38. *An Investigation of the Occurrence of the Co-ordinate or Dative Link by Electric Dipole-moment Measurements.*

By G. M. PHILLIPS, J. S. HUNTER, and L. E. SUTTON.

In the early formulations of the higher oxides and oxy-acids of elements in Groups V, VI, and VII, the oxygen atoms attached only to a central atom were supposed to be held by double bonds. According to Lewis, however, they are held by co-ordinate or dative links; and this view received support from stereochemical investigations.

Subsequent measurements of the bond lengths threw serious doubt on the later formulations for such compounds of elements not in the first short period, and suggested that the earlier ones were more correct. Electric dipole-moment data gave some support to this conclusion.

In this paper, more dipole-moment measurements are reported. The changes of moment which occur when phosphines and sulphides form links to oxygen or sulphur are compared with those when they form *complexes* with boron trifluoride or trichloride, in which the boron must accept a co-ordinate link, and these in turn with the changes when amines or ethers form links to the same atoms or groups.

The results, considered together with thermal data, show that the older formulations are much nearer the truth than the newer ones. The remarkable shortening of the links to less than the values expected for double bonds is shown to be an example of a rather general phenomenon, *viz.*, that abnormally strong bonds tend to be abnormally short.

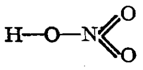
The corresponding bond in a phosphine imine is examined, with a less definite result—it may be derived more nearly equally from the two structures.

The remarkable compound dimethylsulphonium-9-fluorenylidide is found to be highly polar, showing that the attachment of the two parts of the molecule is by a co-ordinate link. It is probable that the substance exists only because of stabilisation by resonance in the ring system.

The structure of ozone is discussed. The low polarity and low stability are shown to be related.

The stable existence of the higher oxy-acids of the halogens can be considered as due to the formation of multiple links. Fluorine cannot form such links, however, nor is it likely to be able to form strong co-ordinate links: so the apparent non-existence of its higher oxy-acids is thus explicable.

In the early " nucleus " formulæ of the higher oxides and oxy-acids of the elements in Groups V, VI, and VII of the Periodic System, two assumptions were made. One was that the oxygen is always bivalent, forming either two single bonds or one double one; the other that the central or nucleus element can have a valency numerically equal to its group number. For example, in such compounds, nitrogen and phosphorus were supposed to be quinquevalent, sulphur sexavalent, and chlorine septavalent, as in (I)—(IV). Werner (" Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," Braunschweig, 1905) objected to these formulæ on the grounds that they implied a distinction, which to him seemed artificial, between the oxy-acids and the halogeno-acids, *e.g.*, chloroplatinic acid; and also because not all of the double bonds postulated actually add on water. He remarked on the frequency with which elements in their most highly oxidised compounds are found associated with *four* oxygen atoms.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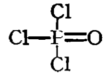
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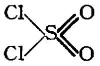
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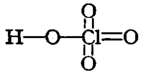
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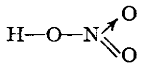
When, later, Lewis placed covalency on a physical basis by introducing the concept of electron sharing, he showed that it was possible to formulate many compounds, including the higher oxides and oxy-acids, with an octet of electrons round each atom (*J. Amer. Chem. Soc.*, 1916, **38**, 762). In place of some of the double bonds in the old formulations, he postulated single covalencies for which the central atom provides both shared electrons. This type of link was termed by Sidgwick (" The Electronic Theory of Valency," Oxford, 1927) the co-ordinate link; * and (I)—(IV) were replaced by (V)—(VIII).

This type of structure gained wide acceptance because it showed that such compounds could be formally unified with many others on the general principle that an atom strives in forming valencies to achieve an inert-gas structure, and so has a covalency limit of four. Application of Bohr's theory of atomic structure, and later of wave-mechanics, to valency problems strongly supported this principle as applied to elements in the first short period (see Pauling, " The Nature of the Chemical Bond," Cornell, 1940, p. 31); and though both theory and the actual existence of such compounds as phosphorus pentafluoride and sulphur hexafluoride showed that the limit of covalency is higher in the later periods, parachor measurements and observations on stereochemical properties appeared to support the octet formulæ for the oxy-compounds (see Sidgwick, *op. cit.*). The large electric moments, 4·1 and 5·1 D. respectively, for diphenylsulphoxide and diphenylsulphone (Bergmann, Engel, and Sandor, *Z. physikal. Chem.*, 1930, *B*, **10**, 397; de Vries and Rodebush, *J. Amer. Chem. Soc.*, 1931, **52**, 2888; Bergmann and Tschudnowsky, *Ber.*, 1932, **65**, 457) also appeared to do this. For a long time, therefore, these formulæ were accepted without serious question.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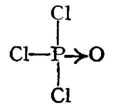
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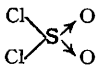
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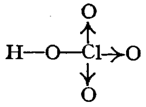
(VIII.)

This view was challenged in 1937 when Pauling and Brockway (*J. Amer. Chem. Soc.*, **59**, 13) drew attention to certain theoretical and practical difficulties. For dithionic and hypophosphoric acids the octet structures lead to large formal charges of like sign on adjacent atoms, which should cause marked instability. These authors suggested, therefore, that there is resonance between several possible structures in which double bonds hold one or more of the extra oxygen atoms. Their adjacent charge rule appears not to be of universal application (see Sutton, J., 1940, 551); but they also produced a more concrete objection, *viz.*, that the bond lengths in the common oxy-acid ions are much shorter than single bonds should be, being in fact as short as double bonds, or even shorter. Either, therefore, must co-ordinate links be much shorter than normal single bonds, or the bonds in question cannot be co-ordinate links.

Further investigations, on the one hand, revealed more examples of very short bonds to extra oxygen or sulphur atoms (which may conveniently be termed " oxy-bonds "), and on the other hand they gave information about the length of true co-ordinate links. Palmer and Elliott (*J. Amer. Chem. Soc.*, 1938, **60**, 1852)

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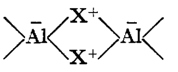
* Objection has been made to this term (see, *e.g.*, Laubengayer and Finlay, *J. Amer. Chem. Soc.*, 1943, **65**, 884), but it has the merit of brevity; and provided that it be not applied to the solid state it does not cause confusion. Of the alternatives suggested, dative bond (Menzies, *Nature*, 1928, **121**, 457) seems the best.

measured the Al–X distance in the four-membered ring (IX) in the dimeric aluminium trihalides: these bonds may be regarded as hybrids between normal single bonds (Al–X) and co-ordinate links ($\overset{-}{\text{Al}}-\overset{+}{\text{X}}$). For the chloride, bromide, and iodide they are 2·21±0·04, 2·33±0·04, and 2·58±0·04 A., in good agreement with the sums of the tetrahedral single-bond radius for aluminium (1·26 A., Pauling and Huggins, *Z. Krist.*, 1934, *A*, **87**, 205) and the normal radii for the halogens (Pauling, *op. cit.*, p. 164), *viz.*, 2·25, 2·40, and 2·59 A. Lister and Sutton (*Trans. Faraday Soc.*, 1939, **35**, 495) reported that the length of the N–O bond in trimethylamine oxide is 1·36±0·03 A. The length found for the N–O single link in *O*-methylhydroxylamine is *ca.* 1·43 A.; this length is that calculated by Schomaker and Stevenson (*J. Amer. Chem. Soc.*, 1941, **63**, 37), whereas the Pauling normal radii give 1·36 A., and 1·15 A. for a double bond, N=O; so the actual length is nearer to that expected for a single bond than for a double one,* and certainly is not *shorter* than the latter.



(IX.)

Moreover, Bauer, Finlay, and Laubengayer (*ibid.*, 1943, **65**, 889), from an electron-diffraction investigation of dimethyl ether–boron trifluoride, report that the length of the B–O bond therein is 1·52±0·06 A., *i.e.*, rather longer than the mean, 1·47 A., of the B–O bond lengths in the tetrahedrally co-ordinated boron phosphate and arsenate (Schultze, *Z. physikal. Chem.*, 1933, *B*, **24**, 215) wherein each boron, phosphorus, or arsenic atom is surrounded by four oxygen atoms, and each of the latter is shared between a phosphorus or arsenic and a boron atom. It is very close to the sum, 1·54 A., of the Pauling single-bond radii, or to the sum of Pauling's radius for oxygen and Bauer and Beach's radius for boron (0·85 A.), *i.e.*, 1·51 A., but somewhat larger than the value got by Bauer and Beach (*J. Amer. Chem. Soc.*, 1941, **63**, 1394) using their boron radius and Schomaker and Stevenson's correction (*loc. cit.*) for the supposed electronegativity difference, *viz.*, 1·45 A. True co-ordinate links appear, therefore, to be nearly of the length to be expected for a normal, single covalency between the same two elements.

In contrast, the bonds between elements of the second short period and the extra oxygen or sulphur atoms always prove to be as short as, or shorter than the normal double-bond length. This is shown by Table I (an elaboration of that in *Ann. Reports*, 1940, **37**, 75).

Two facts are especially striking. One is that the P–O′ bonds in $P_4O_6O_4'$ are extremely short and are thus differentiated from the P–O bonds which, although also shorter than theoretical single bonds, are much less abnormal. Secondly, from the lengthening of the C–S bond in dimethylsulphone ($l_{C-S} = 1·90\pm0·03$ A. instead of 1·81; see Lister and Sutton, *loc. cit.*) the sulphur radius appears to be larger than it is in the normal bivalent state; yet the S–O bonds are very short. Bond-length data therefore suggest very strongly that the oxy-bonds are not co-ordinate links.

On more careful examination, electric dipole-moment data prove also to support this conclusion. The N–O bond in trimethylamine oxide is 1·36 A. long; so if an electron were completely transferred in the formation of the bond, and there were symmetrical sharing of the bonding electrons, the moment would be (electronic charge) × (bond length), *i.e.*, 6·53 D. The value derived by Linton (*J. Amer. Chem. Soc.*, 1940, **62**, 1945) and ourselves (see later) is 4·22—4·37 D., *i.e.*, 66—68% of theory. Moreover, the very large moments of certain co-ordination complexes show that they contain highly polar bonds, although it is true that in some of these the unco-ordinated molecules are themselves quite polar. Examples are: $(Et_2O)_2,BeCl_2$, 6·71 D.; $MeCN,BCl_3$, 7·74 D.; Et_2O,BCl_3, 6·04 D.; $EtNH_2,AlCl_3$, 6·94 D.; $Et_2O,AlCl_3$, 6·68 D.; $C_6H_5{\cdot}NO_2,AlCl_3$, 9·25 D.; $COPh_2,AlCl_3$, 8·32 D. (Nespital, *Z. physikal. Chem.*, 1932, *B*, **16**, 153); $(Et_2S)_2,PtCl_2$, 9·5 D.; $(Et_3P)_2,PtCl_2$, 10·7 D.; $(Et_3As)_2,PtCl_2$, 10·5 D.; $(Et_3Sb)_2,PtCl_2$, 9·2 D. (Jensen, *Z. anorg. Chem.*, 1935, **225**, 97; 1936, **229**, 225; 1937, **231**, 365).

If the S–O, P–O, and P–S bonds were co-ordinate links they should be even more polar than the N–O link, because they are actually longer: the moments for full transference would be 6·86, 7·44, and 9·31 D., respectively. The actual values ascribed are, however, 2·16—2·6 (Coop and Sutton, *Trans. Faraday Soc.*, 1939, **35**, 505), 3·5, and 2·5 D. (Smyth, *J. Amer. Chem. Soc.*, 1938, **60**, 183), respectively, *i.e.*, only 31·5—38%, 47%, and 27% of the theoretical values.

There is, therefore, a strong case against the theory that the S–O, P–O, and P–S bonds in these compounds are co-ordinate links. The data are, however, still relatively unsystematic. Moreover, it is not certain that

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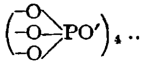
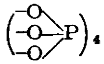
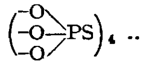
* On the very simple argument that, in the bond $\overset{+}{A}-\overset{-}{B}$, the formal positive charge on A probably decreases its radius as much as the negative charge on B increases its radius, Elliott (*J. Amer. Chem. Soc.*, 1937, **59**, 1380) predicted that the length of the co-ordinate link would be the same as that of a normal single bond between A and B. This is almost certainly an over simplification. A better, though still arbitrary, analysis would be to suppose that there are two effects: (i) the change of radii of the donor and acceptor atoms, brought about by the formal charges and the changes in valency state; (ii) the attraction between the formally charged atoms. The second factor will obviously tend to shorten the link; but it is by no means certain what the first will do. Some data indicate that the radius of a donor nitrogen atom is greater than the Pauling normal valency radius which is valid in amines (see Lister and Sutton, *loc. cit.*): Albrecht and Corey (*J. Amer. Chem. Soc.*, 1939, **61**, 1087) find, however, that in the glycine " zwitterion " the C–N distance in the group CH_2–NH_3^+ is only 1·39 A., *i.e.*, 0·08 A. less than predicted. Bauer, Finlay, and Laubengayer (*loc. cit.*) find no shortening of the C–O bonds in dimethyl ether–boron trifluoride, but rather a slight extension.

The effective radius of boron increases when it becomes an acceptor: l_{B-F} in boron trifluoride is 1·30 ± 0·02 A., but in dimethyl ether–boron trifluoride it is 1·41 ± 0·02 A. It therefore seems possible that both the donor and the acceptor atoms undergo an increase of radius, but that this is more or less counterbalanced by the increased mutual attraction arising from their formal charges.

TABLE I.

Oxy-bond Lengths.

Compound.	$l_{obs.}$, A.	Method.	Ref.
Sulphur–oxygen bonds.			
$l_{calc.}$, A. (Pauling's radii) ‡ : single, 1·70*; double, 1·49; triple, 1·37.			
$SOMe_2$	1·46	E.D.†	(a)
SO_2Me_2	1·44 ± 0·03	—	(a′)
SO_2	1·43 ± 0·01	—	(b)
SO_3, SO_2Cl_2, SO_2F_2	1·43 ± 0·02	—	(c), (d)
$SOCl_2$	1·45 ± 0·02	—	(c)
$S_2O_8^{--}$, $S_3O_6^{--}$, SO_4^{--} (Li_2SO_4)	1·50	*X*-Ray cryst.	(e), (f), (g)
SO_4^{--} ($CaSO_4$, Na_2SO_4)	1·49	—	(h), (i)
SO_4^{--} (Ag_2SO_4)	1·48	—	(j)
SO_3^{--} (Na_2SO_3)	1·39	—	(k)
$S_2O_5^{--}$	1·46	—	(l)
$K{\cdot}SO_3{\cdot}NH_2$	1·44 ± 0·03	—	(m)
Phosphorus–oxygen bonds.			
$l_{calc.}$, A. : single, 1·76*; double, 1·57; triple, 1·43.			
POF_3, POF_2Cl, $POFCl_2$, $POCl_3$	1·55 ± 0·03	E.D.	(n)
	PO′ 1·39 ± 0·02 PO 1·62 ± 0·02	—	(o)
	PO 1·65 ± 0·02	—	(o)
$NH_4H_2PO_4$	1·51 ± 0·11	*X*-Ray cryst.	(p)
KH_2PO_4	1·56	—	(p′)
Ag_3PO_4	1·61 ± 0·03	—	(q)
Phosphates	1·56	—	(r)
$(BPO_4)_n$	1·55	—	(s)
Phosphorus–sulphur bonds.			
$l_{calc.}$, A. : single, 2·14*; double, 1·94; triple, 1·80.			
$PSCl_3$	1·94 ± 0·03	E.D.	(t)
PSF_3	1·85 ± 0·02	—	(u)
	1·85 ± 0·02 (PO = 1·61 ± 0·02)	—	(u)
Chlorine–oxygen bonds.			
$l_{calc.}$, A. : single, 1·65*; double, 1·44.			
ClO_3^- ($NaClO_3$, $KClO_3$)	1·48	*X*-Ray cryst.	(k)
ClO_4^- ($KClO_4$, NH_4ClO_4)	1·44, 1·49	—	(v)
ClO_4^- ($MClO_4$)	1·56	—	(w)

* The single-bond lengths calculated by the method of Schomaker and Stevenson (*loc. cit.*) are : S–O, 1·69; P O 1·71; P–S, 2·10; Cl–O, $1{\cdot}68_5$ A.

† "E.D." means by electron-diffraction investigation of the vapour. "*X*-Ray cryst." means by *X*-ray diffraction investigation of the crystal.

‡ Pauling, *op. cit.*, p. 164.

(a) Rundle and Stevenson, unpublished. (a′) Lister and Sutton, *loc. cit.* (b) Schomaker and Stevenson, *J. Amer. Chem. Soc.*, 1940, **62**, 1270. (c) Palmer, *ibid.*, 1938, **60**, 2360. (d) Stevenson and Russell, *ibid.*, 1940, **62**, 3264. (e) Mooney and Zachariasen, *Physical Rev.*, 1933, (ii), **44**, 327. (f) Zachariasen, *Z. Krist.*, 1934, **89**, 529. (g) Albright, *ibid.*, 1932, **84**, 150. (h) Wooster, *ibid.*, 1936, **94**, 375. (i) Zachariasen and Ziegler, *ibid.*, 1932, **81**, 92. (j) Zachariasen and Hermann, *ibid.*, 1932, **82**, 161. (k) Zachariasen, *J. Amer. Chem. Soc.*, 1931, **53**, 2123. (l) *Idem, Physical Rev.*, 1932, (ii), **40**, 923. (m) Brown and Cox, J., 1940, 1. (n) Brockway and Beach, *J. Amer. Chem. Soc.*, 1938, **60**, 1836. (o) Hampson and Stosick, *ibid.*, p. 1814. (p) Zachariasen and Mooney, *J. Chem. Physics*, 1934, **2**, 34. (p′) West, *Z. Krist.*, 1930, **74**, 306. (q) Helmholtz, *J. Chem. Physics*, 1936, **4**, 316. (r) Wyckoff, "Structure of Crystals," 2nd Edn., 1931, pp. 192, 193. (s) Schulze, *Z. physikal. Chem.*, 1933, *B*, **24**, 215. (t) Beach and Stevenson, *J. Chem. Physics*, 1938, **6**, 75. (u) Stosick, *J. Amer. Chem. Soc.*, 1939, **61**, 1130. (v) Gottfried and Schresterius, *Z. Krist.*, 1932, **84**, 65. (w) Zachariasen, *ibid.*, 1931, **80**, 137.

a direct comparison of the moments of bonds to oxygen formed by elements in the first and the second short period can settle the point at issue, since the greater polarisability of the latter elements may affect the moments. We really need to know more certainly what the moments of the latter bonds would be if they were co-ordinate links.

We therefore determined the changes of moment which occur when phosphines and sulphides form links to oxygen or to sulphur, and those when they form complexes with boron trifluoride or trichloride; and, as far as possible, those when amines and ethers form links to the same atoms or groups.

Since the covalency of boron is limited to 4, the only kind of definite link which it can form in the complexes is a co-ordinate one. It cannot form a multiple link. Thus, we know the changes which occur when an element of the first short period forms dative links to oxygen or to boron, and when the corresponding element in the second short period forms one to boron : therefore we can predict roughly what should be the change if the latter formed a dative link to oxygen. We can then say with some certainty whether or not the actual change is as great as it should be for the formation of a bond of this kind.

This work has been only briefly mentioned before (Sutton, *Ann. Reports*, 1940, **37**, 75). Some results recently reported by Jensen (*Z. anorg. Chem.*, **1943**, **250**, 268) overlap ours, and will be considered with them.

As related matters of interest, attempts were made to establish the nature of the P–N link in triphenylphosphinephenylimine, and of the S–C link in the remarkable compound dimethylsulphonium-9-fluorenylidide.

This task was begun by one of us (J. S. H.) in 1937—1938, and continued (by G. M. P.) in 1938—1939; but then it was interrupted, and so is itself not really complete. A parallel investigation of bond lengths, by electron-diffraction studies, was commenced in 1938—1939, but it had to be abandoned.

EXPERIMENTAL.

Preparation and Purification of Materials.—Benzene (B.D.H. " AnalaR ") was purified by being frozen out three times, refluxed over phosphoric oxide in a stream of dry air, and finally distilled in the dry air stream. It was stored under dry air until used (Hampson, Farmer, and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **143**, 147).

(Preparations by J. S. HUNTER.)

Triphenylphosphine, prepared by Dodonow and Medox's method (*Ber.*, 1928, **61**, 907) from phenylmagnesium bromide and phosphorus trichloride, was recrystallised three times from ethanol; m. p. 79° (uncorr.); Dodonow and Medox give m. p. 79·5°. Its oxide was prepared both by Sauvage's method (*Compt. rend.*, 1904, **139**, 675), *i.e.*, reaction of phenylmagnesium bromide with phosphorus oxychloride, and also by that of Michaelis and von Soden (*Annalen*, 1885, **229**, 306), *i.e.*, oxidation of triphenylphosphine with bromine and alkali. The product of the first method was recrystallised three times, that of the second method once, from benzene–ligroin. Both products had m. p. 159° (uncorr.); Sauvage gives m. p. 156°.

Tri-*p*-chlorophenylphosphine was very kindly provided by Dr. Mann, having been prepared by the method of Mann and Chaplin (J., 1937, 527); m. p. 104° (uncorr.) (Mann and Chaplin give m. p. 103°). Its oxide was made by bromine oxidation, as for the phenyl compound, and had m. p. 178° (uncorr.) after several recrystallisations from ethanol (Mann and Chaplin give m. p. 175°).

Triphenylphosphine–boron trichloride was prepared by the action of excess of the trichloride on the phosphine in benzene solution, there being an appreciable evolution of heat on reaction. After the excess of trichloride and some benzene had been distilled off, the product separated, and was recrystallised from benzene–ligroin under anhydrous conditions. It is readily hydrolysed by water to the phosphine and boric and hydrochloric acids; it fumes slightly in moist air, and is decomposed without melting above 100°. Hydrogen peroxide or bromine and alkali both attack it readily, yielding the phosphine oxide and hydrolysis products. Owing to this instability the analytical data are not very satisfactory (Found : C, 55·4; H, 4·1; Cl, 30·4. $C_{18}H_{15}Cl_3PB$ requires C, 56·9; H, 3·95; Cl, 28·0%).

Trimethylamine oxide was prepared by the method of Dunstan and Goulding (J., 1899, **75**, 1005). Its hydrate, recrystallised once from ethanol, had m. p. 96° (uncorr.) (Dunstan and Goulding, *ibid.*, p. 795, give m. p. 96°); it was converted into the oxide by heating to 110° in a vacuum, and purified by vacuum sublimation at 150°.

As the oxide is very hygroscopic, solutions for dipole measurements were prepared as follows. A suitable quantity of oxide was heated to 110° in a vacuum in an 8-mm. bore glass tube until thoroughly dried, and then sublimed up the tube. Dry air having been admitted, the tube was cooled, and the section containing the sublimate cut out and immediately closed with rubber bungs. After weighing, the solid was rapidly pushed with a glass rod into the dry benzene against a stream of dry air, and the tube weighed again before hydration of the residue could occur.

(Preparations by G. M. PHILLIPS.)

Triphenylphosphine sulphide was prepared by the method of Michaelis and Gleichmann (*Ber.*, 1882, **15**, 803; cf. Michaelis and v. Soden, *ibid.*, p. 307) from triphenylphosphine and sulphur, the phosphine having been prepared as above (m. p. 81·5°, uncorr., after two recrystallisations, one with animal charcoal, from ethanol). The sulphide was recrystallised once from ethanol, giving m. p. 163° (uncorr.). Michaelis and v. Soden give m. p. 157·5° but Strecker and Grossmann (*Ber.*, 1916, **49**, 74) give 161°.

Triphenylphosphinephenylimine was prepared by the method of Staudinger and Meyer (*Helv. Chim. Acta*, 1919, **2**, 643) from triphenylphosphine and phenyl azide, the latter having been prepared as described by Dimroth (*Ber.*, 1902, **35**, 1032) and purified by distillation in a vacuum (b. p. 59°/15 mm.). After two recrystallisations from ether, the imine had m. p. 134° (uncorr.) (Staudinger and Meyer give m. p. 131—132°).

Trimethylphosphine–boron trichloride was prepared by distilling the phosphine off its silver iodide complex into an excess of boron trichloride, in a high vacuum. A white solid was formed immediately, the reaction being markedly exothermic. Excess of boron trichloride was distilled off, and the product purified by two vacuum sublimations (120°/0·5—1 mm.) and two recrystallisations from benzene [Found : C, 18·9; H, 4·7; Cl, 55·6 (by peroxide fusion). $C_3H_9Cl_3PB$ requires C, 18·6; H, 4·7; Cl, 55·0%]. The trimethylphosphine was prepared by the method of Hibbert (*Ber.*, 1906, **39**, 160) from methylmagnesium iodide and phosphorus trichloride, and was collected as the silver iodide complex (Mann, Wells, and Purdie, J., 1937, 1828).

The complex is a white solid, crystallising from benzene in fine needles. It is very stable to heat and to water : it sublimes at atmospheric pressure above 275° without any sign of decomposition, and is only very slowly hydrolysed by boiling with 5N-sodium hydroxide. Its solubility in benzene is low and it is, in general, very similar to its nitrogen analogue.

Diethyl ether–boron trifluoride was prepared from its components by the method of Gasselin (*Ann. Chim.*, 1894, **3**, 50) and purified by vacuum distillation; b. p. 60°/20 mm.

Trimethylamine–boron trifluoride was prepared by distilling the foregoing ether complex into a bulb containing excess of trimethylamine, in a vacuum apparatus (see Kraus and Brown, *J. Amer. Chem. Soc.*, 1929, **51**, 2690). The product, after three vacuum sublimations (60—70°/1—2 mm.), melted at 142—144° (corr.). After three further sublimations it melted at 146—146·5° (corr.) (Burg and Green, *J. Amer. Chem. Soc.*, 1943, **65**, 1838, give 139—147°) (Found : C, 28·5; H, 7·2; N, 11·1. Calc. for $C_3H_9NF_3B$: C, 28·4; H, 7·15; N, 11·0%). It is a white crystalline substance forming fine needles when sublimed slowly. When pure, the solid is stable and may be kept in a well-corked tube. When impure, it slowly turns brown, as did the triethylamine compound described by Kraus and Brown. It hydrolyses readily when in solution, and so is better purified by sublimation than by recrystallisation. Its solubility in both benzene and ether is rather low.

Trimethylamine–boron trichloride (Wiberg and Sütterlin, *Z. anorg. Chem.*, 1931, **202**, 35) was prepared by the same method as the triphenylphosphine compound. Trimethylamine, generated from sufficient hydrochloride to give an excess, was absorbed in benzene, and the trichloride was then distilled in. The product was recrystallised twice from benzene to a constant m. p. 245° (corr.; slight decomp.). Wiberg and Sütterlin give m. p. 243—244° without decomposition.

Diisobutyl sulphide–boron trichloride was prepared by the reaction of excess of the trichloride with the sulphide in ligroin (b. p. 40—60°) solution. The sulphide was prepared by the method of Beckmann (*J. pr. Chem.*, 1878, **17**, 445) as modified by Hammick and Williams (J., 1938, 211), and the trichloride was a commercial specimen purified in a MacGillivray–Podbielniak vacuum-jacketed fractionating column. After removal of the ligroin, the product was distilled in a vacuum (b. p. 87°/1—2 mm.). The complex is very unstable to heat and moisture. It fumes strongly in moist air; and a considerable black residue is left on vacuum distillation owing to thermal decomposition. It is a white solid (m. p. with marked decomposition *ca.* 50°) which rapidly becomes pink on standing. It is very soluble in light petroleum and in benzene. Owing to the instability the analytical results are very unsatisfactory (Found : C, 39·1; H, 7·0. $C_8H_{18}Cl_3SB$ requires C, 36·45; H, 6·9%).

This substance proved unsuitable for accurate electric dipole moment measurements; but since it seemed possible that the diethyl compound would distil with less decomposition and, if it were a liquid, be easier to manipulate, it was prepared.

Diethyl sulphide–boron trichloride, prepared just as was the di*iso*butyl compound, was purified by two distillations in a vacuum. It is a colourless, slightly oily liquid, b. p. 90°/1—2 mm. It was analysed by hydrolysis and silver titration of the chloride ion (Found : Cl, 51·6, 51·3, 51·4. $C_4H_{10}Cl_3SB$ requires Cl, 51·3%). Although it fumes slightly in moist air, is vigorously hydrolysed by water, and leaves a very slight residue on vacuum distillation, it is very much more stable both to heat and to moisture than is the di*iso*butyl compound and can be kept for a week in a well-stoppered tube before decomposition is significant. It is completely miscible with dry benzene or ligroin.

Fluorenyl-9-dimethylsulphonium bromide was prepared from 9-bromofluorene and methyl sulphide as described by Ingold and Jessop (J., 1930, 713). The 9-bromofluorene was obtained from fluorene by the stages, fluorenone (Huntress, Hershberg, and Cliff, *J. Amer. Chem. Soc.*, 1931, **53**, 2720), 9-hydroxyfluorene (Werner and Grob, *Ber.*, 1904, **37**, 2895), 9-bromofluorene (Ingold and Jessop, J., 1929, 2357).

Dimethylsulphonium-9-fluorenylidide was precipitated from the aqueous solution of the sulphonium bromide with alkali on the day it was required for use, washed with alcohol and ether, and dried in a vacuum for about 3 hours. The m. p. was 126—127° with decomposition after melting, but Ingold and Jessop recorded 70—75° with decomposition on rapid heating. It seems possible that this decomposition was caused by occluded alkali; for, although most of our samples, which were precipitated from very dilute solutions (0·25%), gave the high m. p., yet one sample, precipitated from a 2% solution, melted at 81—86°. A sample, m. p. 127—129°, was analysed (Found : C, 78·4; H, 5·9. Calc. for $C_{15}H_{14}S$: C, 79·65; H, 6·2%). As methyl sulphide is readily lost above the m. p., these results were accepted as adequate.

Because of the instability of the compound in solution, Ingold and Jessop's method of measuring the molecular weight cryoscopically was adapted to the dipole moment measurement; *i.e.*, dielectric constant was plotted against time, and the curve extrapolated to zero time. The density was shown not to vary significantly with time.

Physical Measurements.—Electric dipole moments were determined from measurements of the dielectric constant, refractive index, and density of benzene solutions at the same temperature. Dielectric constants were determined by a heterodyne beat method using an apparatus and a technique essentially the same as those described before (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668; Hampson, Farmer, and Sutton, *loc. cit.*), the solution condenser being similar to that described by H. O. Jenkins and Sutton (J., 1935, 609).

Densities were determined with a 10-ml. Sprengel–Ostwald pyknometer.

Refractive indices were measured relative to the solvent with a Pulfrich refractometer fitted with a divided cell, the mercury green line (5461 A.) being used for illumination.

For several reasons, including the instability and the low solubility of some of the compounds, it was not always possible to obtain molecular refractivities of the usual accuracy; so for these substances calculated values were used. Fortunately, since the moments were large, errors of a few c.c. in this quantity were immaterial. The following values of atomic refractivities were used in the calculations. From tables : C, 2·43; H, 1·11; CH_2, 4·69; O^{II}, 1·65; N^{III}, 2·89; Cl, 6·01; F, 0·99; S^{II}, 7·77; P, 9·09; double bond 1·69 c.c. From other results in this paper : increase on co-ordination of BCl_3, 18 c.c. (from $PPh_3,BCl_3 - PPh_3 = 18$, and $SEt_2,BCl_3 - SEt_2 = 18$); increase on co-ordination of BF_3, 2·7 c.c. (from $BCl_3 + 3F - 3Cl = 3$, and $OEt_2,BF_3 - Et_2O = 2{\cdot}4$).

The dielectric constant of pure dry benzene was taken to be 2·2727 at 25° (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, **123**, 664; Sugden, J., 1933, 768), that of dry air 1·0000. The refractive index of pure dry benzene at 25° was taken to be 2·25714.

Atom polarisations were allowed for by adding 5% to the electron polarisation calculated for the wave-length 5461 A.

The usual symbols are used in the tables; n refers to λ 5461 A., and the subscripts " soln." and " vap." are used when moments in solution and those measured in the vapour phase (or those approximately corrected for solvent effect) need to be distinguished.

Results.—All measurements are in benzene solution at 25°. Moments are expressed in Debye units (1 D. = 10^{-18} e.s.u.).

(Measurements by J. S. HUNTER.)

Triphenylphosphine.

f_2.	$d_{4^\circ}^{25^\circ}$.	ε.	n^2.	P_2.	${}_EP_2$.
0·00000	0·8740	2·2727	2·25714	—	—
0·00661	0·8776	2·3012	2·2568	136·9	94·04
0·01053	0·8810	2·3204	2·2573	138·4	93·31
0·01951	0·8857	2·3584	2·2574	136·9	93·84
0·03213	0·8933	2·4154	2·2580	136·4	93·21

$${}_\infty P_2 = 138{\cdot}4;\ {}_EP_2 = 93{\cdot}6;\ {}_AP_2 = 4{\cdot}7;\ {}_OP_2 = 40{\cdot}1\ \text{c.c.};\ \mu = 1{\cdot}39 \pm 0{\cdot}04\ \text{D.}$$

Bergmann and Schütz (*Z. physikal. Chem.*, 1932, *B*, **19**, 401) report 1·45 D. for the moment of this substance (m. p. given as 78°).

Triphenylphosphine oxide.

0·00000	0·8738	2·2727	2·2571	—	—
0·00630	0·8792	2·4534	2·2662	474·4	91·02
0·01325	0·8853	2·6653	2·2683	472·9	90·81
0·01892	0·8903	2·8359	2·2750	468·0	90·36
0·02836	0·8980	3·1337	2·2805	466·3	90·33

$${}_\infty P_2 = 477;\ {}_EP_2 = 91;\ {}_AP_2 = 5;\ {}_OP_2 = 381\ \text{c.c.};\ \mu = 4{\cdot}28 \pm 0{\cdot}02\ \text{D.}$$

Jensen (*Z. anorg. Chem.*, 1943, **250**, 268) reports $\mu = 4{\cdot}31$ D.

Tri-p-*chlorophenylphosphine.*

f_2.	$d_{4°}^{25°}$.	ε.	n^2.	P_2.	$_{E}P_2$.	f_2.	$d_{4°}^{25°}$.	ε.	n^2.	P_2.	$_{E}P_2$.
0·00000	0·8742	2·2727	2·2571	—	—	0·01381	0·8931	2·3028	2·2639	113·6	100·43
0·00759	0·8848	2·2894	2·2636	114·3	100·61	0·02374	0·9059	2·3244	2·2643	113·3	100·36

$_{\infty}P_2 = 114{\cdot}4$; $_{E}P_2 = 100{\cdot}5$; $_{A}P_2 = 5$; $_{O}P_2 = 8{\cdot}9$ c.c.; $\mu = 0{\cdot}65 \pm 0{\cdot}07$ D.

Tri-p-*chlorophenylphosphine oxide.*

0·00000	0·8742	2·2727	2·2571	—	—	0·01463	0·8974	2·4723	2·2652	278·2	97·84
0·00609	0·8842	2·3559	2·2629	277·6	98·03	0·02239	0·9103	2·5819	2·2662	275·9	97·94
0·00719	0·8856	2·3716	2·2639	279·5	97·91						

$P_2 = 281$; $_{E}P_2 = 98$; $_{A}P_2 = 5$; $_{O}P_2 = 178$ c.c.; $\mu = 2{\cdot}93 \pm 0{\cdot}03$ D.

Triphenylphosphine–boron trichloride.

0·00000	0·8741	2·2727	2·2571	—	—	0·00526	0·8771	2·8104	2·2781	1132	111·6
0·00253	0·8754	2·4458	2·2751	1112	112·5	0·00971	0·8796	3·1620	2·2801	1094	111·2

$_{\infty}P_2 = 1140$; $_{E}P_2 = 112$; $_{A}P_2 = 6$; $_{O}P_2 = 1022$ c.c.; $\mu = 7{\cdot}01 \pm 0{\cdot}06$ D.

(Measurement by N. J. LEONARD.)

Trimethylamine oxide.

0·0000	0·8740	2·2727	—	—	—	0·000351	0·8740*	2·28390	—	490·8	—
0·000295	0·8740*	2·28322	—	545·9	—	0·000450	0·8740*	2·28821	—	529·6	—

* The densities were all taken to be the same as that of the pure solvent, since it was found in some preliminary experiments that the differences are inside the experimental error in the case of such dilute solutions.

$_{\infty}P_2 = 522 \pm 30$; $_{E}P_2 = 30$; $_{O}P_2 = 492 \pm 30$ c.c.; $\mu = 4{\cdot}87 \pm 0{\cdot}15$ D.

Linton (*J. Amer. Chem. Soc.*, 1940, **62**, 1945) reports values for the moment of this substance of 5·04 D. in dioxan solution at 25°, and 5·02 D. in benzene solution at 45°. Since these solutions are more concentrated than those above, his values are probably more accurate than ours.

(Measurements by G. M. PHILLIPS.)

Triphenylphosphine sulphide.

0·00000	0·8729	2·2727	—	—	—	0·00465	0·8773	2·4244	—	537·8	—
0·00112	0·8741	2·3107	—	564·2	—	0·00850	0·8809	2·5588	—	544·9	—
0·00208	0·8747	2·3426	—	562·5	—						

$_{\infty}P_2 = 568$; $_{A}P_2 = 5$; $_{E}P_2 = 97$ (calc. from $PPh_3O + S^{II} - O^{II}$); $_{O}P_2 = 466$ c.c.; $\mu = 4{\cdot}73 \pm 0{\cdot}02$ D.

Jensen (*loc. cit.*) reports $\mu = 4{\cdot}74$ D.

Triphenylphosphinephenylimine.

0·00000	0·8737	2·2727	—	—	—	0·00365	0·8802	2·3871	—	515·5	—
0·000938	0·8753	2·3023	—	528·7	—	0·00724	0·8864	2·4993	—	507·0	—
0·00180	0·8770	2·3290	—	516·9	—						

$P_2 = 525$; $_{A}P_2 = 6$; $_{E}P_2 = 117$ (calc. from $PPh_3O + NPh - O$); $_{O}P_2 = 402$ c.c.; $\mu = 4{\cdot}40 \pm 0{\cdot}03$ D.

Jensen (*loc. cit.*) reports $\mu = 4{\cdot}45$ D.

Trimethylphosphine–boron trichloride.

0·00000	0·8740	2·2727	—	—	—	0·00174	0·8753	2·3931	—	1032	—
0·00101	0·8748	2·3434	—	1049	—	0·00241	0·8759	2·4388	—	1017	—

The low solubility prevented direct measurements of $_{E}P_2$. By subtracting the normal values for $3(C_6H_5)$ from the observed value for PPh_3,BCl_3 and adding the normal values for $3(CH_3)$ a value of 54 c.c. is obtained. This is 10 c.c higher than the sum of the atomic refractivities for $P(CH_3)_3$ plus 18 c.c. for BCl_3. The anomaly is the same as that between the observed and calculated values for PPh_3 itself, and so seems to be associated with the presence of phenyl groups. Therefore the second value, 44 c.c., was taken.

$_{\infty}P_2 = 1070$; $_{E}P_2 = 44$; $_{A}P_2 = 2$; $_{O}P_2 = 1024$ c.c.; $\mu = 7{\cdot}03 \pm 0{\cdot}01$ D.

Trimethylamine–boron trifluoride.

0·00000	0·8737	2:2727	—	—	—	0·00171	0·8740	2·3484	—	676·2	—
0·00091	0·8739	2·3144	—	700·5	—	0·00213	0·8741	2·3684	—	683·3	—
0·00115	0·8739	2·3251	—	697·6	—						

$_{\infty}P_2 = 713$; $_{A}P_2 = 1$; $_{E}P_2 = 23$ (calc. from sum of atomic refractivities + 2·7 c.c. for BF_3); $_{O}P_2 = 689$ c.c.; $\mu = 5{\cdot}76 \pm 0{\cdot}02$ D.

Bright and Fernelius (*J. Amer. Chem. Soc.*, 1943, **65**, 735) show that this substance is associated in benzene solution. Their weakest solution was, however, stronger than the strongest of those above; and, in any case, the effect of association should be eliminated by extrapolating the polarisation to infinite dilution.

Trimethylamine–boron trichloride.

0·00000	0·8732	2·2727	—	—	—	0·000356	0·8734	2·2920	—	829·4	—
0·000283	0·8734	2·2883	—	841·3	—	0·001003	0·8739	2·3285	—	845·5	—
0·000545	0·8736	2·3028	—	843·0	—	0·001783	0·8746	2·3729	—	842·4	—

$_{\infty}P_2 = 846$; $_{A}P_2 = 2$; $_{E}P_2 = 38$ (calc. as sum of atomic refractivities + 18 c.c. for BCl_3); $_{O}P_2 = 806$ c.c.; $\mu = 6{\cdot}23 \pm 0{\cdot}02$ D.

Diethyl ether–boron trifluoride.

f_2.	$d_{4°}^{25°}$	ε.	n^2.	P_2.	${}_{E}P_2$.	f_2.	$d_{4°}^{25°}$.	ε.	n^2.	P_2.	${}_{E}P_2$.
0·00000	0·8740	2·2727	2·2571	—	—	0·00000	0·8735	2·2727	—	—	—
0·01408	0·8801	2·8602	2·2466	575·4	23·59	0·01092	0·8772	2·7021	—	564·3	—
0·02529	0·8843	3·2708	2·2406	509·1	25·67	0·02148	0·8814	3·1261	—	526·9	—

${}_{\infty}P_2 = 608$; ${}_{E}P_2 = 25$; ${}_{A}P_2 = 1$; ${}_{O}P_2 = 582$ c.c.; $\mu = 5{\cdot}29 \pm 0{\cdot}03$ D.

Laubengayer and Finlay (*J. Amer. Chem. Soc.*, 1943, **65**, 884) find the moment of this substance to be 4·35 ± 0·12 D.; but their solutions were evidently partly hydrolysed, so we consider our result to be the more reliable.

Diethyl sulphide–boron trichloride.

0·00000	0·8733	2·2727	2·2571	—	—	0·01088	0·8824	2·8718	2·2583	758·9	45·95
0·00500	0·8774	2·5371	2·2580	779·2	47·65	0·01778	0·8877	3·2926	2·2601	733·9	47·70

${}_{\infty}P_2 = 797$; ${}_{E}P_2 = 47$; ${}_{A}P_2 = 2$; ${}_{O}P_2 = 748$ c.c.; $\mu = 6{\cdot}00 \pm 0{\cdot}01$ D.

Dimethylsulphonium-9-fluorenylidide.

Variation of dielectric constant with time.

f_2, 0·000364.		f_2, 0·000629.		f_2, 0·000735.		f_2, 0·001509.	
Time, mins.	ε.	Time, mins.	ε.	Time, mins.	ε.	Time, mins.	ε.
11·75	2·2865	25·75	2·2905	18	2·2991	22·5	2·3154
17·25	2·2842	33·25	2·2865	23·5	2·2962	27·25	2·3108
24·25	2·2824	40·75	2·2838	29	2·2937	33·25	2·3074
31·5	2·2809	52	2·2809	35·5	2·2911	38	2·3051
42·75	2·2801	57·5	2·2803	40·5	2·2892	43·75	2·3028
53·75	2·2800	70	2·2794	53·75	2·2850	49·5	2·3009
						55·75	2·2990

Density, dielectric constant, and polarisation as a function of molar fraction.

f_2.	$d_{4°}^{25°}$	ε_{zero}, measd.	ε_{zero}, mean.	P_2.
0·00000	0·8735	2·2727	2·2727	—
0·000505	0·8738	—	—	—
0·000889	0·8743	—	—	—
0·000364	0·8738 *	2·2936 ± 0·0004	2·2934	882 †
0·000629	0·8740 *	2·3116 ± 0·0010	2·3081	871 †
0·000735	0·8741 *	2·3147 ± 0·0010	2·3141	872 †
0·001509	0·8747 *	2·3519 ± 0·0050	2·3580	868 †

${}_{\infty}P_2 = 876$; ${}_{E}P_2 = 70$ (calc. as sum of atomic refractivities, no allowance being made for the C$\leftarrow$S link);
${}_{A}P_2 = 4$; ${}_{O}P_2 = 802$ c.c. (estimated error ± 50 c.c.); $\mu = 6{\cdot}2 \pm 0{\cdot}2$ D.

*† The values of dielectric constant at zero time, obtained by extrapolation, were plotted against mole-fraction, and the best mean curve drawn. Points from this (ε_{zero} mean) were then used for calculating the total polarisation (†) at the several mole-fractions. Since densities had to be determined in separate runs, interpolated values (*) were used in these calculations.

DISCUSSION.

(Throughout this discussion, " D." is omitted after dipole moments.)

The most obvious way in which to analyse the experimental data would be to derive the dipole moments of the particular bonds in which we are interested and to compare them. In practice, however, this cannot be done at all accurately when the bonds are in such complicated molecules, because of the inadequacy of the assumptions which have to be made (cf. Sutton, *Ann. Reports*, 1940, **37**, 54); so the argument would be weakened by the uncertainties thus introduced. Initially, therefore, it is better to follow a simpler procedure, introducing as few assumptions as possible. Hence, we propose first to compare, not the moments of the bonds themselves, but the apparent vector changes of moment which accompany their formation, to do this for a series of related compounds, and to look for irregularities which might reveal changes in bond type.

Accordingly, we have calculated the changes which occur when amines, phosphines, ethers, or sulphides add on oxygen, sulphur, or boron halides. They are the vectors which must be considered to arise along the conjectured directions of the new bonds, if we suppose that when the latter are formed the moment of the donor molecule remains unchanged; this assumption is probably inaccurate, but the comparisons in related series should still be valid.

For symmetrical amines or phosphines, the new bond is along the axis of symmetry; so the required vector is simply the algebraic difference of the moments of the donor molecule and of the complex. To calculate the vector change on formation of ether or thioether complexes, we may reasonably assume the bonds to radiate from a donor atom along the axes of a regular tetrahedron so the new bond makes an angle of 125° 16′ with the resultant of the other two.

The moments used in these calculations are listed below. It is supposed that in the amines, phosphines, ethers, and sulphides the negative end of the dipole is *away from* the carbon atoms. The moments of their oxides, sulphides, and boron complexes are supposed to be in the same general direction, *i.e.*, with the negative end towards the added atom or group. The values quoted are mostly observed in benzene solution: in some cases the value in the gas phase is known and is given also, with a subscript (g) to distinguish it. Numbers in parenthesis in the list of sources relate to the list in " A Table of Dipole Moments " (*Trans. Faraday Soc.*, 1934, **30**).

Substance.	Moment.	Source.
Trimethylamine	$0{\cdot}65_g$	Groves and Sugden, J., 1937, 1779.
	0·74	Estimated.
Triethylamine	$0{\cdot}69_g$	Higasi, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1937, **31**, 311.
	0·79	
Trimethylamine oxide	(4·87)	Present work.
	5·03	Linton, *J. Amer. Chem. Soc.*, 1940, **62**, 1945.
,, –BCl$_3$	6·23	Present work.
,, –BF$_3$	5·76	,,
Ethylamine	0·99	Ghosh (134).
,, –AlCl$_3$	6·94	Ulich (197).
Trimethylphosphine	(1·2)	Estimated.
,, –BCl$_3$	7·03	Present work.
β-Bistriethylphosphine platinochloride	10·7	Jensen, *Z. anorg. Chem.*, 1936, **229**, 225.
Triphenylphosphine	1·39	Present work.
,, oxide	4·28	,, ; Jensen, *ibid.*, 1943, **250**, 268.
,, sulphide	4·73	,, ,, ,, ,,
,, –BCl$_3$	7·01	,,
,, selenide	4·83	Jensen (*loc. cit.*, 1943).
Triethylamine	1	Estimated.
β-Bistriethylarsine platinochloride	10·5	Jensen (*loc. cit.*, 1936).
Triphenylarsine	1·07	Bergmann (226).
,, oxide	5·50	Jensen (*loc. cit.*, 1943).
Triphenylstibine	0·57	Bergmann (226).
,, oxide	~ 2·3	Jensen (*loc. cit.*, 1943).
,, sulphide	5·40	,, ,,
β-Triphenylstibine platinochloride	9·3	Jensen (*loc. cit.*, 1936).
Diethyl ether	1·14	" A Table of Dipole Moments," *loc. cit.*, various authors.
	$1{\cdot}18_g$	Groves and Sugden, *loc. cit.*
,, –BCl$_3$	5·98	Ulich (197).
,, –BF$_3$	5·29	Present work.
	(4·92)	Laubengayer and Finlay, *loc. cit.*
Methyl sulphide	1·40	Partington (147).
Dimethylsulphone	$4{\cdot}44_g$	Coop and Sutton, *Trans. Faraday Soc.*, 1939, **35**, 495.
Dimethylsulphonium-9-fluorenylidide	6·2	Present work.
Ethyl sulphide	1·58	Smyth (260).
,, –BCl$_3$	6·00	Present work.
β-Bisdiethylsulphide platinochloride	9·5	Jensen, *Z. anorg. Chem.*, 1935, **225**, 97.
Diethylsulphone	4·41	Sutton (257).
*iso*Butyl sulphide	1·58	Williams, " A Table of Dipole Moments," *loc. cit.*
,, sulphoxide	3·90	Hammick and Williams, J., 1938, 211.
Phenyl sulphide	1·50	Hampson (269).
Diphenyl sulphoxide	4·00	,,
Diphenylsulphone	5·05	de Vries (149).
Phenyl selenide	1·38	Bergmann (107).
Diphenyl selenoxide	4·44	Jensen (*loc. cit.*, 1943).
Phenyl telluride	1·13	Bergmann (107).
pp'-Ditolyl telluroxide	3·93	Jensen (*loc. cit.*, 1943).

The calculated vector changes are set out on p. 155. The plain figures are calculated from the above data on the assumptions already given, without any corrections for solvent effect or for mesomeric moment changes. The latter can arise only in the phenyl compounds, while the former, according to Frank's theory of the solvent effect (*Proc. Roy. Soc.*, **1935**, **152**, 171), is unlikely to be important for most of the substances concerned. For triphenylphosphine, its oxide and sulphide, however, it seems desirable to allow for these factors, so corrected values are given in italics, the methods of correction being indicated by notes. These should be more comparable with the uncorrected values for the other substances; but it will be seen that the corrections do not affect the main conclusions. Values deemed to be of doubtful accuracy are in parenthesis.

From this table it will be observed that the vector changes, to be referred to hereinafter as $\Delta\mu_{XY}$, are not very different for the formation of the $\geqslant\text{N}\rightarrow\text{O}$, $\geqslant\text{N}\rightarrow\text{BCl}_3$, and $\geqslant\text{N}\rightarrow\text{BF}_3$ groupings, ranging from 4·25 to 5·5; and that $\Delta\mu_{\text{P}\rightarrow\text{BCl}_3}$ is about the same as $\Delta\mu_{\text{N}\rightarrow\text{BCl}_3}$. Assuming that the simple relation $\Delta\mu_{\text{N}\rightarrow\text{O}}/\Delta\mu_{\text{P}\rightarrow\text{O}} = \Delta\mu_{\text{N}\rightarrow\text{BCl}_3}/\Delta\mu_{\text{P}\rightarrow\text{BCl}_3}$ holds, we should expect that $\Delta\mu_{\text{P}\rightarrow\text{O}}$ would be about 4·25; but $\Delta\mu_{\text{PO}}$ is only *ca.* 2·7, so PO appears not to be P→O.

For the $\geqslant$PS and the $\geqslant$PSe link the argument is similar, though the data are less complete. From the values for $\Delta\mu_{\text{N}\rightarrow\text{O}}$, $\Delta\mu_{\text{N}\rightarrow\text{BCl}_3}$, and $\Delta\mu_{\text{P}\rightarrow\text{BCl}_3}$ we should expect the values of $\Delta\mu_{\text{P}\rightarrow\text{S}}$ and $\Delta\mu_{\text{P}\rightarrow\text{Se}}$ to be at least 4·25; whereas the values of $\Delta\mu_{\text{PS}}$ and $\Delta\mu_{\text{PSe}}$ are only 3·1 and 3·2, respectively. It would be better to use values for $\Delta\mu_{\text{P}\rightarrow\text{AlCl}_3}$ and $\Delta\mu_{\text{P}\rightarrow\text{GaCl}_3}$ to derive those for $\Delta\mu_{\text{P}\rightarrow\text{S}}$ and $\Delta\mu_{\text{P}\rightarrow\text{Se}}$, through relations of the type $\Delta\mu_{\text{N}\rightarrow\text{O}}/\Delta\mu_{\text{P}\rightarrow\text{S}} = \Delta\mu_{\text{N}\rightarrow\text{BCl}_3}/\Delta\mu_{\text{P}\rightarrow\text{AlCl}_3}$, in an attempt to allow for the effect of the greater radii of sulphur and of selenium, which should make the values expected larger than 4·25; but these data are not available. A rough value of $\Delta\mu_{\text{P}\rightarrow\text{PtCl}_2}$ is 6·4; which is, as anticipated, considerably larger than $\Delta\mu_{\text{P}\rightarrow\text{BCl}_3}$.

The values of $\Delta\mu_{\text{AsO}}$ and of $\Delta\mu_{\text{SbS}}$ are about the same as $\Delta\mu_{\text{N}\rightarrow\text{O}}$, though they are still considerably less than those for $\Delta\mu_{\text{As}\rightarrow\text{PtCl}_2}$ and $\Delta\mu_{\text{Sb}\rightarrow\text{PtCl}_2}$; so no very definite conclusions can be drawn about these bonds from existing data. $\Delta\mu_{\text{SbO}}$ is so irregular that one would like to see the value confirmed.

The above argument cannot be applied in full to the case of the SO bond, because there is no direct determination of the vector change when ethereal oxygen co-ordinates oxygen, *i.e.*, $\Delta\mu_{\text{O}\rightarrow\text{O}}$; but, assuming that

TABLE II.

Vector Changes, $\Delta\mu_{XY}$.

$\geqslant$NO 4·25^{Me_3}			$\geqslant$N,BCl$_3$ 5·50^{Me_3}	$\geqslant$N,BF$_3$ 5·02^{Me_3}	$-$N,AlCl$_3$ (5·9)^{EtH_2}	
$\geqslant$PO 2·89^{Ph_3} *2·66*			$\geqslant$P,BCl$_3$ 5·62^{Ph_3} (5·8)^{Me_3} *5·39*			
	$\geqslant$PS 3·36^{Ph_3} *3·11*	$\geqslant$PSe 3·44^{Ph_3} *3·21*				$\geqslant$P,PtCl$_2$ (6·4)^{Et_3}
$\geqslant$AsO 4·43^{Ph_3} *4·14*						$\geqslant$As,PtCl$_2$ (6·4)^{Et_3}
$\geqslant$SbO ((1·7))^{Ph_3}		$\geqslant$SbS 4·83^{Ph_3} *4·46*				$\geqslant$Sb,PtCl$_2$ (6·12)^{Ph_3}
	>OO [4·05]		>O,BCl$_3$ 5·29^{Et_2}	>O,BF$_3$ 4·58^{Et_2}		
	>SO 2·5—3·0		>S,BCl$_3$ 4·98^{Et_2}	>S,C$_{13}$H$_8$ (5·3)^{Me_2}		>S,PtCl$_2$ (5·3)^{Et_2}
	>SeO (3·06)^{Ph_2}					
	>TeO (2·3)$^{(PhMe)_2}$					

Notes.—Correction for PO: Gas-phase moment for triphenylphosphine estimated to be 1·12 D.; for the oxide, μ(g) estimated equal to μ(soln.); mesomeric difference in triphenylphosphine and its oxide supposed to be —0·5 D.

Correction for PS: As for PO.

Correction for P,BCl$_3$: μ(g) for triphenylphosphine estd. 1·12 D.; mesomeric moment difference in triphenylphosphine and the BCl$_3$ complex supposed to be $-$0·5 D.; μ(g) for the latter estd. equal to μ(soln.).

The superscript signs—Ph$_3$, Me$_2$, etc.—show that the values so distinguished are derived from data for the triphenyl, dimethyl, etc., compounds.

The values of the PO and the PS vector changes from the data for phosphorus trichloride, phosphoryl chloride, and thiophosphoryl chloride are 3·5 and 2·4, respectively. These are deemed less reliable, because of the greater probability of a considerable mutual alteration of moments by induction. The value from the data for *pp'p''*-trichlorophenylphosphine and its oxide is ambiguous, being 3·6 or 2·3 according to which way round the moment of the former is supposed to be.

the difference between $\Delta\mu_{O\to BCl_3}$ and the hypothetical $\Delta\mu_{O\to O}$ is the same as that between $\Delta\mu_{N\to BCl_3}$ and $\Delta\mu_{N\to O}$, we find $\Delta\mu_{O\to O} = 4{\cdot}04$; or, assuming that $\Delta\mu_{O\to O}/\Delta\mu_{N\to O} = \Delta\mu_{O\to BCl_3}/\Delta\mu_{N\to BCl_3}$, we find $\Delta\mu_{O\to O} = 4{\cdot}09$. A value 4·05 is therefore taken. Thence we estimate $\Delta\mu_{S\to O}$ to be 3·8, whereas $\Delta\mu_{SO}$ is 2·5—3·0. $\Delta\mu_{SeO}$ and $\Delta\mu_{TeO}$ are also less than the estimated $\Delta\mu_{S\to O}$. $\Delta\mu_{S,C_{13}H_8}$ has, however, the high value to be expected if the sulphur–carbon link were a dative bond, as it is in Ingold and Jessop's formulation (J., 1930, 713).

From this simple consideration of magnitudes of moments changes we conclude that the PO, PS, PSe, SO, SeO, and TeO oxy-bonds are not pure co-ordinate links (cf. Smyth, *J. Amer. Chem. Soc.*, 1938, **60**, 183); but the differences between the observed and the calculated values are not always large. This conclusion becomes much more definite, however, when we consider what the observed moments would mean if we supposed that the bonds were, nevertheless, co-ordinate links.

We must first calculate values for the moments of all the relevant bonds, bearing in mind that this can be done only very roughly. If we ignore the possible effects of mutual induction, these bond moments are either, for the links to oxygen, the same as the vector changes given above, or, for the links to boron, they can be taken as the vector changes less the moments of the BCl$_3$ or BF$_3$ parts which are assumed to be equal to those of chloroform (1·2 D.) and of fluoroform (1·6 D.) respectively. The following are the values obtained:

$\mu_{NO} = 4{\cdot}25$ D. $\quad$ $\mu_{NB} = 4{\cdot}3,\ 3{\cdot}4$ D.
$\mu_{PO} = 2{\cdot}66$ $\quad$ $\mu_{PB} = 4{\cdot}2,\ 4{\cdot}6$
$\mu_{PS} = 3{\cdot}11$
$\mu_{OB} = 4{\cdot}1,\ 3{\cdot}0$
$\mu_{SO} = 2{\cdot}5$—$3{\cdot}0$ $\quad$ $\mu_{SB} = 3{\cdot}78$ $\quad$ $\mu_{SC} = 5{\cdot}0$

We then calculate the degree of sharing of the bonding electrons. If they were symmetrically shared between the donor and the acceptor atoms, the bond moment would be 4·80l (l being the bond length in A.). If the moment is actually 4·80lx, then we may suppose that the centroid of the bonding electrons is distant from the donor atom only a fraction $x/2$ of the bond length. By taking the observed interatomic distances for the bonds of disputed character (see Table I),* and observed or estimated ones for the definite co-ordinate links (using the Pauling radii, $r_N = 0{\cdot}70$, $r_O = 0{\cdot}66$, $r_S = 1{\cdot}04$, $r_P = 1{\cdot}10$ A., and the Bauer and Beach radius for boron, 0·85 A., since these give good results for known cases, cf. p. 148), we can calculate the values of x to be the following:

NO 0·65 $\quad$ NB 0·58—0·46
PO 0·36 $\quad$ PB 0·45—0·49
PS 0·33
OB 0·56—0·41
SO 0·36—0·44 $\quad$ SB 0·42 $\quad$ SC 0·575

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* These calculations cannot be done for such bonds when the distance has not been observed, since to use lengths calculated for co-ordinate links, in the case of these bonds of unknown character, would be to beg the question.

In no case is x unity. The values for the PO, PS, and SO bonds show the same irregularities as did the vector changes.

In the limit, when a " co-ordinate link " has no moment and x is therefore zero, there is no bond; so it seems reasonable to suppose that the smaller x is, the weaker is the co-ordinate link.* Hence we should expect that if the PO, PS, and SO bonds were co-ordinate links they would be weak ones, weaker than the others.† We shall show, however, that actually they appear to be much the stronger.

This is indicated qualitatively by the facts that amine oxides have to be made by the action of strong oxygenating agents on amines, and can be reduced back by zinc dust and acid or alkali (" Beilstein," IV, p. 49), whereas the phosphine oxides are formed very readily, sometimes by aerial oxidation, and cannot be reduced back at all easily. Similarly, the pentoxide of phosphorus is much more stable relative to the trioxide than nitrogen pentoxide is to the lower oxides.

From existing thermal data (see Bichowsky and Rossini, " The Thermochemistry of Chemical Substances," New York, 1936) the heat of the reaction $PCl_3(g) + O(g) \longrightarrow POCl_3(g)$, *i.e.*, the apparent heat of formation from the atoms (H_a) of the PO bond, is calculated to be 127·5 kg.-cals./g.-mol. One of 138 kg.-cals./g.-mol. is got from the experimental value of H_a for phosphoric oxide, P_4O_{10}, and an estimated one for the oxide P_4O_6; the latter being taken as that of twelve P–O bonds, the values for which are calculated by Pauling's method (*op. cit.*, Chap. II), from the experimental H_a values for the P–P and the O–O bond and the difference of electronegativity co-ordinates, to be 72·1 kg.-cals./g.-mol each. Similarly, from data for thionyl chloride and sulphuryl chloride a value of 102·6 kg.-cals./g.-mol. is found for H_a of the SO bond. Furthermore, from data for chlorine heptoxide (Goodeve and Marsh, J., 1937, 1161) and monoxide (Bichowsky and Rossini, *op. cit.*) a value of 52 kg.-cals./g.-mol. for the oxy-bond ClO is found. Thus, all three bonds are strong, the first two especially.‡

From the data for nitrogen trioxide and pentoxide and the heat of atomisation of oxygen (Bichowsky and Rossini, *op. cit.*), the apparent heat of formation of the $N \rightarrow O$ link is 68·8 kg.-cals./g.-mol.; while from those for ethyl nitrite and nitrate it is 66·6. These values include an unknown resonance energy which may be as much as 20 kg.-cals. It is therefore obvious that the PO and the SO bond, far from being weaker, are much stronger.

We may also compare the experimental values for $H_a(PO)$ and $H_a(SO)$ with those estimated for $H_a(P \rightarrow O)$ and $H_a(S \rightarrow O)$ by a process like that used for getting the theoretical vector changes of moment, *i.e.*, by supposing that $H_a(N \rightarrow O)/H_a(P \rightarrow O) = H_a(N \rightarrow B \text{ or Al})/H_a(P \rightarrow B \text{ or Al})$. $H_a(S \rightarrow O)$ can be obtained similarly. We now need $H_a(N \rightarrow B \text{ or Al})$, $H_a(P \rightarrow B \text{ or Al})$, and $H_a(S \rightarrow B \text{ or Al})$.

The apparent heat of formation of a co-ordinate link in a complex is the same as the heat of reaction of the donor and acceptor molecules. Such values for the combination of amines with boron compounds have been determined by Schlesinger, Flodin, and Burg (*J. Amer. Chem. Soc.*, 1939, **61**, 1079) and by Burg and Green (*ibid.*, 1943, **65**, 735). They find the following values of $-\Delta H$: NMe_3,BMe_3 (g), 14 kg.-cals./g.-mol.; NMe_3,BMe_2F (g), 18·3; $NMe_3,BMeF_2$ (g), 23·1. $-\Delta H$ could not be obtained for NMe_3,BF_3 by their method (variation of the degree of dissociation of the vapour with temperature), but a value of 28·5 is found by extrapolating the above data. Bauer, Finlay, and Laubengayer (*loc. cit.*) quote a value of 9 ± 1 for $-\Delta H$ of NH_3,BMe_3 (g), got from the data of Stock and Ziedler (*Ber.*, 1921, **54**, 531), one of 51 for C_5H_5N,BF_3 (g) (van der Meulen and Heller, *J. Amer. Chem. Soc.*, 1932, **54**, 4404), and they report that $-\Delta H$ for NH_3,BF_3 (solid) is 42. The heat of the reaction $NH_3 (g) + AlCl_3 (g) \longrightarrow NH_3,AlCl_3$ (cryst.) can be calculated from the tabulated data (Bichowsky and Rossini, *op. cit.*) to be 72 kg.-cals./g.-mol. Laubengayer and Finlay (*loc. cit.*) find $-\Delta H$ for the gaseous dimethyl and diethyl etherates of boron trifluoride to be $13 \cdot 9 \pm 0 \cdot 7$ and $12 \cdot 5 \pm 1 \cdot 0$ kg.-cals./g.-mol., respectively.

No data exist for the heats of formation of phosphine complexes with boron compounds, but $-\Delta H$ for $PH_3 (g) + AlCl_3 (g) \longrightarrow PH_3,AlCl_3$ (cryst.) is 43·7 kg.-cals./g.-mol., *i.e.*, considerably less than for the corresponding amine, and for $PH_3 (g) + TiCl_4 (g) \longrightarrow PH_3,TiCl_4$ (cryst.) it is 27·7. Hydrogen sulphide forms similar complexes, $H_2S,AlCl_3$ (cryst.) and $H_2S,TiCl_4$ (cryst.), for which the corresponding values are 43·1 and 18 kg.-cals./g.-mol., respectively.

In attempting to arrive at the desired values from these obviously incomplete data, several points must be borne in mind. Some of the values given, being heats of forming the solid product, include an unknown heat of vaporisation of perhaps 10 kg.-cals./g.-mol. or more. Those for the formation of the $N \rightarrow O$ link include resonance energy (see above). Obviously, too, the apparent heat of forming a co-ordinate link between a given pair of atoms is greatly affected by the other atoms or groups in the molecule.

For these reasons, only a rough answer can be expected: but it seems, both from these data and from our qualitative observations on the stability of some of the complexes, that the apparent heat of forming a

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* The bearing of this hypothesis on the structure for ozone is discussed later (p. 161).

† This is similar to the possibility considered by Bauer, Finlay, and Laubengayer (*loc. cit.*), and rejected in the case of dimethyl ether–boron trifluoride, that the donor and acceptor components are linked through an electrostatic polarisation of the former by the latter. In any classical electrostatic treatment, the so-called exchange forces are ignored; but if the degree of interaction were small, the difference between this and the quantum mechanical treatment would be small.

‡ It may be noted that the order of strength of the bonds, PO > SO > ClO, is also that of the differences of electronegativity of the elements for their normal valencies, *viz.*, 1·4, 1·0, 0·5; the H_a values given above are, in fact, all about 100 times these differences.

co-ordinate link from phosphorus or sulphur to an acceptor molecule is not greater than the heat of forming one from nitrogen or oxygen to the same molecule (cf. Davidson and Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 316); and that the heat of forming a co-ordinate link from nitrogen to oxygen is very roughly the same as that for one to aluminium chloride. Hence, we conclude that the heat of forming the $S\rightarrow O$ or the $P\rightarrow O$ bond would probably be not greater than 40 and certainly not more than 70 kg.-cals./g.-mol.

Rough as these values are, there seems no real doubt that the PO and SO oxy-bonds are much stronger than they would be if they were co-ordinate links: indeed, they are stronger than any such links yet investigated. Hence, their lengths, strengths, and electric dipole moments all lead to the conclusion that they are not this type of link. For the PS, PSe, SeO, and TeO oxy-bonds the case is not so complete; but the available evidence strongly favours this conclusion for them too.

The Description of the Oxy-Bonds.—Having decided with some certainty what the oxy-bonds are not, we must now consider what they are.

It has been suggested that they are double bonds and that *d* orbitals of the central atom are involved (Pauling and Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 13; Hampson and Stosick, *ibid.*, 1938, **60**, 1814; Brockway and Beach, *ibid.*, p. 1836; Beach and Stevenson, *J. Chem. Physics*, 1938, **6**, 75). Their heats of formation are of the right order: on p. 156 a value of 103 kg.-cals. was given for that of the SO bond, and others of 127·5 and 138 for that of the PO bonds. These are 1·42 and 1·76—1·91 times the respective calculated heats of forming the single $S{-}O$ (72·4 kg.-cals.) and $P{-}O$ (72·1) links. The former value may also be compared with that of the SO ($^3\Sigma^-$) molecule, which is probably 92·3 kg.-cals. (see Herzberg, " Molecular Spectra and Molecular Structure," I, New York, 1939, p. 493), wherein the link, like that in the O_2 ($^3\Sigma_g^-$) molecule, should be similar in strength to a double bond. Furthermore, the heat of formation per SO bond in sulphur dioxide is 127·7 kg.-cals., and in sulphur trioxide it is 112·5 kg.-cals. These compounds may, therefore, also be consistently formulated with double bonds.

This hypothesis would lead us to expect that the oxy-bonds should be quite definite entities, as in fact they seem to be. We have already remarked how near to 1·44 A. are the SO bond lengths in Table I; that of the similar bond in the SO ($^3\Sigma^-$) molecule is 1·49 A. (value estimated for double bond, 1·49 A.). The PO and PS oxy-bonds show rather more variation in length, but are still fairly constant.

Furthermore, the formation of an oxy-bond often has no effect upon the length of the other bonds (Brockway and Beach, *loc. cit.*; see also phosphorous and phosphoric oxide in Table I) though in thionyl chloride (Palmer, *ibid.*, 1938, **60**, 2360), dimethylsulphone, and the trithionate ion the other bonds are appreciably lengthened (see p. 148). This is much what would be expected, since an increase in covalency brings about a slight increase in bond length in other cases, *e.g.*, the octahedral covalent radii are about 3% longer than the tetrahedral ones (Pauling, *op. cit.*, p. 184); and l_{PF} in phosphorus pentafluoride is 1·57 A. against 1·52 A. in the trifluoride, likewise l_{PCl} in the pentachloride is 2·04—2·11 A. against 2·00 A. in the trichloride.

The dipole moments of the bonds are also relatively constant. Values calculated for the SO bond all lie between 2·2 (see Coop and Sutton, *Trans. Faraday Soc.*, 1939, **35**, 505) and 2·9, except in sulphur dioxide, wherein it is only 1·6; those for the PO bond between 2·7 and 3·5; those for the PS bond between 2·4 and 3·1.

From the discussion of bond lengths, it follows that the shortness of the oxy-bonds, compared with the lengths predicted for normal double bonds in the lower valency states, is abnormal and needs explanation. Palmer (*J. Amer. Chem. Soc.*, 1938, **60**, 2360) suggested that triple-bonded structures of the type $\overset{-}{X}\equiv\overset{+}{O}$ make a considerable contribution. If this were so, however, the dipole moments of the bonds should be very small, or even have the positive pole on the oxygen; and this is not the case (Lister and Sutton, *Trans. Faraday Soc.*, 1939, **35**, 495).* Such effect of the polar triple bond could only be compensated by an equal contribution from the single, co-ordinate linked structure $\overset{+}{X}{—}\overset{-}{O}$; but since this individual structure would, according to the previous evidence, be much less stable than either the double- or the triple-bonded ones, and since furthermore there is no automatic relation between the contribution of this and of the triple-bonded one as there is for example in carbon dioxide, where the contributory structures may be written $O{=}C{=}O$, $\overset{+}{O}{\equiv}C{—}\overset{-}{O}$, $\overset{-}{O}{—}C{\equiv}\overset{+}{O}$, there is no apparent reason why this structure should make more than a minor contribution (cf. Pauling, *op. cit.*, Chap. I). In turn, therefore, it is improbable that the triple-bonded structure can be important.

Pauling has attempted to account for the similar abnormalities in the sulphate ion (*op. cit.*, p. 241) by supposing that there is a contraction of radius brought about by the formal charges on the sulphur atom in such contributory structures as (I) and (II), which affects the length of the double bonds therein. This explanation implies that the resultant bond length is determined mainly by the " stiffest " component, *i.e.*, the double bond; but this principle seems to be one of some generality and may therefore be granted (cf. Pauling, *op. cit.*, p. 175). Applying it to the thionyl, sulphuryl, and phosphoryl compounds, we should expect the SO bonds to be of markedly different length in dimethylsulphone and sulphoxide, since ionic structures of the type (III) or (IV), which are at least conceivable in the former, are not in the latter. The actual difference is, however, small; for l_{SO} in the former is 1·44 (Table I) and in the latter 1·46 A. We should also expect

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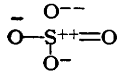
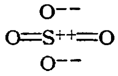
* For further data relating to the SO bond see Hampson, Farmer, and Sutton, *Proc. Roy. Soc.*, 1933, **143**, 147.
This is shown for the PO link by the moments of triphenylphosphine oxide (4·28) and of *pp′p″*-trichlorotriphenylphosphine oxide (0·65) (see experimental section).

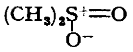
a marked difference for dimethylsulphone and sulphuryl fluoride or chloride, since in the latter it is possible that the positive charge on the sulphur atom would be increased by the partial ionic character of the sulphur–halogen bonds, *e.g.*, (V), whereas in dimethylsulphone any ionic charge from the carbon–sulphur bonds would be negative; yet in both the fluoride and the chloride the length is 1·43 A. Still another objection is that such a change in radius should affect *all* the bonds springing from the central atom; whereas actually the C–S bond in dimethylsulphone, like the S–S bonds in the trithionate ion $[SO_3{-}S{-}SO_3]^{--}$ (Pauling, *op. cit.*, p. 241), is rather *longer* than a normal single bond. Shortening by this sort of polar effect seems, therefore, to be only of minor importance.


$${}^{-}O-\underset{O^{-}}{\overset{O^{--}}{S^{++}}}=O$$

(I).


$$O=\underset{O^{--}}{\overset{O^{--}}{S^{++}}}=O$$

(II.)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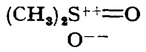
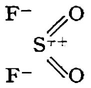
(III.)


$$(CH_3)_2\underset{O^{--}}{S^{++}}=O$$

(IV.)


(V.)

The best course is to abandon for the present these attempts to find a detailed, mechanistic explanation of the phenomenon, and to relate it to a general principle which is gaining recognition, *viz.*, that there is a connection between the length and strength of a bond, inasmuch as abnormally strong bonds tend to be abnormally short, and weak ones long (cf. Hampson and Stosick, *loc. cit.*; Lister and Sutton, *loc. cit.*; Sutton, *Ann. Reports*, 1940, **37**, 78; Schomaker and Stevenson, *loc. cit.*, 1941). The system for calculating single-bond lengths from covalent radii and the Pauling electronegativity co-ordinates proposed by Schomaker and Stevenson is an attempt to state this principle precisely and quantitatively for a special case, since the co-ordinates in question are derived from abnormalities of bond energies (Pauling, *op. cit.*, Chap. II).

Although, as we have seen, the bond length in phosphorus pentafluoride is greater than it is in the trifluoride (1·57 and 1·52 A., respectively), it still is less than the sum of the single covalent radii (1·80 A., using the revised fluorine value; see Schomaker and Stevenson, *loc. cit.*); and in sulphur hexafluoride it is 1·57 instead of 1·76 A. Similarly, we should expect that double bonds to oxygen X=O, which almost certainly have heats of formation greater than the mean of X=X and O=O, would have lengths less than those calculated from normal radii. The values of these radii are by no means certain (see tables in Pauling and Huggins, *Z. Krist.*, 1934, *A*, **87**, 205; Pauling and Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 1223; Pauling, *op. cit.*, p. 164): that for O= has been variously given as 0·59, 0·55, and 0·57 A., while from the oxygen molecule ($^3\Sigma_g^-$), with a bond very similar to a double one, it is 0·604 A. Those used in Table I are from Pauling's list; and they probably allow for some contraction, such as would occur in a bond of moderate strength, as did the older single-bond covalent radii. Taking the normal O= radius as 0·60, and those for S=, Se=, P=, Cl=, and C= as 0·94, 1·07, 1·00, 0·89, and 0·665 A. (Pauling, *loc. cit.*), we derive the calculated double bond lengths: S=O, 1·54; Se=O, 1·67; P=O, 1·60, P=S, 1·94; Cl=O, 1·49; and C=O, 1·27 A. If now the Schomaker and Stevenson correction $[-\ 0{\cdot}09(x_A - x_B)]$ be applied, Pauling's electronegativities being used for the elements in their lower valency states, these become 1·43, 1·57, 1·46, 1·91, 1·49, and 1·18 A., the observed values being 1·44, 1·61 (in selenium dioxide), 1·39—1·55, 1·85—1·94, 1·44—1·48, and 1·21 A. Although this procedure is very arbitrary, the rough consistency of the results indicates that the underlying principle is at least qualitatively correct.

Two arguments have been advanced against the double-bond formulations; and they must be answered. One (p. 147) is that the so-called double bonds do not all add on water (Werner, *loc. cit.*). The other may be stated as follows. Elements in the second short period, unlike those in the first, show little tendency in general to form multiple links in their lower-valent states (Pauling, *op. cit.*, p. 232); *e.g.*, the S_8 and P_4 molecules have been shown to contain single bonds only, and $S_8 \longrightarrow 4S_2\ (^3\Sigma^-) - 96{\cdot}8$ kg.-cals., $P_4 \longrightarrow 2P_2 - 28{\cdot}2$ kg.-cals. (Rossini and Bichowsky, *op. cit.*); phosphorus trioxide exists as P_4O_6 with a single-bonded cage structure (Maxwell, Hendricks, and Deming, *J. Chem. Physics*, 1937, **5**, 626; Hampson and Stosick, *loc. cit.*) and not as O=P—O—P=O; silicon dioxide exists as a single-bonded, three dimensional polymer $(SiO_2)_n$ instead of O=Si=O. Therefore, it is argued, the oxy-bonds are unlikely to be multiple. These two arguments prove to be related.

Addition of water, $XO + H_2O \longrightarrow X{<}\begin{smallmatrix}OH\\OH\end{smallmatrix}$, or polymerisation, $nXO \longrightarrow (-O-X-)_n$, will occur, roughly speaking,* only if $2H_a(X{-}O) > H_a(XO)$, *i.e.*, $H_a(XO)/H_a(X{-}O) < 2$. The oxides of second short period elements readily add on water or polymerise in such a way as to produce that number of single bonds which is equal to the lower or contra-valency, but not more. This shows that the above condition is satisfied for double bonds relative to single ones which in number do not exceed this limit. Werner's argument assumes, however, that it is also satisfied when the number of single bonds is increased further; but this is not a necessary consequence. Sidgwick and Bowen (*Ann. Reports*, 1931, **28**, 387; cf. Sidgwick, "The Covalent Link in Chemistry," Cornell, 1933, p. 120) have shown that the ratio of the heats of forming a double bond to that for the corresponding single one is sometimes less than 2 and sometimes more; *e.g.*, it is less than 2 for the

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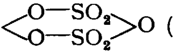
* In this statement, changes of entropy are ignored. So also are changes in intermolecular energies and heats of ionisation. The last should encourage addition of water; so the critical value of the ratio for this process may actually be more than 2. The effect of changes of intermolecular energy can be minimised by taking reactants and products in the same phase.

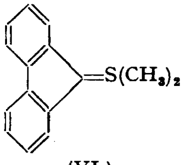
homoatomic links formed by carbon and all the elements after the first short period for which there are data; and for those formed by nitrogen and oxygen it is more, as it is also for carbon–oxygen links (2·0—2·2). This suggests that for elements of variable valency the ratio may possibly be less than 2 if the number of single bonds formed does not exceed the lower valency, but greater than 2 relative to any extra single bonds; and therefore that further hydration does not occur because of the relative weakness of the latter. This view, that single bonds formed in going from the lower to the higher covalency are weaker than the first type, is supported by the non-existence of any covalent higher halides of sulphur except the fluoride, and by the observed differences between the heats of forming the three P–Cl bonds in phosphorus trichloride (62·8 kg.-cals. each) and the two extra ones in the pentachloride (39·4 each). The difference in strength may be due to steric effects, to the extra bonds involving *d* orbitals of the central atom—though the oxy-bonds, if double, must do this too—or to both causes. It is much less marked in the heavier elements. For example, whereas triphenyl-phosphine and -arsine oxides form hydrates which are polar, yet triphenylstibine oxide forms a five-covalent dihydroxide $SbPh_3(OH)_2$ (Jensen, *Z. anorg. Chem.*, 1943, **250**, 268). Telluric acid hydrates up to $Te(OH)_6$, $Te(OCH_3)_6$ is known, and $TeCl_4$ is quite stable. Periodic acid hydrates to $IO_2(OH)_3$ and to $IO(OH)_5$; and ICl_3 is comparatively stable. These facts suggest that the phenomenon may be steric in origin; but the detailed structure of phosphorus pentachloride (Pauling, *op. cit.*, p. 109) indicates that there is a difference of the bonding orbitals for the two bonds along the axis from the three in the belt of the trigonal pyramid (cf. Wells, *Z. Krist.*, 1938, **99**, 367, on the trimethylstibine dihalides).

In the other argument, it is supposed that the reason for the polymerisation is the absolute weakness of the multiple bonds. We have shown, however, that this is only proof of a relative weakness. The $P{\equiv}P$ link may be weak ($H_a = 42{\cdot}1$ kg.-cals., Bichowsky and Rossini, *op. cit.*; but Herzberg, *op. cit.*, gives 116); but the $S{=}S$ ($^3\Sigma_g^1$) bond is quite strong (103·4, Rossini and Bichowsky; Herzberg gives 83) and the $Si{=}O$ bond is still more so [162 in SiO_2(g), Bichowsky and Rossini; 170 in SiO, Herzberg]. Hence, we should not expect multiple bonds to oxygen, formed in attaining the higher valency, to be weak on an absolute scale; nor, as we have seen above, need they be weak relatively.

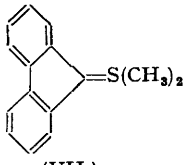
The behaviour of sulphur dioxide and trioxide illustrates the relation between polymerisation and addition of water developed above. The former does not polymerise; but the latter does (the Trouton constants are 23·1 and 32·4 cals./degree respectively)—in the α- or γ-form to  $O_2S\begin{smallmatrix}\diagup O{-}SO_2 \diagdown \\ \diagdown O{-}SO_2 \diagup\end{smallmatrix}O$ (Smits and Moerman, *Rec. Trav. chim.*, 1937, **56**, 169) and in the β-form to $({-}O{-}SO_2{-})_n$ (Gerding and Moerman, *Z. physikal. Chem.*, 1937, *B*, **35**, 216). This indicates that $H_a(S{=}O)/H_a(S{-}O)$ is greater than 2 for the former and less than 2 for the latter; *i.e.*, since $H_a(S{=}O)$ is 127·7 and 112·5 kg.-cals., respectively (p. 157), that the estimated value on p. 157 for $H_a(S{-}O)$ is too large and that it really is between 63·75 and 56·25 kg.-cals. Correspondingly, sulphur dioxide should not add water to form hydroxyl groups so readily as does the trioxide. This is so (see Ley and König, *ibid.*, 1938, *B*, **41**, 365); but, no doubt owing to the rather small margin, even the latter does not do so completely—100% sulphuric acid gives off the trioxide.

From this discussion we see that a reasonably consistent explanation of the physical characteristics and chemical properties of the oxy-compounds of phosphorus, sulphur, selenium, and chlorine can be given on the assumption that the oxy-bonds are double. It is still possible, of course, that the co-ordinate link structures make some contributions; but unless the values for their energies previously estimated (p. 157) are much too small, these contributions are minor. If we assume that they are the sole cause of the bond dipole moments, they are equal to x of the table on p. 155, *i.e.*, 0·35—0·44; but it is very probable that the double covalent bonds themselves are polar (Mulliken's "homopolar dipole," *J. Chem. Physics*, 1935, **3**, 573; cf. Coulson, *Trans. Faraday Soc.*, 1942, **38**, 433), and hence that the contributions are much smaller. These oxy-bonds are, therefore, best described as double. For those formed by arsenic and antimony no such definite opinion can yet be expressed, owing to the lack of data.

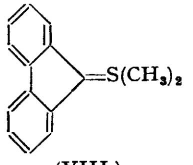
The Sulphur–Carbon Link in Dimethylsulphonium-9-fluorenylidide.—From the foregoing arguments, it might be expected that this bond would be double. It can be so formulated in an otherwise reasonable structure (VI). The dipole-moment data in Table II show, however, that this is not the case. We must, therefore, seek the reason for this apparent anomaly. The theory of the stabilisation of molecules by resonance (Pauling, *op. cit.*, Chap. IV) supplies it. If the sulphur–carbon link were double, the only resonance stabilisation possible would be that provided by the alternative Kekulé structures for the benzene rings (VII, VIII), *i.e.*, there is none peculiar to the system as a whole. If, however, the link is single, there are many possibilities of new component structures, for the unshared electrons which would be left on the carbon skeleton could be on any of the 13 atoms composing it. A few of these are shown in (IX)—(XII). All would be highly



(VI.)

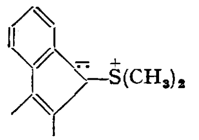


(VII.)



(VIII.)

polar, because the donor atom carrying the positive charge and the unshared pair of electrons carrying the negative one are widely separated.



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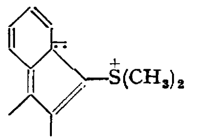
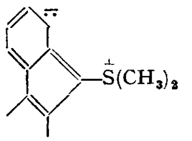
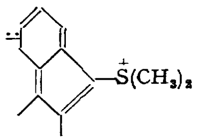


(X.)



(XI.)



(XIII.)

Hence, the single-bonded would be stabilised relative to the double-bonded structure; and it would be very important, or possibly predominant, even if the $\rangle S{=}C\langle$ link were as strong as the $\rangle S{=}O$ link. If the S=C link were very weak, the single-bonded structure would still be possible: the resonance stabilisation then would probably be the only reason why the complex hangs together.

The substance loses methyl sulphide very readily. The other product is probably a large condensed hydrocarbon which is also considerably stabilised by resonance. Unless there is a large difference between the resonance energies in reactant and product, this instability indicates that the two sulphur–carbon links are weak relative to one double carbon–carbon bond, and hence that the latter of the two possibilities considered above is correct.

The Phosphorus–Nitrogen Link in the Phosphinimines.—The nature of this bond in triphenylphosphinephenylimine, $PPh_3{:}NPh$, is not clear from the present data. The numerical difference of the moments (in solution) of triphenylphosphine and its phenylimine is 3·01; but, since the molecule lacks an axis of symmetry, this is less than the vector change. A rough estimate of the moment of the phosphorus–nitrogen bond, got by assuming $\mu_{Ph-N} = 1{\cdot}5$, $P\!-\!\widehat{N}\!-\!Ph = 125°$, and making corrections for the solvent effects and resonance moments, is 4·2. If, however, we try also to allow for the mutual induction between moments, following Groves and Sugden (J., 1937, 1992), the moment obtained is 3·0. So μ_{PN} is probably 3—4.

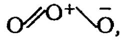
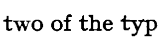
The bond may therefore be more nearly a co-ordinate link than is either the P–O or the P–S bond. It appears also to be rather weaker, since treatment of the phenylimine with mineral acids readily gives the phosphine oxide, while boiling with carbon disulphide gives the sulphide (Staudinger and Meyer, *Helv. Chim. Acta*, 1919, **2**, 664). These facts could be explained if the $\geqslant P{=}N{-}$ bond were for some reason less stable than the others. There is no obvious reason why it should be—the difference of the Pauling electronegativities for phosphorus and nitrogen is almost the same as that for sulphur and oxygen—but in this particular substance the possibilities of resonance complicate the discussion of its structure or reactions, and data for simpler phosphinimines are desirable.

Brockway and Beach (*J. Amer. Chem. Soc.*, 1943, **65**, 1551) found the phosphorus–nitrogen distance in the six-membered ring of the polymer $(PNCl_2)_3$ to be 1·65 ± 0·04 A., and concluded from this that the bonds are, like those in benzene, intermediate in order between single and double, therefore that the ring is of benzenoid type, and hence that the phosphorus is quinquevalent. This conclusion is consistent with the new system of calculating bond lengths. If the following covalent radii for phosphorus and nitrogen be assumed, *viz.*, P—, 1·10 (Pauling); N—, 0·74 (Schomaker and Stevenson); P=, 1·00 (Pauling); N=, 0·65 A. (*i.e.*, 0·05 A. greater than the O= radius from O_2), and the Schomaker and Stevenson correction is applied as before, l_{P-N} is calculated as 1·76, and $l_{P=N}$ as 1·57 A. From these values, the length of the benzenoid P–N bond should be 1·62 A.

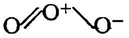
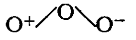
Stereochemical Considerations.—The non-planar configurations of the sulphoxides and related compounds, like the bent one of sulphur dioxide, are no longer regarded as decisive evidence against the sulphur–oxygen bond being double. It is realised that the stereochemistry of sulphur with a decet of electrons in the valency group would probably be based not on the regular tetrahedron but on the trigonal bipyramid, like that of quinquecovalent phosphorus (Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360; Lister and Sutton, *Trans. Faraday Soc.*, 1939, **65**, 495; Stevenson and Schomaker, *J. Amer. Chem. Soc.*, 1940, **62**, 1267; Kimball, *J. Chem. Physics*, 1940, **8**, 188).

The stereochemistry of sexacovalent sulphur should be based on the regular octahedron, as in the hexafluoride (Braune and Knoke, *Z. physikal. Chem.*, 1933, *B*, **23**, 297; Brockway and Pauling, *Proc. Nat. Acad. Sci.*, 1933, **19**, 860). Hence, the trioxide, if all three bonds were double, should be planar, as in fact it is (Smits, Moerman, and Pathuis, *Z. physikal. Chem.*, 1937, *B*, **35**, 60; Palmer, *loc. cit.*): sulphuryl chloride and the sulphones should, however, be tetrahedral (Kimball, *loc. cit.*).

Brockway and Beach (*J. Amer. Chem. Soc.*, 1938, **60**, 1836) showed that the stereochemistry of the phosphoryl halides is not based on the regular tetrahedron, the X—P—X angles being close to 106° instead of 109·5°. It may be noted that the sum of the three angles between three neighbouring bonds in a trigonal bipyramidal arrangement is 300°; the mean is therefore 100°. Our data for the moments of triphenylphosphine oxide and its *pp'p''*-trichloro-derivative give a value of 112° ± 5° for the Ph—P—Ph angle, indicating enlargement by the steric repulsion of the phenyl groups. No definite value for the Ph—P—Ph angle in triphenylphosphine can be got from our data for this and its trichloro-derivative, because the direction of the latter moment relative to the first is not known: hence there are two possible answers, 117° ± 5° and 101° ± 5°.

The Structure of Ozone.—No completely satisfactory explanation of the properties of ozone has yet been given. Its electric dipole moment is only 0·49 (Lewis and Smyth, *J. Amer. Chem. Soc.*, 1939, **61**, 3063); the bonded O–O distance is 1·26 ± 0·02 A. (Shand and Spurr, *ibid.*, 1943, **65**, 179), *i.e.*, it is intermediate between the single-bond length, 1·46 A. (Giguère and Schomaker, *ibid.*, p. 2025) and that in the oxygen molecule, 1·20 A. (see above); the angle $O-\hat{O}-O$ is 127° ± 3°; and the heat of forming each bond from the atoms is only 71·4 kg.-cals. (data from Bichowsky and Rossini, *op. cit.*). Shand and Spurr sought to explain the small moment by supposing that there is hybridisation not only between two structures of the type , but also with two of the type  which cancel each other's polarity. Calculating the contribution of the latter from the observed O–O bond distance, and hence calculating the electric moment, they find it still to be 1·62; and if they had taken the oxygen double bond radius as 0·60 instead of 0·55 A., they would have got a still bigger value. So the small one observed remains puzzling.

On p. 155 it was shown that the moments of complexes are not as large as they would be if the electrons forming the co-ordinate link were symmetrically shared. The actual bond may, therefore, be formally described as a hybrid between an unbound state A B and a symmetrical or perfect co-ordinate link $\overset{+}{A}-\overset{-}{B}$. The former obviously has a high energy content because the unbound atoms repel each other. The latter is stabilised relative to the former by having a covalent link and an ion-pair bond too, but it is destabilised by the difference between the energy required for the ionisation of A and that given out by the corresponding addition of an electron to B. An intermediate state may therefore be more stable than either extreme: the greater the energy content of the extreme polar state, the nearer would the actual one be to the unbound extreme; and consequently the less its polarity, and the less its stability relative to the dissociated state A plus B.

The low moment and low heat of formation of ozone are therefore related. Ozone and the nitro-group make an interesting contrast: the moment of the former being 0·49, and of the latter *ca.* 2·5 ($\mu_{CH_3\cdot NO_2} = 3\cdot1$; $\mu_{CH_3N} = 0\cdot6$) and the heat of the reaction $O_2 + O \longrightarrow O_3$ being only 14·6 kg.-cals. against *ca.* 68 for $-N{=}O + O \longrightarrow -NO_2$. It seems probable that the structure may be best described as a hybrid between two component structures of the type  and two of the type  O, the latter predominating. The possible components  are likely to be of an even higher energy content, and so to be unimportant. On the principle that the resultant bond length is disproportionately near to that with the greater stretching force constant (cf. p. 157), we should expect the O–O distance to be greater than, but quite close to, that in the oxygen molecule which also is paramagnetic, and the valency angle to be greater than 120°. In this way, therefore, the salient characteristics of the molecule can be explained.

The Existence of the Halogen Oxy-acids.—Although the oxy-acids of the heavier halogens have long been known, fluorine has not yet been shown definitely to form any (*Ann. Reports*, 1936, **33**, 147). From the present discussion we may conclude that it probably cannot, save possibly hypofluorous acid.

Generalising from what we have learnt about oxy-bonds, we may suggest that the higher oxy-acids of chlorine, bromine, and iodine exist only because these elements are able to utilise *d* orbitals to form double bonds to oxygen. Nitrogen forms nitric acid, with a co-ordinate link to oxygen; but it is much more easily reduced than is phosphoric acid. Oxygen forms no oxy-acid in this sense, though sulphur forms many. Covalent fluorine would not be expected to form co-ordinate links more readily than covalent nitrogen or oxygen, but less so, for it has a greater nuclear charge. Therefore we should not expect it to form any oxy-acid other than hypofluorous acid in which it is univalent.

Conclusions.—Two general conclusions emerge. One is that co-ordinate links occur much less commonly than they were once thought to do. To emphasise this, we may recall that bond-length measurements provide evidence for the bonds in several types of complex formed by transition elements being partly or wholly double in character (Pauling, *op. cit.*, pp. 250—258), instead of the single, co-ordinate links they were formerly thought to be. They do occur; but on the whole they seem to be relatively weak. Their occurrence is sometimes favoured by the increase of resonance energy of a system into which they bring possibilities of more component structures, as in the nitro-group, ozone, and in dimethylsulphonium-9-fluorenylidide.

The factors which determine their strength seem fairly obvious, although they have not been quantitatively sorted out in any particular case: they are (1) the strength of a covalent link between the two elements in their charged states, which probably will be much the same as that of a pure covalency one between the uncharged ones, (2) the energy of ionisation and the electron affinity of the donor and acceptor atoms, respectively, (3) the energy of the ionic link, (4) the repulsion energy of the two parts of the complex when brought to within bond-forming distance, excluding the repulsion terms between the actual donor and acceptor atoms which are included in (1) and (3), but including such terms as repulsion energy between attached groups, and distortion energy.

The sharing of the bonding electrons between the donor and the acceptor atoms is found not to be symmetrical: they are always nearer the former. Polarity and strength should increase or decrease together.

The second general conclusion is that the properties of the oxy-bonds in the higher oxides and oxy-acids of phosphorus, sulphur, selenium, and chlorine can be very well explained on the hypothesis that they are double. Certain minor premises involved in this explanation, adopted rather as empirical generalisations, themselves require to be elucidated in terms of more fundamental concepts, *e.g.*, the generalisation that abnormally strong bonds are short and weak ones long, and the limited generalisation that the single bonds formed in reaching the lower covalency are stronger than the extra ones formed in reaching the higher covalency although double bonds are not similarly affected. But the general correctness of the hypothesis now seems well established; and its recognition leads to the solution of a number of problems of long standing.

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