Temperature and the Optical Rotatory Power of Solutions. 9 : 10-*Dihydro*-3 : 4-5 : 6-*dibenzophenanthrene.*

By M. K. HARGREAVES.

The specific rotatory powers of solutions of 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene do not decrease with rise of temperature but appear to rise slightly.

IT was recently shown (Hargreaves, *J.*, 1953, 2953) that the rotatory power of octan-2-ol in *n*-heptane varies little, if at all, with change of temperature in the region 25—60°, the slight general rise with increase of temperature being of the order of the probable error of the measurements. The effect of temperature on the rotatory power of solutions of simple organic solutes has hardly been investigated at all, most of the available data referring to homogeneous active liquids in which a reduction of rotatory power usually, though not invariably, obtains (Pickard and Kenyon, *J.*, 1912, **101**, 1427; 1913, **103**, 1933; Kenyon, *J.*, 1914, **105**, 2247; Hargreaves, *loc. cit.*). Rule and Chambers (*J.*, 1937, 149) found that the rotatory power of (+)-pinane is reduced with rising temperature when in solution in nitrobenzene or mesitylene, whilst with (+)-pinene the rotatory power decreases in the first solvent and increases in the second. Rule attributed this difference of behaviour to the polarity of the solute. Rule, Barnett, and Cunningham (*J.*, 1933, 1222) have related the effect of solvent on the rotatory power of the solute to the refractive indices of the solvents.

Through the kindness of Dr. D. Muriel Hall it has been possible to examine, with this point in view, the rotatory dispersion in the visible region of 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene in dilute solution. This substance is particularly suitable since it has a very high rotatory power, is a hydrocarbon, and presumably has only one configuration. Its chief disadvantage is its low solubility—the solutions employed had a concentration of about 0·2%.

TABLE 1. *Specific rotatory powers of solutions of* 9 : 10-*dihydro*-3 : 4-5 : 6-*dibenzo-phenanthrene.*

The rotatory powers have been corrected for the change in the number of active molecules in the light path with temperature (by density corrections) and also for the evaporation of the solvent. In the series (*a*) the correction has been for half the gain in activity of the solution due to evaporation; in series (*b*) it has been corrected for the full amount.

Solvent ($l = 2$)	t		d	C (g./100 c.c.)	6438	5780	5461	5086	4800	4678	4358	$\dfrac{[\alpha]_{4358}}{[\alpha]_{5461}}$	$\dfrac{[\alpha]_{4358}^{(b)}}{[\alpha]_{5461}^{(a)}}$
CCl₄	25°		1·5843	0·2297	847°	1099°	1265°	1502°	1720°	1824°	2099°	1·659	
	40	(*a*)	1·5550	0·2254	—	1121	1282	—	—	—	2176	1·697	} 1·689
		(*b*)	—	—	—	1115	1276	—	—	—	2165	1·697	
	51	(*a*)	1·5333	0·2223	—	—	1300	—	—	—	2198	1·691	} 1·688
		(*b*)	—	—	—	—	1298	—	—	—	2194	1·690	
Benzene	25		0·87341	0·1620	935	1309	1494	1812	2068	2173	2528	1·692	—
	37	(*a*)	0·86053	0·1596	—	1313	1503	—	—	—	2549	1·696	} 1·689
		(*b*)	—	—	—	1308	1497	—	—	—	2538	1·695	
	46		0·85083	0·1578	—	1318	1508	—	—	—	2583	1·714	—
cyclo-Hexane	25		0·77429	0·1774	871	1144	1310	1570	1778	1874	2266	1·730	—
	37	(*a*)	0·76297	0·1748	—	1153	1316	—	—	—	2271	1·726	} 1·727
		(*b*)	—	—	—	1150	1313	—	—	—	2267	1·726	
	50	(*a*)	0·75151	0·1722	—	1157	1322	—	—	—	2291	1·733	} 1·725
		(*b*)	—	—	—	1152	1316	—	—	—	2281	1·733	

The measurements given in Table 1 were made in the order : mercury-green, -yellow, and -violet. It is likely that for the green line either no correction or the (*a*) series correction should be applied, whilst for the violet line the full correction should be used, since in this case a relatively large number of slowly taken readings are required to give reasonable

accuracy. From the expanded results the order of error is judged to be $\leq \pm 3$ units for $\lambda = 5461$ and 5780 and about ± 15 for $\lambda = 4358$; from the curves of $[\alpha]-t$ it would appear to be rather less than this, being 1—2 and up to 5 units respectively. In Table 2 are given the values of the slope of the curve $[\alpha]-t$ as calculated for the (a) and the (b) series corrections, the latter being in parentheses.

TABLE 2.

Solvent	$[\alpha]_{5780}-t$		$[\alpha]_{5461}-t$		$[\alpha]_{4358}-t$	
CCl$_4$	1·47°	(1·01°)	1·34°	(1·02°)	4·04°	(3·9°)
Benzene	0·4	—	0·7	(0·25)	2·1	(0·8)
cycloHexane	0·65	(0·4)	0·6	(0·3)	0·95	(0·55)

DISCUSSION

The effect of a rise in temperature on the specific rotatory power of homogeneous liquids is generally to cause a reduction in their rotatory power when their dispersion is simple. Kauzman, Walter, and Eyring (*Chem. Reviews*, 1940, **26**, 373, 381) have discussed this effect from the theoretical point of view and conclude that in simple substances such as 2-chlorobutane there should be a considerable decrease in the numerical value of the rotatory power with rise in temperature. However, they point out that the optical rotation of simple substances generally decreases only slightly with rising temperature. They also consider that the first- and second-order contributions to the rotatory power (arising from groups respectively far from and close to the chromophoric group) may be of opposite sign. A rise in temperature might thus result in an increase in the rotatory power if the first- and second-order contributions are affected to a different extent. It is noteworthy in this connection that the rotatory power of (—)-menthol shows a maximum value of the rotatory power at 60° although the substance exhibits simple dispersion (Kenyon and Pickard, *J.*, 1915, **107**, 35).

In their discussion no account is taken of the fact that rotatory power is to be considered as the resultant of several rotatory strengths and that not only the rotatory power but also the rotatory dispersion may be markedly affected by temperature changes (Balfe, Hargreaves, and Kenyon, *J.*, 1950, 1861). The change of the rotatory dispersion of octan-2-ol (Hargreaves, *loc. cit.*) with temperature shows that the rotatory strengths of $-\overset{|}{\text{C}}\text{H}$, $-\overset{|}{\text{C}}-\overset{|}{\text{C}}-$, and $-\overset{|}{\text{C}}-\text{OH}$ absorption bands may be differently affected by temperature changes.

The dispersion ratios of solutions of 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene vary only slightly with temperature. The variation is particularly small when the series (a) corrections are applied for $\lambda = 5461$ Å and the series (b) for $\lambda = 4358$ Å. There is clearly no loss in rotatory power accompanying a rise in temperature (within the range 25—50°), and a slight rise in rotatory power with rise in temperature would be the simplest explanation of the results here reported. (Details of the various corrections which must be applied are given in the Experimental section.) In view of the possibly subjective nature of measurements of optical rotatory power, the author attaches some importance to the fact that the density corrections were not applied until some weeks after the conclusion of the experiments. Although the increases in the rotatory power reported are only 0—10 times the observational error the general trend of the results is all in one direction, and it seems clear that, failing some unidentified error in the measurements, there must be a small rise in the optical activity of these solutions with rise in temperature. Since $\Omega = 3[\alpha]/(n^2 + 2)$, it seems clear that the rotivity (Ω) will rise with temperature rather more than $[\alpha]$.

It is interesting that 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene should show this effect since it has a rather rigid structure. This implies that this small observable rise in the rotatory power is not due to rotational isomers or freedom of configuration but is associated with the field within the molecule.

EXPERIMENTAL

Polarimeter.—A Bellingham and Stanley variable half-shadow two-field instrument was used, fitted with a ground glass in the aperture at the light end. Usually about 6 rather quick

readings were taken for the green and yellow lines, and 10—20 laborious readings for the violet line.

Polarimeter Tubes.—These were of fused silica with integral end-plates. The expansion of the tubes is negligible compared to other factors. A small correction was necessary for the rotatory power of the end-plates. This correction was determined as $0.05°$ for the mercury-green line, and the correction for other wave-lengths was calculated by means of the values for the rotatory dispersion of quartz (International Critical Tables, McGraw-Hill, New York, 1929, **6**, 342). The variation of the rotatory power of the end-plates with temperature for $\lambda = 5461$ Å was found to be less than $0.01°$. This is in agreement with the values for quartz given in the I.C.T. (p. 343) which show a variation of $< +0.0004°$ for a rise from $0°$ to $50°$. This comparison would not be strictly valid, however, if the rotatory power of the end-plates were due to strain, since an increase of temperature might be expected to increase the strain. The rotatory power of the end-plates is of opposite sign to that of the solutions, so if temperature were to have any effect it would be expected partially to mask the increase in the rotatory power of the solutions.

TABLE 3. *Actual rotations* α, *and tube and evaporation corrections.*

Solvent ($l = 2$)	t	Wave-length, Å							α^{25}_{5461} corr. for tube		Evaporation correction : Series	
		6438	5780	5461	5086	4800	4678	4358	before heating	after heating	(a)	(b)
CCl$_4$	25°	3.86°	5.01°	5.76°	6.84°	7.83°	8.31°	9.56°	—	—	—	—
	40	—	5.04	5.76	—	—	—	9.78	5.81°	5.87°	5.81 / 5.84	5.81 / 5.87
	51	—	—	5.79	—	—	—	9.79	5.87	5.88	5.81 / 5.87	5.81 / 5.88
Benzene	25	3.00	4.20	4.79	5.81	6.63	6.97	8.11	—	—	—	—
	37	—	4.17	4.77	—	—	—	8.09	4.84	4.88	4.84 / 4.86	4.84 / 4.88
	46 *	—	4.12	4.71	—	—	—	8.08	4.84	4.84	—	—
*cyclo*Hexane	25	3.06	4.02	4.60	5.51	6.24	6.58	7.96	—	—	—	—
	37	—	4.00	4.56	—	—	—	7.88	4.65	4.67	4.65 / 4.66	4.65 / 4.67
	50	—	3.97	4.53	—	—	—	7.86	4.67	4.70	4.65 / 4.68	4.65 / 4.70
Tube correction to be added to figures above		0.03	0.04	0.05	0.06	0.07	0.07	0.08				

* Run at $46°$ before $37°$ experiment.

Densities.—The decrease in the concentration of the active molecules with rise of temperature was calculated from the variation of the densities of the solvents with temperature (I.C.T., 1928, **3**, 28). The variation with temperature of the densities of 0.2% solutions of 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene was assumed to be the same as that of the pure solvent. This assumption seems reasonable in view of the nature of the solute and solvent molecules.

Evaporation Corrections.—In Table 3 are given the actual values of α at different temperatures and the values of α^{25}_{5461} observed before and after heating to each higher temperature.

Temperature Control.—Water from a thermostat controlled to $0.2°$ was rapidly circulated. Temperature was measured by direct insertion of the thermometer into the active liquid.