# **91.** *The Infra-red Spectra of Some Organo-phosphorus Esters.*

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The infra-red spectra of 33 esters of phosphorus have been examined. Characteristic frequencies are suggested for the P–O–Ar (2) and the P–O–C (aliphatic) linkage. Frequencies already suggested for the P=O, P–H, P=S, and P–F links are discussed in the light of our findings.

PREVIOUS studies of the infra-red spectra of organo-phosphorus compounds have been few although this class of compound is of rapidly growing importance both on the commercial side—where they find applications as plasticisers, resins, lubricating oil additives, insecticides, etc.—and the biochemical side for studies on phosphate metabolism. In all these fields it is important to know whether characteristic frequencies exist, which can be correlated with the various units of molecular structure, and the primary aim of this work has been to examine as many compounds as possible from this point of view, although it was hoped that some data on the structure of the materials might be obtained at the same time. It will be appreciated that all the correlations suggested are liable to be affected by changes in the polarity or weight of the substituent groups, especially where skeletal vibrations are concerned, but they appear to show sufficient consistency to be likely to be of some value in structural diagnosis provided that the necessary caution is observed.

Previous work along these lines has been carried out by Meyrick and Thompson (*J.*, 1950, 225) who examined the infra-red and Raman spectra of some ten alkyl esters of phosphorus oxy-acids, and suggested correlations for the P=O, P–H, and P–O linkages; and after the completion of this work, Gore (Symposium of the Faraday Soc. on Spectrography and Molecular Structure, 1950, in the press) and Smith (*ibid.*) have also suggested a number of likely correlations. These will be discussed in the light of our own findings.

*Experimental.*—The compounds whose spectra have been measured were largely synthetic products prepared in these laboratories, although a few have been supplied by Dr. W. Gerrard, of Northern Polytechnic, and Dr. Kilby, of Leeds University. All were believed to be of reasonably high purity and the phosphorus content, refractive index, b. p. or m. p., etc., were checked in all cases.

The spectra were obtained by using the Perkin-Elmer 21B recording double-beam spectrometer with a rock-salt prism.

Liquid samples were examined as films pressed between rock-salt plates and/or as solutions in carbon disulphide. Solid samples were similarly examined by using the Nujol grinding technique and/or solution methods. All the solution studied were examined in the same amalgam-sealed cell 0·05 mm. thick at 5% concentration.

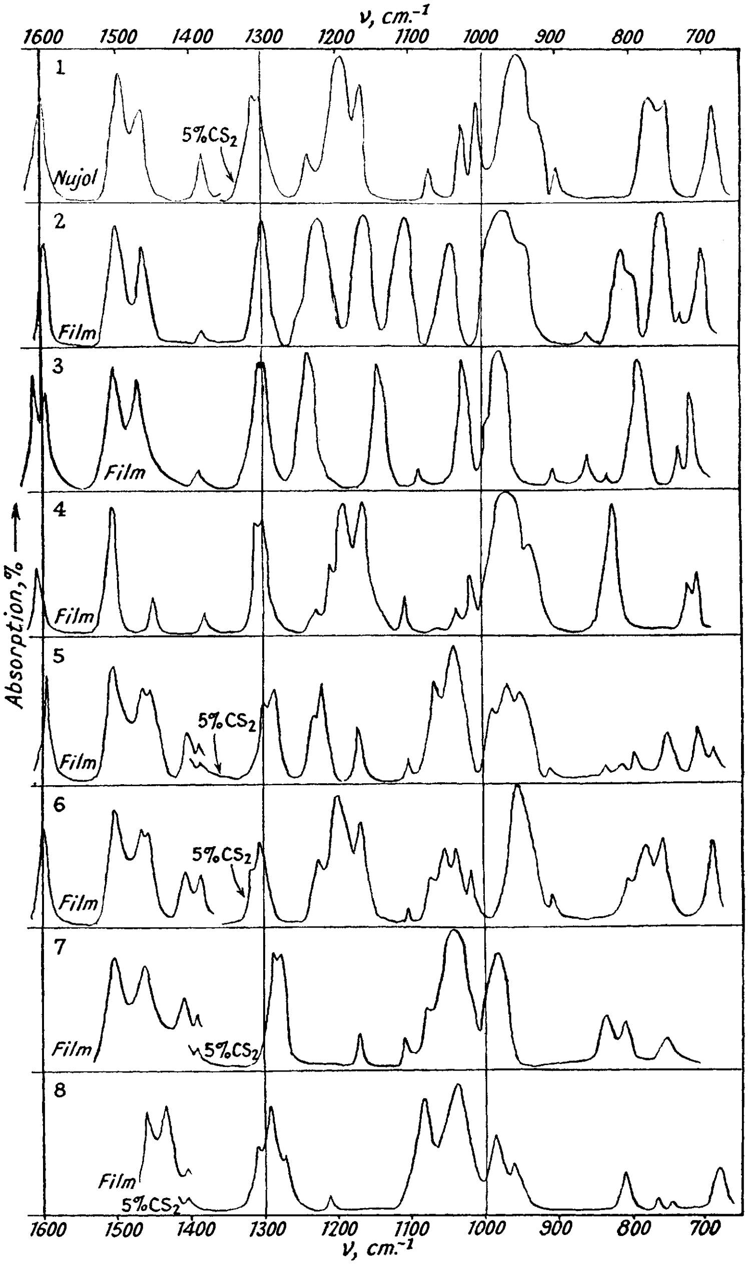
*The* P=O *Grouping.*—The position of this grouping is fairly well defined. Phosphorus oxychloride shows a strong band near 1274 cm.$^{-1}$ which is absent in phosphorus trichloride, and this band also appears in the Raman spectrum of the oxychloride, where it has been assigned to the P=O vibration. On this basis, Meyrick and Thompson (*loc. cit.*) have assigned a similar band which they find in five phosphonates to this vibration. This is strongly supported by our own findings (see Table), particularly in compounds in which the P=O is replaced by the P=S link when there is almost no alteration of spectra other than the disappearance of the 1280 cm.$^{-1}$ vibration. Gore (*loc. cit.*) has recently published data on some hundred phosphates and thiophosphates in which the same appearance and disappearance of this band with the P=O linkage are noted, and Smith (*loc. cit.*) has independently come to the same conclusion on other phosphates and phosphonates. There can therefore be little doubt of the validity of this assignment, although the limiting range in which the band can occur is rather more open. Thompson suggested 1250—1260 cm.$^{-1}$, which is obviously too narrow a range in the light of our results. Gore suggested 1250—1300 cm.$^{-1}$, and all our compounds run close to this range. Smith associates the position of the P=O link with the degree of electro-negativity of the substituents, as he finds considerable shifts when hydroxyl groups are present or when phenyl compounds are bonded directly to carbon. However, all his normal esters fall in the range 1250—1300 cm.$^{-1}$, as do our own, and this would be, therefore, the expected position of the P=O absorption, although it may be that it is liable to larger shifts in special circumstances.

The other point of interest in this connection is the doublet nature of the P=O vibration in many cases. Gore (*loc. cit.*) has suggested that this might arise from an O–$C_2H_5$ vibration close to that of the P=O itself. This will not explain the doublet character of this vibration in a number of fully aromatic compounds which we have prepared, although it may be the reason for the weaker absorption shown in this region by some of the alkyl phosphites and not shown by aromatic phosphites.

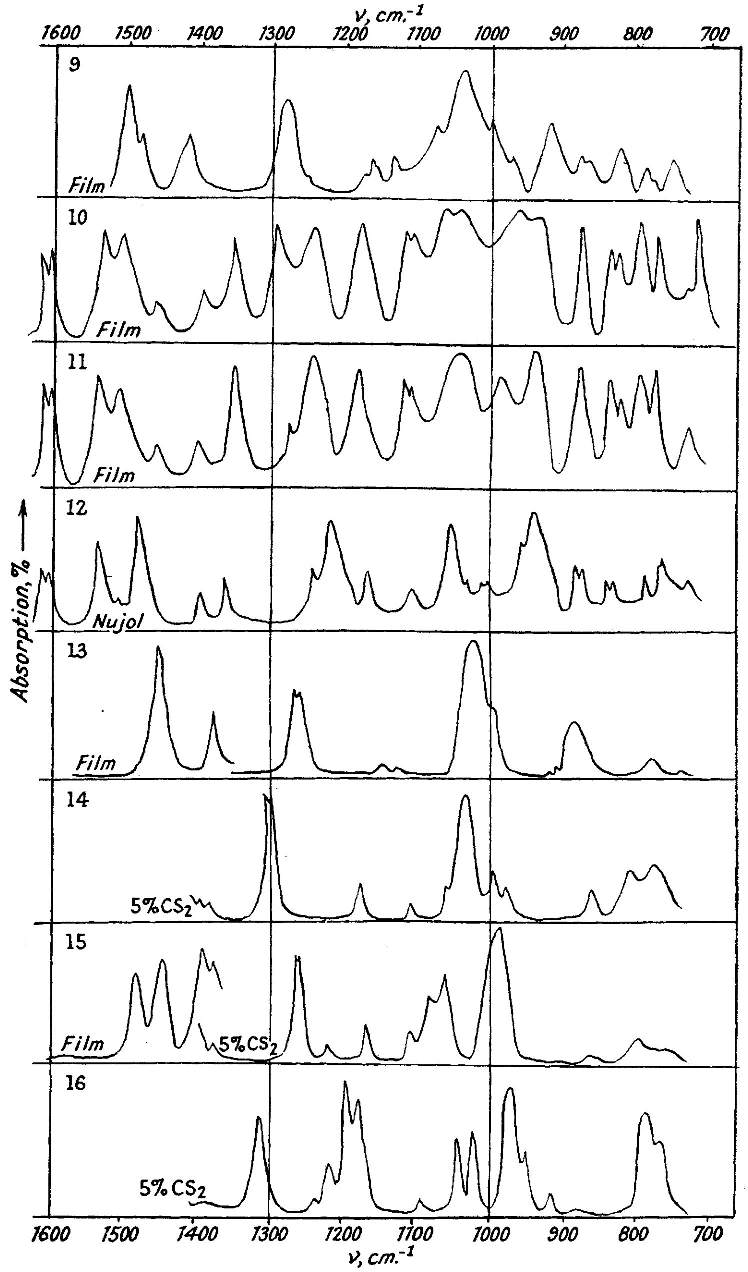
*The* P–O–C *Bond.*—The P–O–C bond might be expected to give rise to two characteristic frequencies, one arising from the P–O vibration, modified by the O–C link, and the other from the O–C linkage modified by the phosphorus atom. As skeletal vibrations they will be difficult to differentiate, as they are likely to occur in the wide regions of C–O or C–C stretching frequencies. However, the C–O–C– linkage gives rise to strong bands, so there is no reason to suppose that they will not arise with the P–O–C linkage also. By analogy with the carbon ether links it is to be expected that such characteristic bands would occupy different positions depending on whether the carbon atom is aromatic in nature or not.

(a) *The* P–O–C (*Aromatic*) *Linkage.*—A study of the spectra obtained shows that in all cases in which the P–O–C(Ar) grouping is present, an intense band appears in the region 1190—1240 cm.$^{-1}$. The figures obtained are indicated in the Table, and it will be seen from

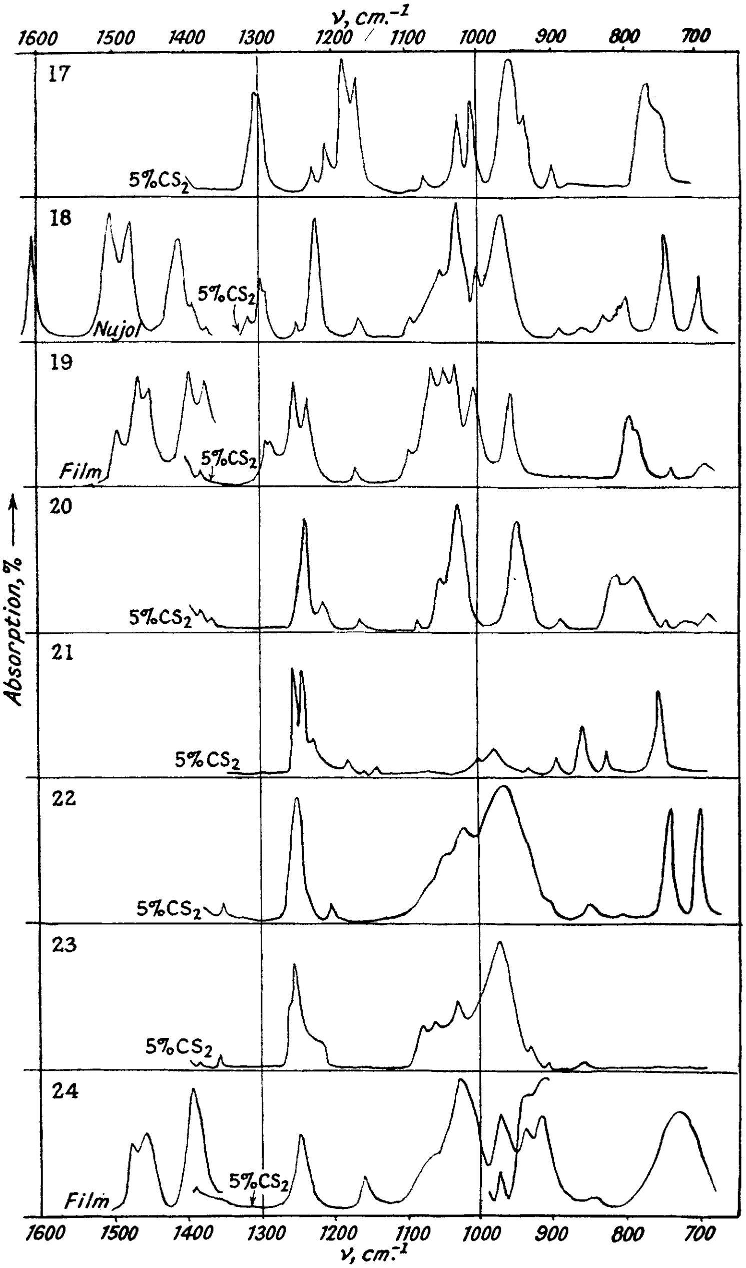
FIGS. 1—8.


ν, cm.⁻¹
1600
1500
1400
1300
1200
1100
1000
900
800
700
1
Nujol
5%CS₂
2
Film
3
Film
4
Film
5
Film
5%CS₂
6
Film
5%CS₂
7
Film
5%CS₂
8
Film
5%CS₂
Absorption, %
1600
1500
1400
1300
1200
1100
1000
900
800
700
ν, cm.⁻¹

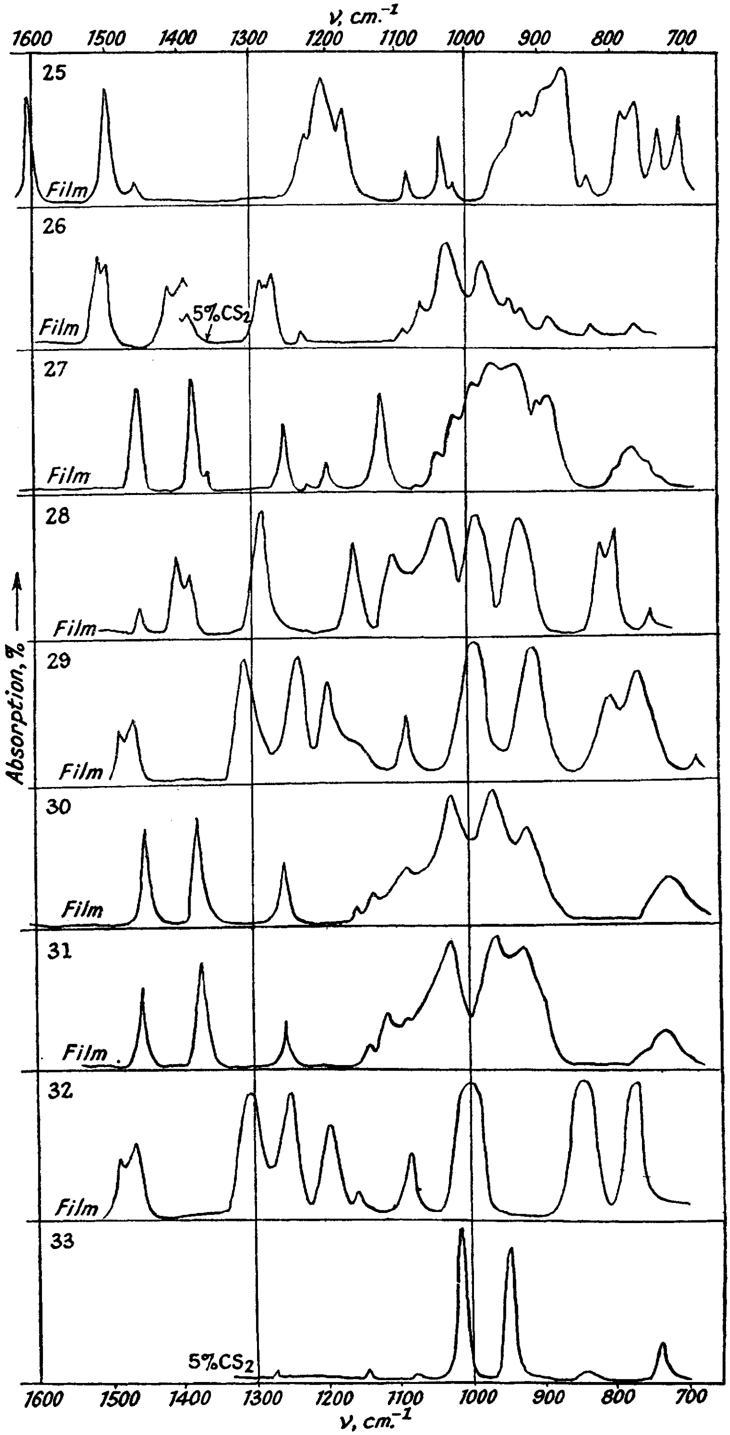
FIGS. 9—16.


ν, cm.⁻¹
1600
1500
1400
1300
1200
1100
1000
900
800
700
9
Film
10
Film
11
Film
12
Nujol
13
Film
14
5% CS₂
15
Film
5% CS₂
16
5% CS₂
Absorption, %
ν, cm.⁻¹

FIGS. 17—24.


ν, cm.⁻¹
1600
1500
1400
1300
1200
1100
1000
900
800
700
17
5%CS2
18
5%CS2
Nujol
19
Film
5%CS2
20
5%CS2
21
5%CS2
22
5%CS2
23
5%CS2
24
Film
5%CS2
Absorption, %
1600
1500
1400
1300
1200
1100
1000
900
800
700
ν, cm.⁻¹

FIGS. 25—33.


ν, cm.$^{-1}$
1600
1500
1400
1300
1200
1100
1000
900
800
700
25
Film
26
Film
5%CS$_2$
27
Film
28
Film
29
Film
30
Film
31
Film
32
Film
33
5%CS$_2$
Absorption, %
1600
1500
1400
1300
1200
1100
1000
900
800
700
ν, cm.$^{-1}$

the spectra that compounds lacking the P–OAr group do not show this band. Dibenzyl phosphonate does not show more than a weak band in this region. Perhaps the strongest evidence for this assignment is given by the studies of a 5% solution in carbon disulphide of the related series triethyl phosphate, diethyl phenyl phosphate, ethyl diphenyl phosphate, and triphenyl phosphate. These were all measured in the same cell at the same concentration and it will be seen that this band is absent in the first and shows gradually increasing intensity throughout the series up to triphenyl phosphate. Similarly, there is an increase in the intensity of this band on going from phenyl dichlorophosphinate to diphenyl chlorophosphonate to triphenyl phosphate. It is considered that this fact together with the evidence given in the Table, represents a strong case for this assignment, which is also supported by Gore's tentative suggestion (*loc. cit.*) that the P–O–Ph grouping may occur in the region 1200—1250 cm.$^{-1}$.

| | | Assignments made (band head position, cm.$^{-1}$) | | | | |
|---|---|---|---|---|---|---|
| Compound | Fig. No. | P–O–C (Aromatic) | | P–O–C (Aliphatic) | P=O | Other assignments |
| *Phosphates, etc.* | | | | | | |
| Triphenyl phosphate | 1 | 1190 | 1029 | — | 1311 1299 | — |
| Tri-*o*-tolyl phosphate | 2 | 1220 | 1042 | — | 1299 | — |
| Tri-*m*-tolyl phosphate | 3 | 1242 | 1029 | — | 1307 1299 | — |
| Tri-*p*-tolyl phosphate | 4 | 1190 | 1022 | — | 1311 1297 | — |
| Ethyl diphenyl phosphate | 6 | 1192 | 1035 | 1046 | 1314 1297 | — |
| Diethyl phenyl phosphate | 5 | 1218 | * | 1037 | 1290 1279 | — |
| Triethyl phosphate | 7 | — | — | 1037 | 1280 1264 | — |
| Tri-2-chloroethyl phosphate | 8 | — | — | 1030 | 1282 | — |
| Tributyl phosphate | 9 | — | — | 1030 | 1274 | — |
| Diethyl *p*-nitrophenyl phosphate | 10 | 1232 | * | 1030 | 1282 | — |
| Diethyl *p*-nitrophenyl thiophosphate | 11 | 1232 | * | 1027 | — | P=S, 763, s. |
| Ethyl di-*p*-nitrophenyl thiophosphate | 12 | 1205 | * | 1037 | — | P=S, 766, m. |
| Tri-2-ethylhexyl phosphate | 13 | — | — | 1026 | 1282 1266 | — |
| *Phosphonates.* | | | | | | |
| Diethyl phosphonate | 14 | — | — | 1053 | 1261 | PH (unbonded), 2427 |
| Diethyl chlorophosphonate | 15 | — | — | 1030 | 1311 | — |
| Diphenyl chlorophosphonate | 17 | 1176 | 1027 | — | 1305 1297 | — |
| Phenyl dichlorophosphinate | 16 | 1186 | 1028 | — | 1305 | — |
| Diethyl anilinophosphonate | 18 | — | — | 1026 | 1290 | — |
| Diethyl ethylphosphonate | 19 | — | — | 1040 1025 | 1250 | — |
| Diethyl butylphosphonate | 20 | — | — | 1031 | 1242 | — |
| *cyclo*Hexyldichlorophosphine oxide | 21 | — | — | 1036 (weak) | 1274 1258 | — |
| Dibenzyl phosphonate | 22 | — | — | 1031 | 1258 | PH (unbonded), 2410 |
| Di*neo*pentyl phosphonate | 23 | — | — | 1026 | 1250 | PH (unbonded), 2381 |
| *Phosphites.* | | | | | | |
| Triethyl phosphite | 24 | — | — | 1030 | — | Several of these show weaker absorption in the region of 1250 |
| Triphenyl phosphite | 25 | 1198 | 1026 | — | — | |
| Tri*neo*pentyl phosphite | 26 | — | — | 1022 | — | |
| Tri-2-ethylhexyl phosphite | 27 | — | — | 1031 | — | |
| Ethyl di-2-ethylhexyl phosphite | 31 | — | — | 1026 | — | |
| Diethyl 2-ethylhexyl phosphite | 30 | — | — | 1026 | — | |
| *Pyrophosphates, etc.* | | | | | | |
| Tetraethyl pyrophosphate | 28 | — | — | 1030 | 1280 | — |
| Bisdimethylaminophosphinic anhydride | 29 | — | — | — | 1305 | — |
| Bisdimethylaminofluorophosphine oxide | 32 | — | — | — | 1305 | P–F, 833 |
| Ethyl dichlorophosphinate | 33 | — | — | 1026 | — | — |

All the above are strong bands except where otherwise indicated.

* Denotes that band is obscured by that due to P–O–C(Alk.).

It is noteworthy that this frequency is within the region of the normal aromatic C–O–C assignment and may indicate that in fact the O–C stretching frequency is not materially altered by the substitution of a phosphorus for a carbon atom. If this were to be the case, a second band of medium intensity in the range 1000—1060 cm.$^{-1}$, comparable with the second C–O–C band, might also be expected from the P–O–C (aromatic) link.

Further study of the spectra indicates that the aromatic esters show two sharp absorption bands at 1012 and 1030 cm.$^{-1}$ which undergo intensification with increase of aromatic content in related series. The first of these can be identified as being due to the aromatic ring itself, as it is displaced in *o*- or *p*-disubstituted compounds but not with *m*- or monosubstitution. It would therefore seem likely that the P–O–C (aromatic) linkage is responsible for the second band observed near 1030 cm.$^{-1}$. It is sometimes obscured by the intense P–O–C (aliphatic) absorption band (see below) but the differences in intensity are sufficient to avoid confusion between them.

(b) *The* P–O–C (*Aliphatic*) *Linkage.*—The occurrence of two bands assigned to P–O–C (aromatic) close to similar bands arising from the C–O–C (aromatic) grouping suggests that the P–O–C (aliphatic) bands might also occur in the 1000—1100-cm.$^{-1}$ region close to the C–O–C (aliphatic) vibrations, especially as the Si–O–C (aliphatic) band has also been found in the region close to the C–O–C position, indicating that the change of mass has not in this case markedly altered the frequency of the O–C vibration (Richards and Thompson, *J.*, 1949, 124).

Examination of the spectra shows that in all cases where the P–O–C (aliphatic) linkage is present (24 compounds) a very intense band occurs between 1030 and 1050 cm.$^{-1}$ which can be assigned to this link. As in the case just quoted, this band shows progressive changes in intensity as the number of alkyl groups is increased through a related series, and the band is absent from fully aromatic compounds. The actual band positions are indicated in the Table. The narrow range in which this band falls is remarkable for a skeletal vibration, and only slight shifts appear to be produced on alteration of the substituent groups through ethyl, butyl, *neo*pentyl, or 2-ethylhexyl or on changes in the substitution pattern through phosphates, phosphites, thiophosphates, phosphonates, etc.

The ten compounds examined by Meyrick and Thompson (*loc. cit.*) are in agreement with this assignment. These authors have tentatively suggested that absorption near 795 cm.$^{-1}$ may also be connected with the P–O–C linkage. The spectra which we have obtained bear out this suggestion to some extent, although we find the bulk of the band heads to be nearer 760 cm.$^{-1}$, and in this region we differ from their findings as regards the relative strengths of bands in two of the three compounds of theirs which we have re-examined. However, the bands in this region are usually broad, and are weak compared with those in the 1030—1050-cm.$^{-1}$ range. They also show large changes on solution in some cases, which suggests that they may arise from hydrogen-bonded linkages. They are therefore less likely to be of value in structural diagnosis work.

*Other Assignments.*—All the compounds examined were prepared with a view to working out the correlations given above, but some of them are also useful in providing a check—insofar as their numbers will allow—on other assignments proposed for this series.

(i) P–H. Meyrick and Thompson (*loc. cit.*) have given strong evidence for the assignment of the absorption band at 2300—2400 cm.$^{-1}$ to this group, and Smith (private communication) has confirmed this with seven other compounds. This is further supported by our spectra of dibenzyl phosphonate and di*neo*pentyl phosphonate which show a band in this region. This is also interesting in indicating that the existence of dialkyl hydrogen phosphite in the tautomeric phosphonate form is not confined to short-chain aliphatic materials. We have also re-examined the spectrum of diethyl phosphonate and differ from Meyrick and Thompson in that we find a sharp band at 2427 cm.$^{-1}$ in solution and in the liquid film, whereas they find a broad band in this region which they ascribe to hydrogen bonding. However, Kosolapoff and Powell (*J. Amer. Chem. Soc.*, 1950, **72**, 4291) have adduced from molecular weights that many dialkyl phosphites are monomeric and therefore unbonded.

(ii) P=S. Gore (*loc. cit.*) has found a weak band in many thiophosphates near 750 cm.$^{-1}$ which he ascribes to this linkage, and this has been confirmed by Smith (*loc. cit.*). We find both diethyl *p*-nitrophenyl thiophosphate and ethyl di-*p*-nitrophenyl thiophosphate to give absorption in this region.

(iii) P=F. Smith assigns this linkage to the region 750—900 cm.$^{-1}$. In a single compound, *viz.*, bisdimethylaminofluorophosphine oxide we find a very strong band at 833 cm.$^{-1}$ which is absent in the closely related bisdimethylaminophosphinic anhydride, and which may therefore be due to the P–F band.

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