406. *Some Physical Properties of* cis-*Stilbene.*

By D. S. BRACKMAN and P. H. PLESCH.

Some physical constants are recorded for highly purified *cis*-stilbene.

A NEW method of purifying *cis*-stilbene is described below. The *cis*-stilbene thus obtained had m. p. 5—6°, higher than any value recorded in the literature (see Table 1), and n_D^{25} 1·6218. New vapour-pressure measurements combined with recorded values gave 15·8 ± 0·3 kcal./mole for the latent heat of vaporisation.

The infra-red spectrum of *cis*-stilbene is recorded in Fig. 2, and the wave-numbers of the main absorption bands in the spectra of *cis*- and *trans*-stilbene are given in Table 2.

EXPERIMENTAL

cis-Stilbene has been prepared by many workers, using a variety of methods, but without full agreement on the physical properties of the pure compound. The present authors prepared *cis*-stilbene by Taylor and Crawford's method (*J.*, 1934, 1130). Purification by repeated high-vacuum fractionation at 80° yielded a colourless oil, which readily froze to a white crystalline solid, m. p. 5—6°, n_D^{25} 1·6223 ± 0·0005. Because this method was tedious it was abandoned. Instead, the crude reaction product was fractionally distilled once under a high vacuum at 80°, and the fractions with the same refractive index (yellow oils) were combined and further purified by repeated crystallisation from *n*-hexane cooled in solid carbon dioxide–methanol. After removal of the residual hexane in high vacuum, a colourless product was obtained which had m. p. 5—6° and n_D^{25} 1·6214 ± 0·0005. The melting point of the specimens purified by both

---

* It may be worth noting that the high π-electron coupling energy for this structure (17·82β, new calculation) seems to make it possible that the free radical corresponding to it may have considerable stability and little tendency to dimerization.

methods decreased when they were kept for several days in subdued light, reaching a steady value of 0·62° ± 0·04°. This decrease of the melting point may be due to the spontaneous formation of traces of *trans*-stilbene or of oxidation products from atmospheric oxygen. The infra-red spectrum shows that the proportion of the impurity, if it is *trans*-stilbene, is certainly small.

The fact that both our methods of purification give the same melting point and, within experimental error, the same refractive index, leads us to propose a m. p. of 5—6°, and n_D^{25} 1·6218. The refractive index agrees well with the most recent result (Coops and Hoijtink, *Rec. Trav. chim.*, 1950, **69**, 358), but our melting point exceeds that found by the Dutch workers; the reason for this is almost certainly our improved method of purification.

FIG. 1. *The relation between the logarithm of the vapour pressure* (p *in mm. Hg*) *and the absolute temperature* (T) *for* cis-*stilbene.*

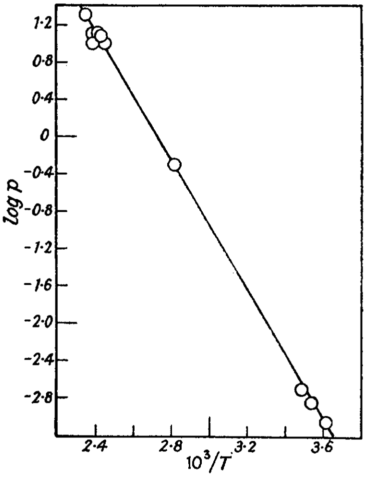
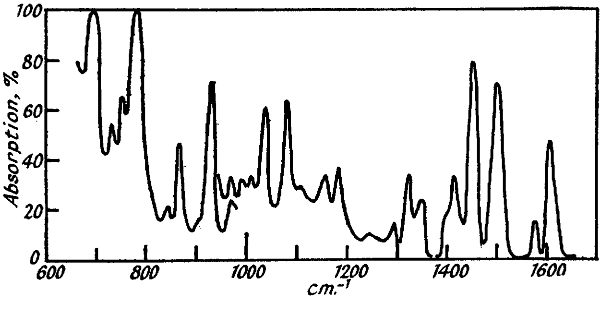


FIG. 2.



We are indebted to Mr. T. Charnley and Dr. H. A. Skinner for vapour-pressure measurements on our *cis*-stilbene with a quartz-fibre viscosity gauge (see Charnley and Skinner, *J.*, 1951, 1921) over the range 3—13°. When these results (shown in Table 1) are combined with the vapour pressures at various temperatures found in the literature, so that the temperature range is

TABLE 1.

Ref.	Method of prepn.	Method of purifn.	M. p.	Refractive index: temp.	n_D	Vapour pressure: temp.	p (mm. Hg)
1	a	—	—	—	—	145°	13
2	a	—	—	13°	1·620	139—140°	12
3	b	—	—	—	—	134°	10
4	a	—	—	—	—	145°	10
5	a	—	—	—	—	140·5—141°	13
6	c	I	—	25°	1·6032	—	—
7	a & b	II	1°	—	—	—	—
8	a	—	—	13°	1·6234	—	—
9	a	—	−28° to −26°	—	—	82·5°	0·5
10	b	III	2°	25°	1·62167	152°	20
11	b	IV	5—6°	25°	1·6218	3°	$(9·1 \pm 0·5) \times 10^{-4}$
						9°	$(1·49 \pm 0·11) \times 10^{-3}$
						13°	$(2·00 \pm 0·22) \times 10^{-3}$

References: 1, Schlenk and Bergmann, *Annalen*, 1928, **463**, 112. 2, Bourguel, *Bull. Soc. chim.*, 1929, [iv], **45**, 1067. 3, Taylor and Crawford, *J.*, 1934, 1130. 4, Kistiakowsky and Smith, *J. Amer. Chem. Soc.*, 1934, **56**, 638. 5, Price and Meister, *ibid.*, 1939, **61**, 1595. 6, G. N. Lewis, Nagel, and Lipkin, *ibid.*, 1940, **62**, 2973. 7, Weygand and Rettberg, *Ber.*, 1940, **73***B*, 771–3. 8, Downing and Wright, *J. Amer. Chem. Soc.*, 1946, **68**, 141. 9, Lewis and Mayo, *ibid.*, 1948, **70**, 1533—6. 10, Coops and Hoijtink, *Rec. Trav. chim.*, 1950, **69**, 358—67. 11, This paper.

Method of preparation: a, Catalytic hydrogenation of tolane. b, Decarboxylation of α-phenylcinnamic acid in quinoline. c, Isomerisation of *trans*-stilbene by ultra-violet light.

Method of purification: I, High-vacuum distillation at 80°. II, Impurities removed by complex formation. III, Distillation at 20 mm. Hg. in absence of air and light. IV, This paper.

extended to 152°, the best line is given by $\log p = 9{\cdot}4 - 3453\,T^{-1}$, where T is the absolute temperature and p the vapour pressure in mm. Hg. The latent heat of vaporisation (L) is 15·8 ± 0·3 kcal./mole (see Fig. 1).

The data found in the literature are summarised in Table 1.

The infra-red spectrum of *cis*-stilbene has not been published before. It was recorded for us (see Fig. 2) by Mr. M. St. C. Flett of the Blackley Laboratories of Imperial Chemical Industries Limited on a Hilger D.209 instrument, with single-beam photographic recording, using thin layers of the undiluted *cis*-stilbene. The spectrum could not be obtained immediately after purification, so that the material which was used, although initially our purest, had m. p. 0·62° at the time when the spectrum was recorded.

The spectrum of *trans*-stilbene (Thompson, Vago, Corfield, and Orr, *J.*, 1950, 214) was recorded on the same instrument for comparison.

Table 2. *Wave-numbers* (cm.$^{-1}$) (± 2) *of the main absorption bands of* cis- *and* trans-*stilbene.*

cis-Stilbene					*trans*-Stilbene				
695	864	1035	1321	1578	687	986	1156	1318	1600
730	927	1077	1346	1605	762	1003	1182	1340	1753
751	968	1168	1413	1910	847	1031	1221	1391	1826
780	986	1183	1450	1950	909	1072	1266	1455	1878
845	1005	1296	1500		964	1105	1299	1498	1935

The spectrum of *trans*-stilbene has a strong band at 1221 cm.$^{-1}$, and the absence of this from the spectrum of our *cis*-stilbene shows that it could not have contained more than a very small proportion of the *trans*-isomer.

The wave-numbers of the main bands for both *cis*- and *trans*-stilbene obtained from our spectra are given in Table 2.

This work was carried out at the University of Manchester. We thank Dr. H. A. Skinner, Mr. T. Charnley and Mr. M. St. C. Flett for their kind help and advice.

THE UNIVERSITY, MANCHESTER.
UNIVERSITY COLLEGE OF NORTH STAFFORDSHIRE,
KEELE, NORTH STAFFORDSHIRE.

[*Received, January 25th,* 1952.]