

LXXV.—*The Magnetic Rotation of Hexatriene,  $\text{CH}_2\text{:CH}\cdot\text{CH}\text{:CH}\cdot\text{CH}\text{:CH}_2$ , and its Relationship to Benzene and other Aromatic Compounds: also its Refractive Power.\**

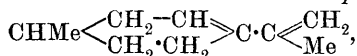
By SIR WILLIAM HENRY PERKIN.

IN a paper on magnetic rotatory power, especially of aromatic compounds (Trans., 1896, **69**, 1025), attention is repeatedly drawn to the very high rotations of aromatic compounds, and the difficulty of finding a satisfactory explanation of these abnormally high values is especially emphasised. That the values for aromatic compounds should be much higher than those of aliphatic saturated compounds was to be expected, because rotations increase for every unsaturated grouping which the substance contains, but that they should be so abnormally high as they have been found to be, admitted, at that time, of no satisfactory explanation. The examination of hexylene, diallyl, and dipropargyl showed that their magnetic rotations appeared to be about normal, and the value for each unsaturated grouping rose only slightly as the number of these groupings increased (Trans., 1895, **67**, 255 †). The two acetylene groupings in dipropargyl,  $\text{CH}\text{:C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}\text{:CH}$ , also seemed to act like four ordinary unsaturated groups, but when dipropargyl was compared with its isomeride benzene, a very striking difference in rotation was observed, the value for dipropargyl (10·435) being much lower than that of benzene (11·284). It was supposed at the time that this difference was due, in some way, to the ring formation of benzene.

\* Compare J. W. Brühl (Trans., 1907, **91**, 115, and Ber. 1907, **40**, 878).

† Griner (*Ann. Chim. Phys.*, 1892, [vi], **26**, 323, 346) has shown that diallyl and dipropargyl as ordinarily prepared are not pure products, but contain small quantities of isomeric hydrocarbons, so that the true magnetic rotations of the pure substances may be found to differ to some slight extent from those given in this paper.

That this was the chief reason became, however, very doubtful when the remarkable observation was made that  $d\text{-}\Delta^{3:8(9)}\text{-}p\text{-menthadiene}$ ,



which contains two unsaturated groupings in conjunction, yielded abnormally high numbers for the magnetic rotation (Trans., 1906, 89, 854). This result seemed to point to the possibility that the high rotations of benzene derivatives and other substances containing unsaturated groups in conjunction was, in fact, chiefly due to the presence of these groups.

In order to test this supposition, it seemed very desirable, in the first place, to examine some open chain compounds in order that the effect of association might be determined without any disturbing influence due to ring formation. Fortunately this was rendered possible by the discovery of P. van Romburgh and W. van Dorssen (*Proc. K. Akad. Wetensch., Amsterdam*, 1905, 8, 565) of *hexatriene*,  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ , which contains three contiguous unsaturated groups, and I have to thank these gentlemen for their kindness in placing about 25 c.c. of this rare substance at my disposal for the purpose of examination. Two separate determinations of the magnetic rotation of the freshly fractionated hydrocarbon were made and these gave concordant results, the average value being 12.196. This is a remarkably high number, higher indeed than that of benzene itself (11.284), from which hexatriene only differs in containing 2 atoms of hydrogen more.

The difference in the formulæ of hexatriene and benzene is simply the difference of ring formation due to the loss of two atoms of hydrogen, and is exactly the same as the difference between hexane and hexamethylene; the latter value has been determined experimentally and found to be 0.982 (Trans., 1902, 81, 295).

If we subtract this difference from hexatriene, we obtain a value for the magnetic rotation of benzene based on the assumption that benzene contains three unsaturated groupings.

Magnetic rotation of hexatriene .....	12.196
Difference for ring formation .....	0.982
<hr/>	
Calculated rotation of benzene.....	11.214

It is interesting to note that this number is practically identical with that actually found for the rotation of benzene (11.284), and this fact seems to point to two important conclusions, namely, that benzene contains three contiguous unsaturated groupings (Kekulé's formula), and secondly that these have substantially the same value as in the

case of open chain compounds. Another set of comparisons which point in the same direction is the following :

Hexatriene.....	12·196	Benzene.....	11·284
Hexane .....	6·646	Hexamethylene ..	5·664
Difference .....	5·550	Difference .....	5·620

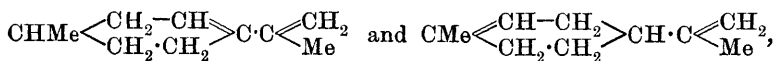
These comparisons of such widely differing substances are, moreover, interesting for another reason, namely, because the difference (5·6 approx.) gives us a reliable value for the association of three double linkings.\* In this connexion, the following comparisons of hexatriene,  $\text{CH}_2\text{:CH}\cdot\text{CH}\text{:CH}\cdot\text{CH}\text{:CH}_2$ , and diallyl,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\text{:CH}_2$ , serve to show the remarkable effect which is produced when two unsaturated groups become united by means of a third. In the formula for diallyl, there are two unsaturated groups separated by  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot$ ; in hexatriene this intermediate group is displaced by  $\cdot\text{CH}\text{:CH}\cdot$ , a displacement which, in ordinary circumstances, would cause a rise of rotation of about 0·730. The actual determinations gave, however, the following figures :

Hexatriene .....	12·196
Diallyl .....	8·420
Difference .....	3·776

and it is seen that the rise in rotation is about three whole numbers more than would have been the case had the unsaturated groupings not been associated.

In making some attempt to estimate approximately the effect of association in connexion with unsaturated groupings, the following points are worthy of consideration.

$d\text{-}\Delta^{3,8(9)}$ -*p*-Menthadiene and *d*-limonene,



both contain two unsaturated groupings, and are exactly similarly constituted, with the exception that in *d*-menthadiene the two unsaturated groupings are associated, whereas in *d*-limonene they are separated by the group  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot$ . The difference in the observed rotations of these two terpenes is 1·815, or 0·907 for each associated

\* By the value for an associated double linking is understood the number which represents the conversion of the group  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot$  into an *associated* double linking  $\cdot\text{CH}\text{:CH}\cdot$ . The actual effect due to association would be obtained by subtracting from this the value for unsaturation (that is, the value obtained when the group  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot$  is converted into an *ordinary* unsaturated group).

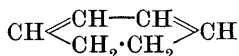
unsaturated group, as seen from the following comparison of their respective rotations :

<i>d</i> - $\Delta^{3:8(9)}$ - <i>p</i> -Menthadiene .....	13.061
<i>d</i> -Limonene .....	11.246
	<hr/>
	2)1.815
	0.907

If 0.730 (the ordinary value for unsaturation) is added to this, we obtain 1.637 as the rise in rotation due to the conversion of a group,  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot$ , into an associated double linking,  $\cdot\text{CH}:\text{CH}\cdot$ . It is interesting to note that this value is considerably less than that observed in the case of *three* associated double linkings, because, if the difference between hexatriene and hexane (namely, 5.550, see above) is divided by three, we obtain 1.85 as the value for each of the three double linkings in hexatriene.

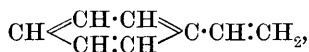
In the case of *d*- $\Delta^{3:8(9)}$ -*p*-menthadiene, we have the interesting condition that one of the associated double linkings is situated within whilst the other is outside the ring, and it is evident that in these circumstances there is a similar rise in value to that observed when both associated linkings are inside or outside a ring, although there may, of course, be some slight difference in the amount of the rise.

The only case of the association of two unsaturated groupings within the ring which has been directly measured is the case of  $\Delta^{1:3}$ -dihydrobenzene,



(Crossley, Trans., 1904, **85**, 1418), which was found to have a rotation of 8.093. If the value for hexamethylene (5.664) is deducted from this, we obtain 2.429 as the value of the two associated double linkings or 1.218 for each, and this is perhaps a rather smaller value than might have been expected. No open chain compound has, so far, been measured which contains two associated double linkings, but a substance of this type is in the course of preparation, and the determination of its magnetic rotation should yield very interesting results.

In comparing *d*- $\Delta^{3:8(9)}$ -*p*-menthadiene with hexatriene it was indicated that rotation rises in a remarkable manner as the number of associated double linkings in the molecule increases, and that this rise quickly becomes enormous may be shown from the following considerations. Styrene,



is benzene to which an associated double linking has been added, and the effect of this addition may be estimated as follows.

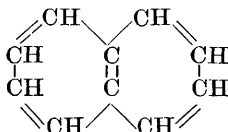
When styrene is compared with ethylbenzene, it is clear that the former is derived from the latter by the conversion of the group  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot$  into the associated double linking  $\cdot\text{CH}:\text{CH}_2\cdot$ .

If, then, we deduct the rotation of ethylbenzene (13·382) from that of styrene (16·041) we obtain the high figure 2·659 as the result of this change. This number does not, of course, represent the value of the additional associated double linking; it is obviously the increase in value of the three double linkings contained in benzene by association with a fourth. It has already been pointed out that the three associated double linkings in benzene have a value of 5·620 or 1·87 for each, and therefore the value of the four associated double linkings in styrene may be calculated as 8·279 (5·620 + 2·659) or 2·07 for each. Clearly then there has been a considerable rise in the value for each associated linking in passing from a compound containing three to one containing four such linkings. If the molecule contains still more associated double linkings, the rise in rotation increases enormously with the number of such linkings and, in this connexion, the case of stilbene,



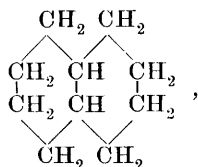
which contains seven associated double linkings, is worthy of special attention. The rotation of stilbene is 33·143, and if from this we deduct the rotation of dibenzyl, 24·997, we obtain 8·146 as the result of introducing the seventh associated double linking. The total rise in rotation due to the seven double linkings is therefore 19·386 (8·146 + 11·240 from two benzene rings) or about 2·77 for each.

Another interesting case is that of naphthalene, the enormous rotation of which is probably of a similar kind to that suggested in considering the other cases mentioned above. If naphthalene is represented by the formula



it contains five associated double linkings, and is derived from benzene by the addition of two such linkings. The rotation of naphthalene is 25·125, and if the value of benzene,  $-2\text{H}$ , 10·776, is deducted from this we obtain the enormous value 14·349 for the introduction of the grouping  $\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}\cdot$ . The actual value of each of the five associated double linkings in naphthalene may be roughly calculated thus. The rotation of hexamethylene is 5·664 and two-thirds of this, or 3·776, represents the value of  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot$  in the ring.

The value for decahydronaphthalene,



calculated on this basis is therefore

Hexamethylene - 2H .....	5.156
$\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2$ .....	3.776
Decahydronaphthalene.....	8.932

If this is deducted from the rotation of naphthalene (25.125) we obtain 16.193 as the value for five associated double linkings or 3.24 for each of these. One of the most interesting examples of the rise due to association is brought to light when a comparison is made between the rotations of benzene and diphenyl. Diphenyl is produced when 2 molecules of benzene unite with the loss of 2 atoms of hydrogen. The rotation of diphenyl is 25.304, and if from this we deduct the value of 2 molecules of benzene less 2 atoms of hydrogen, 22.060, we have a rise of rotation of 3.244, which can only be due to the association of the two sets of three double linkings which is brought about when the two phenyl groups combine.

In other words, the value of each of the three double linkings in benzene has risen from 1.87 to 2.41 in diphenyl simply as the result of causing the two sets of three to combine and become six.

Leaving out the case of naphthalene, which is not quite comparable, the above deductions may be conveniently summarised and we then obtain a clear representation of the remarkable fact that rise of rotation due to association increases more or less uniformly with the number of associated linkings contained in the molecule.

In dihydrobenzene, *two* associated double linkings have a value of 1.22 each; in benzene, *three* have the value of 1.87 each; in styrene, *four* have the value of 2.07 each; in diphenyl *six* have the value of 2.61 each, and in stilbene, *seven* have the value of 2.77 each.

In my paper on "The Magnetic Rotatory Power of Aromatic Compounds" (Trans., 1896, 69, 1161) attention was repeatedly called to the "screening" effect which is observed when a group enters the molecule in such a way as to prevent double linkings from becoming associated. The value of  $\text{C}_6\text{H}_5\cdot$  in benzene is 11.03; when two of these groups are united, in diphenylmethane, by a  $\cdot\text{CH}_2\cdot$  group, the value of each,  $\text{C}_6\text{H}_5\cdot$  rises to 11.411.

When, however, the intervening  $\cdot\text{CH}_2\cdot$  in diphenylmethane is

removed, so that the two phenyl groups come into direct union, the influence of each  $C_6H_5\cdot$  group rises to 12.657.

It seems therefore that when the associated double linkings are screened by  $\cdot CH_2\cdot$ , they still exert a certain although comparatively slight influence on the rotation of the molecule. When the screening group contains oxygen, the effect is still more marked, as is evident from the consideration of the two following cases. In allyl benzoate,  $CH_2:CH\cdot CH_2\cdot CO_2\cdot C_6H_5$ , the screening effect of the group  $\cdot CH_2\cdot CO_2\cdot$  is so pronounced that the group  $CH_2:CH\cdot$  is scarcely influenced by the presence of the phenyl group and has an almost normal value, and again in the case of phenyl allyl ether,  $C_6H_5\cdot O\cdot CH_2\cdot CH:CH_2$ , the group  $\cdot O\cdot CH_2\cdot$  greatly minimises the effect of the phenyl group on the unsaturated grouping  $\cdot CH:CH_2\cdot$  (Trans., 1896, 69, 1141).

Attention had previously been called (Trans., 1896, 69, 1095, 1098, 1162) to the very remarkable difference which had been observed in the influence of the  $\cdot NO_2$ ,  $NH_2$ , and  $\cdot NMe_2$  groups, when introduced into the benzene nucleus. The  $NO_2$  group, in which nitrogen is quinquivalent, causes a diminution in the rotation of benzene, whereas the  $NH_2$  and  $NMe_2$  groups with trivalent nitrogen raise the rotation to an extraordinary extent, as the following comparisons show :

	Mag. rot.		Mag. rot.
Nitrobenzene .....	9.361	Aniline..... ..	16.076
Benzene .....	11.284	Benzene .....	11.284
Difference .....	- 1.923	Difference.....	+ 4.792

The cases of dimethylaniline (22.888) and dimethyl- $\beta$ -naphthylamine (47.377) are even more remarkable, because in the first instance the introduction of the  $\cdot NMe_2$  group into benzene raises the rotation by 11.604, and in the second that of naphthalene by 22.252, whereas this group, in the aliphatic series, has only a very small rotation, as is shown by the fact that the rotation of ethylamine (dimethylamine has not been measured) is only 3.609. It seems probable that the large effect produced by the introduction of the  $NH_2$  and  $NMe_2$  groups is due, as in the case of the introduction of the  $\cdot CH:CH_2\cdot$  group (p. 810), in part at least, to the association of the unsaturated groups with the associated double linkings of the nucleus. This view is borne out by the observation that the hydrochlorides of aniline and dimethylaniline in which the nitrogen atoms have become saturated have in the case of aniline a rotation very little higher than that of this base, and in dimethylaniline a considerably lower rotation (aniline 16.076 aniline hydrochloride = 16.394; dimethylaniline 22.888, dimethylaniline hydrochloride = 18.326). When therefore the value of hydrogen chloride (2.245) is taken into account, it is seen that the addition with consequent saturation of the nitrogen atom has produced a remarkable

lowering in the rotation. It is worth noting that the introduction of a second  $\text{NO}_2$ ,  $\text{NH}_2$ , or  $\text{NMe}_2$  group does not act like the first. In the case of the second  $\text{NO}_2$  group there is no longer a reduction, but a slight rise in the rotation, and in the case of the second  $\text{NH}_2$  and  $\text{NMe}_2$  groups the rise is much smaller than in the case of the first introduction.

*Comparison of the Refractive Power of Hexatriene with that of Benzene.*

The careful examination of freshly distilled hexatriene,  $\text{C}_6\text{H}_8$ , has shown that the refraction, and especially the dispersion, of this substance are both considerably higher than the calculated.

$$\text{Refraction } \frac{\mu_a - 1}{d} p.$$

$$51\cdot650$$

$$\text{Dispersion } H_\gamma - H_\alpha.$$

$$4\cdot472$$

The calculated refractive power of a substance,  $\text{C}_6\text{H}_8$ , containing three double linkings is 47·300, or 4·350 less than was actually found, and it is remarkable that the dispersion of benzene, containing 2 atoms of hydrogen less, is only 2·426, or not much more than half that of hexatriene.

The comparison of the above values for hexatriene with those of benzene show that the differences do not run parallel with the magnetic rotation results. As stated on p. 808, the differences in rotation between hexatriene and hexane (5·550) and between hexamethylene and benzene (5·620) are practically the same. But when a similar comparison of the refractive powers is made an entirely different result is obtained.

	$H_\alpha$ .		$H_\alpha$ .
Hexatriene.....	51·650	Benzene .....	44·087
Hexane .....	48·630	Hexamethylene ...	45·824
Difference .....	+ 3·020		- 1·737

It is very difficult to account for these striking differences, but it may be stated generally that, although there is often a similarity between refractive powers and magnetic rotations, many cases have been observed in which very little relationship seems to exist between the two sets of values. Thus, for example, the magnetic rotation of benzene is *much larger* than that calculated on the assumption that it is a compound,  $\text{C}_6\text{H}_6$ , containing three double linkings of the *ordinary value*, whereas the refractive power is *actually less* than that calculated on the same basis. Similar peculiarities have been observed in



a number of other cases, and these tend to show that magnetic rotation not infrequently detects differences which the determination of the refractive power fails to reveal.

#### EXPERIMENTAL.

The specimen of hexatriene (about 25 c.c.) was received in a sealed glass flask. When opened, it was found that a few drops of the substance, when placed on bibulous paper, did not entirely evaporate, but left an oily stain; it had therefore apparently polymerised to some extent, as its original boiling point was  $79.5-81^{\circ}$ . On distillation, most of it passed over between  $77^{\circ}$  and  $80^{\circ}$ , chiefly  $78-80^{\circ}$ . The temperature was then allowed to rise to  $95^{\circ}$ , when the distillation almost ceased, about 3 c.c. of a viscid oily product being left behind. The fraction  $77-80^{\circ}$  was examined as to its density, magnetic rotation, and refractive power. Seventeen days later this product was re-fractionated; it then passed over mostly between  $77.5^{\circ}$  and  $79^{\circ}$ , only a small amount of polymerised product being left behind. This fraction was also examined, and was found to have practically the same density, magnetic rotation, and refractive power as the previous product. On keeping this for several weeks it underwent scarcely any change, only a minute quantity of polymerised product being formed. It almost appears as though the original product contained two isomeric hydrocarbons, one polymerising quickly and the other slowly, the specimen I examined consisting of the latter, but as very small changes of conditions often greatly influence the rate of polymerisation, this is a point that cannot be decided without further experiment. Strong sulphuric acid causes polymerisation to take place instantly with formation of a solid substance. It was also found that if hexatriene is placed in a tube full of oxygen over mercury it undergoes oxidation, the volume of gas soon becoming greatly reduced.

The following results are the averages obtained from the examination of the two fractions above referred to, obtained after different intervals of time:

Av. b. p.  $77.7-79^{\circ}$ .

Density:  $d_{4^{\circ}/4^{\circ}}$ , 0.75190;  $d_{15^{\circ}/15^{\circ}}$ , 0.74229;  $d_{25^{\circ}/25^{\circ}}$ , 0.73444.

Magnetic rotation:

<i>t.</i>	Sp. rot.	Mol. rot.
$13.75^{\circ}$	2.0402	12.196

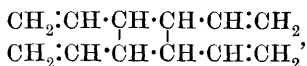
*Refractive power :*

$$d_{16\cdot2^\circ/4^\circ} = 0\cdot74067$$

	$\mu_{16\cdot2^\circ}$	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d} p$
$\text{H}_\alpha$	1·47819	0·64562	51·650
$\text{H}_\beta$	1·50272	0·67878	54·302
$\text{H}_\gamma$	1·51958	0·70155	56·124

$$\text{Disp. } \text{H}_\gamma - \text{H}_\alpha = 4\cdot472.$$

It was thought that it would be interesting to determine the magnetic rotation and refraction values of the crude polymerised product left from the distillation of hexatriene, because if it were formed from the hydrocarbon with the production of



this substance would contain no associated double linkings and would therefore give very much lower values than two molecules of hexatriene itself. The following results were obtained :

*Polymerised hexatriene distilling above 95°.**Density :*  $d_{15^\circ/15^\circ} 0\cdot88494$  ;  $d_{25^\circ/25^\circ} 0\cdot87920$ .*Magnetic rotation :*

$t$	Sp. Rot.	Mol. Rot.	
		For $\text{C}_6\text{H}_8$ .	For $(\text{C}_6\text{H}_8)_2$ .
14°	1·7605	8·836	17·673

*Refractive power :*

$$d_{16\cdot75^\circ/4^\circ} = 0\cdot88295$$

	$\mu_{16\cdot75^\circ}$	$\frac{-1}{d}$	$\frac{\mu-1}{d} p$	
			For $\text{C}_6\text{H}_8$ .	For $(\text{C}_6\text{H}_8)_2$ .
$\text{H}_\alpha$ .....	1·51569	0·58406	46·725	93·450
$\text{H}_\beta$ .....	1·53348	0·60421	48·337	96·674
$\text{H}_\gamma$ .....	1·54481	0·61703	49·362	98·724

The following are the results obtained compared with those of hexatriene :

*Magnetic rotation :*

Rot. of 2 mols. of Hexatriene	...	...	24·380
” ” polymerised product	}	...	17·672
taken as $(\text{C}_6\text{H}_8)_2$			
Reduction due to polymerisation	...		6·708

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*Refractive power :*

H <sub>α</sub> 2 mols. of Hexatriene	...	...	...	103·300
” polymerised product	}	...	...	93·449
taken as (C <sub>6</sub> H <sub>8</sub> ) <sub>2</sub>				
Reduction due to polymerisation			...	9·851

The magnetic rotation of a polymeride of the above constitution should be about equivalent to that of 2 molecules of diallyl less 4H, thus :

Rot. of 2 mols. diallyl	(8·420 × 2) = 16·840
less 4H	1·016
	15·824

Considering the product still contained traces of hexatriene which would raise its rotation (which is about 1·85 too high), it would appear not unlikely that polymerisation takes place in the direction indicated above.