

(3) The absorbers consisted of hollow spheres or cylinders so large compared with the test piece in the centre that those neutrons which reach the test piece must traverse the absorber nearly normally.

The absorption of cadmium and silver was measured. The logarithms of the measured intensities are plotted in Fig. 1, against the thickness of absorber. The absorption is in both cases exponential so far as the observations extend, that is, down to one fifth of the original intensity. The half values are 1.25 gm./cm.<sup>2</sup> for Ag and 24 mgm./cm.<sup>2</sup> for Cd. Fermi's values for cadmium are given as the dotted line in Fig. 1.

This result, that slow neutrons are absorbed exponentially under suitable experimental conditions, suggests either that the active neutrons are of fairly homogeneous speed or that, in the region of velocity of the neutrons concerned, the nuclear cross-section does not depend appreciably on the velocity of the neutrons.

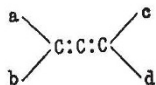
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<sup>1</sup> *Proc. Roy. Soc., A.*, **149**, 522; 1935.

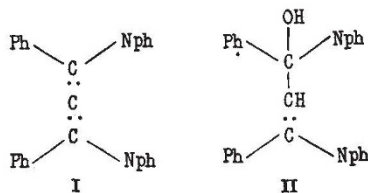
#### Experimental Demonstration of the Allene Asymmetry

WE have succeeded in verifying the prediction made by van't Hoff in 1875, but hitherto unverified, that unsymmetrically substituted allenes,



would be found to exhibit enantiomorphism.

The difficulty in demonstrating the association of optical activity with this structural type lay chiefly in the synthesis of a substituted allene with suitable salt-forming groups. This difficulty can be avoided by the employment of asymmetric catalysis, and we have by this means obtained diphenyl-di- $\alpha$ -naphthyl allene (I)



in optically active forms. (It has long been recognised that the dissymmetry of van't Hoff's type persists when  $a$  is identical with  $c$  and  $b$  with  $d$ .)

The different forms of the allene were obtained by dehydration of the alcohol (II). The inactive form, produced by ordinary methods of dehydration, melts at 242°–244°. When the dehydration is carried out catalytically by heating with  $d$ -camphorsulphonic acid in benzene solution, there is produced, together with the inactive form, a certain proportion of a powerfully dextrorotatory isomeride with  $[\alpha]_{5461} + 437^\circ$ . This optically active modification is much more soluble than the inactive allene and can be isolated in well-formed crystals melting at 158°–159°. When  $l$ -camphorsulphonic acid is used as the catalyst the corresponding levorotatory enantiomorph with  $[\alpha]_{5461} - 438^\circ$  is formed.

It was shown that these optically active isomerides of m.p. 158°–159° were actually enantiomorphous forms of the allene by mixing their saturated solutions at the ordinary temperature, when the inactive (racemic) allene of m.p. 242°–244° crystallised.

The active forms have very considerable optical stability, though they gradually lose their activity when heated above 160°.

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#### The Straight Chain- and the Many Membered CH<sub>2</sub> Ring-Molecule

THE heats of combustion of a CH<sub>2</sub> group are the same in a normal and in the cyclo molecule, except the first members of the two series. Almost the same holds for the refractivities if the very small differences in the cyclo series are disregarded. From these two facts it must be concluded that the carbon-carbon and the carbon-hydrogen distances are the same in both series, and that the whole electronic configuration of an individual CH<sub>2</sub> group is nearly identical in both structures.

Yet it is found that there is a marked difference in the densities or molecular volumes in the two series when these measurements are made at temperatures near the melting point. This fact was first noticed and has been fully discussed by L. Ruzicka and his collaborators. A summary of their systematic work has recently been published in the *Journal of the Society of Chemical Industry* (January 1935).

Owing to the kindness of Prof. Ruzicka, who supplied me with a number of these cyclo compounds, I was able to measure their molecular volumes by means of X-rays, the substances being in the solid state<sup>1</sup>. In this paper I came to much the same conclusion as Ruzicka and his co-workers, and ascribed the high density of the cyclo compound as due to the strain produced by the bending of the chain into a ring.

Looking into this matter since, I calculated the molecular volume of a CH<sub>2</sub> group both in a straight chain and in a cyclo compound, using for this calculation some earlier measurements on hydrocarbons at low temperature<sup>2</sup>. These are the figures:

Average volume of a CH<sub>2</sub> group in the cyclo hydrocarbon C<sub>12</sub>H<sub>24</sub> and in the  $n$ -C<sub>12</sub>H<sub>26</sub>, in 10<sup>-14</sup> c.c.

Temp. (abs.)	solid	cyclo	solid	normal
90°	23.3	23.3	23.7	23.7
290°	24.6	24.6	28.8	28.8
330°	27.6	27.6	30.0	30.0

(C<sub>12</sub>H<sub>24</sub> has a particularly high density in the whole series of cyclo compounds).

The striking fact is that the molecular volumes become identical at a low temperature; or in other words, the two substances differ only in their coefficient of thermal expansion. This is not surprising. Although the CH<sub>2</sub> groups in both series are nearly the same, there must be a difference in their mobility, since one group is part of a chain with two free ends and the other group is in a closed chain which as a whole must have a higher rigidity.

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May 27.

<sup>1</sup> *Helvet. Chim. Acta*, **16**, 155; 1933.  
<sup>2</sup> *Proc. Roy. Soc., A*, **127**, 417; 1930.