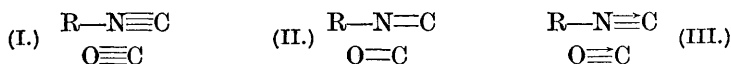


CCXLIV.—*Structure of the isoCyanides and Other Compounds of Bivalent Carbon.*

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THREE types of formula have been proposed for the bivalent carbon compounds, the *isocyanides* [carbylamines], the fulminates, and carbon monoxide :



The first has long been abandoned on stereochemical grounds, and is obviously inconsistent with modern views of covalency; it was replaced more than thirty years ago by the second, mainly through the work of Nef (*Annalen*, 1892, **270**, 267; 1895, **287**, 265). The third was suggested by Langmuir (*J. Amer. Chem. Soc.*, 1919, **41**, 1543) and accepted by G. N. Lewis ("Valence," 1923, p. 127), Lowry, Sugden ("The Parachor and Valency," 1930, p. 171), and others; but it has never been definitely proved to be true, nor have its implications been discussed in detail, so that it has not displaced the Nef formula (II) in general use.

We have now obtained direct evidence of the truth of this formula (III), mainly from the measurement of the parachors and the dipole moments of the *isocyanides*.

EXPERIMENTAL.

Preparation of Materials.—Benzene. A. R. Benzene was frozen out four times, dried over calcium chloride, and then distilled over sodium; m. p. 5.50° (corr.).

p-Nitrobenzonitrile. A laboratory specimen was recrystallised repeatedly from ethyl alcohol; m. p. 148—149° (146°, Sandmeyer, *Ber.*, 1885, **18**, 1492; 149°, Borsche, *ibid.*, 1909, **42**, 3597).

Ethyl isocyanide. Made by Guillemard's modification (*Ann. Chim.*, 1908, **14**, 412) of Gautier's method (*ibid.*, 1869, **17**, 233); dried over barium oxide and distilled several times. The main fraction (b. p. 77.8—78.3°) was used for the surface-tension measurements.

Aromatic isocyanides. Made (from carefully purified amines) by the Hofmann reaction. Biddle and Goldberg (*Annalen*, 1900, **310**, 7) claim to have raised the yield of phenyl *isocyanide* to 35—40% by using powdered alkali instead of the alcoholic solution, but they give no precise details. We found that by the following method a 50% yield (calculated on the amine used) can be obtained. The amine (1/5 g.-mol.), dissolved in chloroform (13 c.c.) and methyl

alcohol (20 c.c.), is heated nearly to boiling under reflux, and powdered sodium hydroxide (3 g.) added : on shaking, the mixture boils gently, and when the reaction is nearly over, 5 c.c. of a mixture of chloroform (40 c.c.) and methyl alcohol (60 c.c.) are added, and a further 3 g. of powdered alkali. The process is repeated until 60 g. of sodium hydroxide and 100 c.c. of the chloroform-alcohol mixture have been added.

p-Tolyl isocyanide. Care must be taken to avoid decomposition of the product by prolonged heating. The mixture obtained as above was filtered from sodium chloride, the salt washed with ether, and the filtrate and washings were evaporated to a small bulk as quickly as possible in about 5 portions. The residue was steam-distilled in small portions, the distillate extracted with ether, the extract well washed with dilute sulphuric acid (1 : 10) to remove amine and formamidine, and then with water; it was dried over potassium hydroxide, and the ether removed. The product was fractionated at least twice in a vacuum : b. p. $94^{\circ}/25$ mm. ($99^{\circ}/36$ mm., Nef, *Annalen*, 1892, **270**, 321; $99^{\circ}/32$ mm., Smith, *Amer. Chem. J.*, 1894, **16**, 374). It was then frozen out two or three times, about one-third being rejected. So obtained, it was always dark green, owing to its rapid polymerisation; it was freed from the polymeride by sublimation, usually at the ordinary temperature, in a high vacuum, the receiver being cooled in liquid air. It is thus got as a perfectly white, finely crystalline mass, which slowly turns yellow in the cold. The m. p. was consistently 19.6° , and could not be raised (Smith, *loc. cit.*, gives 21°).

p-Methoxyphenyl isocyanide. This compound, which has not previously been described, was prepared as above, but without steam distillation. The residue from ether was twice recrystallised from dilute alcohol, frozen out, and sublimed. It forms long colourless prisms, m. p. 30° , and turns green above its m. p., but much more slowly than the tolyl compound. It has a typical carbylamine smell, but rather weaker than that of tolyl isocyanide (Found : C, 72.08; H, 5.24; N, 10.62. C_8H_7ON requires C, 72.18; H, 5.26; N, 10.52%). With alcoholic hydrogen sulphide at 110° it gives *thioform-p-anisidide*, $MeO \cdot C_6H_4 \cdot NH \cdot CHS$ (hitherto undescribed), yellow needles, m. p. $127-129^{\circ}$, with an extremely bitter taste (Found : N, 8.14. C_8H_9ONS requires N, 8.4%).

p-Chlorophenyl isocyanide. Made as before, but the vacuum distillation and the freezing out were omitted, as the carbylamine rapidly polymerises above its m. p. It was purified by conversion into a double compound by shaking in benzene solution with silver cyanide for an hour; the solid was washed with ether, decomposed with potassium cyanide solution, and the isocyanide extracted with

ether. The extract was washed with water, dried over potassium hydroxide, and the ether removed. It was then sublimed; m. p. 72.5° (Ingold, J., 1924, **125**, 97, gives m. p. 71°).

Measurement of Parachor.—The method of surface-tension measurement used was essentially that of Sugden (J., 1924, **125**, 27) as modified by Hammick and Andrew (J., 1929, 754). The densities were measured with a modification of Sugden's U-shaped pycnometer (J., 1924, **125**, 1171).

p-Tolyl isocyanide. Owing to its rapid polymerisation in the pure liquid state, a solution in carbon tetrachloride was used, and the results were calculated by the method of Hammick and Andrew (*loc. cit.*). The values obtained were as follows :

Mols. % R·NC.	Temp.	Density, g./c.c.	Surface tension, dynes/cm.	Parachor of soln.	Mean parachor of soln.	Parachor of R·NC.
0	25°	1.5868	26.31	219.5	219.5	—
22.35	7.8	1.4485	30.1	235.4	235.4	291 ± 6
"	11.3	1.4430	24.6	235.4 f		
27.65	10.3	1.4075	30.0	238.8	238.4	288 ± 5
"	14.4	1.4010	29.6	238.0 f		
54.41	6.34	1.2353	32.6	258.6	258.8	292 ± 3
"	8.76	1.2322	32.4	258.9 f		

The last column gives the parachor of the isocyanide with the computed errors, which are rather large, owing to the instability of the compound. The figures extrapolate (if we assume a straight-line relation, which is to be expected on Hammick and Andrew's principles) to a value of 295 ± 5 for the pure substance. The *p*-chloro-compound could not be examined, as it polymerised too rapidly even in solution.

p-Methoxyphenyl and ethyl isocyanides were measured in the pure state :

<i>p</i> -Methoxyphenyl isocyanide.				Ethyl isocyanide.			
Temp.	Density.	Surface tension.	Para- chor, R·NC.	Temp.	Density.	Surface tension.	Para- chor, R·NC.
31.3°	1.0574	39.4	315.0	17.3°	0.7457	24.4	163.9
33.3	1.0553	39.1	315.0	12.1	0.7510	25.0	163.8
35.2	1.0536	38.9	315.2	7.5	0.7558	25.6	163.7
36.8	1.0523	38.7	315.2			Mean	163.8
39.1	1.0504	38.4	315.1				
		Mean	315.1				

Measurement of Electrical Dipole Moments.—These were measured by the convenient approximate method used by Lange (*Z. Physik*, 1925, **33**, 169), Williams (*J. Amer. Chem. Soc.*, 1927, **49**, 1676), Höjendahl (Diss., Copenhagen, 1928) and others, in which the polarisation due to dipole orientation is determined as the difference between the total polarisation obtained from the dielectric constants

of solutions in benzene, and the electron polarisation obtained from the refractive indices of these solutions at the same temperature; the results are extrapolated to infinite dilution (see Debye, "Polare Molekeln," Leipzig, 1929).

The apparatus used will be fully described later. It was of the heterodyne type, and was modified in various ways so as to improve the ease and accuracy of working. The refractive indices were measured in a special Pulfrich refractometer provided with a double cell.

The data are given in Table I. The first column gives f_2 , the molar fraction of solute, the second the density of the solution, the third ϵ , the dielectric constant, the fourth P_2 , the total molecular polarisation of the solute, the fifth the refractive index, and the sixth eP_2 , the electron polarisation calculated from the latter. The temperature was 25°; the light was that of the mercury green line.

TABLE I.
p-Nitrobenzonitrile.

f_2 .	d^{25° .	ϵ .	P_2 .	n .	eP_2 .
0.02698	0.8880	2.2992	47.4		
0.01743	0.8828	2.2907	47.9		
0.01198	0.8798	2.2853	47.6		
0.02596	(0.8875)	2.2978	47.45		
0.01874	(0.8838)	2.2920	47.50		
0.01333	(0.8809)	2.2870	47.71		
0.02732	0.8882	—	—	1.50469	38.21
0.01940	0.8840	—	—	1.50394	38.15
0.00929	0.8785	—	—	1.50294	38.53

P_2 at infinite dilution = 47.6; eP_2 = 38.6.

Hence $P_2 - eP_2$ = 9.0, and μ = 0.66×10^{-18} E.S.U.

p-Tolyl isocyanide.

0.0293	0.8764	2.9278	324		
0.0198	0.8754	2.7155	335		
0.0097	0.8742	2.4928	353		
0.01606	0.8752	2.6440	350		
0.01074	0.8747	2.5249	361		
0.00827	0.8745	2.4547	345		
0.01874	0.8756	2.7093	348		
0.01280	0.8753	2.5656	353		
0.00918	(0.8745)	2.4822	355		
0.00470	(0.8741)	2.3763	348		
0.06396	0.8806	—	—	1.50388	37.37
0.04566	0.8784	—	—	1.50341	37.47

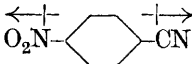
P_2 at infinite dilution = 365 ± 7 ; eP_2 = 37.42; μ = 3.98 ± 0.03 or 4.0×10^{-18} E.S.U.

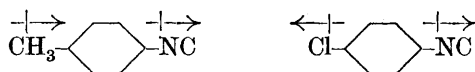
p-Chlorophenyl isocyanide.

0.0300	0.8853	2.4659	125.4	1.50400	37.50
0.0214	0.8821	2.4121	127.1	1.50348	37.52

P_2 at infinite dilution = 126; eP_2 = 37.5; μ = 2.07×10^{-18} E.S.U.

The moments of the $-\text{NO}_2$ and $-\text{CN}$ groups in aromatic compounds are known to be 3.9 and 3.84 respectively (these and other values of dipole moments quoted without authority are taken from Debye, "Polare Molekeln," Leipzig, 1929, including the supplementary list issued by him in January 1930 : they are expressed in *E.S.U.* $\times 10^{-18}$). The low value of 0.66 given by *p*-nitrobenzonitrile shows that in this molecule the moments of the two groups are opposed to one another, that is, are similarly directed with respect to the ring; hence, since in $-\text{NO}_2$ the negative pole is away from the ring, the same must be true of the $-\text{CN}$ group,

 (This symbol $\text{---}|\text{---}\rightarrow$ for the dipole avoids the ambiguity of the simple arrow, which physicists write with the head pointing to the positive, and chemists to the negative end of the dipole.) In the two *isocyanides* examined, the $-\text{NC}$ group is in the para-position to CH_3 and Cl respectively, and the moment in the first case is 4.0 and in the second 2.07. The moment of $\text{CH}_3\text{---C}<$ has been shown to be 0.5 ($\text{---}|\text{---}\rightarrow$) and that of $\text{Cl---C}<$ ($\leftarrow|\text{---}$) 1.55. (The symbol $\text{R---C}<$ implies that the group R is attached to a benzene nucleus.) Hence if the negative pole of the $>\text{C---NC}$ group is remote from the ring, its moment will be increased by that of a para-methyl group, and diminished by that of the para-chlorine :



This is what we find to occur. The moment of $>\text{C---NC}$ calculated from the *p*-tolyl compound is $4.0 - 0.5 = 3.5$; from the *p*-chloro-compound it is $2.07 + 1.55 = 3.62$: mean value 3.6 ($\text{---}|\text{---}\rightarrow$).

Discussion of Results.

The parachors found for the three *isocyanides* are collected in the following table, the third column giving the value for the $-\text{NC}$ group obtained by subtracting that of the attached radical : the calculated values for the alternative formulæ of Nef and Langmuir are added ; the atomic and structural parachors of Sugden ("The Parachor and Valency") are used throughout.

<i>isoCyanide.</i>	Parachor of R---NC .	Parachor of $-\text{NC}$.	Parachor calc., for $-\text{N}=\text{C}$. for $-\text{N}\equiv\text{C}$.	
<i>p</i> -Tolyl	295	66		
<i>p</i> -Methoxyphenyl	315	66		
Ethyl	164	69		
	Mean 67	40.5	62.3	

It will be seen that the results agree fairly well with those required by the co-ordinate structure, but differ widely from those calculated

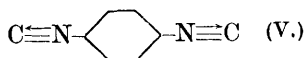
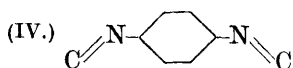
for the Nef formula. It is true that we cannot say what effect the sextet of electrons in the carbon of the latter would have on the parachor, but the basis of the calculation for the Langmuir structure is clear, and the result agrees with observation. The same is the case with carbon monoxide, as Sugden (*loc. cit.*) has pointed out. The observed parachor (61.6) is much nearer to that of $\text{C}\equiv\text{O}$ (69.6) than to that of $\text{C}=\text{O}$ (48.0).

The dipole moments are even more convincing. They show (1) that in the nitrile group the nitrogen is the negative pole, and (2) that the *isocyanide* group has a moment of about 3.6, and that here the carbon atom is the negative pole. The moment 3.8 of $-\text{C}\equiv\text{N}$ is due to unequal sharing of the six electrons. We may assume as a first approximation that there is the same inequality of sharing of the electrons in a single and in a double link of carbon to nitrogen, so that the moment of $-\text{C}-\text{N}$ is $1/3$ of $3.8 = 1.3$, and that of $-\text{C}=\text{N}$ is $2/3$ of $3.8 = 2.6$ (both with the nitrogen negative). Such calculations are of course only rough; we cannot tell what allowance, if any, to make for a possible distortion of the orbits of the unshared electrons; but we may assume that this does not seriously affect the conclusions. The moment of the group $>\text{C}-\text{N}-\text{C}$ would therefore be the resultant of two opposing moments of 2.6 and 1.3 inclined at an angle of about 125° , and so would have a value of about 2 with the negative pole towards the ring, while the observed value is 3.6 in the opposite direction. In the alternative formula $>\text{C}-\text{N}\equiv\text{C}$, the multiple link is formed of six shared electrons as in the nitriles, from which it differs only in that four of these six are derived from the nitrogen; this is the same as if one electron was transferred from the nitrogen to the carbon, and then a triple link was formed in the ordinary way. The observed moment is thus the resultant of three: (1) that of $>\text{C}-\text{N}$ (1.3, \rightarrow), (2) that of the 6 shared electrons of the $-\text{N}\equiv\text{C}$ group, assumed to be shared as in the nitriles (3.8, \leftarrow), and (3) that due to the transferred electron, which is $e \times d$, where e is the electronic charge of 4.77×10^{-10} E.S.U., and d is the distance of the transference in Å.U. The observed value of 3.6 thus gives us $3.6 = e \times d + 1.3 - 3.8$, so that $e \times d = 6.1$, or $d = 1.3 \times 10^{-8}$. This is a probable value for the distance between the atoms, especially as the corresponding distance in carbon monoxide has been shown (see below) to be 1.16×10^{-8} . Thus the observed moment agrees with that required by the formula both in magnitude and in direction.

A similar argument applies to carbon monoxide, which on our view should have the structure $\text{C}\equiv\text{O}$, with a link exactly like that between the carbon and the nitrogen in the *isocyanides*. The moment of the double link $\text{C}=\text{O}$ in the aldehydes and ketones is

about 2.7; a molecule $\text{C}=\text{O}$ should therefore have a considerable moment. But the observed value (Debye, *op. cit.*) for carbon monoxide is 0.12. This can only be explained by the presence of a large counterbalancing moment, such as that due to a transferred electron. In $\text{C}\equiv\text{O}$ the six shared electrons would give a moment of about $3/2 \times 2.7 = 4.1$ ($-\rightarrow$). The transfer will produce an opposing moment of $4.77 \times d$, as before. The distance between the nuclei in carbon monoxide has been shown from the infra-red absorption spectrum to be 1.16 Å.U. (Schaefer and Philipps, *Z. Physik*, 1926, **36**, 399). If we assume the charges produced by the co-ordination to be located at this distance apart, which is probably roughly but not accurately true, the second moment will have a value of 5.5 units ($\leftarrow-$), and is thus of the same order as that due to the shared electrons, but in the opposite direction. The resulting moment should therefore be small, as it actually is. That the observed value is smaller than the calculated is no doubt due to the various approximations involved in the calculation, and especially to the neglect of a possible distortion of the unshared orbits, and to the assumption that the degree of inequality of the sharing is unaffected by the electronic transference.

A crucial test of the structure of the isocyanides would be the measurement of the dipole moment of *p*-diisocyanobenzene. On the Nef formula the two links of the $>\text{C}-\text{N}=\text{C}$ group must be inclined to one another as in the oximes, and the terminal carbon atom must lie off the straight line passing through the two para-carbon atoms of the ring (formula IV) :



Hence the two groups by their rotation round this line would produce asymmetry, and therefore a finite moment, as occurs in the diethyl ether of quinol ($\mu = 1.7$; Williams, *Physikal. Z.*, 1928, **29**, 683; Weissberger and Williams, *Z. physikal. Chem.*, 1929, *B*, **3**, 367; Hassel and Naeshagen, *ibid.*, *B*, **6**, 152) and in tetramethyl-*p*-phenylenediamine ($\mu = 1.23$; Weissberger and Sängewald, *ibid.*, *B*, **5**, 237). On the other hand, the co-ordinate formula, with a triple link between the carbon and the nitrogen, requires that these atoms should lie on the same straight line with the carbon of the ring (formula V). The molecule would therefore be symmetrical, and hence non-polar. This point is being investigated.

Further evidence is given by the values of the heats of rupture of these links, as calculated by the method of Grimm and Wolff (Geiger-Scheel, "Handbuch der Physik," 1926, **24**, 536; quoted by Eucken, "Lehrb. d. chem. Physik," 1930, p. 882). The mean

value (in kg.-cals. per g.-mol.) is for —C—O— 92, for $\text{C}\equiv\text{C}$ in ketones 188, for the link in carbon monoxide 250 (ratio 1 : 2.04 : 2.75), clearly indicating a triple link in the last. (A similar argument was used by Holroyd, *Chem. and Ind.*, 1923, p. 632.) The falling off in the last figure indicates the relative weakness of the co-ordinate link. Similar results are given by the *isocyanides*, but here the values of Grimm and Wolff must be corrected for the recent redetermination of the heat of dissociation of nitrogen (220 kg.-cals.). The corrected values, calculated from the heats of combustion quoted by Kharasch (*Bur. Standards J.*, 1929, 2, 410), are : —C—N— 60, $\text{—C}\equiv\text{N}$ (from 3 aliphatic nitriles, range 193—197) mean 195; $\text{—N}\equiv\text{C}$ (from 5 aliphatic *isocyanides*, range 181—187) mean 184. The relative weakness of the co-ordinate link is again apparent, though less than in the oxygen compound.

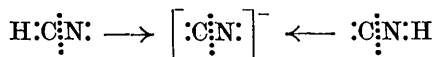
The presence of a co-ordinate link normally depresses the volatility of a compound, but, except when it arises through association, it does so only in virtue of the dipole moment which it produces (see Sidgwick, "Electronic Theory of Valency," p. 123). In the bivalent carbon compounds the co-ordinate link does not increase the moment : in carbon monoxide it almost destroys it. The minute polarity of the latter explains the close agreement in critical data between this gas and nitrogen to which Langmuir (*loc. cit.*) drew attention, an agreement which seemed incomprehensible when it was supposed that carbon monoxide was highly polar. The cyanides and *isocyanides* having nearly identical moments, their b. p.'s should lie near together : as a fact the cyanides boil about 20° higher than their isomerides, which corresponds to a difference in the heats of evaporation of only about 0.4 kg.-cal.

We may therefore take it that the co-ordinate structure is established by the physical data. It is also in accordance with the chemical properties. The *isocyanides* (and the fulminates), as Nef (*loc. cit.*) pointed out, are distinguished by the fact that the unsaturated character is confined to the carbon, and does not extend, as it does in the cyanides, to the nitrogen, their addition compounds (*e.g.*, with chlorine, oxygen, and ethyl hypochlorite) being always of the type $\text{R—N}\equiv\text{CX}_2$. In a molecule $\text{R—N}\equiv\text{C}$ the nitrogen has a fully shared octet, and so cannot co-ordinate either as donor or as acceptor. The carbon has a lone pair of electrons, so that it can act as a donor : also the co-ordinate link with the nitrogen is readily broken, as such links always are, by the return of the two electrons to the exclusive control of the nitrogen, and the carbon can then act as an acceptor. Hence the reactivity of the group resides in the carbon alone. In the nitriles, on the other hand, the nitrogen has a negative charge and a lone pair, so that it can

act as a donor (as it does in many complexes), but any further reaction involves the rupture of a link between the nitrogen and the carbon, and hence addition to both atoms.

The behaviour of the *isocyanides* and carbon monoxide in complex formation gives support to these structures. The complexes formed by carbon monoxide (especially the carbonyls) are not fully understood, but it is clear that the CO groups are separately attached to the central atom (since they always come away separately); that they invariably act as donors and never as acceptors; and that each occupies one co-ordination place on the central atom, *i.e.*, provides one pair of electrons, like a molecule of water or ammonia. These last points follow from the composition of the "mixed" carbonyl complexes, such as those formed by bivalent platinum, *e.g.*, $[\text{Pt}(\text{NH}_3)_2(\text{CO})_2]\text{Cl}_2$, $[\text{Pt}(\text{NH}_3)_2(\text{CO})\text{Cl}]\text{Cl}$ (Schutzenberger and Tommasi, *Compt. rend.*, 1870, **70**, 1288); $[\text{Pt}(\text{CO})\text{Br}_3][\text{H}, \text{C}_5\text{H}_5\text{N}]$, $[\text{Pt}(\text{CO})(\text{SCN})_3]\text{NH}_4$ (Mylius and Foerster, *Ber.*, 1891, **24**, 2438, 3752). The same is true of the complexes formed by the *isocyanides* with metallic cyanides (Ag, Cu, Cd, Co, Ni), with other salts such as CoCl_2 and FeCl_3 , and again in the platinum compounds such as $[\text{Pt}(\text{CH}_3\text{NC})_4]\text{PtCl}_4$ and $[\text{Pt}(\text{CH}_3\text{NC})_2\text{Cl}_2]$ (Hofmann and Bugge, *Ber.*, 1907, **40**, 1774; Tschugaev and Teearu, *ibid.*, 1914, **47**, 570). It is evident that both carbon monoxide and the *isocyanides* form a link as donors, sharing a lone pair of electrons with the central atom. This is in complete agreement with the co-ordinated structure, in which the carbon has such a lone pair, and, to judge from the stability of the fully shared octet in carbon, must be very ready to share it. If, however, the Nef formula were correct, and the carbon had only six valency electrons, it is incredible that it should never complete its octet by acting as an acceptor.

With the adoption of this formula for the *isocyanides*, the arguments as to the tautomerism of the cyanogen ion lose their meaning, as Lowry and others have pointed out; the ions produced by the two tautomeric forms of hydrocyanic acid are identical :



The same is true in general of the ions of any tautomeric acid belonging to Laar's dyad class (*i.e.*, in which the hydrogen migrates from one atom of a chain to the next) as in nitrous or sulphurous acid.

The general characteristic of carbon is to be stable only in the normal 4-covalent state, and to refuse to form either co-ordinate links or electrovalencies. But it is clear that in these bivalent compounds we have an exception to this rule, and the carbon is acting as an acceptor. This suggests that the same thing may

happen elsewhere, and that, for example, in some compounds in which the linkage $>\text{C}=\text{X}$ is assumed to exist, this should be written $>\text{C}\leftarrow\text{X}$. The presence of the co-ordinate link would be detected through the properties of the compound and the consequent difference in the valency group of the atom X. Ingold and Jessop (J., 1929, 2359, note) have already suggested this possibility for the link of carbon to nitrogen, and have verified it (this vol., p. 713) for that of carbon to sulphur in an analogous compound; they obtained a fluorenyl-sulphonium derivative containing a group which they showed should be written $>\text{C}\leftarrow\text{SMe}_2$ and not $>\text{C}=\text{SMe}_2$. The latter formula involves an unco-ordinated 4-covalent sulphur atom, which is almost if not quite unknown in chemistry, while in the former the sulphur is in the familiar sulphonium state. It would be interesting to know if this compound has the other properties to be expected from the presence of the $\text{C}\leftarrow$ link.

The recognition of this structure in the compounds of bivalent carbon removes an apparent anomaly in the behaviour of carbon as compared with its allies in the fourth group of the periodic table. In the later members of the group, the "inertness" of two of the valency electrons (compare Grimm and Sommerfeld, *Z. Physik*, 1926, **36**, 36; Sidgwick, *op. cit.*, p. 178) is very evident, reducing the valency from 4 to 2. But as in the other periodic groups, this effect diminishes as the atomic number decreases, being most marked in lead, where the only stable ion is bivalent, less in tin (Sn^{++}), faint in germanium, and practically absent in silicon. That it should reappear in force in carbon is against all analogy.

It may be pointed out that it is still permissible to describe the *isocyanides* and carbon monoxide as compounds of bivalent carbon. The only satisfactory numerical definition of the valency of a combined atom is that of Grimm and Sommerfeld, that it is the difference between the number of unshared electrons that it has in the isolated state (atomic number) and the number that it has when combined. In these compounds the carbon has the valency group of two unshared and six shared electrons; it has shared two of its four valency electrons, and in this sense its valency is 2. But its covalency, which on the Nef formulæ was 2 in carbon monoxide and in the *isocyanides*, now appears as 3 in both.

The supposed tautomerism of acetylene and its derivatives, $\text{H}\cdot\text{C}=\text{C}\cdot\text{H} \rightleftharpoons \text{H}_2\text{C}=\text{C}$, suggested by Nef (*Annalen*, 1897, **298**, 332; Lawrie, *Amer. Chem. J.*, 1906, **36**, 487; Mrs. Ingold, J., 1924, **125**, 1528; see, however, Biltz, *Ber.*, 1913, **46**, 143) cannot be explained in this way, since the central carbon atom of the second formula has a fully shared octet and cannot co-ordinate. It can only occur if it is possible for carbon to exist with a valency sextet.

The structure adopted above for carbon monoxide gives some support to analogous formulæ for nitric and nitrous oxides. For nitric oxide a structure $\text{:N}\ddot{\text{O}}\text{:}$, in which the nitrogen shares 3 electrons belonging to the oxygen, and the oxygen 2 from the nitrogen, has been proposed; but until we know the dipole moment of nitric oxide we cannot judge of its truth. Of nitrous oxide, however, the dipole moment has been investigated and found to be zero (Ghosh, Mahanti, Mukherjee, *Z. Physik*, 1929, **58**, 200; Williams, private communication quoted by Debye, *op. cit.*). This implies that the molecule is symmetrical with respect to its moments, which is only possible if it contains a rectilinear chain N-O-N , with two similar links. The only formula which seems to satisfy this requirement is N=O=N : we know that an atom joined by 4 shared electrons to each of two others lies in the same straight line with them, not only as a deduction from the tetrahedral atom, but also from the exact analogy of the non-polar O=C=O ; if either of the two links in nitrous oxide were single, it must be inclined at an angle to the other one, as in water or the oxides, and the molecule would have a moment. The close resemblance in physical properties between nitrous oxide and the "isosteric" carbon dioxide was pointed out by Langmuir (*loc. cit.*; see also Clusius, Hiller, and Vaughan, *Z. physikal. Chem.*, 1930, *B*, **8**, 427; compare Snow, *Proc. Roy. Soc.*, 1930, **128**, 294).

[Note, added July 28th, 1930.] After this paper was sent in, Lindemann and Wiegrebé published (*Ber.*, **63**, 1650; July, 1930) a paper on the same subject, in which they record the parachors of a series of isocyanides, and draw from them the same conclusions as to the structure of bivalent carbon compounds that we do. Their measurements, where they deal with the same substances, are identical with ours; the two sets are given below, together with the values calculated for the co-ordinate structures.

Parachors of isocyanides, R-NC.

R.	[P] obs.	[P] obs.	[P] calc.	Anomaly.
	L., W.	H., N., S., S.		
Methyl	122.1	—	118.4	+3.7
Ethyl	—	164	157.3	+6.7
Phenyl	255.2	—	252.3	+2.9
o-Tolyl	292.9	—	291.3	+1.6
p-Tolyl	295.5	295	291.3	+4.2
o-Anisyl	314.1	—	311.3	+2.8
p-Anisyl	314.5	315	311.3	+3.2

In conclusion we wish to express our gratitude to Prof. Debye for his kind help in the construction of the dipole apparatus; to the

Department of Scientific and Industrial Research for a grant which enabled one of us (L. E. S.) to take part in this work; and to Imperial Chemical Industries Ltd. for a grant towards its cost.

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[*Received, June 19th, 1930.*]
