588. *The Measurement of Optical Rotatory Dispersion. (+)-Octan-2-ol.*

By M. K. HARGREAVES.

The methods available for the investigation of the relation between optical rotatory power and wave-length are reviewed. A photoelectric device for the control of an iron arc is described, by which the scope of Lowry's ultra-violet polarimeter is increased.

As a first step in an investigation of the relation between optical rotatory power and molecular configuration, the optical rotatory dispersion of (+)-octan-2-ol has been re-examined in greater detail than hitherto, both in the homogeneous state and in solution in *n*-heptane. The dispersion curve in the ultra-violet region shows no marked deviation from the simple hyperbolic form, but the dispersion ratio of the *n*-heptane solution clearly indicates complexity.

IT is now generally realised that work on optical rotatory dispersion should include measurements in the ultra-violet region of the spectrum and that it is dangerous to draw conclusions from measurements of optical rotatory power made under differing conditions at only one wave-length. The methods hitherto used for this purpose are briefly as follows.

The photographic method of Cotton and Descamps (*Compt. rend.*, 1926, **182**, 22) and the photoelectric method of Bruhat and Chatelain (*ibid.*, 1932, **195**, 462) have not found favour; Brode (*J. Opt. Soc. Amer.*, 1951, **41**, 987) and Broser and Lautsch (*Z. Naturforsch.*, 1951, **6**, *b*, 369) have recently devised other photoelectric methods, the latter authors employing a photo-multiplier, but insufficient data are available for an evaluation of these methods for a determination of the rotatory power of organic liquids in the ultra-violet region. Two new techniques which may be expected to have application in the study of optical-rotatory dispersion are as follows.

The rotating-sector method. The chief disadvantage of the photoelectric method in the ultra-violet region is that at the extinction point the light passing through the optical system is of very low intensity, and the amplitude of the electrical response to the photo-cell is of the order of the " background " noise of the amplifier. This problem has now been virtually surmounted for many purposes, *e.g.*, in electron-diffraction measurements (Roth, *Ann. Reports Phys. Chem.*, 1951, **2**, 218), by application of various modifications of the rotating-sector technique. Since the accuracy is proportional to the exposure a number of exposures at different settings of the analyser would be required, the advantages of this method might not be as great in this as in other work.

The image converter. This device has an obvious application to polarimetry, both in the infra-red and in the ultra-violet region, if it should be capable of the necessary accuracy in the reproduction of the image intensity. Unfortunately, the commercial instruments available for conversion of an ultra-violet into a visible image show little gain in brilliance over direct vision with a fluorescent screen (Messrs. Mullard, Ltd., personal communication). There is, therefore, little point in considering the accuracy of the representation of the image intensity.

Lowry and Coode-Adams's method (*Phil. Trans.*, 1927, **226**, *A*, 391) seems to provide the best available combination of accuracy with simplicity of the optical working parts. Its chief disadvantage is that it is extremely tedious, the apparatus requiring constant attention to ensure that the fields of the polarimeter are evenly illuminated. The following development of a photo-electronic device to control the iron arc largely overcomes this disadvantage.

EXPERIMENTAL

Apparatus.—Polarimeter. Basically, the apparatus is similar to that of Lowry and Coode-Adams (*loc. cit.*). Instead of the large metal scale of the earlier instrument, there is a glass scale divided to 0·005° whose image can be projected on to the photographic plate of the spectrograph. However, the deviation of the beam from the objective (L_2, Fig. 1) is such that for large rotations the spectrograph must be moved so as to continue to receive the image of the polariser on the slit (S). In this case the necessity for refocusing the image of the scale on the plate offsets any advantage accruing from the recording of the reading. The optic of the polarimeter consists of standard Hilger Foucault prisms, with a 9″-focus quartz condenser (L_1, Fig. 1) and a 15″ quartz–fluorite achromatic projection lens of 1″ aperture (L_2). The quartz wedge supplied with the analyser was found to increase the deviation of the beam, and was discarded.

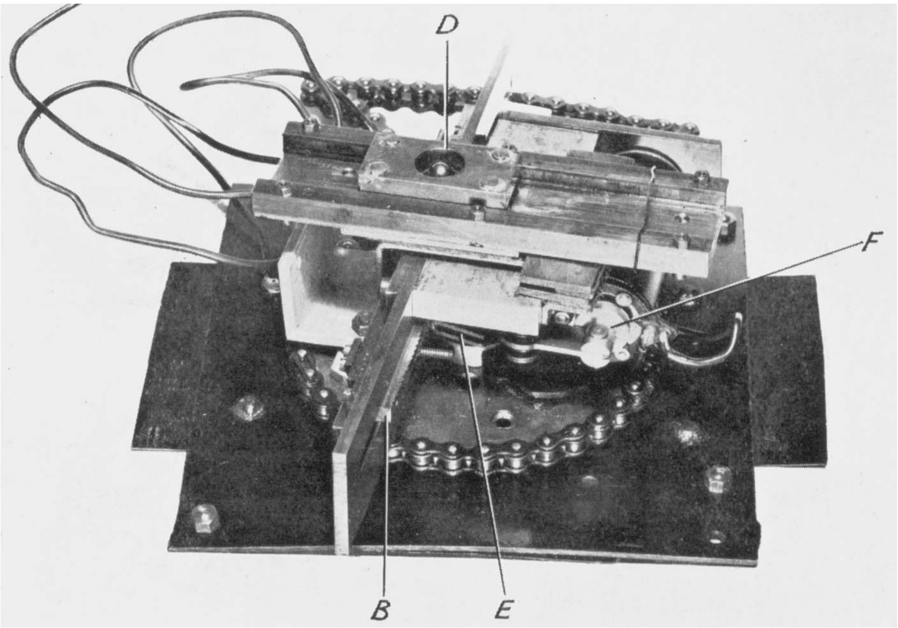
Polarimeter tubes. These were of fused silica with integral end-plates and detachable brass jackets. The temperature was controlled to $<0{\cdot}1°$ at 25° and to 0·2° at the higher temperatures. A small correction is required for the rotation due to imperfections in some of the end-plates.

Arc. An iron arc is used as a high-intensity source of light and to provide an accurate wave-length scale. Its disadvantages are its inconstancy and unevenness. With substances of low dispersive power the latter can cause considerable error, which can be seen clearly by the use of a three-field polarimeter, particularly when readings are taken to determine the zero of the instrument, there being no dispersion.

A new photoelectric method of arc control (Figs. 1 and 2, and Plate) ensures that the beam of light passes centrally through the optical system of the polarimeter, and thus that the three fields of the polarimeter are evenly illuminated. A circuit diagram of the photo-cell amplifier is given in Fig. 2, and the Plate shows the mechanism by which the arc is moved to the correct position.

The control system only operates when light falls on the photo-cell. The slides (B, D on the Plate) must be very free-running since movement of the axial arm of the arc (H, Fig. 1) is restrained only by the friction of the ball support. When light falls on the photo-cell the amplifier emits an intermittent current which causes a relay to oscillate with a low frequency. This in turn provides an intermittent current to a solenoid, at each oscillation of which a pawl engages with the teeth of a ratchet rack, moving the arm of the arc in such a way that the beam from the arc passes along the axis of the polarimeter.

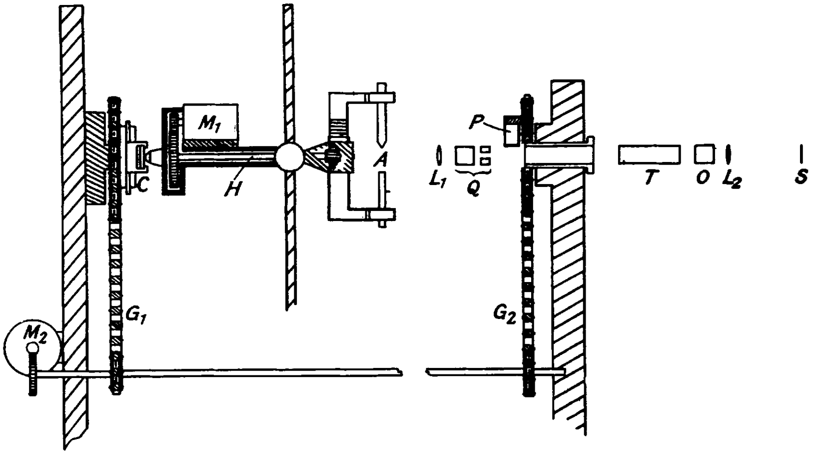
The continuous operation of the arc is ensured by placing it in one arm of a Wheatstone bridge (Fig. 3). The armature coils of the motor (M_1), controlling its opening, are placed in the position normally occupied by the galvanometer. This mechanism works satisfactorily for periods up to 2 hr. without attention.



Showing detail of the solenoid mechanism (*C*, Fig. 1).

Spectrograph. A Hilger medium quartz spectrograph is used with Ilford Zenith Super Sensitive or Special Rapid plates. The position of the extinction on the plates is determined by means of a microphotometer in the region of high photographic density and low dispersion; below *ca.* 3000 Å visual inspection with a low-power microscope is better.

FIG. 1. *Elevation of the polarimeter and arc control (partly sectional—not to scale). The photo-cell rotates about the axis of the polarimeter. It is coupled by G_1 and G_2 to the solenoid mechanism so that an impulse from the cell is transmitted to the arc at the appropriate point in the revolution of the solenoid.*



Key to Fig. 1 *and to Plate:*

A,	Arc.
B,	Ratchet rack in slide.
C,	Solenoid control mechanism.
D,	Trolley running in cross slide, showing the ball which transmits the impetus of the solenoid to the axial arm of the arc (*H*, Fig. 1).
E,	Pawl actuated by solenoid.
F,	Solenoid.
G_1 & G_2,	Chain drive.
H,	Axial arm of arc.
L_1,	Quartz condensing lens of 9″ focus.
L_2,	Quartz–fluorite achromatic lens of 15″ focus.
M_1,	Arc-control motor.
M_2,	Driving motor for photo-cell and solenoid mechanism.
O,	Analyser (Foucault prism).
P,	Photo-cell.
Q,	Polariser (Foucault prisms).
S,	Slit of medium quartz spectrograph.
T,	Polarimeter tube.

FIG. 2. *Circuit diagram of the photocell amplifier and oscillating relay:* *P*, Photo-cell; *U*, relay controlling the solenoid (*F*, on plate).

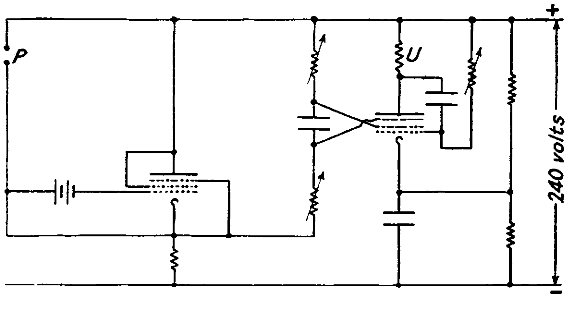
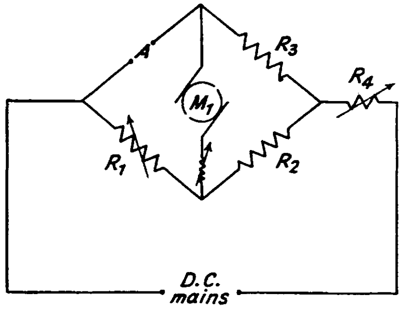


FIG. 3. *Arc-control circuit: A*, Arc. M_1, Armature coils of arc-control motor. R_1, R_2, R_3, and R_4, Resistances.



Refractive Indices.—A Pulfrich refractometer was used for these measurements.

Densities.—A 2-c.c. density bottle, with temperature control to within 0·1°, was used. Intermediate values were obtained by interpolation.

(+)-*Octan-2-ol.*—Prepared by Kenyon's method (*Org. Synth.*, 1926, **6**, 68), this had b. p. 85—86°/20 mm., $[\alpha]_D^{18}$ 11·76°.

n-*Heptane.*—Hydrocarbon supplied by the Anglo-American Oil Co. was dried (P_2O_5) and fractionally distilled, the fraction, b. p. 98·4°, being collected and stored over phosphoric oxide. It was redistilled immediately before use.

Accuracy.—Measurements made by finding the wave-length at which the three fields of the polarimeter appear of equal density on the plate have an accuracy of 0·3—1·0%. In view of the usual steep slope of the curve α/λ in the ultra-violet region the error in α may be several times larger. Where only the general shape of the curve is required, this method is satisfactory. For greater accuracy the method of " bracketting " (Lowry and Coode-Adams, *loc. cit.*) is employed, the limit of accuracy of which is often set by the absorption of light by the substance under investigation. For substances with strong absorption bands above 2000 Å the permissible path length is the chief factor governing accuracy and practicability of an investigation. A 2-dm. tube is suitable for aliphatic alcohols to 2500 Å, where an exposure of upwards of 2 hr. is required. For substances containing the phenyl chromophore, on the other hand, only a fraction of a centimetre is permissible for work below 4000 Å.

DISCUSSION

Variations in Optical Rotatory Power.—The validity of Drude's equation, $[\alpha]_\lambda = \Sigma k_x/(\lambda^2 - \lambda_x^2)$, relating the specific rotatory power $[\alpha]$ and the wave-length λ at which it is measured, has been established by Lowry and his school (Lowry and Coode-Adams, *loc. cit.*; Lowry and Richards, *J.*, 1924, **125**, 1593). Subsequent theoretical expressions relating rotatory power and fundamental constants of the molecule (Condon, *Rev. Mod. Phys.*, 1937, **9**, 432; Kirkwood, *J. Chem. Phys.*, 1937, **5**, 479) embody a dispersion term of the Drude type. Whereas Lowry was interested to show that the dispersion curve could be represented by a very few Drude terms, Condon regards these terms as having average values resulting from the combination of several terms with more fundamental significance.

One of the interesting features of rotatory power is its marked dependence upon solvents (see Balfe, *J.*, 1950, 1871). The theoretical expressions obtained by Condon and others refer to an isolated molecule possessing freedom of rotation in all its single bonds. Such a state of affairs will generally exist only at relatively high temperatures in the dilute vapour phase, under which conditions optical rotatory power is not easily measured accurately. For this reason very few measurements of the rotatory power of vapours have been made, available data mainly referring to organic compounds in the liquid phase or in solution.

The aim of the present work is the study of the effect of conditions on the rotatory dispersion of simple organic substances. In this way, information as to the molecular state of the dissolved molecules can be obtained, and also, by eliminating the secondary factors, data can be provided for the estimation of the rotatory power of the free molecule for comparison with calculated values.

As a preliminary step, the optical rotatory disperion of (+)-octan-2-ol has been examined in the homogeneous state and in solution in *n*-heptane.

Results.—The early work on optical rotatory dispersion was concerned with the " simplicity " or " complexity " of the dispersion, *i.e.*, whether one or two terms of Drude's equation were required to represent the experimental curve. Condon (*loc. cit.*) has shown, theoretically, that the complexity of the dispersion has little fundamental significance. Whereas most previous authors had insisted that optical activity could only arise as a result of two or more oscillators coupled together, Condon, Altar, and Eyring (*J. Chem. Phys.*, 1937, **5**, 753) showed that a single electron moving in an asymmetric field could give rise to optical activity. In the light of this theory it is reasonable to suppose that all electronic transitions, in an active molecule, are optically active. This does not, however, imply that all absorption bands will show optical activity, since two transitions of approximately the same wave-length and intensity, and of opposite rotation, would cancel each other. The validity of the argument is rendered doubtful by the existence of substances exhibiting *simple* dispersion and yet containing well-spaced absorption bands : octan-2-ol is often quoted as a typical example. It is of interest, therefore (Tables 1 and 2), that the dispersions ratio $[\alpha]_{4358}/[\alpha]_{5461}$, which for the homogeneous material is 1·65, drops to 1·53 in a 10% *n*-heptane solution. If the *simple* dispersion law holds, then a dispersion ratio of 1·57 corresponds to an absorption band at zero wave-length, and a lower value to one of negative wave-length. Octan-2-ol must, therefore, be considered to show *complex* dispersion.

At higher temperatures the dispersion ratio of the pure substance rises slightly, and on dilution with *n*-heptane it appears to have a minimum value at about 5% concentration. At the greater dilutions the value approaches that of the hot homogeneous substance. Small changes in the value of this quantity are not of much significance, being very sensitive to error. For this reason the values for the 1·25% solution are not given.

TABLE 1. *Specific rotatory power of* (+)-*octan*-2-*ol* (all wave-lengths in Å).

(*a*) Visible region.

Temp.	d_4^t *	λ								$\frac{[\alpha]_{4358}}{[\alpha]_{5461}}$
		6438	5893	5780	5461	5086	4800	4678	4358	
24·6°	0·8174	7·92°	9·56°	10·06°	11·30°	13·13°	14·96°	15·57°	18·64°	1·65
38·0	0·8066	7·18	9·20	9·76	10·98	12·75	14·66	15·02	17·87	1·64
56·0	0·7918	7·09	8·87	9·34	10·43	12·50	14·16	14·71	17·54	1·68
92·0	0·7615	—	8·77	9·30	10·40	12·37	14·02	—	17·40	1·68

* By interpolation from $d_4^{25\cdot0}$ 0·8174, $d_4^{50\cdot0}$ 0·7968, $d_4^{75\cdot0}$ 0·7766, d_4^{100} 0·7547.

(*b*) Ultra-violet region.

t = 24·6°.				*t* = 38·0°				*t* = 56·0°.		*t* = 92·0°.	
l = 2 dm.		*l* = 0·5 dm.		*l* = 2 dm.		*l* = 0·5 dm.		*l* = 0·5 dm.		*l* = 0·5 dm.	
λ	[α]	λ	[α]	λ	[α]	λ	[α]	λ	[α]	λ	[α]
4260	20·31°	3260	37·97°	4460	17·14°	3440	33·52°	4130	20·91°	4450	17·12°
4050	23·31	3070	45·31	4150	20·57	3140	40·96	3950	22·79	3780	25·00
3810	26·29	2900	52·65	3930	23·59	2900	48·40	3850	24·05	3320	32·88
3640	29·29	2770	60·00	3760	26·64	2810	55·84	3450	31·62	3140	40·76
3490	32·28	2630	67·33	3600	29·67			3180	39·20		
3330	35·26	2540	74·67	3500	30·86			2950	46·78		
		2490	82·02					2810	54·36		

TABLE 2. *Specific rotatory power of solutions of* (+)-*octan*-2-*ol in* n-*heptane* (all wave-lengths in Å).

(*a*) Visible region.

Temp.	*l* (dm.)	*c* (g./100 c.c.)	λ								$\frac{[\alpha]_{4358}}{[\alpha]_{5461}}$
			6438	5893	5780	5461	5086	4800	4678	4358	
24·6°	2	10·817	10·8°	13·1°	13·7°	15·1°	17·3°	19·1°	19·8°	23·1°	1·53
37·0	2	9·746	10·7	12·3	12·7	14·2	16·5	—	—	21·9	1·54
56·5	2	9·459	10·1	11·9	12·4	13·7	16·1	—	—	21·1	1·54
24·6	2	7·504	10·9	13·1	13·7	14·9	17·1	19·2	19·7	23·1	1·55
36·5	2	7·384	10·7	12·5	13·1	14·4	17·0	18·7	19·4	21·8	1·51
54·5	2	7·195	10·6	12·5	13·2	14·5	16·4	18·0	19·5	21·9	1·51
24·6	2	4·973	10·9	14·1	15·0	15·5	17·6	19·0	19·9	23·5	1·52
36·5	2	4·899	10·7	13·4	14·0	15·1	17·4	18·7	19·6	23·0	1·52
55·0	2	4·762	10·7	13·4	13·9	15·1	17·0	18·6	19·5	23·0	1·52
24·6	2	3·752	—	—	14·7	16·4	—	—	—	27·7	1·69
36·5	2	3·695	—	—	14·2	16·2	—	—	—	27·3	1·69
56·0	2	3·602	—	—	14·2	16·3	—	—	—	27·4	1·70
24·6	4	2·489	—	—	14·8	16·6	—	—	—	28·3	1·70
36·5	4	2·452	—	—	15·0	16·7	—	—	—	28·1	1·68
55·0	4	2·402	—	—	15·0	16·8	—	—	—	28·5	1·70
24·6	4	1·246	—	—	14·5	16·4	—	—	—	27·8	—
36·5	4	1·228	—	—	14·7	16·6	—	—	—	27·6	—
56·0	4	1·196	—	—	15·1	16·8	—	—	—	27·8	—

(*b*) Ultra-violet region.

t = 24·6°; *c* = 10·817.				*t* = 56·5°; *c* = 10·301.							
l = 2 dm.		*l* = 2 dm.		*l* = 2 dm.		*l* = 2 dm.		*l* = 0·5 dm.		*l* = 0·5 dm.	
λ	[α]	λ	[α]	λ	[α]	λ	[α]	λ	[α]	λ	[α]
4270	24·6°	3190	49·5°	4900	17·4°	3900	27·7°	3680	32·0°	2980	67·8°
3750	32·8	3000	57·9	4150	23·7	3730	30·6	3570	34·0	2880	74·3
3410	41·1							3100	53·1		

Although there may be numerous factors influencing the dispersion, it is clear that at least two different absorption wave-lengths are involved and that more than one molecular species is contributing to the resultant effect. In its more general aspect, this emphasises the danger of drawing conclusions from measurements of rotatory power made at only one wave-length, and measurements are required over as wide a range of wave-lengths as possible. In this case the range covered was from 6400 to below 3000 Å. No marked deviation from the simple hyperbolic form of the curve was observed, either in the homogeneous material or in the 10% *n*-heptane solution. The more dilute solutions were not examined in the ultra-violet region, since their low dispersion would make the estimation of the extinction position inaccurate. No attempt was made to achieve the accuracy of the earlier work of Lowry and Richards (*loc. cit.*) since this accuracy was obtained at the cost of a very restricted wave-length coverage. In this investigation the range of conditions under which the substance was examined was much wider, and the examination was carried to much shorter wave-lengths. The agreement with the earlier work is satisfactory. The dispersion constant λ_x^2, determined for the homogeneous material at 24·6°, was 0·0243, and the rotation constant *k*, 3·091. Lowry and Richards found 0·0244 and 3·176, respectively, but did not state the temperature at which their measurements were made.

TABLE 3. *Refractive indices of octan-2-ol and* n-*heptane at 24·6°.*

	Wave-length (Å).						
	6438	5893	5780	5461	5086	4800	4678
Octan-2-ol	1·4227	1·4237	1·4245	1·4260	1·4283	1·4300	1·4309
n-Heptane	1·3842	1·3802	1·3859	1·3872	1·3893	1·3909	1·3919

The dispersion curves for the homogeneous alcohol, and for the solutions, at the higher temperatures run parallel to the corresponding curve at 25°, and are practically superimposable, being indistinguishable at the shorter wave-lengths. The accuracy of the measurements in the ultra-violet region is of the order of 0·3—1·0%, the error being in the determination of the wave-length rather than of the rotatory power, which is known to the accuracy of setting of the polarimeter.

The specific rotatory power of solutions of (+)-octan-2-ol in *n*-heptane increases progressively with dilution until a concentration of about 3% is reached, whereat it becomes constant within the limits of experimental error. The reduction in rotatory power accompanying a rise in temperature is greatest in the 10% solution. When the results are corrected for the expansion of the solutions, as are the figures in Table 2, it is seen that if rise of temperature has any effect on the rotatory power of the dilute solutions it is to increase it slightly. This increase is, however, of the order of the individual error of the observation and may well have no significance.

It has been suggested (Kauzman, Walter, and Eyring, *Chem. Reviews*, **1940**, **26**, 339) that the quantity $\Omega = 3[\alpha]/(n^2 + 2)$, called the " rotivity," should show less variation with change of solvent and temperature than the specific rotatory power itself. For (+)-octan-2-ol the proportional variation in Ω with temperature is rather less than that of $[\alpha]$, but with change of solvent the rotivity shows no greater constancy than does the rotatory power. Hence, although use of Ω instead of $[\alpha]$ may be of value with hydrocarbons such as pinane (Rule and Chambers, *J.*, **1937**, 145), it is of much less value in the case of octan-2-ol, where stronger intermolecular forces come into play.

In conclusion, it may be said that the existence of more than one optically active absorption band in octan-2-ol is proved, and that the one-electron theory is supported. There are still insufficient data to enable the molecular state of the solute molecules to be determined, but at least two molecular species would appear to contribute to the rotatory power. It seems probable that the values of the rotatory power of (+)-octan-2-ol shown in dilute solution in *n*-heptane approximate more closely to those of the individual molecule than do those of the substance itself.

The behaviour of octan-2-ol is clearly too complicated to permit its use as a yardstick in the investigation of other substances. It is hoped to extend this work by investigating the effect of solvents and of temperature on the rotatory power of simpler substances.

The author thanks the Central Research Fund Committee of the University of London for a grant towards the construction of the polarimeter. Thanks are also offered to Professor R. G. W. Norrish, F.R.S., for the loan of a set of Foucault prisms, to Dr. V. I. Little for the design of the circuit given in Fig. 2, and to the laboratory staff of Bedford College for their help with the construction of the apparatus. The author also expresses his grateful appreciation of the help given by Mr. H. Yates and Mr. C. Godfrey, of Messrs. Hilger and Watts, in matters of construction and design.

BEDFORD COLLEGE, REGENT'S PARK, N.W.1.

[*Received, February 24th,* 1953.]