

### 378. The Dependence of Optical Rotatory Power on Chemical Constitution. Part XXXIX. (–)-2-Thienylmethylcarbinol.

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Though the linear  $1/\alpha-\lambda^2$  plots of the carbinol (homogeneous and in solution) and of its hydrogen phthalate (in solution) are consistent with simple rotatory dispersion in the visible spectrum, the values for  $\lambda_0$  of a one-term Drude equation (obtained by extrapolation of  $1/\alpha-\lambda^2$ ) are not related to the  $\lambda_{\max}$  of the observed absorption bands. It is therefore suggested that the dispersion is in fact complex, which is supported by the high values of the dispersion ratios.

The values for  $\lambda_0$  of the carbinol in different solvents vary over a rather wide range. Its rotatory powers vary in different solvents, but not over an exceptionally wide range, and the rotatory powers of the homogeneous carbinol are relatively insensitive to temperature.

THE ultra-violet absorption spectrum of 2-thienylmethylcarbinol [1-(2-thienyl)ethanol] between 2900 and 2200 Å. has a maximum at 2335 ( $\epsilon_{\text{molar}}$  7840) and an inflexion at 2750 Å. ( $\epsilon_{\text{molar}}$  14). The main band presumably corresponds to the 2350-Å. band of thiophen with  $\epsilon_{\text{max}}$  4500 in hexane (Braude, *Ann. Reports*, 1945, **42**, 128): substitution in the ring nearly doubles the extinction coefficient without displacing  $\lambda_{\text{max}}$ . The low-intensity inflection at 2750 Å. may be compared (a) with the extremely weak band at ca. 2700 Å. ( $\epsilon_{\text{max}}$  ca. 0.16) in thiophen itself, which was recorded by Menczel\* (*Z. physikal. Chem.*, 1927, **125**, 161) though not by later workers (cf. Sease and Zechmeister, *J. Amer. Chem. Soc.*, 1947, **69**, 270; Appleby, Sartor, Lee, and Kapranos, *ibid.*, 1948, **70**, 1553; A.P.I. Research Project 44, Ultra-violet Absorption Spectrograms, nos. 38, 136), and with (b) similar features in pyrrole and furan (cf. Menczel, *loc. cit.*). All of these may be caused by cyclic conjugation related to the partly aromatic character of the five-membered heterocyclic rings. In 2-thienylmethylcarbinol the nuclear substituent causes a marked increase in intensity of the long-wave band, as is frequently observed with low-intensity "forbidden" transitions.

TABLE I.  
Specific rotatory powers of (–)-2-thienylmethylcarbinol.

Solvent and $\mu$ .	Concn., g./100 c.c.	$t$ .	$\lambda$ , Å.							
			6438.	5893.	5780.	5461.	5086.	4800.	4358.	$\Omega_D$ .†
None .....	—	20°	–19.0°	–23.7°	–24.3°	–28.0°	–33.0°	–37.9°	–49.0°	16.26
None .....	—	43.5	19.2	—	25.0	28.5	33.5	—	–49.9	—
None .....	—	64	18.8	—	23.4	26.8	32.0	—	46.3	—
None .....	—	95	18.1	—	23.0	26.2	31.0	—	43.9	—
Ethyl ether, 1.22 ...	5.01	16	26.0	32.0	32.9	37.5	44.6	50.7	63.3	24.96
Carbon disulphide, 0	5.06	16	28.4	35.2	36.7	41.8	50.3	58.4	76.0	22.65
Ethyl alcohol, 1.74...	5.10	20	15.1	17.7	18.7	21.4	24.8	28.3	35.2	13.68
Benzene, ‡ 0 .....	2.16	19	—	22.9	24.1	27.3	31.7	36.6	46.1	16.17

‡ – 21.6° at 6104, –17.4° at 6708 Å.

† Rotivity.

Table I gives the rotatory powers of the carbinol in the visible spectrum. The plots of  $1/\alpha-\lambda^2$  for the carbinol, homogeneous at 20°, or in solution (except in carbon disulphide), are linear. However, the dispersion ratios of the homogeneous carbinol (Table II) are not consistent with simple rotatory dispersion, and the dispersion ratios in different solvents vary considerably. Two-term equations, in which  $\lambda_1$  and  $\lambda_2$  are respectively greater and less than  $\lambda_0$ , are therefore probably required for an exact expression of the dispersions. The  $\lambda_1$ 's may be related to one of the observed absorption bands.

\* We are indebted to a Referee for drawing our attention to Menczel's results.

TABLE II.  
Dispersion ratios and extrapolated  $\lambda_0$  values for (-)-2-thienylmethylcarbinol and its hydrogen phthalate.

Solvent :	Carbinol.								Hydrogen phthalate.	
	Homogeneous.				Ethyl ether.	Carbon disulphide.	Ethyl alcohol.	Benzene.	Benzene.	Carbon disulphide.
$t$ :	20°	43·5°	64°	95°.	16°.	16°.	20°.	19°.		
Dispersion ratio	1·74	1·75	1·73	1·68	1·69	1·82	1·65	1·69	1·8	1·8
$[\alpha]_{4358}$										
$[\alpha]_{5461}$										
$\lambda_0$ from extrapolated $1/\alpha - \lambda_0^2$	2170	2190	2030	1760	1950	2313	1600	1960	2390	2700

TABLE III.

Specific rotatory powers of (-)-2-thienylmethylcarbinol hydrogen phthalate (1, 2 ;  $t$ , 18°).

Solvent.	Concn., g./100 c.c.	$\alpha$ , A.							
		6438	5893	5780	5461	5086	4800	4358	
Benzene .....	1·87°	-46·6°	-57·9°	-60·5°	-70·0°	-82·3°	-90·0°	-123°	
Carbon disulphide .....	2·10	62·6	79·0	84·7	97·7	116	135	178	

The wide variation of  $\lambda_0$  in different solvents (compare the constancy of  $\lambda_0$  for phenylcyclohexylcarbinol in different solvents : Part XXXVII) suggests that there are interactions between solvent and carbinol. These may be of dipolar origin, as discussed by Rule (see, *e.g.*, *J.*, 1931, 674), though neither  $\lambda_0$  values, rotatory powers, nor rotivities lie in the order of the dipole moments of the solvents and the spread of the rotivities is as great as that of the rotatory powers. The rotatory power of 2-thienylmethylcarbinol is much less sensitive than those of glycidic phenyl ether (Part XXXVIII) or of 2-(2-hydroxy-*n*-propyl)pyridine (Part XL) to change of solvent, and is not extremely sensitive to temperature changes. It is therefore unnecessary to postulate for 2-thienylmethylcarbinol any form of molecular association such as is suggested for glycidic phenyl ether and 2-(2-hydroxy-*n*-propyl)pyridine.

The rotatory dispersions of 2-thienylmethylcarbinyl hydrogen phthalate in benzene and in carbon disulphide (Table III) both give linear plots of  $1/\alpha - \lambda^2$  and dispersion ratios 1·8, the latter indicating that absorption in the near ultra-violet is affecting the rotatory powers. The extrapolated values for  $\lambda_0$  are in both cases above 2300 Å. It is therefore not unlikely that the rotatory dispersion of the phthalate in the visible spectrum is dominated by a Drude term derived from the 2750 Å. band of the carbinol, or from the much stronger chromophore in the phthalate radical, at about the same wave-length (Goslowski and Marchlewski, *Bull. Acad. Polon. Sci., A*, 1934, 42). Levene and Rothen (in Gilman's "Organic Chemistry," 1st edn., New York, 1938) have shown that anisotropy in a phenyl chromophore may sometimes make an important contribution to rotatory power.

## EXPERIMENTAL.

(±)-2-Thienylmethylcarbinol was obtained by the Grignard reaction from 2-iodothiophen (Minnis, *Org. Synth.*, 1932, 12, 44) and acetaldehyde in 36% yield calc. on the iodo-compound. Better yields were obtained by reduction of 2-thienyl methyl ketone, which was obtained in 75–80% yield (calc. on thiophen) by the methods described by Johnson and May (*ibid.*, 1938, 18, 1) and Hartough and Kosak (*J. Amer. Chem. Soc.*, 1946, 68, 2639) : the molar proportions stated in the Experimental section of the latter paper were used. The ketone yielded a semicarbazone, m. p. 189–190°; Steinkopf and Jaffe (*Annalen*, 1917, 413, 339) record m. p. 190–191°. Meerwein-Ponndorf reduction of the ketone (Kuhn and Dahn, *ibid.*, 1941, 547, 293; Nazzaro and Bullock, *J. Amer. Chem. Soc.*, 1946, 68, 2121) gave the carbinol in 70% yield from 20 g. of ketone, the duration of reduction being 1 hour : lower yields were obtained if larger quantities or longer periods of reduction were employed, di-(1-2'-thienylethyl) ether being formed (b. p. 145–147°/14 mm.,  $n_D^{20}$  1·5615; cf. Kuhn and Dahn, *loc. cit.*). Though Kuhn and Dahn (*loc. cit.*) report the preparation of the phenylurethane from the carbinol, Campaigne and Dietrich (*J. Amer. Chem. Soc.*, 1948, 70, 391) were unable to isolate this derivative, and we also have not been able to prepare it. We have obtained the 5-chloromercuri-derivative, m. p. 158–160°, reported by Kuhn and Dahn (*loc. cit.*) to have m. p. 157°.

*Hydrogen Phthalate of (±)-2-Thienylmethylcarbinol.*—A mixture of the carbinol (53·6 g.), phthalic anhydride (69 g.), and pyridine (50 c.c.) after 5 hours at 70° and 18 hours at 20° was diluted with acetone (250 c.c.) and poured into hydrochloric acid (1 l. of *N.*) at 0°. The washed precipitate was dissolved in sodium hydrogen carbonate solution and, after extraction of the solution with ethyl ether, the *hydrogen phthalate* was reprecipitated with hydrochloric acid and recrystallised from carbon disulphide; it (42 g.) had m. p. 94° (Found : equiv., 278.  $C_{14}H_{12}O_4S$  requires equiv., 276).

The brucine salt which separated from a solution of brucine (204 g.) and (±)-(hydrogen phthalate) (144 g.) in hot ethyl acetate (1 l.) was recrystallised 4 times from ethyl acetate, yielding the brucine salt

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(68 g.), m. p. 156°,  $[\alpha]_{5780}^{25} - 50.5$ ,  $[\alpha]_{5461}^{25} - 60.0$ ,  $[\alpha]_{4359}^{25} - 141.5^\circ$  in chloroform ( $c$ , 2.45;  $l$ , 2.0), of the (–)-phthalate. The salt, covered with twice its weight of acetone, was mixed with ice-cold hydrochloric acid. The precipitated (–)-(hydrogen phthalate), recrystallised from carbon disulphide, had m. p. 84°. Rotatory powers are in Table III.

(–)-2-Thienylmethylcarbinol.—Potassium hydroxide (4.95 g.) in water (2 c.c.) was added to a solution of the (–)-(hydrogen phthalate) (9.8 g.) in ethyl alcohol (250 c.c.). The mixture was heated for 10 minutes on the steam-bath, cooled, and diluted with water (50 c.c.). Ether (500 c.c.) was added and the mixture washed with brine until neutral. The ethereal solution was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated at 25°. From the residue, (–)-2-thienylmethylcarbinol (3.1 g.), b. p. 88–89°/11 mm., was obtained. Rotatory powers are in Table I. This carbinol yielded a (–)-(hydrogen phthalate) with  $[\alpha]_{5893}^{19.5} - 56.2^\circ$  in benzene ( $c$ , 1.655), *i.e.*, 97% of the rotatory power of the phthalate from which the carbinol was prepared.

Rotivities  $\Omega$  were calculated from  $\Omega = 3[\alpha]/(n^2 + 2)$ , by using the weighted means of refractive indices of solvents and solute.

The absorption spectrum was determined by Dr. G. H. Beaven, using a Beckman photo-electric quartz spectrophotometer. Thanks are expressed to the Government Grants Committee of the Royal Society and to Imperial Chemical Industries Limited for grants, and to the Department of Scientific and Industrial Research for a maintenance grant (to I. G. A.).

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