

**187.** *The Structure of the isocyanides. Part II.*

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IN a previous communication (Hammick, New, Sidgwick, and Sutton, *J.*, 1930, 1876; see also Sidgwick, *Chem. Rev.*, 1931, **9**, 77), it was shown from the magnitude and sense of the electric dipole moment of the *isocyanide* [carbylamine] group, as given by the moments of *p*-tolyl *isocyanide* and *p*-chlorophenyl *isocyanide*, that the group probably has the co-ordinate structure  $R-N\equiv C$ , first proposed by Langmuir (*J. Amer. Chem. Soc.*, 1919, **41**, 1543), and not the double-bond structure proposed by Nef,  $R-N=C$  (*Annalen*, 1892, **270**, 267; 1895, **287**, 265). Moreover, the magnitude of the moment of carbon monoxide was shown to be in accord with a similar structure for this substance. The evidence provided by the parachor, the heats of rupture, and the chemical properties was shown further to support these structures.

There is a second and independent method of applying dipole measurements to distinguish between the two formulæ. In the Nef formula, the R-N and N-C links, by analogy with the oximes, will not lie in a straight line, whereas in the Langmuir formula they will, as the H-C and C-N links do in the analogous case of hydrogen cyanide (Schaefer and Matossi, "Das Ultrarote Spectrum," Berlin, 1930, p. 248), since the  $N\equiv C$  link will be identical with a normal triple link in its stereochemical properties; once it is formed, the six electrons composing it would be indistinguishable from one another. From the latter structure it would therefore be anticipated that the observed moments of para-substituted phenyl *isocyanides*, provided that the para-substituent also be a group which is sym-

metrical about the valency uniting it with the benzene ring, should be approximately equal to the sum or the difference of the moments of the two monosubstituted benzenes. From the former structure this would be expected not to be so.

The moment calculated for *p*-chlorophenyl isocyanide from the moments of phenyl isocyanide ( $3.49 \times 10^{-18}$  e.s.u.; Eide and Hassel, *Tydskr. Kemi Berg.*, 1930, **8**, 93) and chlorobenzene ( $1.56 \times 10^{-18}$ )\* is  $1.93 \times 10^{-18}$ ; that observed is  $2.07 \times 10^{-18}$  (H., N., S., S., *loc. cit.*). The moment calculated for *p*-tolyl isocyanide, the moment of toluene being taken as  $0.45 \times 10^{-18}$ , is  $3.94 \times 10^{-18}$ ; that observed is  $3.98 \times 10^{-18}$ . In view of the possibility of the para-groups producing a small mutual alteration of moment, this is, however, not an exact way of applying the criterion. As was pointed out previously (*idem, loc. cit.*), a more certain way would be to measure the moment of *p*-diisocyanobenzene, which would have a finite moment if the isocyanide group had the Nef structure, but not if it had the Langmuir structure. This has therefore been done. The moment of ethyl isocyanide has also been measured.

#### EXPERIMENTAL.

*Preparation and Purification of Materials.*—Benzene. A. R. Benzene was frozen out four times, dried over calcium chloride, and then distilled over sodium.

*Carbon tetrachloride.* Pure carbon tetrachloride (as supplied by Messrs. Albright and Wilson, specially purified for medicinal purposes) was distilled over phosphoric oxide.

*p*-Diisocyanobenzene. Kaufler (*Sitzungsber.*, 1901, **110**, IIb, 912) obtained a 10—20% yield of this substance by boiling *p*-phenylenediamine in chloroform with aqueous-alcoholic potash, but a repetition of his preparation, with exact adherence to his directions, produced only very small yields (1% or less). A number of experiments were made to improve the yield, and it was finally found possible to obtain yields of the order claimed by Kaufler by carrying out the preparation in two stages; an intermediate compound, previously undescribed, has been isolated and shown to be *p*-aminophenyl isocyanide.

(1) *Preparation of p*-aminophenyl isocyanide. A mixture of 30 g. of *p*-phenylenediamine (B.D.H., pure), 200 g. of potassium hydroxide, 800 c.c. of water, 120 c.c. of alcohol, and 400 c.c. of chloroform was boiled under reflux for 2 hours. The chloroform layer was then removed, and the aqueous layer extracted with more chloroform; the combined chloroform solutions were washed with

\* This and other moments quoted without authority are taken from Debye, "Polare Molekeln," Leipzig, 1929, including the supplements issued in 1930 and 1931.

a little water, dried over magnesium sulphate, and evaporated, finally under reduced pressure. The tarry residue was shaken vigorously with three or four successive quantities of ligroin (b. p. 60—80°), each of 1500 c.c., which on cooling deposited yellow crystals of the amino-*isocyanide*; a second crop was obtained from mother-liquors; yield about 30% of the theoretical.

The crude substance forms pale yellow needles, which darken in the course of a few days, particularly in the light; it can be obtained colourless by sublimation under reduced pressure, but has not yet been obtained quite pure; m. p. about 74°. It has a characteristic *isocyanide* smell, stronger than that of *p*-diisocyanobenzene, and a bitter taste. It is very soluble in all the ordinary organic solvents except ligroin. It is fairly soluble in water, from which it can be recrystallised, and readily soluble in dilute acid (probably with decomposition). For analysis, a specimen was recrystallised from ligroin (b. p. 60—80°) and sublimed (Found: C, 71.34; H, 5.3.  $C_7H_6N_2$  requires C, 71.2; H, 5.1%).

The constitution of the *isocyanide* is proved (1) by its hydrolysis to *p*-phenylenediamine on boiling with dilute hydrochloric acid; (2) by the formation of *p*-aminobenzonitrile on heating at 235° for 2 hours; (3) by its probable reduction to *N*-methyl-*p*-phenylenediamine with sodium and amyl alcohol; the reduction product was not obtained pure, but it gave the colour reactions described by Bernthsen and Goske (*Ber.*, 1887, **20**, 930), and an *oxalate*, m. p. 153—154° (decomp.) (Found: C, 51.31; H, 5.9.  $C_9H_{12}O_2N_2$  requires C, 50.9; H, 5.7%); (4) by its forming *p*-diisocyanobenzene by the Hofmann reaction (see below).

The amino-*isocyanide* has basic properties as is shown by its solubility in acid, and it forms an *oxalate*, m. p. about 120° (efferv.), from which it can be recovered. On boiling in aqueous solution, the *oxalate* decomposes, forming a yellow solid, m. p. 155—160° (decomp.); the decomposition of *isocyanides* by oxalic acid, with formation of formamidines, is a normal reaction.

Bromination of the amino-*isocyanide* in ether gave a grey precipitate, which on heating gave off hydrogen bromide but did not melt below 280°; a complex product might be expected to result from the condensation of an amino-group with a brominated *isocyanide* group.

In preparing the diisocyanide, Kaufler removed amine by washing with dilute acid, and this explains why he did not obtain the amino-*isocyanide*.

(2) *Conversion of mono- into di-isocyanide*. This was carried out by a method similar to that developed for the other aromatic *isocyanides* (see H., N., S., S., *loc. cit.*). 2 G. of *p*-aminophenyl *isocyanide* were dissolved in 8 c.c. of methyl alcohol and 10 c.c. of

chloroform; the solution was heated in a very small flask under reflux, and 6.5 g. of solid sodium hydroxide, finely powdered, were added in small quantities. The mixture was cooled only sufficiently to prevent its frothing into the condenser, and the reaction was allowed to slacken before each addition; all the alkali was added in 6—10 minutes. The mixture was then cooled and diluted with several times its volume of ether.

The products from this process, repeated a number of times, were filtered, washed with water, and evaporated to dryness; the residue was washed with a little ether to remove tarry products and unchanged amino-isocyanide, dissolved in more ether, and shaken with 10% sulphuric acid to remove any remaining amine. The solution was then washed with water, dried over magnesium sulphate, and concentrated under reduced pressure until most of the diisocyanide had crystallised out; yield, 20—30% of that calculated on amino-isocyanide used.

The substance decomposes before melting, and we have no satisfactory criterion of purity. A colourless specimen analysing correctly was obtained by recrystallisation from ligroin (b. p. 60—80°), followed by sublimation under *ca.* 1 mm. pressure; a special apparatus was used with 5 mm. between the vaporising surface and the water-cooled condensing surface; at 70—75°, 2 g. sublimed in 30 minutes (Found: C, 75.00; H, 3.3.  $C_8H_4N_2$  requires C, 75.00; H, 3.1%). In view of the probable weakness of *p*-aminophenyl isocyanide as a base (compare *p*-chloroaniline and *p*-nitroaniline) and of the ease with which it could be produced by hydrolysis of the diisocyanide, it is possible that the above method of purification did not entirely remove all of this substance.

*p*-Diisocyanobenzene forms colourless needles having a comparatively weak isocyanide smell; it is fairly soluble in methyl or ethyl alcohol, ether, benzene, cyclohexane, and carbon disulphide, but less so in ligroin and carbon tetrachloride. Its solutions, particularly in benzene, gradually become green with a strong blue fluorescence on standing at the ordinary temperature, and more rapidly on heating. A preliminary experiment showed that this decomposition has no measurable effect on the polarisation during the time of one dipole determination. On standing for several weeks, a benzene solution deposits a dark resin.

On being heated, *p*-diisocyanobenzene darkens at about 135°, is black at 155°, and at 165° it decomposes suddenly with evolution of gas.

A bromination product, m. p. 141—142° (Kaufler, *loc. cit.*, gives 137—138°) was obtained (Found: Br, 71.13. Calc. for  $C_8H_4N_2Br_4$ : Br, 71.42%).

Kaufler, by determining the elevation of the boiling point of ether, showed that the substance is approximately unimolecular in solution.

*Ethyl isocyanide*. This was made by Guillemard's modification (*Ann. Chim.*, 1908, [viii], **14**, 412) of Gautier's method (*ibid.*, 1869, [iv], **17**, 233); it was dried over barium oxide and fractionated. The major fraction, b. p.  $78.2-78.7^{\circ}/782$  mm., was used.

*Measurements of Electric Dipole Moments*.—These were measured in benzene solution at  $25^{\circ}$  by the method used before (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668). The results are tabulated below:  $f_2$  is the molar fraction of the solute,  $d_2^{25}$  the density of the solution, and  $n$  its refractive index at  $25^{\circ}$  (Hg green line,  $\lambda$  5461 Å.U.),  $P_2$  is the total polarisation of the solute, and  $eP_2$  its electron polarisation. To minimise errors in the density determination, the experimental values have been plotted against  $f_2$ , and the values used in the calculations have been obtained from the mean line; these interpolated densities are quoted below.

*p-Diisocyanobenzene in benzene.*

	$f_2$ .	$d_2^{25}$ .	$e$ .	$n$ .	$P_2$ .	$eP_2$ .
(1)	0.01833	0.8783	2.2868	1.5034	46.15	39.0
	0.01258	0.8769	2.2828	—	45.96	—
	0.00856	0.8758	2.2798	1.5027	45.89	39.2
	$P_2$ at infinite dilution = 45.7 c.c.					
(2)	0.02216	0.8793	2.2918	1.5037	47.54	38.8
	0.01510	0.8775	2.2870	1.5033	48.15	39.0
	0.01032	0.8763	2.2830	—	47.78	—
	0.00708	0.8755	2.2805	—	48.56	—
	$P_2$ at infinite dilution = 49 c.c.					
(3)	0.01860	0.8784	—	1.5033	—	38.4
	0.01428	0.8773	—	1.5030	—	38.5
	0.01266	0.8769	—	1.5032	—	39.6

Two further runs, carbon tetrachloride being used as solvent, gave  $P_2$  at infinite dilution = *ca.* 55 and 52 c.c.  $eP_2$  at infinite dilution = *ca.* 39 c.c. The dielectric constant found for carbon tetrachloride at  $25^{\circ}$  (referred to benzene as a standard  $e = 2.2747$  at  $25^{\circ}$ ) was 2.2287.

*Ethyl isocyanide in benzene.*

0.04168	0.8696	2.9820	1.4973	233.8	16.4
0.03836	0.8695	2.9259	1.4977	236.9	16.9
0.02290	0.8717	2.6608	1.4994	247.6	16.3
0.01640	0.8723	2.5506	1.5002	252.8	16.0
0.01270	0.8719	2.4875	1.5006	255.3	15.9

$P_2$  at infinite dilution = 266 c.c.;  $eP_2$  at infinite dilution = 16.0 c.c.;  
 $\mu = 3.47 \times 10^{-18}$  e.s.u.

*Discussion of Results.*

Throughout this discussion, dipole moments are given in terms of  $10^{-18}$  e.s.u.

The values obtained for  $P_2$  of *p*-diisocyanobenzene in benzene

at different concentrations are consistent in each run to within 1 c.c., but extrapolate to values of  $P_2$  at infinite dilution which vary among themselves by 3.5 c.c.; if the values in carbon tetrachloride be included, the variations are still greater. These values are, however, all greater than  $\epsilon P_2$ , the minimum difference corresponding to a moment of 0.6, and the maximum to one of 0.9.

The variations of  $P_2$  suggest, however, that the specimens examined were mixtures of a non-polar and a polar substance in various proportions. In fact it seemed very probable that small quantities of *p*-aminophenyl isocyanide would be present, since, as already pointed out (p. 1418), it was obviously difficult to remove this. This substance would have a moment of about 5—6 (compare *p*-nitroaniline,  $\mu = 6.4$ ; Tiganik, *Z. physikal. Chem.*, 1931, *B*, **14**, 135), and therefore, since the apparent moment conferred by small quantities of such a substance on a non-polar one would be equal to the product of its dipole moment and the square root of its molar fraction, only 1% of it would be required to produce an apparent moment of 0.6. It therefore seems justifiable to take the smallest difference between  $P_2$  and  $\epsilon P_2$  to obtain the maximum possible moment of *p*-diisocyanobenzene. This difference includes the atom polarisation, for which no allowance has been made; its effect is always to increase the apparent value of the moment (Ebert, *Z. physikal. Chem.*, 1924, **113**, 5; 1925, **114**, 431; J. Errera, "Polarisation diélectrique," Paris, 1928, p. 104; Smyth, "Dielectric Constant and Molecular Structure," New York, 1931, p. 163). We may therefore conclude that the moment of *p*-diisocyanobenzene is indistinguishable from zero.

The Nef structure would lead us to expect a much larger moment than the apparent value obtained; an estimate of the moment in such a case may be made by assuming that the ratio between the moment of *p*-diisocyanobenzene and that of phenyl isocyanide would be approximately equal to that between other para-disubstituted and monosubstituted compounds having unsymmetrical groups. Comparable pairs of substances are tetramethyl-*p*-phenylenediamine ( $\mu = 1.23$ ) and dimethylaniline ( $\mu = 1.58$ ) which give a ratio of 1 : 1.28, or terephthalaldehyde ( $\mu = 2.31$ ) and benzaldehyde ( $\mu = 2.75$ ), which give a ratio of 1 : 1.19. Taking a mean value of 1.23 for the ratio, and the moment of phenyl isocyanide as 3.49, we find that the probable moment of *p*-diisocyanobenzene, if it had the Nef formula, would be 2.8, which is much greater than the largest apparent value found. The chemical properties, as a whole (compare H., N., S., S., *loc. cit.*), do not indicate tautomerism between the Nef and the Langmuir structure. The present measurements therefore support the latter structure.

The Raman spectra of methyl and ethyl *isocyanides* (Dadiou, *Wien. Ber.*, 1930, 139, 629; *Monatsh.*, 1931, 57, 437) also support this; they have a line in the same region as those lines attributed to triple bonds in nitriles and acetylene compounds. The measurements of Rasetti (*Nature*, 1929, 123, 205) provide similar evidence for carbon monoxide. This is in agreement with the evidence from the heats of rupture which were previously cited.

Moreover, from their treatments of the chemical bond upon the principles of wave mechanics, Pauling (*J. Amer. Chem. Soc.*, 1931, 53, 1367) and Hund (*Z. Physik*, 1931, 73, 1) have shown that it is possible for the *isocyanides* and carbon monoxide respectively to have the triple-link structure. The Langmuir structure may therefore be considered as definitely established.

The moment of ethyl *isocyanide* is 3.47, and since this is almost exactly equal to that of phenyl *isocyanide*, it indicates that there is no electromeric effect in the latter (Sutton, *Proc. Roy. Soc.*, 1931, A, 133, 668). The nitrile group, on the other hand, though it has a similar electronic structure, shows a marked electromeric effect

( $m_e = -0.43$ ), which may be represented as  $R-C \equiv \overset{\curvearrowright}{N}$ . This difference may be attributed to carbon having a greater tendency than nitrogen to share electrons. It is, unfortunately, impossible to determine the orientating power of the *isocyanide* group directly on account of the ease with which it is hydrolysed by acids, and oxidised or attacked by halogens.

With the more reliable data now available, it is possible to perform the calculation, made previously, of the distance between the carbon and nitrogen atoms in the *isocyanide* group with more certainty. The moment of the group  $C-N \equiv C$  may be taken as the numerical difference (3.27) between the moment of ethyl *isocyanide* (3.47) and of the ethyl group (which is equal to that of the C-H link and is therefore 0.2; Sutton, *loc. cit.*, p. 689). The moment of the C-N link has been calculated to be approximately 1.0 (Hammick, New, and Sutton, this vol., p. 742), and the moment of the  $C \equiv N$  link may be taken as the numerical difference between those of acetonitrile (3.34) and the methyl group, which gives 3.14. The moment due to the transference of an electron from nitrogen to carbon will be  $4.77 \times d \times 10^{-10}$ , where  $d$  is the distance between the atoms, and therefore we have :

$$\begin{array}{c}
 C-N \equiv C \\
 \begin{array}{ccc}
 \overleftarrow{|} & & \overleftarrow{|} \\
 1.0 & & 3.14 \\
 \overrightarrow{|} & & \overrightarrow{|} \\
 \hline
 4.77 \times d \times 10^8 \\
 \hline
 \overrightarrow{|} \\
 3.27
 \end{array}
 \end{array}$$

whence  $3.27 = 1.0 + 4.77 \times d \times 10^8 - 3.14$ , and therefore  $d = 1.13 \text{ \AA.U.}$  The value observed for  $d$  in the nitrile triple bond is  $1.15 \text{ \AA.U.}$  (Mecke, "Band Spectra," 1929, p. 23). Although the closeness of the agreement is to some extent fortuitous, yet the reality of the transference is convincingly demonstrated.

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