

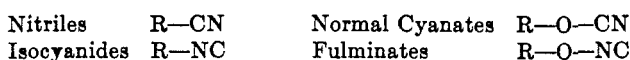
STRUCTURE OF DIVALENT CARBON COMPOUNDS

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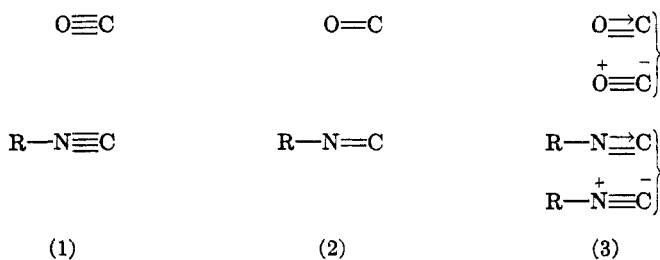
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The divalent carbon atom is recognized as occurring in three classes of compounds—carbon monoxide, the isocyanides or carbylamines, and the fulminates. The last of these needs no separate treatment; it was proved by Nef that the fulminates have the same relation to the isocyanides that the normal cyanates have to the nitriles,



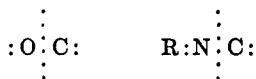
and any conclusions as to the structure of the —NC group in the isocyanides apply equally to the fulminates. For carbon monoxide and the isocyanides three types of formulas have been proposed:



The first of these has long been discarded on stereochemical grounds, since the tetrahedral atomic model does not admit of a quadruple link; it is also inconsistent with the modern view that the covalence of nitrogen cannot exceed four. It was replaced more than thirty years ago by the second type, mainly through

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the work of Nef (1), which will be discussed later. The third, which can be written in two ways both meaning the same thing, namely that an electron is transferred from the oxygen or nitrogen to the carbon and that six electrons are shared between the two atoms,



was suggested by Langmuir (2), and has been accepted by G. N. Lewis (3), Lowry, Sugden (4), and others; but it has not been definitely established, nor have its implications been discussed in detail, so that it has not displaced the Nef formula in general use, especially among organic chemists, who are those mainly interested in this question.

In this paper is discussed further evidence that seems to put the correctness of the Langmuir formula beyond doubt.

The most striking is that of the dipole moments. We know now that in the covalent link the two electrons are not as a rule shared equally between the two atoms, so that the system forms an electrical dipole, more positive towards one end and more negative towards the other. The moment of a dipole is the product of the electric charge into the distance of separation; the sum of the moments in a molecule can be determined experimentally, and the deduction of the moments of individual links, though it is only approximate, is near enough to give us valuable information. The moments are expressed in terms of the unit 10^{-18} E.S.U.

Carbon monoxide has been found to be almost non-polar; its moment² is 0.12. Now a single C—O link has a moment of 0.7, and the double C=O link in aldehydes and ketones has one of about 2.3, the oxygen being at the negative end. Hence if carbon monoxide had the structure C=O it should have a moment of 2 or 3. The fact that it is almost non-polar shows that there is a counterbalancing moment in the molecule. This is provided

² Moments quoted in this paper without authority are taken from Debye, *Polare Molekeln*, Leipzig, 1929, including the supplementary list issued in January, 1930.

by the transferred electron of the Langmuir formula. We can even calculate approximately what its effect should be. The distance between the atomic centers in carbon monoxide has been shown to be 1.14 A.U. (5). If we may assume the electron to be transferred through this distance, it will produce a moment of $1.14 \times 4.77 = 5.44$ units. This differs from the moment of the triple C \equiv O link, and we may assume exceeds it, by 0.12. Thus it appears that the moment of the triply linked C \equiv O without the effect of the transferred electron would be 5.3. It may be pointed out that this makes the ratio of the moments of C \equiv O and C—O ($5.3 \div 0.7 = 7.6$) almost the same as that of the triple and single links of carbon to nitrogen ($3.8 \div 0.4 = 9.5$). At any rate the effect is of the right order, and in the right direction.

Coming to the nitriles and isocyanides, we know that the nitrile group —C \equiv N has a large moment (benzotrile, 3.9), and we might assume that the nitrogen would be at the negative end; but to make certain, this was determined by the ingenious method of J. W. Williams of balancing the group against another in the *para* position in the benzene nucleus. *p*-Nitrobenzotrile was found to have a moment of 0.7 (6), showing that the two groups oppose one another. In —NO₂ the negative end of the dipole must be remote from the ring; hence this is so with the nitrile group as well.

The magnitude and direction of the moment of the isocyanide group were determined in the same way (6). *p*-Tolyl isocyanide was found to have a moment of 3.98, and *p*-chlorophenyl isocyanide one of 2.07. Now toluene has a moment of 0.43, and the positive end is away from the ring: chlorobenzene has a moment of 1.56 in the opposite direction (see table 1). It is evident that the moment of —NC is strengthened by methyl and weakened by chlorine; the carbon must therefore be negative to the nitrogen. The magnitude of the moment is from the tolyl compound $3.98 - 0.43 = 3.55$, and from the chloro compound $2.07 + 1.55 = 3.62$. The moment of phenyl isocyanide itself has since been determined (7), and was found to be 3.49, which is in satisfactory agreement with our results.

If the isocyanide had the formula $C_6H_5-N=C$ its moment would be essentially the resultant of two, $C-N$ and $N=C$; in both the nitrogen is negative, but more strongly in the double

TABLE 1
Dipole moments ($\times 10^{18}$ E.S.U.)

$\begin{array}{c} \overleftarrow{+} \\ \text{---C---O} \\ \text{0.7} \end{array}$	$\begin{array}{c} \overleftarrow{+} \\ \diagup \text{C=O} \\ \text{2.3} \end{array}$	Carbon monoxide: $\begin{array}{c} \overleftarrow{+} \\ \text{C}\equiv\text{O} \\ \overrightarrow{+} \end{array}$
$\begin{array}{c} \overleftarrow{+} \\ \text{O}_2\text{N---C}_6\text{H}_5 \\ \text{3.9} \end{array}$	$\begin{array}{c} \overleftarrow{+} \quad \overrightarrow{+} \\ \text{O}_2\text{N---} \langle \text{C}_6\text{H}_4 \rangle \text{---CN} \\ \text{0.7} \end{array}$	$\begin{array}{c} \overrightarrow{+} \\ \text{C}_6\text{H}_5\text{---CN} \\ \text{3.9} \end{array}$
$\begin{array}{c} \overrightarrow{+} \\ \text{H}_3\text{C---C}_6\text{H}_5 \\ \text{0.43} \end{array}$	$\begin{array}{c} \overrightarrow{+} \quad \overrightarrow{+} \\ \text{H}_3\text{C---} \langle \text{C}_6\text{H}_4 \rangle \text{---NC} \\ \text{3.98} \end{array}$	Difference 3.55
$\begin{array}{c} \overleftarrow{+} \\ \text{Cl---C}_6\text{H}_5 \\ \text{1.56} \end{array}$	$\begin{array}{c} \overleftarrow{+} \quad \overrightarrow{+} \\ \text{Cl---} \langle \text{C}_6\text{H}_4 \rangle \text{---NC} \\ \text{2.07} \end{array}$	Sum 3.63
	$\begin{array}{c} \overrightarrow{+} \\ \text{C}_6\text{H}_5\text{---NC:} \\ \text{Observed 3.49} \end{array}$	
$\begin{array}{c} \overrightarrow{+} \\ \text{C---N} \\ \text{0.4} \end{array}$	$\begin{array}{c} \overrightarrow{+} \\ \text{C} \\ \text{1.5} \\ \text{N} \\ \text{C} \end{array}$	$\begin{array}{c} \overrightarrow{+} \\ \text{C---N}\equiv\text{C} \\ \overrightarrow{+} \quad \overleftarrow{+} \\ \text{0.4} \quad \text{3.8} \\ \text{3.5} \end{array}$
$\begin{array}{c} \overleftarrow{+} \\ \text{About 1} \end{array}$		

link. The value for $C-N$ is 0.4, and that for $N=C$ would presumably be from 1 to 1.5. The whole group should thus have a moment of about 1, of which the positive end would be remote from the ring. The observed facts, that the moment is about

3.5, and still more that it is in the opposite direction, are incompatible with this structure, but are explained by the coördinate formula as due to the transferred electron, which, as in carbon monoxide, but much more strongly, overcomes the moment due to the inequality of sharing of the six electrons of the triple link. Here too we can make an approximate calculation. In the group $\text{>C}-\text{N}\equiv\text{C}$ we have three moments concerned: (1) that of $\overset{\rightarrow}{\text{C}}-\overset{\leftarrow}{\text{N}}$ (0.4); (2) that of six shared electrons in $\overset{\leftarrow}{\text{N}}\equiv\text{C}$, which may be assumed to be 3.8, as in the nitriles; and (3) that due to the transferred electron in $\overset{\rightarrow}{\text{N}}\equiv\text{C}$, which is $4.77 \times d$, where d is the distance of transference. Since the total moment is found to be 3.5, we have

$$3.5 = 4.77 \times d + 0.4 - \text{about } 3.8$$

whence

$$4.77 \times d = 6.9$$

or

$$d = 1.4 \text{ A.U.}$$

The distance between the atoms in the $-\text{NC}$ group is unknown; but it may be taken to be about the same as that between the triply linked atoms of carbon in acetylene (1.2 A.U.) or of nitrogen in nitrogen gas (1.1 or 1.2 A.U.), and so to be 1.2 A.U. This again agrees well with the value deduced from the moments.

These calculations have an interest outside this particular group of compounds. There is a tendency to assume that the idea of the transferred electron in the coördinate link should not be taken too seriously; and it is important to realize that when the idea can be tested quantitatively by dipole measurements, it is found to be in accord with experiment.

The coördinated formulas for these compounds are further supported by the heats of formation of the links from their atoms, as calculated by the method of Grimm and Wolff (8). The relevant values are given in table 2, expressed in kilogram-calories per gram-molecule. They have been recalculated in the light of recent determinations of the heats of dissociation of oxygen and nitrogen.

It will be seen that in each case the heat of formation is approximately proportional to the multiplicity of the link, and that both carbon monoxide and the isocyanides behave as triply linked compounds.

The parachors are also in agreement with these formulas. The meaning of the parachor is still to some extent a mystery, but it is a definite additive property, particularly suitable for detecting multiple linkage. The parachors of the isocyanides were measured simultaneously at Oxford (6) and by Lindemann

TABLE 2
Heats of formation of links

LINK	COMPOUND	HEAT OF FORMATION	
		Abs.	Rel.
		<i>kg.-cal. per gram-molecule</i>	<i>kg.-cal. per gram-molecule</i>
C—O	Alcohols	73.0	1
	Ethers	73.5	1
C=O	Aldehydes	163	2.2
	Ketones	163	2.2
	Carbon dioxide	180.7	2.5
C≡O	Carbon monoxide	237	3.2
C—N	Monamines	58.5	1
C=N	Isocyanates	108.9	1.9
C≡N	Nitriles	185.4	3.2
	Isocyanides	179.7	3.1

(9) in Germany. The results for carbon monoxide (10) and the isocyanides are given in table 3, along with the values calculated for the Nef and Langmuir formulas. In calculating the value for the Nef formula it is assumed that the carbon exerts its normal effect on the parachor. Although this is not certain, all analogy shows that the reduction which that formula requires, of the valence octet to a sextet, and of the covalence from four to two, if it had any effect would diminish the parachor, so that the value given in the table is a maximum. With carbon monoxide the observed value is at least much nearer to that required for the

second formula, and with the isocyanides the agreement with the latter is reasonably good.

The volatility is also in agreement with this theory, although that property depends directly on the dipole moments, and not on the formula assigned to the group. The presence of a coördinate link normally depresses the volatility of a compound, but, except where association occurs, this is only because it increases the dipole moment. In the compounds we are considering, the coördination does not increase the moment; in carbon monoxide

TABLE 3
Parachors

CARBON MONOXIDE	P (OBSERVED)		P (CALCULATED)	
			C=O	C≡O
	61.6		48.0	69.6
ISOCYANIDES R-NC	P _{NC} (observed)		P _{NC} (calculated)	
	Lindemann and Wiegrebe	Hammick, New, Sidgwick and Sutton	R-N=C	R-N≡C
R = Methyl.....	66.0			
Ethyl.....		69		
Phenyl.....	65.2			
<i>o</i> -Tolyl.....	63.9			
<i>p</i> -Tolyl.....	66.5	66	40.5	62.3
<i>o</i> -Anisyl.....	65.1			
<i>p</i> -Anisyl.....	65.5	66		
	Mean	65.5		

it almost destroys it. The close agreement in critical data between carbon monoxide and nitrogen to which Langmuir (2) drew attention, was inexplicable as long as it was supposed that the former gas was highly polar, but it is explained by its actual polarity being so small. The cyanides and the isocyanides having nearly equal moments should be about equally volatile, and as a fact the cyanides boil about 20° higher than their isomers, which corresponds to a difference in the heats of evaporation of only about 5 per cent.

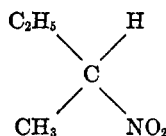
The coördinate structure with the triple link is thus supported by the physical data. It is also in accordance with the chemical properties. The main point on which Nef based his formula was the evidence he obtained that in the isocyanides (and in the fulminates) the unsaturated character is confined to the carbon, and does not extend, as it does in the nitriles, to the nitrogen, their addition compounds (for example with chlorine, oxygen, and ethyl hypochlorite) being always of the type $R-N=CX_2$. This behavior is equally to be expected from the Langmuir formula. In a molecule $R-N\equiv C$ the nitrogen has a fully shared octet, so that, like carbon in the tetrachloride, it cannot coördinate either as donor or as acceptor. The carbon has a lone pair of electrons, and from its strong tendency to assume the 4-covalent state, it is to be expected that these will readily react. Further, the coördinate link with the nitrogen is easily 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 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 formed by nitriles, but as its covalence is limited to four, it cannot use these two electrons to form two new covalences; any further reaction involves the rupture of a link between the nitrogen and the carbon, and hence addition to both of these atoms.

Further support is given to this view by the behavior of carbon monoxide and the isocyanides in complex formation. The complexes formed by carbon monoxide, especially the carbonyls, are not fully understood, but it is clear (1) that the CO groups are separately attached to the central atom, since they always come away separately; (2) that they invariably act as donors and not as acceptors, since they always attach themselves to atoms which can take up other donors like ammonia; and (3) from the composition of the "mixed" carbonyl compounds such as $[Pt(NH_3)_2(CO)_2]Cl_2$, that each CO occupies one coördination place, that is, provides one pair of electrons, like a molecule of water or ammonia. The complexes formed by the isocyanides, for example

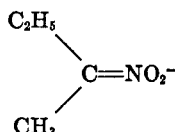
[Pt(CH₃·NC)₂Cl₂] show that they behave in the same way. This is in complete agreement with the coördinate structure, in which the carbon has a lone pair, and, to judge from the stability of the fully shared octet in carbon, must be very willing to share it. If, however, the Nef formula were correct and the carbon had only six valence electrons, it is incredible that it should never complete its octet by acting as acceptor.

The recognition of these structures removes an apparent anomaly in the behavior of carbon as compared with its allies in the fourth group of the Periodic Table. The "inertness" of a pair of valence electrons, changing the valence by two units, is common among the elements of the B subgroups, but in any group it is always found to be most marked in the heaviest members. Thus its intensity is in the order I > Br (Cl, F); Te > Se (S, O); Bi > Sb > As (P, N). The elements in brackets are those which show no sign of this inertness. In the fourth group this order is very clearly defined; the inertness is most marked in lead, where the only stable ion is divalent, less in tin (Sn⁺⁺), faint in germanium, and practically absent in silicon. It would be against all analogy that it should then reappear in force in the lightest member, carbon.

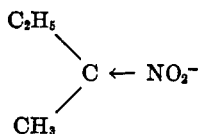
The whole of organic chemistry shows that the general characteristic of carbon is to be stable only in the normal 4-covalent state, and to refuse to form either coördinate links or electrovalences. But it is evident that in these divalent compounds we have an exception to this rule, and the carbon is acting as acceptor. This suggests that the same thing may happen elsewhere, and may have been overlooked; that, for example, in some compounds in which the grouping C=X has been assumed, this should be written C←X. The presence of the coördinate link would be detected through the properties of the compound, and through the difference involved in the valence group of the atom X. An instance of this, where X is a sulfur atom, has been suggested by Ingold and Jessop (11), but perhaps the most interesting example is the following one. Kuhn has shown (12) that the optically active form of



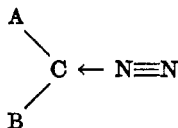
retains a considerable part of its activity after solution in alkali. This remarkable result has been confirmed by Shriner and Young (13). Now in the alkaline derivatives the metallic atom is undoubtedly ionized, and it has always been assumed, since the work of Hantzsch, that the ion had the structure



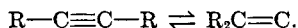
But this is symmetrical, and if it were formed, solution in alkali must destroy the optical activity. Kuhn, however, points out that if we assume that the nitrogen is joined to the carbon in the ion by a coördinate link,



the ion is not symmetrical, and the persistence of the activity is explained: the central carbon atom has the same possibility of activity as the 3-covalent sulfur atom in the compounds of Phillips and Kenyon (14). If the optical activity found by Levene and by W. A. Noyes (15) in the aliphatic diazo compounds, which has recently been confirmed by Lindemann (16), is really due to these compounds and not to an impurity, we must assign to them a similar structure



Another group of compounds was supposed by Nef to contain divalent carbon: he maintained that acetylene and its derivatives could occur in tautomeric forms



These cannot be explained in the same way; the central carbon atom of the second formula has a fully shared octet and no lone pair, so that it cannot coördinate. If this formula is correct the terminal carbon here has only a valency sextet. These views of Nef are however doubtful (17). Recent work on the band spectrum of acetylene has shown that at least the greater part consists of symmetrical linear molecules $\text{H}-\text{C}\equiv\text{C}-\text{H}$. It should be easy to settle the question by measuring the dipole moment of such a compound as diiodoacetylene. $\text{I}-\text{C}\equiv\text{C}-\text{I}$ would be non-polar, and $\text{I}_2\text{C}=\text{C}$ would be highly polar. The existence of the supposed acetal of carbon monoxide, $\text{C}(\text{O}\cdot\text{C}_2\text{H}_5)_2$ (18), seems from the recent work of Arbusow (19) to be very doubtful.

We may still call the isocyanides, the fulminates, and carbon monoxide compounds of divalent carbon. The only satisfactory definition of the numerical valency of a combined atom is that suggested by Grimm and Sommerfeld, that it is the difference between the number of unshared electrons that the atom has in the uncombined state (atomic number) and the number that it has when combined. In these compounds the carbon has a valence group of two unshared and six shared electrons; it has shared two of its valence electrons, and in this sense its valence is two, but its covalence, which according to the Nef theory was two in all three classes of compounds, now appears as three.

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