

the absorption due to iodide, iodate and undissociated iodic acid is negligible, even at 2400 Å. Correction was made for the absorption of perchloric acid.

The accuracy of the maximum molar extinction coefficients given in Table I is 1%; that of the curves in Fig. 1 is somewhat less.

The spectra of I^- , IO_3^- , $S_4O_6^{2-}$ and $S_2O_3^{2-}$ were measured by dissolving the sodium or potassium salt in doubly distilled water and measuring the optical density of the solutions with a Cary recording spectrophotometer. The accuracy of the molar extinction coefficients shown in Fig. 2 is about 10%. The values for tetrathionate are in agreement with those in the literature,³ but for thiosulfate there is a discrepancy of the order of a factor of 1.5 between these data and those reported elsewhere.^{3,4}

The Heat of Dissociation of Triiodide Ion.—The triiodide ion concentration in a solution containing $2.00 \times 10^{-3} M$ potassium iodide and $10^{-4} M$ perchloric acid was measured spectrophotometrically at different temperatures. The total iodine concentration was determined from the known equilibrium constant⁵ at 25.0°, and the equilibrium constant at the other temperatures then calculated. The data are given in Table II.

TABLE II
THE TRIIODIDE EQUILIBRIUM CONSTANT AT DIFFERENT TEMPERATURES

Temp., °C.	log (I_0/I) at 3530 Å.	$(I_3^-) \times 10^6 M$	$(I_2) \times 10^6 M$	$K \times 10^3 M$	$1/T_{abs.} \times 10^3$
1.0	0.538	2.038	0.667	0.654	3.648
16.1	.460	1.743	0.962	1.10	3.458
25.0	.420	1.591	(1.114)	(1.40)	3.356
25.0	.418	1.583	(1.109)	(1.40)	3.356
33.4	.379	1.436	1.256	1.75	3.264
39.2	.350	1.321	1.371	2.08	3.202

Allowing a 1% error in each spectrophotometer reading, the error in the equilibrium constants calculated in this way is about 5%. An experiment at high iodide ion concentration showed that the extinction coefficient of triiodide ion at 3530 Å. does not change with temperature.

A semi-logarithmic plot of K against the reciprocal of the absolute temperature gives a straight line, within experimental error. The value of ΔH calculated from the slope of this line is -5100 cal., with a maximum uncertainty of ± 400 cal. A value of -4300 is obtained from the data of Jones and Kaplan⁵ at 0° and 25°.

(3) L. Lorenz and R. Samuel, *Z. physik. Chem.*, **B14**, 219 (1931).

(4) H. Ley and E. König, *ibid.*, **B41**, 365 (1938).

(5) (a) G. Jones and B. B. Kaplan, *THIS JOURNAL*, **50**, 1845 (1928);

(b) W. C. Bray and G. M. J. Mackey, *ibid.*, **32**, 914 (1910).

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The *cis* and *trans* Isomers of 1,2-Dichloro-1-propene

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The *cis* and *trans* isomers of 1,2-dichloropropene have been prepared recently² and have boiling

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(2) Huntress and Sanchez-Nieva, *THIS JOURNAL*, **70**, 2813 (1948).

points of 76 and 93°. The assignment of *cis* and *trans* configurations had not been made but by analogy with the dichloroethylenes the low boiling isomer might be expected to have the *trans* configuration. The configuration of these isomers was then more fully investigated by King and Smith³ who measured the electric moment of the molecules in the vapor phase. Since they found that the high boiling isomer had a moment of 2.2 debye units and the low boiling isomer had a moment of 0.8 debye unit the configurations were identified as *cis* and *trans*, respectively.

The investigation of the structure as a problem in spectroscopy was undertaken before the results of King and Smith were available and our results are in agreement with the finding of these authors.

The *cis*- and *trans*-dichloropropenes and their completely deuterated analogs were prepared by Dr. L. Leitch.⁴ The spectra were obtained with a

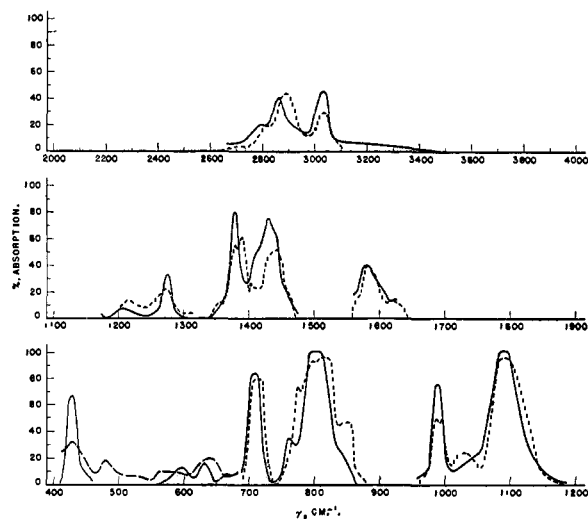


Fig. 1.—Infrared spectrum of $CH_2Cl-CHCl$ low boiling, *trans* isomer: —, liquid, 0.025 mm.; ---, gas, 65 mm.; — — —, gas, 65 mm.

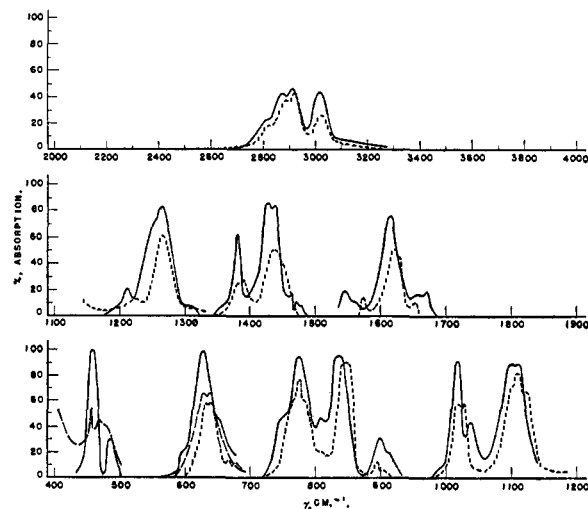


Fig. 2.—Infrared spectrum of $CH_2Cl-CHCl$ high boiling *cis* isomer: —, liquid, 0.025 mm.; ---, gas, 45 mm.; — — —, gas, 36 mm.

(3) W. H. King and H. A. Smith, *ibid.*, **72**, 3459 (1950).

(4) L. Leitch, *Can. J. Chem.*, in press.

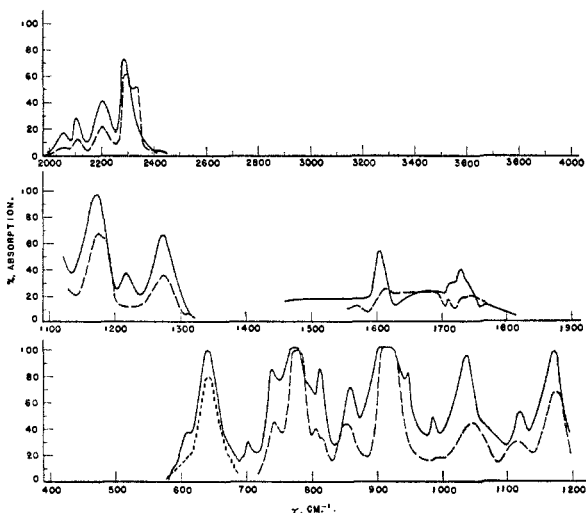


Fig. 3.—Infrared spectrum of $\text{CD}_2\text{CCl}=\text{CDCl}$ low boiling, *trans* isomer: —, liquid, 0.025 mm.; ---, gas, 60 mm.; — · —, gas 36 mm.

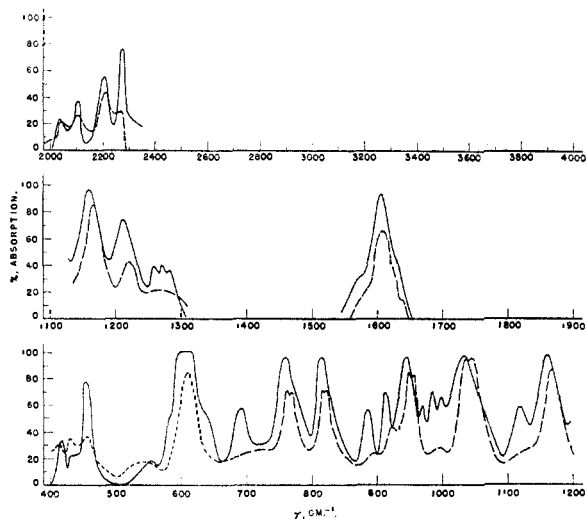


Fig. 4.—Infrared spectrum of $\text{CD}_2\text{CCl}=\text{CDCl}$, high boiling *cis* isomer: —, liquid, 0.025 mm.; ---, gas, 50 mm.; — · —, gas, 36 mm.

Perkin-Elmer infrared spectrometer (Model 12C) used in conjunction with a Brown recorder. Sodium chloride and potassium bromide optics were used where required. The results are recorded in the figures.

Without attempting an assignment of the various bands to particular vibrational modes it is possible to obtain good supporting evidence that the low boiling isomer has the *trans* configuration from the following considerations. The selection rules forbid the presence in the infrared spectrum of the band corresponding to the mode of vibration associated with the stretching and contraction of the $\text{C}=\text{C}$ bond in a pure *trans* compound with a center of symmetry such as *trans*-dichloroethylene, whereas the corresponding band in the *cis* compound is quite strong.⁵ Substitution of a CH_3 group for H in *trans*-dichloroethylene hardly alters the over-all electrical symmetry (since the

(5) H. J. Bernstein and D. A. Ramsay, *J. Chem. Phys.*, **17**, 556 (1949).

electric moment of CH_3 is about the same as the electric moment of CH) of the molecule and allows the CC vibration to be observed in the infrared almost entirely because of the mass asymmetry. One might expect therefore that the $\text{C}=\text{C}$ band in *trans*-dichloropropene would be considerably weaker than the $\text{C}=\text{C}$ band in the *cis* compound. The same argument would also predict that the number of strong bands in the infrared spectrum of the *cis* compound would be far greater than in the *trans* compound. Both criteria should be useful therefore in distinguishing between the *trans* and *cis* spectra. In fact one observes that the $\text{C}=\text{C}$ band in heavy *trans*-dichloropropene is 1605 cm^{-1} , and 1615 cm^{-1} for the light compound and that the bands in both *trans* forms are very much weaker than the corresponding bands in the *cis* forms, *viz.* 1606 cm^{-1} and 1614 cm^{-1} for the heavy and light *cis* compound, respectively. Also as can be seen from the figures there are about 20 strong bands in the *cis* spectrum and only about one-half as many in the spectrum of the *trans* compound. The spectroscopic evidence then can be interpreted unambiguously in terms of *cis* and *trans* structures.

Thanks are due to Miss K. West for reduction of the spectra.

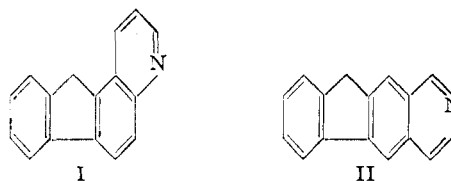
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The Synthesis of 1-Hydroxy-11-indeno(2,1-f)quinoline

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While studying the behavior of fluorene compounds, Diels and Staehlin¹ applied the Skraup reaction to 2-aminofluorene and showed that an indenoquinoline was formed, but they were unable to decide between the angular structure I and the linear structure II for the substance. Apparently only one quinoline derivative was produced, indicating definite predisposition toward ring closure in a particular way.



Hughes, Lions and Wright² condensed ethyl acetoacetate with 2-aminofluorene at 100° in the presence of a very small amount of hydrochloric acid to form ethyl β -(2-fluorenylamino)-crotonate. Upon cyclization of this compound, a solid was obtained to which they gave the formula corresponding to 1-hydroxy-3-methyl-11-indeno(2,1-f)quinoline, thus assuming ring closure in the 1-position.

Neish³ condensed 2-aminofluorene with pyruvic

- (1) Diels and Staehlin, *Ber.*, **35**, 3275 (1902).
- (2) Hughes, Lions and Wright, *J. Proc. Roy. Soc. N. S. Wales*, **71**, 449 (1938).
- (3) Neish, *Rec. trav. chim.*, **67**, 349, 357 (1948).