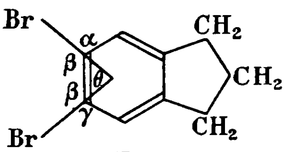
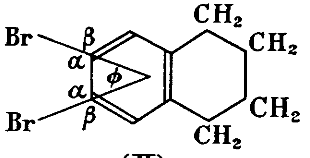
336. *Dipole Moments and the Fixation of Aromatic Double Links: Bromohydrindenes and Bromotetralins.*

By Nevil V. Sidgwick and Harold D. Springall.

Mills and Nixon (J., 1930, 2510) pointed out that if benzene consists of a system of alternate single and double links, then the external valencies will not be directed towards the centre of the hexagon; and hence the side ring in hydrindene (I) will be less strained if the link common to the two rings is single, while in tetralin (II) there will be less strain if the common link is double. They further showed that the chemical reactivity of certain hydroxy- and acetamido-hydrindenes and -tetralins, in bromination and in coupling with diazo-compounds, was in accordance with the fixation of the double links in these positions.



(I)



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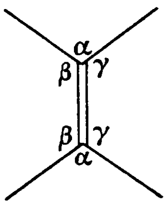

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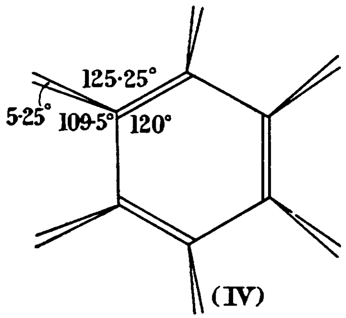

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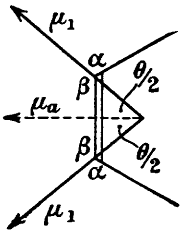

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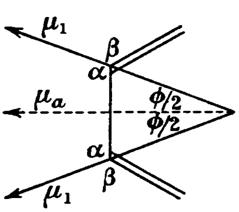


(VI)

It seemed possible to obtain evidence for or against this view by measuring the dipole moments of 5 : 6-*dibromohydrindene* (I) and 6 : 7-*dibromotetralin* (II); this we have done, and the results obtained agree with the assumption that there is fixation of the double links in hydrindene but not in tetralin. On the Mills–Nixon hypothesis the angles between the C—Br valencies in these two compounds (I) and (II) should differ, and hence the moments of the systems should also differ, by an amount which can be calculated within narrow limits, and which should be easily detected experimentally. On the van 't Hoff model the spatial arrangement of the free bonds in the system $>C{=}C<$ is planar, with the angles (see III) $\beta = \gamma = 125{\cdot}25°$, and $\alpha = 109{\cdot}5°$. When γ is the angle of the aromatic ring it is reduced to 120°, so that $\alpha + \beta$ is increased by 5·25°. We do not know how this increase is distributed between α and β, but the extreme limits are (*a*) when it all goes to α, and (*b*) when it all goes to β. On hypothesis (*a*) we get $\alpha = 114{\cdot}75°$ and $\beta = 125{\cdot}25°$, and on hypothesis (*b*) $\alpha = 109{\cdot}5°$ and $\beta = 130{\cdot}5°$. The diagram (IV) shows the possible limits. (Since the opposite sides of the hexagon must be parallel, the fact that the double links are some 10% shorter than the single will not affect the conclusion.)

The angle θ between the two ortho-linkages separated by a double C=C link is equal to $2\beta - 180°$ and hence is 70·5° on hypothesis (*a*), and 81° on (*b*): while the angle ϕ, where the C—C link is single, is $2\alpha - 180°$, and so ranges from 49·5° for (*a*) to 39·0° for (*b*). The dipole moment of the *o*-dibromo-system is given by

$$\mu_a = 2\mu_1 \cos\psi/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where μ_1 is the moment of the C—Br link in the compound, and ψ is the angle between the valencies.

The moment of bromobenzene is 1·52 D (Tiganik, *Z. physikal. Chem.*, 1931, *B*, **13**, 425). In all ortho-dihalogen-substituted benzenes it is found that (presumably owing to mutual polarisation) the observed moment is about 20% less than that calculated on the simple vector model with all the valency angles 120°. Thus the moment of *o*-dibromobenzene is 2·12 D (see below) while the calculated value is 2·63. Hence the value to be taken for μ_1 is $1{\cdot}52 \times 0{\cdot}8 = 1{\cdot}22$ D. With this value for μ_1, equation (1) gives as the moment of the Br–C–C–Br group in the dibromo-hydrindene derivative the limits (*a*) 1·99 to (*b*) 1·84, and for the tetralin derivative (*a*) 2·21 to (*b*) 2·30 D, a difference of from 0·22 to 0·46. The total moment of each of these compounds is the sum of that of the parent hydrocarbon and that of the Br–C–C–Br group, together with the moment due to the induced polarisation of the side-ring system by the moment of the Br–C–C–Br system. Hence the moments of these parent hydrocarbons were measured, and further, those of their monobromo-derivatives, and also those of 4-bromo- and 4 : 5-dibromo-*o*-xylene (that of *o*-xylene is already known). These values should indicate whether any abnormal variation occurs in these ring-systems, which might destroy the force of the argument from the difference of the moments.

The values of the induced polarisation are calculated by the methods of Smallwood and Herzfeld (*J. Amer. Chem. Soc.*, 1930, **52**, 1919) and Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171) as elaborated by Hampson and Weissberger (this vol., p. 393); in this last paper the method as applied to the chlorinated naphthalenes gives results in good agreement with experiment.

The moment set up through the polarisation induced in a polarisable medium by a permanent dipole μ, may be resolved into two components, one $\acute{\mu}_x$, along the line of the inducing dipole; and the other, $\acute{\mu}_y$, perpendicular to this line.

$$\acute{\mu}_x = \frac{\varepsilon + 2}{3}\alpha\frac{3\cos^2\theta - 1}{\varepsilon r^3}\mu, \qquad \acute{\mu}_y = \frac{\varepsilon + 2}{3}\alpha\frac{3\sin\theta\cos\theta}{\varepsilon r^3}\mu$$

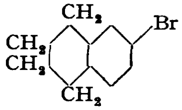
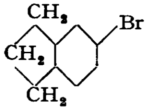
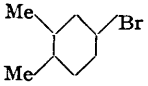
ε is the dielectric constant of the polarisable medium, *i.e.*, the side system; the value taken for the tri- and tetra-methylene group is 2·016, the observed value for *cyclo*hexane : for the dimethyl group in *o*-xylene, a value of 2·00 is used.

α is the polarisability of the side system in the plane of the ring, assumed equal along the x and y axes. This is calculated for the tri- and tetra-methylene side-ring groups from the electron polarisation and depolarisation data for *cyclo*hexane (Hampson and Weissberger, *loc. cit.*). For each of the methyl groups of *o*-xylene, spherical symmetry is assumed.

r, the distance of the dipole from the centre of polarisation, and θ, the inclination of r to the dipole axis, are both taken from geometrical models. The distances used were

$C_{al.}$—$C_{al.}$, 1·54 A.; $C_{arom.}$—$C_{arom.}$, 1·42 A.; radius of Br atom 1·13 A. The reduced ring in tetralin was treated as planar, since this introduces no sensible error.

TABLE I.

Type.	Inducing moment.	r, A.	θ.	α, c.c. × 10^{-23}	ϵ.	μ_x.	μ_y.
	1·52	5·1	19°	0·7988	2·016	0·10	0·05
	1·52	4·85	18	0·6013	2·016	0·09	0·05
	1·52	4·44	17	0·2294	2·00	0·07	0·04

The results of the induced moments in the side-systems of the dibromo-derivatives are obtained by compounding the separate moments induced by the two separate C—Br linkages, and correcting for the 20% deficit in the actual compared with the theoretical inducing moment. Owing to the symmetry of the systems there is no component of induced moment perpendicular to the line of the inducing moment. The induced moments are 0·18 D for 6 : 7-dibromotetralin, 0·17 for 5 : 6-dibromohydrindene and 0·14 for 4 : 5-dibromo-*o*-xylene.

The results of applying this method of correction to the monobromo-derivatives are given in Table II, in which the moments observed for these compounds are compared with those calculated from the observed moments for the parent hydrocarbons; the inducing moment, 1·52 D (the value of μ for C—Br in bromobenzene); and the induced moments.

TABLE II.

Monobromo-derivatives.

Type.	Moment of parent hydrocarbon.	Induced moment. μ_x.	μ_y.	Total resultant moment. Calc.	Obs.
Tetralin	0·52	0·10	0·05	2·12	2·23
Hydrindene	0·53	0·09	0·05	2·08	2·15
o-Xylene	0·59 *	0·07	0·04	2·10	2·07

* Tiganik, *Z. physikal. Chem.*, 1931, *B*, **13**, 425.

The agreement between the last two columns shows the accuracy of the method of correction adopted, and also indicates that there is nothing abnormal in the behaviour of the hydrindene compound.

In Table III are given the results for the dibromo-derivatives. For the Br–C–C–Br system the " observed " moment is that of the dibromide minus the sum of that of the parent hydrocarbon and the induced moment; the " calculated " values are those derived from the Mills–Nixon theory for fixation of the double links, on the limiting hypotheses for the valency angles described above. If there is no fixation, the moment of the Br–C–C–Br system should be 2·12 D throughout.

TABLE III.

Type.	Moment of hydrocarbon.	Moment of dibromide.	Induced moment.	Moment of Br–C–C–Br. Obs.	Calculated. (*a*).	(*b*).
Hydrindene	0·53	2·48	0·17	1·78	1·99	1·84
Tetralin	0·52	2·81	0·18	2·11	2·21	2·30
o-Xylene	0·59	2·86	0·14	2·13	No fixation	
Benzene	0	2·12	0	2·12	No fixation	

It will be seen that the moments of the Br–C–C–Br system in the dibromotetralin and the dibromo-*o*-xylene are the same and are equal to that found for *o*-dibromobenzene; on the other hand, in the dibromohydrindene the moment is 0·34 D lower than the mean value of 2·12 D found in the above compounds, and is only 0·06 D lower than the lower limit calculated on the Mills–Nixon hypothesis.

The suggestion that the strain in the 5-membered ring may cause an abnormal value of the electron polarisation, or refractive power, is negatived by the observation that the increase in this in going from the 5- to the 6-ring (due to the extra CH_2) has very nearly the theoretical value of 4·71 c.c. (for the H_γ line at 20°), being 4·24 for the parent hydrocarbons, 4·32 for the monobromo-derivatives, and 5·02 for the dibromo-derivatives (for the Hg green line at 25°).

To bring the moment of dibromohydrindene up to the value (2·81 D) of the tetralin compound, we should have to assume that the electronic and atomic polarisations together only amounted to 19·4 c.c., whereas the refractivity gives for the electronic polarisation the value of 52·4 c.c., in close agreement with the theoretical value.

The suggestion is further negatived by the smallness of the difference between the moments of the parent hydrocarbons, and the agreement between calculation and observation in Table II.

Thus the observed moment of the dibromohydrindene agrees very closely with that required by the Mills–Nixon theory, and there are no indications that this can be due to any other cause than an increase in the valency angles of the Br–C–C–Br system. The whole problem of the fixation of links in aromatic systems is so complicated * that we do not wish to do more than offer a contribution to the evidence on the subject. It should be noticed that evidence from dipole moments is of a different kind from that derived from reactivity, such as was given by Mills and Nixon. In the latter, a relatively small difference in the heat of activation between two molecules may produce a large change in the rate of reaction, as was pointed out by Sutton and Pauling (*Trans. Faraday Soc.*, 1935, **31**, 939), who concluded that a difference of 6% in the ratio of the coefficients (*i.e.*, in the predominance) of the two Kekulé forms was enough to account for the experimental results of Mills and Nixon. The moments, on the other hand, express the mean positions of the atoms in the resting molecule, and our results certainly seem to indicate that the difference found is exactly what is required for the fixation of the links in hydrindene, and free resonance in tetralin and *o*-xylene.

EXPERIMENTAL.

The dipole moments were determined in benzene solution at 25° by the refractivity method, using the heterodyne apparatus for the measurement of dielectric constant as described by Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668), Hampson, Farmer, and Sutton (*ibid.*, 1933, *A*, **143**, 147), Jenkins (J., 1934, 481), and Jenkins and Sutton (J., 1935, 609).

The published values of the moment of *o*-dibromobenzene (see *Trans. Faraday Soc.*, 1934, **30**, Appendix) do not wholly agree; this was therefore redetermined; the value we obtained (2·12 D) agrees with that of Tiganik (*loc. cit.*).

Preparation of Materials.—The bromohydrindenes were made by acetylating hydrindene in the 5-position, converting the product into its oxime, and then through the Beckmann transformation into the acetamido-compound: this by hydrolysis and the Sandmeyer reaction gives the 5-bromo-derivative. The acetamido-compound is also converted into its 6-bromo-derivative and so into 5 : 6-dibromohydrindene. The bromotetralins were made in a similar way; 6-acetamidotetralin was (1) converted into 6-bromotetralin, and (2) nitrated in the 7-position, the acetamido-group replaced by bromine, and the nitro- reduced to the amino-group, and this replaced by bromine.

Benzene. Hopkin and Williams's thiophen-free material was frozen out four times, refluxed over phosphorus pentoxide, and distilled in a current of dry air into a receiver from which it could be pumped for immediate use.

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* See, for example, the crystal structure of cyanuric triazide (Knaggs, *Proc. Roy. Soc.*, 1935, **150**, 576) and of *p*-dinitrobenzene (James, King, and Horrocks, *ibid.*, 1935, **153**, 225). Cf. *Ann. Reports*, 1935, **32**, 232.

Hydrindene.

f_2.	d_s.	ϵ.	n^2.	P_2.	${}_eP_2$.
0·037161	0·87652	2·29725	2·26315	48·50	41·416
0·025791	0·87570	2·28959	2·26120	47·23	41·139
0·020657	0·87510	2·28599	2·26043	47·30	40·861
0·012468	0·87439	2·28072	2·25924	47·00	41·230

${}_\infty P_0 = 5·6$ c.c. $\mu = 0·53$ D.

Tetralin.

0·036909	0·8773	2·30105	2·26309	54·73	45·82
0·028928	0·8765	2·29556	2·26182	53·85	44·98
0·021790	0·8757	2·28863	2·26061	53·10	45·53
0·015267	0·8752	2·28404	2·25961	51·01	45·38

${}_\infty P_0 = 5·2$ c.c. $\mu = 0·52$ D.

4-*Bromo*-o-*xylene.*

0·041656	0·9024	2·50831	2·26645	122·23	44·17
0·024671	0·8913	2·41802	2·26516	125·91	45·91
0·022601	0·8898	2·40631	2·26200	126·42	44·36
0·010568	0·8812	2·33564	2·25969	128·22	45·42

${}_\infty P_0 = 88·6$ c.c. $\mu = 2·07$ D.

7-*Bromotetralin.*

0·021244	0·89123	2·42537	2·26505	149·72	51·88
0·014170	0·88546	2·37850	2·26197	151·505	51·62
0·013946	0·88541	2·37431	2·26117	152·467	50·46
0·0092396	0·88144	2·34092	2·26001	153·598	49·98

${}_0P_2 = 105·4$ c.c. $\mu = 2·23$ D.

6-*Bromohydrindene.*

0·038226	0·90468	2·52725	2·26962	136·16	46·63
0·021038	0·89095	2·41145	2·26746	136·65	46·18
0·010581	0·88264	2·34349	2·26055	138·45	46·48
0·010594	0·88255	2·34596	2·26056	138·48	46·48

${}_0P_2 = 94·42$ c.c. $\mu = 2·15$ D.

o-*Dibromobenzene.*

0·029588	0·9166	2·4756	2·26661	132·78	40·37
0·019587	0·90225	2·4063	2·26639	133·32	42·59
0·022354	0·9060	2·4250	2·26613	133·25	41·86
0·018459	0·9006	2·3987	2·26095	133·54	40·99

${}_\infty P_0 = 93·6$ c.c. $\mu = 2·12$ D.

4 : 5-*Dibromo*-o-*xylene.*

0·025135	0·91019	2·5704	2·26808	210·43	51·45
0·017519	0·89936	2·4806	2·26547	211·86	50·93
0·014315	0·89454	2·4441	2·26386	216·15	51·06
0·011364	0·89031	2·4087	2·26197	216·94	50·53

${}_\infty P_0 = 170·56$ c.c. $\mu = 2·86$ D.

5 : 6-*Dibromohydrindene.*

0·024062	0·9122	2·50024	2·27042	178·2	52·55
0·020451	0·9066	2·46612	2·26850	179·2	52·57
0·016012	0·8992	2·24241	2·26590	179·8	52·44
0·010365	0·8901	2·37012	2·26293	180·9	53·70

${}_\infty P_0 = 130·0$ c.c. $\mu = 2·48$ D.

6 : 7-*Dibromotetralin.*

0·031198	0·9261	2·6501	2·2806	213·6	57·34
0·02559	0·9164	2·5823	2·2763	216·0	57·78
0·02003	0·9077	2·5144	2·2721	216·6	57·04
0·01040	0·8916	2·3971	2·26505	218·5	56·69

${}_\infty P_0 = 163·1$ c.c. $\mu = 2·81$ D.

Hydrindene. Pure indene is reduced in dry methyl-alcoholic solution, in the presence of palladised strontium carbonate under a pressure of 45 lb. per sq. inch of hydrogen. The hydrindene is distilled at 73° under 13 mm.; b. p. 177°/760 mm. Perkin (J., 1896, **69**, 1249) gives 177°.

Tetralin. Technical tetralin is dried over calcium chloride and distilled. The fraction, b. p. 91°/17 mm., is used; von Auwers (*Ber.*, 1913, **46**, 2990) gives b. p. 90·8—91·2°/17 mm.

4-*Bromo*-o-*xylene.* This is prepared by the direct bromination of *o*-xylene (Jacobsen, *Ber.*, 1884, **17**, 2372). It distils (a colourless oil) at 92°/12 mm. and at 215°/760 mm. (Jacobsen gives b. p. 214°).

5-*Bromohydrindene.* 5-Acetamidohydrindene is prepared by the method of Borsche and Bodenstein (*Ber.*, 1926, **59**, 1912); m. p. 108° (Borsche gives m. p. 108°). This is hydrolysed to the amine and subjected to the Sandmeyer reaction with cuprous bromide in a manner analogous to that given for the conversion of *p*-toluidine into *p*-bromotoluene (" Organic Syntheses," New York, 1923, **5**, 21). The 5-bromohydrindene distils (a colourless oil) at 107°/11·5 mm. (Borsche and Bodenstein give b. p. 113—114°/16 mm.).

6-*Bromotetralin.* 6-Acetamidotetralin is prepared by the method of Scharwin (*Ber.*, 1902, **35**, 2513), but using a mixture of acetic acid and acetic anhydride saturated with hydrogen chloride as the medium for the Beckmann oxime rearrangement; m. p. 106—107° (Scharwin gives m. p. 107°). This is hydrolysed to the amine and subjected to the Sandmeyer reaction as with 5-bromohydrindene. The 6-bromotetralin distils (a colourless oil) at 121·5°/10 mm. and at 239°/760 mm. (Smith, J., 1904, **85**, 729, gives b. p. 238°).

4 : 5-*Dibromo*-o-*xylene.* This is prepared by the direct bromination of 4-bromo-*o*-xylene, m. p. 88° (Jacobsen, *Ber.*, 1884, **17**, 2376, gives m. p. 88°).

5 : 6-*Dibromohydrindene.* 6-Bromo-5-aminohydrindene is prepared by the method of Borsche and Bodenstein (*loc. cit.*); m. p. 41—42° (Borsche and Bodenstein give m. p. 42°). This is subjected to the Sandmeyer reaction with cuprous bromide (as above). The 5 : 6-*dibromohydrindene* is distilled at 142—144°/10 mm., and solidifies in the receiver. It is recrystallised from ethyl alcohol at 0°; colourless plates, m. p. 76—77° (Found : Br, 58·12. $C_9H_8Br_2$ requires Br, 57·96%).

6 : 7-*Dibromotetralin.* 6-Acetamidotetralin is prepared as above. From this, 7-nitro-6-aminotetralin is prepared by the method of Schröter (*Annalen*, 1921, **426**, 66); m. p. 125° (Schröter gives m. p. 124·5—126°). The separation of 7-nitro-6-acetamidotetralin from the simultaneously formed 5-nitro-compound is very laborious. It was found desirable to rub the tarry product obtained from the nitration of 6-acetamidotetralin with small quantities of alcohol to remove some of the tar, before proceeding to recrystallisation from alcohol. From this, according to Veselý and Chudožilov (*Bull. Soc. chim.*, 1925, **37**, 1440), 6-bromo-7-nitrotetralin is prepared; m. p. 50° (Veselý gives m. p. 50—51°). This is reduced to 6-bromo-7-aminotetralin, by stannous chloride and hydrochloric acid, and the bromoamine is subjected to the Sandmeyer reaction with cuprous bromide (as above). The 6 : 7-*dibromotetralin* distils at 164°/10 mm., and solidifies in the receiver. It is recrystallised from ethyl alcohol at 0°. Pale yellow plates, m. p. 54—55° (Found : Br, 55·23. $C_{10}H_{10}Br_2$ requires Br, 55·18%).

o-*Dibromobenzene.* This is prepared from *o*-bromoaniline (m. p. 31°; Hübner and Alsberg, *Annalen*, 1870, **156**, 317, give m. p. 31°) by the Sandmeyer reaction with cuprous bromide. It distils, a colourless oil, at 96°/11 mm. (Holleman, *Rec. trav. chim.*, 1906, **25**, 191, gives b. p. 104°/15 mm.).

We wish to express our gratitude to Prof. R. Robinson for suggesting the methods of synthesis adopted, and for his help in carrying them out. We are indebted to Dr. G. C. Hampson for his assistance in the calculation of dipole induction.

We are also grateful to Imperial Chemical Industries for a grant towards the cost of the work, and one of us (H. D. S.) to Magdalen College for a Senior demyship and to the Department of Scientific and Industrial Research for a grant.

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