56. *Epimeric Alcohols of the* cyclo*Hexane Series. Part IV. The Parachor as a Criterion for* cis–trans-*Isomerism.*

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The parachors of ten pairs of geometrical isomerides of the *cyclo*hexane series have been measured. The epimers examined show definite differences in parachor, and, with the exception of the menthones and menthyl acetates, the *trans*-isomer gives a higher value. The magnitude of the difference appears to depend more upon the chemical nature of the compound than the relative size of the substituent groups.

During the early investigations on the relation between surface tension, density, and chemical constitution, Sugden and Whittaker (J., 1925, **127**, 1868) measured the parachors of five pairs of geometrical isomerides over a wide range of temperature. All the compounds examined contained a non-polar double bond, and the *cis*-compounds, in which two bulky groups were adjacent, had slightly higher parachors than the corresponding *trans*-epimers. In the *cyclo*hexane series the double bond is replaced by a six-membered carbon ring, and it seemed desirable to examine the parachors of certain epimeric compounds, which had become available during other investigations, to see whether the experimental values might be applied as a discriminative test of configuration. While investigating the isomerism of borneol and *iso*borneol, Lipp (*Annalen*, 1930, **480**, 298) measured the parachors of the *dl*-bornyl acetates. Bornyl acetate (*trans*) gave a higher value (463·3) than *iso*bornyl acetate (*cis*, 462·6). These values are in good accord with those obtained with simple geometrical isomers of this series.

In the present work every precaution has been taken to ensure complete accuracy of results, and usually the maximum error in the parachor measurements is less than 1 in 4000 (compare Sugden, 1 in 200). Two cells were used for most of the measurements, and a large number of readings taken with each. The results reported below represent a mean value of these readings, but in every case the limits of experimental error are indicated.

Carter (J., 1927, 1278) determined the parachors of the menthones, and considered that the results indicated a *cis*-configuration for *iso*menthone. No experimental details are given, but it would appear probable that the values are not altogether reliable, as he obtained different results for the active and the racemic ketones. Moreover the *iso*menthone used was prepared directly from piperitone by catalytic hydrogenation, and was thus contaminated with menthone. Redeterminations on the carefully purified ketones differed appreciably from most of Carter's values, and any difference between the epimers was less than the experimental error. Determinations were also made in the case of the various menthyl acetates, but these do not throw any light on the configurations of the parent alcohols (see Tables I and II).

In every case the *trans*-epimer has the higher parachor. Further generalisations may be suggested, although the number of compounds examined does not allow any definite conclusions to be stated. The difference in the parachor values appears to depend not so much on the relative size of the substituent groups as on the chemical nature of the compound. The two primary alcohols both give only a small difference (0·4 unit), but the secondary alcohols show a larger difference, the effect increasing in the 1 : 3-positions. A 1 : 2-substituted *cyclo*hexane was not available, but an even greater difference would be expected in this case. Both esters examined have the same difference of **1·9** units.

TABLE I.

	Cell.	$A \times 10^3$.	P.	$d^{30°}_{4°}$.	$\gamma^{30°}$.	[P] obs.	Mean.	Carter.
l-Menthone	A	3·095	9·290	0·8869	28·39	401·1$_7$	401·08 ± 0·19	403·2
	B	4·289	6·661		28·30	400·9$_9$		
*dl-iso*Menthone	A	3·095	9·463	0·8908	28·87	401·1$_1$	401·19 ± 0·08	405·3
	B	4·289	6·815		28·92	401·2$_7$		

TABLE II.

Acetates.	Cell.	$A \times 10^3$.	P.	$d^{30°}_{4°}$.	$\gamma^{30°}$.	[P] obs.	Mean.	Difference.
l-Menthyl	A	3·095	9·096	0·9158	27·77	496·7$_8$	496·6$_9$ ± 0·09	
	B	4·307	6·491		27·73	496·6$_0$		−1·4
*dl-neo*Menthyl	A	3·095	9·040	0·9124	27·64	498·0$_0$	498·1$_0$ ± 0·10	
	B	4·307	6·477		27·61	498·2$_0$		
*dl-iso*Menthyl	A	3·112	9·212	0·9232	28·33	495·2$_9$	495·3$_9$ ± 0·10	
	B	4·144	6·892		28·35	495·4$_8$		−2·9
*dl-neoiso*Menthyl	A	3·112	9·121	0·9138	27·86	498·4$_0$	498·3$_1$ ± 0·09	
	B	4·144	6·511		27·82	498·2$_2$		

The remainder of the compounds examined fall into five classes, and the results are summarised below.

TABLE III.

Compound.	Cell.	$A \times 10^3$.	P.	$d^{30°}_{4°}$.	$\gamma^{30°}$.	[P] obs.	Mean.	Difference.
1. *trans-p*-Menthane	A	3·095	8·024	0·7837	24·49	397·8$_0$	397·8$_1$ ± 0·02	
	B	4·307	5·746		24·48	397·8$_3$		+2·2
cis-p-Menthane	A	3·095	8·120	0·7913	24·82	395·5$_0$	395·5$_7$ ± 0·08	
	B	4·307	5·822		24·86	395·6$_5$		
2. *trans*-4-Methyl*cyclo*-hexylcarbinol	A	3·095	9·489	0·8962	28·89	331·5$_0$	331·4$_3$ ± 0·07	
	B	4·312	6·762		28·86	331·3$_6$		+0·4
cis-4-Methyl*cyclo*-hexylcarbinol	A	3·095	9·870	0·9074	30·11	330·9$_2$	331·0$_3$ ± 0·11	
	B	4·312	7·095		30·26	331·1$_5$		
trans-4-*iso*Propyl-*cyclo*hexylcarbinol	A	3·095	9·754	0·9007	29·75	404·9$_2$	404·9$_8$ ± 0·06	
	B	4·312	6·981		29·80	405·0$_4$		+0·4
cis-4-*iso*Propyl*cyclo*-hexylcarbinol	A	3·095	9·905	0·9051	30·21	404·5$_9$	404·6$_0$ ± 0·07	
	B	4·312	7·089		30·22	404·6$_1$		
3. *trans*-Dihydrocryptol	A	3·118	9·771	0·9074	30·03	366·7$_0$	366·7$_3$ ± 0·03	
	B	4·308	7·048		30·05	366·7$_5$		+2·8
cis-Dihydrocryptol	A	3·118	9·668	0·9121	29·72	363·8$_7$	363·9$_4$ ± 0·06	
	B	4·308	6·980		29·76	364·0$_0$		
4. *trans*-3-Methyl*cyclo*-hexanol	A	3·112	9·514	0·9072	29·18	292·3$_4$	292·3$_7$ ± 0·03	
	B	4·144	7·122		29·21	292·4$_0$		+3·1
cis-3-Methyl*cyclo*-hexanol	B	4·144	7·020	0·9139	28·80	289·2$_5$	289·2$_5$ ± 0·04	
5. *trans*-Hexahydro-cuminic ester	A	3·095	9·408	0·9234	28·87	497·4$_8$	497·4$_3$ ± 0·05	
	B	4·308	6·760		28·85	497·3$_9$		+1·9
cis-Hexahydro-cuminic ester	A	3·095	9·382	0·9264	28·78	495·5$_0$	495·5$_4$ ± 0·04	
	B	4·308	6·749		28·80	495·5$_8$		
trans-Dihydrocryptyl acetate	C	5·123	5·648	0·9271	28·74	460·0$_3$	459·9$_8$ ± 0·06	
	C	5·123	5·644		28·71	459·9$_2$		+1·9
cis-Dihydrocryptyl acetate	C	5·123	5·647	0·9308	28·73	458·1$_5$	458·1$_0$ ± 0·05	
	C	5·123	5·643		28·70	458·0$_5$		

EXPERIMENTAL.

Surface tension measurements were made by the maximum bubble pressure method of Sugden (J., 1922, **121**, 858; 1924, **125**, 27). The apparatus and procedure was essentially that described by Mills and Robinson (J., 1931, 1629) and it is necessary here only to describe those details which it was found convenient to modify.

As some of the liquids to be examined were available in small quantities only, the cells, made of Monax glass, were designed to give 15—20 mm. depth with 3 c.c. of substance. The jets, also of Monax glass, had radii approximately 1·4 mm. and 0·04 mm. The apparatus was always dried in a vacuum at 100—110° after cleaning in hot nitric–chromic acid and thorough washing with good quality distilled water.

The rate of bubbling was found to be important, if consistent results were to be obtained. For the large jet a rate of one in 4—6 seconds was used, but the most satisfactory rate for the fine jet varied somewhat with the type of liquid under examination. A rate as high as 1 bubble per second gave good results with less viscous liquids, but for other substances this was varied to one in 1½—3 seconds.

The cell constants were frequently checked, usually before and after each pair of determinations. The standard used was "analytical reagent" benzene (Merck) which had been redistilled, rejecting head and tail fractions. For this liquid at 30° the constants used were $\gamma = 27{\cdot}58$ dynes/cm., and $d_{4^\circ}^{30^\circ}$ 0·868.

Density measurements were made in pyknometers of 4—6 c.c. capacity, and in every case at least two determinations in different pyknometers were done.

Each liquid was freshly distilled before a determination. Below is a summary of the compounds examined; all have been described fully elsewhere.

cis- and *trans*-*p*-Menthanes : *dl*-*iso*Menthone and *l*-menthone were electrolytically reduced, and the products purified by the method of Keats (J., 1937, 2005). The hydrocarbons had the following physical constants : *cis*- b. p. 171°, $n_D^{20^\circ}$ 1·4411, $d_{4^\circ}^{30^\circ}$ 0·7913; *trans*- b. p. 170°, $n_D^{20^\circ}$ 1·4371, $d_{4^\circ}^{30^\circ}$ 0·7837.

l-Menthone (α_D − 25·65°) was prepared by the oxidation of pure *l*-menthol by Beckmann's chromic acid mixture.

dl-*iso*Menthone was prepared as described by Hughesdon, Smith, and Read (J., 1923, **123**, 2921), and, when fractionated under 25 mm. pressure through a 50 cm. column, gave a main fraction, b. p. 108—109°. It had $n_D^{20^\circ}$ 1·4540, $d_{4^\circ}^{30^\circ}$ 0·8908, and was therefore practically pure.

l-Menthyl acetate was prepared from *l*-menthol (8 g.) by treatment with glacial acetic acid (30 g.; 10 mols.) and dry hydrogen chloride (2 g.). After standing overnight, it was refluxed for 2 hours, and then washed, in ethereal solution, with dilute sodium carbonate and water. After drying (sodium sulphate) and removal of the ether, the product, distilled in a vacuum, had b. p. 85°/3·1 mm., $n_D^{20^\circ}$ 1·4472, α_D − 72·09°, $d_{4^\circ}^{30^\circ}$ 0·9159.

d-*neo*Menthyl acetate. *d*-*neo*Menthol, obtained by the Ponndorf reduction of *l*-menthone (Grubb and Read, *J. Soc. Chem. Ind.*, 1934, **53**, 52T), on treatment as above, gave the acetate, b. p. 81°/3·0 mm., $n_D^{20^\circ}$ 1·4489, α_D + 28·30°, $d_{4^\circ}^{30^\circ}$ 0·9124.

dl-*iso*Menthyl acetate. *dl*-*iso*Menthol, prepared by reduction of *dl*-piperitone with sodium and alcohol (Hughesdon, Smith, and Read, J., 1923, **123**, 2918), and purified through the hydrogen phthalate, gave an acetate, b. p. 88°/3·8 mm., $n_D^{20^\circ}$ 1·4498, $d_{4^\circ}^{30^\circ}$ 0·9225.

dl-*neoiso*Menthyl acetate. *dl*-*neoiso*Menthol was obtained by the crystallisation of the phosphoric acid compound of the Ponndorf reduction product of *iso*menthone (Read and Grubb, J., 1934, 316). The alcohol, m. p. 11—12°, treated as above, gave the acetate, b. p. 85°/3·5 mm., $n_D^{20^\circ}$ 1·4516, $d_{4^\circ}^{30^\circ}$ 0·9138.

The *cis*- and *trans*-dihydrocryptols and their acetates have been previously described (Cooke, Gillespie, and Macbeth, J., 1939, 518).

cis- and *trans*-*l*-3-Methyl*cyclo*hexanols were prepared by the hydrogenation of *d*-3-methyl*cyclo*hexanone, obtained by the hydrolytic decomposition of *d*-pulegone (Wallach, *Annalen*, 1896, **289**, 340). *trans*-*l*-3-Methyl*cyclo*hexanol, purified through the hydrogen phthalate, had b. p. 65°/5·6 mm., $[\alpha]_D^{16^\circ}$ − 4·28, $n_D^{20^\circ}$ 1·4574, $d_{4^\circ}^{30^\circ}$ 0·9072. *cis*-*l*-3-Methyl*cyclo*hexanol, recovered from the hydrogen phthalate crystallisations (above), was purified by repeated crystallisation of the *p*-nitrobenzoate. The alcohol had b. p. 61°/5·2 mm., $[\alpha]_D^{16^\circ}$ − 7·42°, $n_D^{20^\circ}$ 1·4580, $d_{4^\circ}^{30^\circ}$ 0·9140 (compare Godchot and Cauquil, *Compt., rend.*, 1934, **198**, 663).

The remaining compounds examined were recently described (Cooke and Macbeth, J., 1939, 1245), and the densities are given in Table III.

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