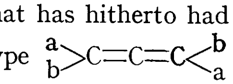
228. *Dipole Moment and Molecular Structure. Part XV. The Spatial Configuration of the Allene System.*

By Ernst Bergmann and G. C. Hampson.

Amongst the conclusions of the classical theory of the tetrahedral carbon atom, there is one that has hitherto had no experimental verification, *viz.*, that an allene derivative of the type  $^{a}_{b}{>}C{=}C{=}C{<}^{b}_{a}$ should be resolvable into optical enantiomerides owing to the fact that the geometrical distribution of the valencies should cause the two pairs of substituents to lie in two different planes perpendicular to each other.

For the combination of one double bond with a planar ring system, van 't Hoff's conclusion has been confirmed experimentally by many workers (*e.g.*, Perkin, Pope, and Wallach, *Annalen*, 1909, **371**, 180; J., 1909, **95**, 1789; 1911, **99**, 1510; Mills and Bain, J., 1910, **97**, 1866; 1914, **105**, 64; Mills and Schindler, J., 1923, **123**, 312; Mills and Saunders, J., 1931, 537; for theoretical treatment, see Dunkel, *Z. physikal. Chem.*, 1930, *B*, **10**, 450), but failure to realise enantiomorphism of the type under discussion has been reported, *e.g.*, by Hurd and Webb (*J. Amer. Chem. Soc.*, 1927, **49**, 546), Ziegler and Sauermilch (*Ber.*, 1930, **63**, 1851), and Faltis, Pirsch, and Berman (*Ber.*, 1927, **60**, 1621; 1930, **63**, 691). The last authors, in view of the failure of all these efforts, suggested that, contrary to van 't Hoff's theory, one should consider the allene system as a simple planar system of the ethylene type, affording, therefore, not enantiomorphic forms of the above derivatives, but geometrical isomerides, since all the four substituents were assumed to lie in one plane.

In spite of the fact that Faltis, Pirsch, and Berman's experimental data have been proved incorrect by Ingold and Shoppee (J., 1930, 1619), we thought it desirable to obtain more exact experimental evidence about the spatial arrangement of the allene system. In favour of Faltis's view one could argue that in the Raman spectrum of the allene system (Bourguel and Piaux, *Compt. rend.*, 1931, **193**, 1333) the characteristic lines of ordinary double bonds could not be observed; but, as Cabannes and Rousset (*ibid.*, 1932, **194**, 706) pointed out, that effect would be expected on theoretical grounds, and moreover, investigation of allene by means of the method of electron diffraction (Wierl, *Ann. Physik*, 1932, **13**, 460) has shown that the distance between the doubly-bound carbon atoms in the molecule is the normal ethylenic one.

The problem could be solved by measurements of dipole moments, for it is clear that in $\alpha\gamma$-di-(*p*-bromophenyl)-$\alpha\gamma$-diphenylallene (III), the moment of which is due entirely to that of the phenyl–bromine link (see below), that moment depends upon whether the phenyl–bromine valencies lie (*a*) in two mutually perpendicular planes (classical model) or in one plane (*b*) in the same or (*c*) in opposite directions. In the first case, suppose the planes are inclined at an angle ϕ to one another (ϕ on the classical model is 90°). In order to derive an expression for the dipole moment of the substituted molecule, we must assume that the allene system itself does not contribute to the dipole moment. In support of this, tetraphenylallene (I) has zero dipole moment and *p*-chlorotetraphenylallene (II) has the dipole moment 1·55 *D*, *i.e.*, the ordinary aromatic chlorine value. If ξ is the moment of the phenyl–bromine linkage (the dipole moment ξ of bromine is 1·49 for aromatic and olefinic linkages; Bergmann, Engel, and Sandor, *Z. physikal. Chem.*, 1930, *B*, **10**, 106), and θ the angle between the two benzene rings which are linked to the same carbon atom, then the polar co-ordinates of the two bromine atoms are given by

(1) $\xi, \frac{1}{2}\theta, 0$; (2) $\xi, 180° - \frac{1}{2}\theta, \phi$
and the ordinary co-ordinates by

(1) $\xi \sin \frac{1}{2}\theta, 0, \xi \cos \frac{1}{2}\theta$; (2) $\xi \sin \frac{1}{2}\theta \cos \phi, -\xi \sin \frac{1}{2}\theta \sin \phi, -\xi \cos \frac{1}{2}\theta$.
The dipole moment μ follows as usual from the equation

$$\mu^2 = \xi^2 \sin^2 \tfrac{1}{2}\theta\,(1 + \cos \phi)^2 + \xi^2 \sin^2 \tfrac{1}{2}\theta \sin^2 \phi,$$

i.e.,

$$\mu = \xi \sin \tfrac{1}{2}\theta \sqrt{2(1 + \cos \phi)}.$$

Evaluation of the three possibilities of configuration (above) gives :

(*a*) classical model, $\phi = 90°$, $\mu = \sqrt{2}\xi \sin \frac{1}{2}\theta$;
(*b*) Faltis's model, *cis*-configuration, $\phi = 0°$, $\mu = 2\xi \sin \frac{1}{2}\theta$;
(*c*) Faltis's model, *trans*-configuration, $\phi = 180°$, $\mu = 0$.

In order to obtain the final figures we must know the value of θ. This can be derived from the dipole moment of $\alpha\alpha$-di-(*p*-chlorophenyl)-$\gamma\gamma$-diphenylallene (IV), since this moment is due to two phenyl–chlorine moments (1·55) inclined at an angle θ. We found the moment 1·57 *D*; θ is therefore 119°.

The moments of $\alpha\gamma$-di-(*p*-bromophenyl)-$\alpha\gamma$-diphenylallene (III) to be expected with this value of θ are 1·85, 2·62, or 0 for cases (*a*), (*b*), and (*c*) respectively. The experimental value is 1·92, which strongly supports van 't Hoff's orthodox stereochemical view.

(I.) $CPh_2{:}C{:}CPh_2$
$C_6H_4Cl{\cdot}CPh{:}C{:}CPh_2$ (II.)
(III.) $C_6H_4Br{\cdot}CPh{:}C{:}CPh{\cdot}C_6H_4Br$
$C(C_6H_4Cl)_2{:}C{:}CPh_2$ (IV.)

A widening of the angle θ beyond the normal tetrahedral value of 109·5° is to be expected *a priori*, from the Thorpe–Ingold valency-deflexion hypothesis (J., 1921, **119**, 305), when two of the carbon valencies are engaged in forming a double bond. For the formaldehyde molecule, indeed, an angle of 120° between the carbon–hydrogen bonds has to be assumed from spectroscopic evidence (see Stuart, " Molekülstruktur," Berlin, 1934, p. 83). Other compounds which resemble the allenes in that the substituents on one side of the molecule are very bulky, and those on the other (corresponding to the middle carbon atom of the allene molecule) very small, such as benzophenone (Bergmann, Engel, and Meyer, *Ber.*, 1932, **65**, 446), *as.*-diphenylethylene and *as.*-dichloroethylene (Errera, *Physikal. Z.*, 1926, **27**, 764; Bergmann and Engel, *Z. physikal. Chem.*, 1930, *B*, **8**, 127), give a value of 130° for θ from dipole-moment determinations, although by the method of electron diffraction (Wierl, *loc. cit.*) the last gives a value of 110°. Possibly the calculation of the angle in this compound from dipole-moment data is rendered inaccurate by electrical forces of unknown nature. On the other hand, further investigation of the Cl–Cl distance may give a greater value, which would correspond better to the dipole moment observed, as well as to the theoretically expected value.

The system of carbodianil, $C_6H_5{\cdot}N{=}C{=}N{\cdot}C_6H_5$, although similar to that of tetraphenylallene, has a very marked dipole moment (1·89; *pp*′-dimethyl derivative 1·96; Bergmann and Schuetz, *Z. physikal. Chem.*, 1932, *B*, **19**, 389). It follows (i) that the molecule is not linear—actually, the usual stereochemical behaviour of nitrogen would not be in accordance with such a structure; and (ii) that the dipole moment is due to the polarity of the N–Ph bond, whilst the C–Ph bond has no marked polarity.

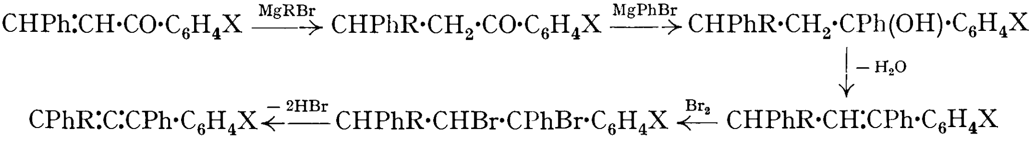
Since, therefore, we can consider carbodianil as analogous, in respect of its dipole properties, to $\alpha\gamma$-di-(*p*-bromophenyl)-$\alpha\gamma$-diphenylallene, the formula given above applies to the nitrogen compound too. Assuming the value of the N–Ph moment to be − 1·34 (see, *e.g.*, Sutton, *Trans. Faraday Soc.*, 1934, **30**, 794) and the angle between the C=N and the N–Ph bond to be 120°—which corresponds to $\varepsilon = 120°$, and is therefore nearly identical with the value used above—the theoretical moment for carbodianil would be 1·64, and for its *pp*′-dimethyl derivative 2·13. The value for the N–(*p*-tolyl) bond is assumed to be

— 1·74. The correspondence of the values is sufficient; the minor differences may be due to an error in the value for the N–Ph bond. In any case, it follows that the structure of the carbodianil, too, supports the classical van 't Hoff theory.

[*Note, added in proof.*] Maitland and Mills (*Nature*, 1935, **135**, 994) have recently described the resolution of $\alpha\gamma$-diphenyl-$\alpha\gamma$-di-(α-naphthyl)allene, thus also supporting the classical theory of the tetrahedral carbon atom.

EXPERIMENTAL.

Tetraphenylallene (I) and its $\alpha\alpha$-di-*p*-chloro-derivative (IV) were prepared by the methods of Vorländer and Siebert (*Ber.*, 1906, **39**, 1024; cf. Schlenk and Bergmann, *Annalen*, 1928, **463**, 234) and of Bergmann, Hoffmann, and Meyer (*J. pr. Chem.*, 1932, **135**, 245) respectively. The allenes (II) and (III) were prepared according to the following scheme, due to Vorländer and Siebert (*loc. cit.*):



$$\begin{tikzcd} CHPh{:}CH\cdot CO\cdot C_6H_4X \arrow[r, "MgRBr"] & CHPhR\cdot CH_2\cdot CO\cdot C_6H_4X \arrow[r, "MgPhBr"] & CHPhR\cdot CH_2\cdot CPh(OH)\cdot C_6H_4X \arrow[d, "-H_2O"] \\ CPhR{:}C{:}CPh\cdot C_6H_4X & CHPhR\cdot CHBr\cdot CPhBr\cdot C_6H_4X \arrow[l, "-2HBr"'] & CHPhR\cdot CH{:}CPh\cdot C_6H_4X \arrow[l, "Br_2"'] \end{tikzcd}$$

(*a*) R = Ph; X = *p*-Cl, giving (II). (*b*) R = *p*-C_6H_4Br, X = *p*-Br, giving (III).

(*a*) *p*-Chloroacetophenone, b. p. 152°/12 mm., was prepared according to the method of Straus and Ackermann (*Ber.*, 1909, **42**, 1812). This ketone (61·6 g.), benzaldehyde (42·4 g.), and absolute alcohol (40 c.c.) were cooled to − 22° and slowly mixed with a cold solution of potassium hydroxide (12 c.c. of a 20% methyl-alcoholic solution and 17 c.c. of alcohol); the orange-red coloration disappeared at once, and the whole mass crystallised; it was then sucked dry, washed with water, and recrystallised from alcohol; m. p. 98·5°; yield 80 g. (Found: Cl, 14·3. Calc. for $C_{15}H_{11}OCl$: Cl, 14·4%) (see Allen and Frame, *Chem. Zentr.*, 1932, ii, 3880).

p-*Chlorophenyl* $\beta\beta$-*diphenylethyl ketone.* The above chalkone (60 g.) was treated with the Grignard solution prepared from magnesium (7·2 g.) and bromobenzene (47 g.); the violent reaction was completed by heating for 1½ hours. On decomposition with ice and sulphuric acid, the product crystallised spontaneously from the ethereal layer. Recrystallised from benzene, it formed colourless needles (53 g.), m. p. 131° (Found: C, 78·4; H, 5·3. $C_{21}H_{17}OCl$ requires C, 78·7; H, 5·3%).

α-p-*Chlorophenyl*-$\alpha\gamma\gamma$-*triphenylpropyl alcohol.* The foregoing compound (45 g.) afforded on treatment with the Grignard solution from magnesium (4 g.) and bromobenzene (26 g.) a clear thick resin, which, after standing for a long time with acetone–light petroleum, crystallised completely. It recrystallised from light petroleum or methyl alcohol in colourless pyramids (40 g.), m. p. 127—128° (Found: Cl, 9·1. $C_{27}H_{23}OCl$ requires Cl, 8·8%).

α-p-*Chlorophenyl*-$\alpha\gamma\gamma$-*triphenyl*-Δ^{α}-*propene.* The above propanol (40 g.) was heated with water (440 c.c.) and concentrated hydrochloric acid (360 c.c.) for 4 hours in an oil-bath. The product, isolated by ether extraction, formed a crystalline mass, which, on purification from alcohol, afforded prisms (35 g.), m. p. 120—121° (Found: Cl, 10·5. $C_{27}H_{21}Cl$ requires Cl, 9·2%).

α-p-*Chlorophenyl*-$\alpha\gamma\gamma$-*triphenylallene* (II). The propene compound (22 g.) in chloroform (70 c.c.) was kept with bromine (3·8 c.c.) in chloroform (7 c.c.) at room temperature for 30 minutes, the solvent evaporated, and the residue boiled for 1½ hrs. with alcoholic potash (62 g. in 440 c.c.). The mass was poured into water (4 l.), extracted with ether, dried, and evaporated. The residue was a resin which crystallised on standing. From alcohol, it recrystallised as hexagonal crystals (7·25 g.), m. p. 90°, but there was much tendency to supercooling (Found: C, 85·5; H, 5·2. $C_{27}H_{19}Cl$ requires C, 85·7; H, 5·0%).

(*b*) *p*-Bromoacetophenone (148 g.) was prepared from bromobenzene by Hale and Thorp's method (*J. Amer. Chem. Soc.*, 1913, **35**, 267); b. p. 162°/11 mm.; leaflets, m. p. 60° (cf. Schweitzer, *Ber.*, 1891, **24**, 550). 66 G. were condensed with benzaldehyde (35 c.c.) as already described. The resulting benzylidene-*p*-bromoacetophenone crystallised from a mixture of methyl and ethyl alcohols in prismatic needles (71 g.), m. p. 102—103° (Found: Br, 27·8. Calc. for $C_{15}H_{11}OBr$: Br, 27·9%) (cf. Kohler, Heritage, and Burnley, *Amer. Chem. J.*, 1910, **44**, 67).

p-*Bromophenyl* β-p-*bromophenyl*-β-*phenylethyl ketone.* To the Grignard solution prepared from magnesium (4·3 g.) and *p*-dibromobenzene (42 g.) (Bergmann, *Ber.*, 1931, **64**, 1483), the chalkone derivative (34 g.) was added. On decomposition, the product crystallised spontaneously. It was dissolved in tetrachloroethylene, and the solution filtered, and evaporated; on recrystallisation from amyl alcohol, the *compound* formed clusters of needles (18 g.), m. p. 126·5° (Found: Br, 35·7. $C_{21}H_{16}OBr_2$ requires Br, 36·0%).

αγ-Di-(p-*bromophenyl*)-*αγ-diphenylpropyl alcohol.* The above ketone (22 g.) was introduced into a Grignard solution (magnesium, 1·4 g.; bromobenzene, 6·2 c.c.) in ether, dry toluene (35 c.c.) added, the ether distilled off on a water-bath, and the toluene solution boiled for 3 hours. The product obtained on decomposition was treated with steam and consisted of an oil, which on standing with acetone or propyl alcohol crystallised slowly. From propyl alcohol, it formed clusters of needles (4 g.), m. p. 130—131° (Found: Br, 30·4. $C_{27}H_{22}OBr_2$ requires Br, 30·6%).

αγ-Di-(p-*bromophenyl*)-*αγ-diphenylallene* (III). The foregoing compound (13 g.) was boiled for 4 hours with a mixture of concentrated hydrochloric acid (90 c.c.) and water (110 c.c.). The propylene isolated by means of ether was an oil, which after standing for a long time in the ice-box gave a small amount of crystals. (The failure to crystallise may be due to the occurrence of the two possible geometrical isomerides.) Crystallisation from propyl alcohol gave beautiful prisms, m. p. 126°. The crude product (30 g.) was brominated as described above (3·8 c.c. of bromine). The substituted allene was obtained as an oil, which crystallised spontaneously after some days. The crystals were triturated with light petroleum, sucked dry, and recrystallised from propyl alcohol. Here again, stirring with a glass rod was necessary in order to prevent oily precipitations; m. p. 139—139·5°; yield 14 g. (Found: C, 64·6; H, 3·8. $C_{27}H_{18}Br_2$ requires C, 64·5; H, 3·6%).

Measurements.—The first three substances were measured according to the procedure of Bergmann, Engel, and Sandor (*loc. cit.*), the symbols having the following significance: c = molar fraction, $\overline{M}$ = mean molecular weight of the solution, ρ = density, ε = dielectric constant, n = refractive index, $P_{\frac{1}{2}}(P_{E\frac{1}{2}})$ = total (electronic) polarisation of the solution, $P(P_E)$ the same for the solute; P_{A+O} = (atomic and) orientation polarisation, which is extrapolated graphically to infinite dilution.

With the Zeiss interferometer, P_E could not always be measured at the same concentrations as were used for the dielectric constants. For the evaluation of the dipole moments, an average of the measured P_E values was chosen (tetraphenylallene 131·0, *p*-chlorotetraphenylallene 136·8). This procedure is reasonable because the electron polarisation is independent of the concentration.

The dipole moment of the fourth substance was measured according to the procedure followed at Oxford.

The electron polarisation values are higher than those calculated for the constituent atoms; there may be a specific influence of the solvent (benzene). In any case, the discussion of the measurements is not seriously affected by these P_E values.

c.	$\overline{M}$.	ρ.	ε.	n^2.	$P_{\frac{1}{2}}$.	$P_{E\frac{1}{2}}$.	P.	P_E.	P_{A+O}.
(I) Tetraphenylallene; $T = 19·3°$.									
0·0	78	0·8795	2·2854	2·2854	26·602	26·602	—	—	—
0·00363	78·97	0·8820	—	2·2940	—	26·981	—	130·86	—
0·00526	79·40	0·8831	—	2·2979	—	27·151	—	131·13	—
0·02048	84·25	0·8956	2·3312	—	28·913	—	125·01	—	0
0·03434	87·14	0·9030	2·3511	—	29·964	—	124·50	—	0
0·04510	90·00	0·9104	2·3720	—	31·024	—	124·64	—	0
$P^{\infty}_{A+O} = 0$; $\mu = 0$.									
(II) *p*-Chlorotetraphenylallene; $T = 22·2°$.									
0·0	78	0·8760	2·2795	2·2795	26·620	26·620	—	—	—
0·00315	78·95	0·8790	—	2·2871	—	26·965	—	136·2	—
0·00462	79·39	0·8804	—	2·2906	—	27·124	—	135·8	—
0·00769	80·31	0·8833	—	2·2994	—	27·480	—	138·5	—
0·01183	81·55	0·8871	2·3468	—	28·483	—	184·1	—	47·3
0·01895	83·69	0·8938	2·3873	—	29·608	—	184·3	—	47·5
0·02390	85·18	0·8985	2·4063	—	30·259	—	178·9	—	42·1
0·03064	87·15	0·9046	2·4499	—	31·385	—	183·2	—	46·4
$P^{\infty}_{A+O} = 50·3$ c.c.; $\mu = 1·55$.									
(III) αγ-Di-(*p*-bromophenyl)-αγ-diphenylallene; $T = 18·9°$.									
0·0	78	0·8795	2·2862	2·2862	26·517	26·517	—	—	—
0·01011	82·29	0·8993	2·3692	2·3165	28·675	27·909	239·87	164·14	75·7
0·01189	83·04	0·9027	2·3880	2·3223	29·100	28·144	243·69	163·33	80·4
0·01613	84·84	0·9108	2·4166	2·3346	29·879	28·681	234·84	160·63	74·2
0·01976	86·38	0·9176	2·4394	2·3445	30·520	29·144	229·05	159·43	69·6
$P^{\infty}_{A+O} = 78·0$ c.c.; $\mu = 1·92$.									

(IV) αα-Di-(*p*-chlorophenyl)-γγ-diphenylallene; $T = 25{\cdot}0°$.

c.	*ρ*.	*ε*.	n^2.	P_2.	$_{E}P_2$.	*c*.	*ρ*.	*ε*.	n^2.	P_2.	$_{E}P_2$.
0·0	0·87430	2·2727	2·25797	—	—	0·002565	0·87758	2·2874	2·26392	185·9	135·2
0·003560	0·87885	2·2930	2·26607	185·6	134·5	0·010335	0·88755	—	—	—	—

$_{\infty}P_2 = 186$ c.c.; $_{E}P_2 = 135$ c.c.; $P_{A+O} = 51$ c.c.; $\mu = 1{\cdot}57$.

THE DANIEL SIEFF RESEARCH INSTITUTE, REHOVOTH, PALESTINE.
THE DYSON PERRINS LABORATORY, OXFORD.

[*Received, March 6th,* 1935.]