964. *Phosphonitrilic Derivatives. Part XI.[1] The Force Constants of Triphosphonitrilic Chloride and Fluoride.*

By A. C. Chapman and D. F. Carroll.

Bond stretching and interaction force constants for P–N, P–Cl, and P–F bonds have been calculated from the assignments previously reported. High values of the P–N stretching constants indicate strong π-bonding, and strong interactions between P–N bonds remote from one another suggest extensive delocalisation. The phosphorus–halogen stretching and interaction constants are high, suggesting exocyclic π-bonding; this effect is more marked in the chloride than in the fluoride.

In Part VIII [2] comprehensive assignments of the vibrational spectra of triphosphonitrilic chloride, $(PNCl_2)_3$, and triphosphonitrilic fluoride, $(PNF_2)_3$, were presented. These assignments confirmed earlier work [3,4] which showed the symmetry of each molecule to be D_{3h}. We now report P–N and P–Hal bond stretching and interaction force constants for the two molecules which have been determined from these assignments.

CALCULATION OF FORCE CONSTANTS

The calculation of the force constants was carried out by the Wilson FG matrix method.[5] Because no data other than the frequencies were available, the force field used was restricted to a simple valence type, comprising diagonal terms only in the factored F matrix, and therefore containing a number of constants equal to the number of frequencies. Because of the high symmetry of the molecules, this function allows a study of the interactions between equivalent internal co-ordinates.

In cases where some of the lower frequencies in a particular symmetry species could not be assigned, a frequency separation was used, the higher frequencies being factored off to give approximate values for the appropriate diagonal force constants.

For some of the symmetry species, the observed frequencies could not be reproduced using the diagonal terms alone, showing that the off-diagonal terms, normally neglected in this type of force field, have an important effect. It was considered that to allow off-diagonal constants to take non-zero values which were largely arbitrary was no worse than the normal practice of arbitrarily taking them to be zero. Therefore, after the solution had proceeded as far as possible using only the diagonal constants, the off-diagonal constant or constants which appeared to be having the greatest effect were allowed to take non-zero values, and an exact solution for the frequencies was obtained. Since more force constants are determined than there are frequencies, this procedure renders the factored diagonal force constants somewhat arbitrary, although less so than would bad frequency reproduction. Also, since it is well known (as instanced by the degree of success achieved by the simple valence force field) that the diagonal constants have the most significant effect on the frequencies, the element of arbitrariness is largely concentrated in the off-diagonal terms.

Bond Lengths and Angles.—Bond lengths and angles for the chloride were taken from the results of the crystal-structure determination by Wilson and Carroll.[6] The values used were: P–N 1·59 Å; P–Cl 1·975 Å; N–P–N = P–N–P = 120°; Cl–P–Cl 101° 55′. For the fluoride, no data were available and assumptions had to be made. The bond-lengths were assumed to be the same as those (1·51 Å for both P–N and P–F) determined for the tetrameric fluoride by McGeachin and Tromans,[7] whilst the angles were assumed to be the same as those given above for the trimeric chloride.

Factored G Matrix.—The individual G elements were derived from published formulæ [5,8]

[1] Part X, Dougill, *J.*, 1963, 3211.
[2] Chapman and Paddock, *J.*, 1962, 635.
[3] Daasch, *J. Amer. Chem. Soc.*, 1954, **76**, 3403.
[4] Becher and Seel, *Z. anorg. Chem.*, 1960, **305**, 148.
[5] Wilson, Decius, and Cross, " Molecular Vibrations," McGraw-Hill, New York, 1955.
[6] Wilson and Carroll, *J.*, 1960, 2548.
[7] McGeachin and Tromans, *J.*, 1961, 4777.
[8] Decius, *J. Chem. Phys.*, 1948, **16**, 1025.

7 Y

(note, however, the misprint in the expression for $G^1_{rr}(\frac{1}{2})$, in ref. 8), or were worked out from first principles as described by Wilson, Decius, and Cross.[5] The individual elements were then grouped into combinations derived from the symmetry co-ordinates in the usual way,[5] giving the factored G matrix elements.

Triphosphonitrilic Chloride.—A_1' *species.* The three highest frequencies in this factor were shown in Part VIII [2] to be 785, 671, and 365 cm.[-1] The lowest frequency was there tentatively assigned to a doubtful line at 76 cm.[-1] During the course of the analysis, however, it became clear that, if the lowest frequency lay below about 200 cm.[-1], no real solution could exist, even if substantial off-diagonal force constants were included. This was because this frequency, though primarily associated with the PCl_2 deformation mode, was also governed to a large extent by the other three diagonal force constants, so that even if the deformation constant were zero the frequency would still be about 200 cm.[-1] It is therefore most likely that the lowest A_1' frequency is either one of the bands otherwise assigned to E'' vibrations at 162, 173, and 210 cm.[-1], the polarisation of the A_1' band having remained undetected, or that it lies underneath these bands. The lowest A_1' frequency was therefore assumed to be 210 cm.[-1], a reasonable figure by comparison with the fluoride, in which the corresponding frequency is 311 cm.[-1]

No exact or reasonably exact solution could be obtained by considering only the four diagonal constants. This was most apparent in the case of the third frequency, which could not be raised above 348 cm.[-1] even by the introduction of ridiculously high values for the factored P–Cl stretching constant. The interaction constant which appeared to be having the greatest effect, namely that between P–Cl stretching and PCl_2 bending, was therefore allowed to take non-zero values, and two solutions were obtained. There is little to choose between these as far as the reproduction of frequencies is concerned; the potential-energy distributions of both confirm the assignments already made.[2] The two sets of values for the diagonal stretching constants differ considerably and probably represent the limits of a range within which the true solutions lie. These differences have only a small effect on the final values of the P–N and P–Cl bond stretching force constants (Table).

Bond stretching and interaction force constants (mdynes/Å) for P–N, P–Cl, and P–F bonds.[a]

P–N *bonds*		$(PNCl_2)_3$		$(PNF_2)_3$		
		1	2	1	2	3
Stretching constant	$f(PN)_{11}$	8·12	8·26	9·03	8·89	8·89
	$f(PN)_{12}$	0·86	1·00	1·44	1·30	1·30
Interaction constants [b]	$f(PN)_{13}$	−1·50	−1·36	−1·41	−1·56	−1·56
	$f(PN)_{14}$	−1·86	−1·73	−1·68	−1·82	−1·82
	$f(PN)_{16}$	−1·02	−0·89	−0·67	−0·82	−0·82

P–Hal *bonds*		$(PNCl_2)_3$		$(PNF_2)_3$		
		1	2	1	2	3
Stretching constant	$f(PX)$	4·47	4·29	5·88	5·84	5·65
	$f(PX)_{gem}$	−1·07	−1·26	−0·18	−0·23	−0·41
Interaction constants	$f(PX)_{cis}$	−0·50	−0·68	−0·29	−0·34	−0·52
	$f(PX)_{trans}$	0·59	0·40	−0·32	−0·37	−0·55

[a] The different sets of force constants for each compound are derived from the different solutions for the A_1' factor in each case. Since the two solutions for the E'' factor of $(PNCl_2)_3$ are very similar only the first solution was used in deriving the above values. [b] Suffices refer to cyclic numbering of P–N bonds; $f(PN)_{12}$ refers to the interaction between bonds having a common nitrogen atom, and $f(PN)_{16}$ to that between bonds having a common phosphorus atom.

A_2'' *species.* Only the highest frequency of this species, the in-phase PCl_2 antisymmetrical stretching band at 620 cm.[-1], has been assigned.[2] However, the other two frequencies, corresponding to rocking of the PCl_2 groups and an out-of-plane ring deformation, are expected at very much lower frequencies and certainly lie below 315 cm.[-1] The highest frequency may therefore be factored off to give a reasonably accurate value for the factored PCl_2 stretching force constant.

A_2' *species.* This species is theoretically inactive, but the trigonal ring-stretching vibration has been tentatively assigned [2] to the weak to medium band at 1368 cm.[-1], and the vibration

must certainly lie in this region. The other vibration in this species corresponds to a PCl_2 wagging vibration and is expected in the region of 200 cm.$^{-1}$, so that a frequency separation may be employed.

E' species. Of the six frequencies in this species, the two ring-stretching vibrations, the PCl_2 stretching vibration, and the ring elongation have been assigned at 1295, 1218, 528, and 336 cm.$^{-1}$, respectively. The remaining two bands, corresponding to PCl_2 deformation and wagging, are expected at lower frequencies. Since the frequencies of primary interest were the first three, and the degree of coupling between the ring-elongation mode and the modes of lower frequency is uncertain, only the three higher frequencies were employed in a frequency separation, the procedure of which was as follows. The two higher frequencies were factored out to give the diagonal force constants describing the two ring-stretching modes.[2] Real solutions could be obtained only for a narrow range of negative values of the off-diagonal constant appropriate to these modes. The intensities of the bands at 1218 and 1295 cm.$^{-1}$ suggest[2] that these bands correspond to the first and second degenerate members of the system of ring vibrations, with little coupling. A value of the interaction constant which gave such a separation was therefore employed in a solution, which was then refined with the inclusion of the third frequency, giving a good solution, which is, however, limited in accuracy by the neglect of the three lower frequencies.

E'' species. The frequencies 875, 210, 173, and 162 cm.$^{-1}$ have previously been assigned to this species.[2] However, the band at 210 cm.$^{-1}$ is now regarded as belonging to the A_1' species, and the three lowest frequencies in the E'' factor, associated with the PCl_2 rocking, out-of-plane deformation, and PCl_2 torsional vibrations, are taken to be 173, 162, and 76 cm.$^{-1}$. The PCl_2 torsional vibration is expected at a lower frequency than the PCl_2 rocking vibration, and does not couple with the other vibrations because of zeros in the corresponding column of the G matrix. It is therefore assigned to the band at 162 cm.$^{-1}$ which appears to be too close to be coupled with the band at 173 cm.$^{-1}$.

After factoring out the PCl_2 torsional mode, approximate solutions were then obtained for the remaining modes by a frequency separation, considering the highest frequency in isolation and the remaining two as a quadratic. An exact solution of the quadratic could only be obtained for a range of non-zero values of the interaction constant between PCl_2 rocking and ring-bending. The approximate solution was then refined, first using the minimum value of this interaction constant, and secondly taking it as zero.

A better reproduction of frequencies was obtained in the first case, but the effect of the introduction of the off-diagonal constant on the diagonal terms is not significant. The differences between the frequency separation value for the P–Cl stretching constant and the final values are small, indicating that the uncertainties in assignment have little effect on the values obtained for this constant.

Bond stretching and interaction force constants. The factored force constants for P–N and P–Cl stretching in the different symmetry species were unfactored to give values of the bond-stretching and -interaction constants for the P–N and P–Cl bonds (Table).

Triphosphonitrilic Fluoride.—A_1' species. Attempts to solve this factor using the four diagonal constants alone were totally unsuccessful. The observed frequencies could only be reproduced by a set of complex force constants; attempts with real positive constants invariably caused the two higher frequencies to be much too high, and the other two far too low. It was clear that to obtain a solution one or more interaction constants would have to be considered, as explained above. The largest and most important interaction constant was expected to be that between P–Cl and P–N stretching, the distribution of modes in the chloride suggesting that two of the frequencies which were too widely spaced in the fluoride might be associated with this constant. Although this association was not confirmed by the results, by allowing this constant to take non-zero values a great improvement in frequency reproduction was achieved. For similar reasons the interaction between P–N stretching and ring bending was also expected to be significant, and further improvements were made by introducing this constant and that between P–F stretching and ring bending, but even with these seven constants an exact solution could not be obtained. Although there are considerable differences between the values of the diagonal constants given by the best solutions employing five, six, and seven constants, these differences have little effect on the final values of the P–N and P–F bond-stretching and -interaction constants (Table).

A_2'' species. Only the two highest frequencies of this species have been assigned,[2] at 973

and 516 cm.⁻¹. As in the chloride, the highest frequency was factored off, giving an approximate value for the PF₂ stretching force constant.

A_2' *species.* The treatment of this species was similar to that of the chloride, with the tentative assignment [2] of the trigonal ring-stretching vibration to the band at 1367 cm.⁻¹.

E' *species.* This factor was treated in the same way as the corresponding factor for the chloride, using the assigned frequencies of 1343, 1297, and 862 cm.⁻¹.

E'' *species.* As only two of the four frequencies for this factor have been assigned,[2] the highest frequency at 962—975 cm.⁻¹, which is widely separated from the remainder, was factored off to give an approximate value for the PF₂ stretching force constant.

Bond stretching and interaction force constants. The factored force constants for P–N and P–F stretching in the different symmetry species were unfactored, to give values of the bond stretching and interaction constants (Table).

DISCUSSION

It is difficult to assess the effect on the bond stretching and interaction constants (Table) of the approximations in the treatment of the E'' factor of the fluoride and the A_2'', A_2', and E' factors of both molecules, but the small differences introduced by the possible solutions for the A_1' factors, and the good results obtained from the frequency separation for the E'' factor of the chloride, suggest that the diagonal constants quoted are close to the true values. The interaction constants can be expected to be correct in sign and approximate magnitude only.

The results for the P–N bonds show a very similar pattern in the two molecules, and show that the P–N bonds in the fluoride are indeed stronger than those in the chloride, as expected from considerations of the effect of the electronegativity of the exocyclic groups on the ring bonds.[9,10] No other values of P–N stretching constants have evidently been reported, so no comparisons can be made with other compounds, but the values obtained are higher than the predictions (for the chloride) of Badger's rule [11] (5·7 mdynes/Å) or Gordy's rule [12] (3·6 mdynes/Å for a single bond, 6·9 mdynes/Å for a double bond), showing that the degree of π-bonding is high, and confirming the inferences drawn from bond lengths and other properties.[10]

The magnitudes and signs of the interaction constants between the P–N bonds are of interest in view of current theories [13,14] of the bonding in these compounds. If the ring π-bonds are of the polyallylic type suggested by Dewar *et al.*,[15] consisting of " islands " of conjugation each of which covers a nitrogen atom and two adjacent phosphorus atoms, one would expect $f(PN)_{12}$ to be much larger in magnitude than the other interaction constants. One might also expect $f(PN)_{12}$ to be positive, since an extension of $(P–N)_1$ may lead to a shortening of $(N–P)_2$ by favouring the structure $P\!\!-\!\!\underset{(1)}{N}\!\!\equiv\!\!\underset{(2)}{P}$ at the expense of $P\!\!\underset{(1)}{=}\!\!N\!\!-\!\!\underset{(2)}{P}$. On the other hand, if the cyclic conjugation suggested by Craig and Paddock [15] is dominant, one would expect all the interactions to be of similar magnitude, and might also expect alternation of signs, for reasons similar to those above. In fact, although $f(PN)_{12}$ is positive it is no larger than the more remote interaction constants, and all the interactions round the ring are of similar magnitude, providing evidence for a system of cyclic conjugation. There is no evidence for any alternation in signs round the ring, since all the interaction constants except $f(PN)_{12}$ are negative. This suggests that an extension of $(P–N)_1$ leads to a general weaking of the system of π-bonds.

The P–Cl stretching constant for the chloride is very much higher than any previously

[9] Paddock, *Endeavour*, 1960, **19**, 134.
[10] Paddock and Searle, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 347.
[11] Badger, *J. Chem. Phys.*, 1935, **3**, 710.
[12] Gordy, *J. Chem. Phys.*, 1946, **14**, 305.
[13] Craig and Paddock, *Nature*, 1958, **181**, 1052.
[14] Craig and Paddock, *J.*, 1962, 4118.
[15] Dewar, Lucken, and Whitehead, *J.*, 1960, 2423.

reported [16,17] for P–Cl bonds (in mdynes/Å, 2·83 for PCl_3, 2·70 for $PFCl_2$, 2·89 for PCl_5,equatorial, and 2·45—3·08 for $POCl_3$), suggesting that the degree of exocylic π-bonding is considerable. The interaction constants between P–Cl bonds, including those on different phosphorus atoms, are also large, providing further evidence for an extensive π-bond system and for participation of the P–Cl bonds in this system.

The P–F bond stretching constant is much higher than the values reported [18] for PF_3 and $PFCl_2$ (4·93 and 4·10 mdynes/Å) but is lower than the value of 6·18 mdynes/Å reported [17] for POF_3. This suggests that the degree of exocyclic π-bonding is smaller than in the chloride. The interaction constants are smaller than in the chloride, thus supporting this view.

RESEARCH DEPARTMENT, ALBRIGHT & WILSON (MFG.) LIMITED,
OLDBURY, BIRMINGHAM.   [*Received, November 5th,* 1962.]

[16] Iwasaki and Hedberg, *J. Chem. Phys.*, 1962, **36**, 596; Wilmshurst and Bernstein, *J. Chem. Phys.*, 1957, **27**, 661; Hariharan, *J. Indian Inst. Sci.*, 1956, **38**, *A*, 16; Mayants, Popov, and Kabachnik, *Optics and Spectroscopy*, 1959, **6**, 384.

[17] Siebert, *Z. anorg. Chem.*, 1953, **274**, 24.

[18] Venkateswarlu and Sundaram, *J. Chim. phys.*, 1957, **54**, 202; Wilson and Polo, *J. Chem. Phys.*, 1952, **20**, 1716.