276. *The Optical Rotatory Dispersion of Hydrocarbons. (+)-3-Methylhexane.*

By B. C. Easton and M. K. Hargreaves.

The effect of certain solvents on the optical rotatory dispersion of (+)-3-methylhexane is recorded. The rotatory powers in these solvents depend on the refractive index in an unusual manner.

The synthesis of 3-methylhexane *via* pentyl-lithium has some advantage over previous methods.

The rotatory powers of 3-methylheptane show quite large variations with solvent.[1] The rotatory dispersion of the simplest optically active paraffin, 3-methylhexane, is similar to that of its homologue. Thus there is a considerable reduction in the optical rotatory power on dissolution in carbon disulphide; this is accompanied by a change in the dispersion ratio $[\alpha]_{4358}/[\alpha]_{5461}$. This change is, however, small when compared with that shown by other substances on change of solvent.[2] These variations are of interest because they cannot be ascribed to interaction or bonding of any appreciable strength. A minor interaction due to polarity at the tertiary hydrogen position is possible but seems unlikely.

Changes in rotatory power and rotatory dispersion with solvent may be correlated with changes in (1) the refractive index of the medium, (2) the wavelength of absorption maxima, or (3) the rotatory strengths of particular absorption bands.

(1) *Refractive Index and Rotatory Power.*—Amongst the factors which influence rotatory power the refractive index of the medium must first be considered since the theoretical expressions[3] for rotatory power show $[\alpha]$ to depend on $(n^2 + 2)$ so that $\Omega = [\alpha]/(n^2 + 2)$ may be expected to vary less than $[\alpha]$ between solvents with different refractive indices and between different temperatures. In a number of cases[3] this is not so, and it seems that the effect of refractive index is masked by some stronger effect due to the solvent. In 3-methylhexane Ω will vary more than $[\alpha]$ between the different solvents, since $[\alpha](n - 1)$ is found to be more constant than $[\alpha]$.

Solvent	3-Methylhexane $[\alpha]^{25\cdot3}(n^{20} - 1)$ (λ 5461 Å)	3-Methylheptane[1] $[\alpha]^{18}(n^{18} - 1)$ (λ 5893 Å)
(Homogeneous)	4·3	2·7
n-Hexane	4·3	—
Benzene	4·5	2·7
CS_2	4·1	2·7
CH_2Cl_2	—	2·4 *

* Interpolated.

Calculations based on Kenyon and Platt's results[1] show that in the case of 3-methylheptane also $[\alpha](n - 1)$ is constant to within the probable experimental error. But for 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene, also a hydrocarbon, there is no apparent correlation between the refractive index or the dielectric constant of the solvent and the rotatory power of the solution:

Solvent	n_D	ε^{20}	$[\alpha]^{25}$ (λ 5461 Å)
CCl_4	1·46305 (at 15°)	2·24	1265
*cyclo*Hexane	1·42900 (at 15°)	2·02	1310
Benzene	1·5033 (at 25°)	2·28	1494

Also, the rotatory power of solutions of 3-methylhexane does not depend on refractive index since $[\alpha]$ is constant for different temperatures (within the limit of accuracy).

Thus these results show that $[\alpha]$ for 3-methylhexane depends on refractive index as between different solvents but not as between different temperatures. The dependence

---

[1] Kenyon and Platt, *J.*, 1939, 633.

[2] Hargreaves and Richardson, *J.*, 1957, 2260.

[3] Kauzmann, Walter, and Eyring, *Chem. Reviews*, 1940, **26**, 339.

observed is not perfect and may well be fortuitous, but the fact that 3-methylheptane shows a similar dependence suggests that there may be a fundamental reason for this behaviour. In view of the wide differences in behaviour which are observed, it is noteworthy that 3-methylhexane and 3-methylheptane both obey this " rule " in the solvents studied. Against this agreement is the fact that (+)-pinane follows an opposite law, Ω being more constant than $[\alpha]$ as between different solvents[5] and that 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene shows no dependence on refractive index.

(2) *Wavelength of Absorption Maxima and Rotatory Power.*—Changes in the wavelength of absorption maxima are, in general, far too small to account for observed changes in rotatory power. This is particularly so where the measurements are in the visible region and all the absorption bands are in the Schumann region, as in the aliphatic hydrocarbons.

(3) *Rotatory Strengths of Absorption Bands.*—Alteration in the rotatory strengths of particular absorption bands may be due to an alteration (*a*) in the proportion of the various conformational species present or (*b*) in the polarisability of the active molecule. With aliphatic hydrocarbons there is little chance that one bond will be especially affected by change of solvent, so that where the variation cannot be correlated with refractive index it seems that the observed changes in rotatory power must be due either to changes in the " average conformation " about single bonds, or to alteration in the polarisability of the molecule, but probably to the former.

In 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene solutions the rotatory power cannot be correlated with the refractive index, and the solute molecule is virtually rigid, there being no possibility of change of conformation without racemisation. Yet the rotatory power varies by 20% between solutions in carbon tetrachloride and in benzene. It is noteworthy that these variations occur between solvents of zero dipole moment and low dielectric constant, and further that the concentrations used in these experiments were so small as to make solute–solute interaction virtually non-existent. A large molecule of this type is likely to be readily polarisable, so the effect of the solvent may be to alter its polarisability (the molecule also probably has a small permanent dipole moment), but the lack of dependence of $[\alpha]$ on refractive index is against this explanation.

It is, however, clear from this work that conformation cannot be the only influence with a major effect on the rotatory power unless the solvent can act by altering the " out-of-plane " or azimuthal angle of the solute molecule.

Effect of Temperature.—In 3-methylhexane and in octan-2-ol[6] the rotatory power of the homogeneous material varies slightly with temperature. For 3-methylhexane (homogeneous) we have:

Temp.	25·3°	40·8°	56·5°	72·3°
$[\alpha]_{5461}$	11·10°	10·96°	10·75°	10·60°
Ω_{5461} *	2·827	2·827	2·789	2·766

* Calculated by using values of n at 25·3° and $(n^2 - 1)/(n^2 + 2) = kd$.

Ω is rather more constant than $[\alpha]$ but with the solutions $[\alpha]$ varies little if at all so that Ω must be the least constant. With the 10% solutions of octanol in *n*-heptane there is still a variation with temperature but at lower concentrations this disappears. Table 1 shows that the rotatory powers of solutions of 3-methylhexane are approximately invariant with temperature. This may be attributed either (1) to the similarity of the rotatory power of the various conformations or (2) to similarity of the energy of the different conformations so that the populations of the respective forms change but little with temperature. A similar argument applies to Ω if this is considered to be the fundamental quantity, but work with the dilute solutions suggests that $[\alpha]$ is, in fact, the more fundamental.

Since the solvent molecules are symmetric, in dilute solutions the solute molecules are

---

[4] Hargreaves, *J.*, 1954, 1781.

[5] Rule and Chambers, *J.*, 1937, 145.

[6] Hargreaves, *J.*, 1953, 2953.

probably sufficiently far apart for the energy of " packing in the solution " to be much the same for all conformations so that there is invariance of rotatory power with temperature. In the homogeneous substance, however, the different conformations will have rather

TABLE 1. *Optical rotatory and refractive dispersions of* (+)-3-*methylhexane.*

Solvent	c * (g./100 c.c.)	t (°c)	Wavelength (Å)						$\frac{[\alpha]_{4358}}{[\alpha]_{5461}}$
			6438	5780	5461	5086	4800	4358	
			[α] (l = 2, except for first set, where l = 1)						
None (homogeneous)		25·3 [a]	7·72°	9·80°	11·10°	12·95°	14·61°	18·34°	1·65
		40·8	7·53	9·73	10·96	12·74	14·43	18·05	1·65
		56·5	7·42	9·52	10·75	12·62	14·38	17·65	1·64
		72·3	7·33	9·36	10·60	12·46	14·20	17·41	1·64
n-Hexane	11·17	25·3 [b]	7·9	10·0	11·3	13·3	14·7	18·0	1·60
		39·7	7·8	9·9	11·1	13·3	14·5	17·8	1·60
		51·0	7·7	9·9	11·1	13·2	14·4	18·0	1·63
	7·58	25·3	8·0	10·0	11·1	13·2	14·8	18·1	1·63
		40·0	—	10·0	11·1	—	—	18·1	1·63
		56·4	—	10·1	11·2	—	—	18·1	1·61
Benzene	8·38	24·3	7·7	8·7	9·3	11·0	12·2	15·4	1·66
		37·7	—	8·5	9·4	—	—	15·8	1·68
		51·3	—	8·6	9·3	—	—	15·5	1·67
		65·6	—	8·7	9·2	—	—	15·4	1·65
	4·19	24·3	—	8·7	9·2	—	—	14·9	1·62
CS_2	8·30	25·3	—	6·0	6·8	—	—	10·6	1·56
		38·5	—	5·7	6·4	—	—	—	
	4·15	24·3	—	5·9	6·4	—	—	—	
		37·9	—	6·0	6·4	—	—	—	
H·CO·NHMe + $COMe_2$	7·82	24·9	—	9·6	10·4	—	—	—	
		37·8	—	9·2	10·1	—	—	—	
			n (homogeneous) †						
		25·3	1·3853	1·3869	1·3881	1·3899	1·3917	1·3950	

Densities (d_4^t)

t	25·3°	40·8°	56·5°	72·3°
d_4	0·6850	0·6716	0·6850	0·6445

* The actual values of c used were corrected for the expansion of the solution, standard values being used for the densities of the solvent except for the solution in monomethylformamide and acetone which had $d_4^{20\cdot4}$ 0·9079, $d_4^{49\cdot8}$ 0·8817. (Acetone, c = 25·89; monomethylformamide, c = 64·15.)

† n_D^{20} 1·3890, $n_{5893}^{25\cdot3}$ 1·3866.

[a] $[\alpha]_{5893}$ = 9·43° at 19·9°, 9·42° at 25·3°. [b] $[\alpha]_{5893}$ = 9·6° at 24·3°.

TABLE 2. *Specific rotatory powers* * *of* (+)-3-*methylhexane in the ultraviolet region.*

λ	[α]	λ	[α]	λ	[α]	
		(a) *Homogeneous liquid* (l = 0·25)				
4326	18·57°	3305	36·09°	2754	59·45°	t = 25·3°
3856	24·41	2970	47·77	2591	71·12	
3514	30·25	2843	53·61	2529	76·96	
4294	18·92	3248	36·77	2718	60·57	t = 40·0°
3840	24·87	3100	42·72	2644	66·52	
3505	30·82	2947	48·67	2599	72·47	
4423	17·45	3180	37·44	2810	55·62	t = 54·0°
3589	28·36	3067	43·50			
		(b) *Solution in* n-*hexane* (c = 11·17; l = 1, t = 25·3°)				
3825	22·98	3490	30·65	2870	57·46	
3631	26·81	3057	45·97	2598	68·95	

* The rotatory powers are exact, the error being in the estimation of the wavelength, the line given being that nearest at match.

different energies owing to the need to pack into holes in a liquid consisting of unsymmetrical molecules. It is difficult to see in what other way a solvent of such similar character to the solute as *n*-hexane could influence the rotatory power.

Summary.—The rotatory power of solutions of 3-methylhexane depends on $(n - 1)$ in the solvents studied, but is independent of n where change of temperature is concerned. The rotatory power of the homogeneous substance varies slightly with temperature, this variation may be correlated, at least in part, with changes in refractive index. In 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene, by contrast, no relation to refractive index was observed. Since only one conformation of this molecule is possible, it is difficult to explain the observed variations of rotatory power with solvent.

TABLE 3. *Rotatory dispersion of* (+)-1-*bromo*-2-*methylbutane at* 20°.

Wavelength (Å)	6438	5893	5780	5461	5086	4800	4358
[α] ($l = 2$)	3·32°	4·07°	4·22°	4·72°	5·44°	6·04°	7·13°

$d_4^{20\cdot0}$ 1·2232; $n_{5893}^{20\cdot0}$ 1·4450.

EXPERIMENTAL

1-*Bromo*-2-*methylbutane*.—(*a*) 2-Methylbutanol (0·46 mole), kept for 3 days at room temperature in a sealed tube with phosphorus tribromide (0·54 mole), gave the bromide, b. p. 116—122°, n_D^{20} 1·4445, in 52% yield. The product contained traces of phosphorus compounds which were difficult to remove.

(*b*) *Modification of Heller's method.*[7] (—)-2-Methylbutanol (47 g.) [$\alpha_{5461}^{20\cdot1}$ $-5\cdot748°$ ($l = 1$)] was saturated with dry hydrogen bromide (from boiling decalin and bromine) at 0°. The temperature was then raised to 100° and the stream of hydrogen bromide continued for 2½ hr., after which the lower layer of hydrogen bromide solution was run off. The remaining 1-bromo-2-methylbutane was washed twice with ice-water, separated, and dried by freezing. The bromide was shaken twice at 0° with an equal volume of sulphuric acid and then, also at 0°, twice with an equal volume of water. The liquid was again " freeze dried " and then left over freshly heated potassium carbonate. The product (68·2 g.) was distilled, giving the bromide (65·7 g., 81·5%), b. p. 38·3°/39 mm., $\alpha_{5461}^{20\cdot1}$ $+5\cdot483°$ ($l = 1$).

Fractionation. The bromide, α_{5461}^{20} $+5\cdot53°$ (67·6 g., from another preparation using 2-methylbutanol with α_{5461}^{20} $-5\cdot65°$), was distilled from a 50 ml. flask in a water-bath at 74—79° through a 20 cm. vacuum-jacketed column, 1 cm. diam., packed with broken glass, giving (1) 11·5 g., b. p. 62—64·8°/140 mm., α $+5\cdot11°$ ($l = 1$), (2) 15·8 g., b. p. 65·0°/140 mm., α_{5461}^{23} $+5\cdot41°$ ($l = 1$), (3) 15·8 g., b. p. 65—65·6°/140 mm., α_{5461}^{20} $+5\cdot77°$ ($l = 1$), $[\alpha]_{5893}^{20}$ $+4\cdot068°$, d_4^{20} 1·2232, n_D^{20} 1·4450 (cf. Brauns,[8] $[\alpha]_{5893}^{20}$ 4·043°, d_4^{20} 1·2234), n_D^{20} 1·4451. Dry hydrogen was passed through the " air-leak " during these preparations. The rotatory power of fraction (3) fell to α_{5461}^{20} $+5\cdot721°$ ($l = 1$) in 14 days, care being taken to exclude moisture.

(±)-3-*Methylhexane*.—(a) *By Heller's method.* Magnesium turnings (7·4 g.) and 1-bromo-2-methylbutane (41·7 g.) in ether (100 ml., Na-dried) under dry nitrogen were blown into an ethereal solution of diethyl sulphate (95·3 g., dried by K_2CO_3), giving a thick paste. After being refluxed and stirred for 15 hr. (shorter time reduces the yield), the cooled mixture was poured into dilute hydrochloric acid and ice. After removal of the ether from the dried ($CaCl_2$) ethereal layer, the residue was treated with an equal volume of concentrated sulphuric acid (in ice). The upper layer was kept over anhydrous potassium carbonate and distilled, giving a main fraction (10·4 g., 38%), b. p. 87·5—94°/760 mm., n_D^{15} 1·3921 (cf. below).

(b) *From ethyl-lithium.* Lithium wire (1 mm. diam., 5 g.) and dry pentane (100 ml.) under dry hydrogen were placed in a 500 ml. flask fitted with a strong stirrer and a CO_2–Methyl Cellosolve condenser (Quickfit air condenser surrounded by an inverted hot-water bottle with a sawn-off base). Ethyl chloride vapour (2 g., dried by silica gel) was added, and the solution gently warmed and stirred. When the reaction was completed a further 28·1 g. of ethyl chloride were

---

[7] Heller, *J. Amer. Chem. Soc.*, 1952, **74**, 4858.
[8] Brauns, *J. Res. Nat. Bur. Stand.*, 1937, **18**, 315.

added during 4 hr., the stream of dry hydrogen being maintained throughout the reaction and during subsequent refluxing for 30 min. The mixture was then filtered by blowing (with hydrogen) through a tube containing glass-wool. The filtered solution was made up to 500 ml. with dry pentane and analysed by the benzyl chloride method,[9] a yield of 77% based on lithium being indicated.

To 0·2 mole of ethyl-lithium (by titration) in 200 ml. of dry *n*-pentane under dry hydrogen, 1-bromo-2-methylbutane (15·1 g., 0·1 mole) in an equal volume of *n*-pentane was slowly added; the mixture was then slowly warmed, allowed to reflux overnight, cooled, and decomposed by pouring on crushed ice. A vigorous reaction ensued (the residue remaining in the flask was very reactive to air). The pentane layer was dried (K_2CO_3) and then fractionated through a column surrounded by warm water (*ca.* 40°), giving 3-methylhexane (1·8 g., 18%), b. p. 85—96°, n_D^{20} 1·3888 (cf. below).

(c) *From pentyl-lithium.* Lithium (5 g., as 1 mm. wire) was pressed into a 3-necked 250 ml. flask in an atmosphere of dry hydrogen, and 30 drops of a solution of 35 g. of 1-bromo-2-methylbutane [α_{5461}^{20} +5·70° ($l = 1$)] in 50 ml. of ether were added with stirring in the presence of a slow stream of dry hydrogen. The mixture was cooled to −10° by immersion in CO_2–acetone. The remainder of the bromide was added during 30 min., the temperature being kept at −10° to −15°. The mixture was then allowed to warm to 0° in 2 hours' standing in ice–salt. The pentyl-lithium solution was filtered through glass wool in a tube and then blown by dry hydrogen through a polyl(vinyl chloride) tube into a separating funnel, the whole apparatus being filled with dry hydrogen. The pentyl-lithium solution was run slowly into diethyl sulphate (60 g., dried by K_2CO_3) and ether (100 ml., dried by Na) in a 500 ml. 3-necked flask, cooled in ice–water when necessary to maintain moderate refluxing. The mixture was then refluxed for a further hour, cooled, and poured into dilute hydrochloric acid and ice. The ethereal layer (dried by $CaCl_2$) was fractionated from a water-bath as before. The residue was shaken with an equal volume of concentrated sulphuric acid at 0°; the upper layer was washed with a little water and dried (K_2CO_3). The crude paraffin (12·7 g.) was fractionated, giving 10·3 g., 44·4%, b. p. 86—106°/760 mm. Refractionation gave 8·3 g., b. p. 91—93°/760 mm., $[\alpha]_{5893}^{19\cdot9}$ +9·43°, n_D^{20} 1·3892, $d_4^{19\cdot9}$ 0·6898 (cf. Gordon and Burwell,[10] $[\alpha]_{5893}^{25}$ +9·10°, n^{20} 1·3889, d_4^{25} 0·6824; Marckwald,[11] $[\alpha]_{5893}^{20}$ +9·5°, d_4^{20} 0·6865).

Measurements.—These were carried out as previously described.[6] The observational error was probably less than 0·01° for 5461 and 5780 Å in the best cases, and about ±0·03° for the other lines. Since it is sometimes necessary to correct for different conditions, mean values for rotatory powers are given to an accuracy greater than that warranted by the individual measurements. This avoids certain losses in accuracy due to "rounding off" in the course of conversion.

We thank the Central Research Fund Committee of the University of London for grants, and Mr. R. K. Mitchell for active 2-methylbutanol.

QUEEN ELIZABETH COLLEGE, UNIVERSITY OF LONDON,
CAMPDEN HILL ROAD, LONDON, W.8.

[*Received, December 17th,* 1958.]

---

[9] Wittig, "Newer Methods of Preparative Organic Chemistry," Interscience, New York, 1948, 575.

[10] Gordon and Burwell, *J. Amer. Chem. Soc.*, 1948, **70**, 3128.

[11] Marckwald, *Ber.*, 1904, **37**, 1046.