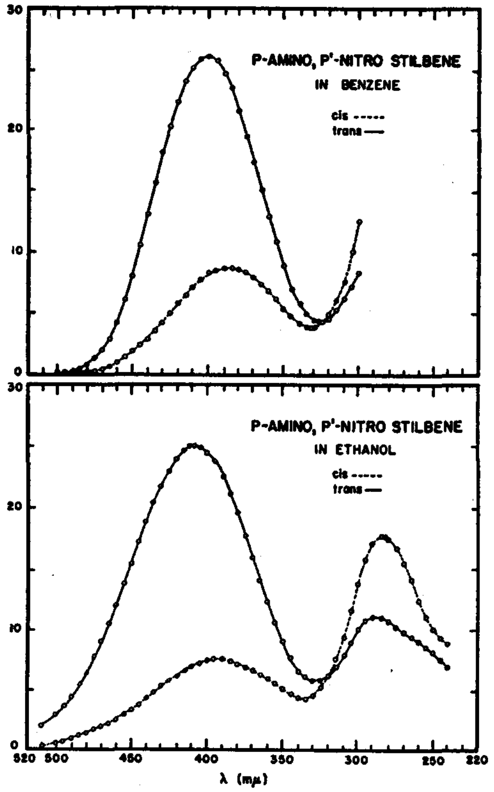

Fig. 3. Absorption spectrum of *p*-amino *p*′-nitro stilbene in benzene (top) and in ethanol (bottom).

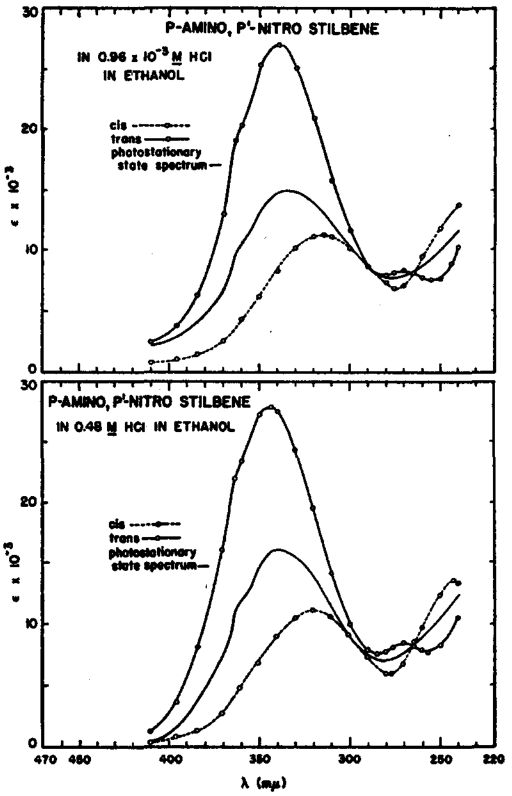

Fig. 4. Absorption spectrum of *p*-amino *p*′-nitro stilbene hydrochloride in 0.96 *M* hydrochloric acid in ethanol (top) and in 0.48 *M* hydrochloric acid in ethanol (bottom).

p-amino *p*′-nitro stilbene is almost completely destroyed in the amine hydrochloride. This is shown by the spectra in ethanolic hydrochloric acid (Fig. 4). Comparison of these spectra with those of free *p*-nitro stilbene shows them to be very similar, as expected.

Earlier work[2] on *trans*-*p*-amino *p*′-nitro stilbene hydrochloride indicated that the spectrum varies to a large extent with the acid concentration in the ethanol. This was tentatively interpreted as being due to a shift in a rapid equilibrium between the geometrical isomers of the salt with acid concentration. That this phenomenon is not due to a rapid equilibrium is shown by the spectra of both *cis* and *trans* salts at two different acidities (Fig. 4). The small differences between the two spectra are probably due to differences in the degree of dissociation of the salts at the two acidities.

The spectra of the photostationary states at two acidities for the hydrochlorides of *cis*- and *trans*-*p*-amino *p*′-nitro stilbene are also shown in Fig. 4. These states were approached from both the *cis* and *trans* sides by illumination of the dilute solutions with a 200-watt tungsten bulb. The photostationary state shows an acid dependence; in 0.48 *M* hydrochloric acid it is at 38 percent *trans*, while in 0.96×10^{-3} *M* hydrochloric acid it is at 22 percent *trans*. It seems reasonable to suggest that in the earlier work photostationary states or approaches to photostationary states were actually observed instead of a rapid thermal equilibrium.