376. *The Dependence of Optical Rotatory Power on Chemical Constitution. Part XXXVII.** cyclo*Hexylphenylcarbinol.*

By Michael P. Balfe, Gilbert H. Beaven, and Joseph Kenyon.

The rotatory dispersions of *cyclo*hexylphenylcarbinol and of its acetate, formate, benzoate, and hydrogen phthalate in the visible spectrum, and their absorption spectra between 2100 and 2900 A., are recorded. The constants are given of one-term Drude equations which fit tolerably well the observed rotatory dispersions. It is suggested that induced anisotropy of phenyl chromophores has an observable effect in the rotatory powers of the acetate, formate, and benzoate, and not of the carbinol itself.

Table I summarises the ultra-violet absorption spectrum between 2100 and 2900 A. of *cyclo*hexylphenylcarbinol and some of its esters. In the carbinol, and its acetate, formate, and chloride, the absorption is due to the phenyl group, since the *cyclo*hexyl and hydroxyl groups and chlorine substituents are all effectively transparent down to about 1900 A. The absorption bands of these four compounds, in wave-lengths, extinction coefficients, and fine structures, are typical of the benzene chromophore containing a saturated substituent (cf. Braude, *Ann. Reports*, 1945, **42**, 124), the spectra being very similar to the absorption spectrum of benzyl alcohol, for which in ethanol, $\lambda_{max.}$ occurs at 2565 A. and $\varepsilon_{max.}$ is 178, with accompanying fine structure (*Tables Annuelles*, **13**, Part 33, p. 61). In the benzoate and hydrogen phthalate, the presence of the second phenyl group, containing carboxyl and carbalkoxy-substituents, has moved the absorption bands to longer wave-lengths and increased $\varepsilon_{max.}$; in the benzoate four maxima remain in the zone of longer wave-length, but in the hydrogen phthalate this detail has been suppressed.

---

* Parts XXXIII, *J.*, 1928, 3000; XXXIV, *J.*, 1939, 633; XXXV, *J.*, 1941, 312; XXXVI, *J.*, 1942, 531.

TABLE I.

Ultra-violet absorption spectra of cyclo*hexylphenylcarbinol and its derivatives.*

	Short-wave band.		Long-wave band.	
Compound (solvent).	$\lambda_{max.}$, A.	ε_{molar}.	$\lambda_{max.}$, A.	ε_{molar}.
Carbinol (light petroleum)	*ca.* 2120	*ca.* 6550	2475	103
			2525	149
			2585	186
			2645	141
			2680	80
Acetate (light petroleum)	2155	3830	2470	141
			2520	171
			2580	207
			2640	165
Formate (light petroleum)	2110	8000	2478	121
			2520	164
			2580	209
			2640	166
Chloride (light petroleum)	*ca.* 2150	7420	2470	552
			2525	535
			2587	474
			2645	*328*
Benzoate (*n*-hexane)	2240	17,700	2595	765
			2665	780
			2740	883
			2815	795
Hydrogen phthalate (*cyclo*hexane)	2280	10,300	2780	1420

Italics denote an inflection.

TABLE II.

Rotatory dispersion of cyclo*hexylphenylcarbinol* (obs. = observed; calc. = calculated from Drude constants in Table IV).

				λ, A.					
Solvent.	Concn., g./100 c.c.	*t.*	$[\alpha]_\lambda$.	6438.	5893.	5780.	5461.	4800.	4358.
Ethanol	9·715	19°	obs.	18·71	22·52	23·42	26·13	34·26	42·24
			calc.	18·71	22·45	23·47	26·37	34·53	42·24
Benzene	3·29	22	obs.	23·71	28·27	28·58	32·83	43·62	52·89
			calc.	23·63	28·27	29·50	33·20	43·48	53·37
Carbon disulphide	4·027	22	obs.	24·83	29·80	30·79	34·27	46·31	55·63
			calc.	24·74	29·71	31·00	34·77	45·66	55·83
*cyclo*Hexane	3·696	22	obs.	27·87	31·80	32·75	37·75	51·95	61·70
			calc.	27·20	32·70	34·03	38·30	50·13	61·50
Pyridine	3·687	22	obs.	27·40	31·61	33·10	37·58	50·46	62·13
			calc.	27·05	32·50	33·80	38·05	49·83	61·13
Ethyl ether	4·030	20	obs.	—	38·8	—	—	—	—
	15·63	20	obs.	—	37·6 *	—	—	—	—

* Levene and Mikeska, *J. Biol. Chem.*, 1927, **75**, 587.

Table II gives the rotatory dispersion of the carbinol in various solvents, and Table III the dispersion of the esters, each in one solvent. The signs of rotatory power have been omitted; it can be shown that the (+)-carbinol, (+)-acetate, (+)-formate, and (+)-(hydrogen phthalate), and the (—)-benzoate have the same relative configuration (Balfe, Beaven, and Kenyon, in preparation). The data for the chloride refer to the preparation of highest rotatory power, and for the carbinol and esters to optically pure preparations.

Specific rotatory powers at λ_{5893} of the carbinol and esters in a number of other solvents can be calculated from concentrations and initial observed rotatory powers (some extrapolated to zero time) which will be given in kinetic data by Balfe, Beaven, and Kenyon.

The one-term Drude equation derived from the rotatory powers of the carbinol in ethanol solution gives calculated values of rotatory power which are in good agreement with the observed. Extrapolated straight-line plots of $1/\alpha$–λ^2 in the other solvents cut the λ^2 axis at values close to the λ_0^2 in this equation. This value for λ_0 (*i.e.*, 1070 A.) was therefore assumed for the data in other solvents, and values for *k* were calculated therefrom. The resulting equations give calculated [α] values which are in tolerable agreement with the observed results; calculation of constants from the observed results by the usual method (Lowry, " Optical Rotatory Power," London, 1935, p. 420) did not give better-fitting equations. For the hydrogen phthalate, acetate, formate, and benzoate in ethanol, one-term Drude equations were calculated which fit reasonably well the observed results. Neither a one-term nor a two-term, three-constant equation could be derived for the dispersion data of the hydrogen phthalate in chloroform, either by the usual method of calculation (Lowry, *op. cit.*) or by successive approximations from selected values for the constants.

TABLE III.

Rotatory dispersion of esters of cyclo*hexylphenylcarbinol* (obs. = observed; calc. = calculated from Drude constants in Table IV).

		Concn.,			λ, A.					
Ester.	Solvent.	g./100 c.c.	*t.*	[α]λ.	6438.	5893.	5780.	5461.	4800.	4358.
Acetate	Ethanol	3·984	20°	obs.	57·9	71·0	73·4	84·2	118·0	147·1
				calc.	57·8	70·8	73·9	84·2	115·2	147·9
Formate	Ethanol	2·307	18	obs.	60·2	75·4	—	90·6	123·1	163·6
				calc.	61·5	75·4	79·0	91·0	126·0	163·6
Benzoate	Ethanol	2·083	28	obs.	25·5	32·2	33·9	40·1	60·0	83·5
				calc.	25·5	32·2	33·9	39·8	59·3	83·5
Hydrogen phthalate	Ethanol	4·085	21	obs.	18·0	21·9	22·4	25·7	—	41·6
				calc.	18·3	21·9	22·9	25·7	33·8	41·6
	Chloroform	2·22	16	obs.	38·9	51·8	55·4	64·0	87·9	113·5
		4·00	20	obs.	—	52·5 *	—	—	—	—
Chloride	Ethyl ether	9·6	20	obs.	—	62·0	—	—	—	—
		9·89	20	obs.	—	29·4 *†	—	—	—	—

* Levene and Mikeska, *loc. cit.* (Table II).
† From carbinol of about half the maximum rotatory power.

TABLE IV.

Constants of one-term Drude equations, lowest λλ *of absorption, dispersion ratios, and plot of* $1/\alpha - \lambda^2$.

	Carbinol.	Acetate.	Formate.	Benzoate.	Hydrogen phthalate.	
Drude constants, *k*	14·35, 18·065, 18·977, 20·835, 20·699 *	49·356 §	48·067 §	24·195 §	24·637 §	indeterminate **
λ_0, A.	1070 †	2145 §	2353 §	3025 §	1224 §	
λ (A.) of main absorption maxima (Table I)	2120 ‡ 2585 ‡	2155 ‡ 2580 ‡	2110 ‡ 2580 ‡	2240 ‖ 2740 ‖		2280 ¶ 2780 ¶
Dispersion ratios	1·62, 1·61, 1·62, 1·63, 1·65 *	1·75 §	1·80 §	2·08 §	1·62 §	1·77 *
Plot of $1/\alpha - \lambda^2$	linear †	linear §	linear §	linear §	linear §	concave to $1/\alpha$ axis **

* In ethanol, benzene, carbon disulphide, *cyclo*hexane, and pyridine, in that order.
† In all solvents. ‡ In light petroleum. § In ethanol.
‖ In *n*-hexane. ¶ In *cyclo*hexane. ** In chloroform.

The plots of $1/\alpha$–λ^2 for the carbinol in the various solvents, and for the acetate, formate, and hydrogen phthalate, are straight lines, suggesting that $\lambda_2 < \lambda_0 < \lambda_1$ (Levene and Rothen, in Gilman's " Organic Chemistry," 1st Edn., New York, 1938, p. 1800 : λ_0 being the characteristic frequency of the one-term Drude equation which fits the observations in the visible spectrum, and λ_1, λ_2 the characteristic frequencies of the two-term equation which would presumably be required to fit observations of the dispersion extended through the visible to the near ultra-violet) : λ_0 is thus a lower limit to λ_1. In the carbinol, λ_0 (1070 A.) is so far below the short-wave absorption bands (*ca.* 2100 A.) associated with the phenyl chromophores (see Table IV), that it seems probable that λ_1 would be derived not from these, but from anisotropy in the C–OH group which has its first absorption region located near 1800 A. The dispersion ratios for the carbinol fall in a range which is consistent with " simple " dispersion, *i.e.*, a one-term equation covering the dispersion in the whole of the accessible spectrum : λ_0 (1070 A.) is the characteristic frequency in this equation. Though similar considerations apply to the comparison of λ_0 (in ethanol) and the observed absorption bands of the hydrogen phthalate, the difference between its dispersion ratios in two solvents, and the high values of the dispersion ratio in chloroform, make it unlikely that a one-term equation would fit the dispersion in the ultra-violet spectrum : in a two-term equation, λ_1 is less likely, than it is in the carbinol, to be the C–OH chromophore at 1800—2000 A., and may be associated with the phenyl chromophores. In the acetate and formate, the dispersion ratios suggest that a two-term equation would be required for the full dispersion range. Comparison of λ_0 and the wave-lengths of the absorption bands suggests that λ_1 could be associated with the phenyl absorption bands, λ_2 being again probably at about 1800 A. Although the $1/\alpha$–λ^2 plot for the benzoate is a straight line (Table IV), λ_0 (3025 A.) cannot be a lower limit for λ_1, since this would place λ_1 in the violet or near ultra-violet and it is most improbable that in such a case $1/\alpha$–λ^2 for the visible spectrum would be a straight line. It is more likely that the dispersion equation involves two terms of opposite sign:

$$[\alpha]_\lambda = \frac{k_1}{\lambda^2 - {\lambda_1}^2} - \frac{k_2}{\lambda^2 - {\lambda_2}^3}$$

The dispersion ratio for the benzoate also suggests that a two-term equation would be necessary, and in this case λ_1 might well be associated with the phenyl chromophore.

The suggestions put forward then are as follows :

(i) In the carbinol, anisotropy in the phenyl group does not make an observable contribution to the rotatory power; its absorption spectrum is only slightly affected by the introduction of the $-CH(OH)\cdot C_6H_{11}$ substituent.

(ii) In the acetate and formate, the effect of the phenyl group on the rotatory power becomes apparent : this group is rendered capable of anisotropic absorption by vicinal action between the phenyl and ester-carbonyl groups; the interaction is trivial (cf. Kuhn, *Trans. Faraday Soc.*, 1930, **26**, 293), as shown by the small increases in extinction coefficients.

(iii) The benzoate contains a second phenyl group which is attached to the polarisable ester-carbonyl group. The phenyl absorption bands are now shifted to longer wave-lengths and their absorption coefficients still further increased : the contribution from the benzoate radical predominates over the similar but less intense contribution from the phenyl group in the carbinol (cf. Braude, *loc. cit.*, p. 126). A new Drude term is introduced by vicinal action in this second phenyl chromophore and is probably opposite in sign to the shorter-wave-length term, as is indicated by the necessity for assuming terms of opposite sign in the dispersion equation, and by the difference in sign of rotatory power between the benzoate on the one hand, and the carbinol and other esters of the same configuration on the other.

(iv) In the hydrogen phthalate, the intense contribution of the phthalate chromophore dominates the absorption spectrum (cf. "A.P.I. Ultraviolet Absorption Spectrograms," Serial Nos. 101—103, U.S. Bureau of Standards, 1945), and the presence of the second phenyl chromophore complicates the rotatory dispersion.

EXPERIMENTAL.

The preparation of the optically active carbinol and esters will be described by Balfe, Beaven, and Kenyon (see also Levene and Mikeska, *loc. cit.*).

Absorption spectra were determined in spectroscopic-grade solvents, using (i) Hilger "medium" quartz spectrograph with "Spekker" or sector UV photometers and high-frequency tungsten spark under water or condensed spark between tungsten-steel electrodes, (ii) Beckman photo-electric quartz spectrophotometer and hot-cathode hydrogen arc source.

Rotatory powers were determined at room temperature in 2-dm. tubes.

Thanks are expressed to the Government Grants Committee of the Royal Society and Imperial Chemical Industries Limited for grants.

BATTERSEA POLYTECHNIC, LONDON, S.W.11. [*Received, March* 16*th*, 1950.]