for *trans* compounds is larger than J_{W-P} for *cis* compounds. Fourth, unlike the results for the monosubstituted compounds, J_{W-P} does not change appreciably from ligand to ligand for compounds of the same stereochemistry. The experimental errors are about the same magnitude as the differences in measurements for the compounds, so no conclusion can be made on the fourth point.

However, the difference noted between the coupling constants for the compounds of different stereochemistry is real, and *trans* J_{W-P} is greater than *cis* J_{W-P} for $(R_3P)_2W(CO)_4$. This is to be compared to $(R_3P)_2PtCl_2$ for which *cis* J_{Pt-P} is greater than *trans* J_{Pt-P}.[7,8,12]

We feel both of these facts are consistent with the π-bonding explanation. Phosphorus competes more effectively with chlorine *trans* to it for platinum d_π electrons in the *cis* isomer than it competes with itself in the *trans* isomer, and phosphorus competes more effectively for tungsten d_π electrons *trans* to itself in the *trans* isomer compared to carbon monoxide *trans* to it in the *cis* isomer.[37]

The assumption here is that the π-acceptor abilities are in the order $CO > P > Cl$, for which there is ample evidence.[38] Moreover, the greater the π bonding becomes, the greater is the phosphorus–metal interaction and the greater is the metal–phosphorus coupling as a result.

We are not prepared at this time to propose an explanation for the greater downfield chemical shift of the phosphorus in the *trans* isomer, except to point out that it probably does not arise mainly from diamagnetic shielding effects as was suggested in the platinum cases.[8] Results with palladium and rhodium complexes[39] indicate also that simple diamagnetic effects are not sufficient to explain the ^{31}P shifts, as has been emphasized for other types of phosphorus compounds.[40]

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(37) S. O. Grim and D. A. Wheatland, *Inorg. Nucl. Chem. Letters*, **4**, 187 (1968).

(38) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, pp 719–759.

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Aryl-Substituted Phosphonitrilic Fluorides. IV. The Crystal and Molecular Structure of 1,1-Diphenylphosphonitrilic Fluoride Trimer[1]

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The crystal structure of the 1,1-diphenylphosphonitrilic fluoride trimer, 1,1-$N_3P_3F_4(C_6H_5)_2$, has been determined by symbolic addition and Fourier techniques. The results have been refined to a conventional R factor of 0.059 by a full-matrix least-squares treatment employing anisotropic temperature factors on 2442 reflections measured by counter methods. The crystals belong to the orthorhombic system, with $a = 14.803$ (4), $b = 12.571$ (5), $c = 16.732$ (8) Å; the space group is Pnma, and there are eight molecules in the unit cell ($\rho_{\text{measd}} = 1.54$ g cm^{-3}, $\rho_{\text{calcd}} = 1.56$ g cm^{-3}). The asymmetric unit contains two independent molecules each of which has C_s crystallographic symmetry. The phosphorus–nitrogen ring has five atoms approximately coplanar, with the phenyl-substituted phosphorus atom 0.20 Å out of this plane. There are three different sets of phosphorus–nitrogen bonds with mean lengths 1.618 (5), 1.558 (4), and 1.539 (5) Å. The exocyclic bond angles are: C–P–C, 107.9 (3)°; F–P–F, 96.9 (2)°. The endocyclic angles are: N–P–N, 115.5 (3)°; 120.6 (3)°; P–N–P, 120.5 (2)°.

Introduction

The investigation of crystal structures of phosphonitrilic halides and their derivatives is of interest for both theoretical considerations and elucidation of stereochemical substitution patterns. The diphenylphosphonitrilic fluoride trimer obtained from the Friedel–Crafts reaction of benzene with the monophenylphosphonitrilic fluoride trimer has been assigned a geminal configuration on the basis of chemical[1] and nuclear magnetic resonance[1,4] evidence. We have investigated the crystal structure of this compound in order to verify the geminal assignment and to investigate further the influence of fluorine as an exocyclic group on the conformation of the phosphorus–nitrogen ring system. The difference between fluorine- and chlorine-substituted phosphonitrilic halides is often dramatic; *e.g.*, tetrameric phosphonitrilic chloride exists in two forms, one with a boat[5] and the other with a chair[6] configuration, whereas tetrameric phosphonitrilic fluoride[7] is planar. Inasmuch as the crystal structure of the 1,1-diphenylphosphonitrilic chloride trimer has been determined,[8] a comparison with the corresponding fluoride is of some

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(2) Gulf Oil Corp. Predoctoral Fellow, 1968–1969.

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interest. A preliminary report of this investigation based on film data has appeared.[9] The present paper deals with the results of a refinement using a set of counter data.

Experimental Section

Preparation of the Compound.—Monophenylphosphonitrilic fluoride trimer was prepared by the reaction of phenyllithium with trimeric phosphonitrilic fluoride.[4,10] The compound 1,1-$N_3P_3F_4(C_6H_5)_2$ was prepared by the reaction of the monophenylphosphonitrilic fluoride trimer with benzene in the presence of aluminum chloride and triethylamine.[1]

The compound 1,1-$N_3P_3F_4(C_6H_5)_2$ can be recrystallized from a wide variety of solvents; crystals grown from both methanol and *n*-heptane were examined. Data were collected from a lath which was cut from a larger crystal obtained from absolute methanol at 0°.

Crystallographic Data

A preliminary examination of the crystal, using the Weissenberg camera, indicated that it belonged to the orthorhombic system. A least-squares fit to the angular settings for six reflections obtained on a Picker FACS-1 four-circle diffractometer (λ(Cu Kα) 1.54178 Å) gave the following cell dimensions at 25 ± 5°: a = 14.803 (4), b = 12.571 (5), c = 16.732 (8) Å. The dimensions for a and c are somewhat larger than those reported previously.[9] Systematic absences, by examination of the $hk0$, $0kl$ (precession, Mo Kα radiation), $h0l$, and hll (Weissenberg, Cu Kα radiation) nets, occur when $0kl$ has $k + l = 2n + 1$ and $hk0$ has $h = 2n + 1$. Therefore, the space group is either Pnma (no. 62) or Pn2$_1$a (no. 33). The density, measured by flotation in aqueous zinc chloride solution, is 1.54 g cm^{-3} as compared with a calculated density of 1.560 g cm^{-3} (assuming eight molecules of 1,1-$P_3N_3F_4(C_6H_5)_2$ (M = 365.15) in the unit cell of volume 3109 × 10^{-24}cm^3). $F(000)$ is 1472 and the linear absorption coefficient for Cu Kα is 39.9 cm^{-1}.

Collection of X-Ray Data

Initially, multiple-film, equiinclination Weissenberg photographs ($h0l$–h,10,l) were taken with nickel-filtered Cu Kα radiation (λ 1.5418 Å) on a crystal mounted about the needle (*i.e.*, the b) axis. A total of 1442 independent, nonzero intensities was estimated by visual comparison with a series of standard exposures prepared from the specimen crystal.

Then a set of data was collected at 25 ± 5°, on a Picker FACS-1 computer-controlled four-circle diffractometer. The crystal (0.02 × 0.02 × 0.05 cm), obtained by careful cleavage of a larger specimen, was initially mounted on the a axis (0.05-cm length) but was displaced from that setting by approximately 20° on each goniometer arc. The takeoff angle was 4°; pulse height analysis and an Ni filter were used to give approximately monochromatic Cu Kα radiation (λ 1.5418 Å). The reflections were measured with a scintillation counter and attenuators were inserted when necessary. All of the symmetry-nonequivalent reflections in the 2θ range of 5–130° were measured using a moving-crystal, moving-counter technique with a 2θ scan rate of 1°/min. A standard reflection was monitored after every 50 measurements. The intensity of the standard fell off approximately linearly with time. After measurement of the independent data set, this intensity was 67% of the initial value. An increasing opacity of the crystal, coupled with a slight darkening, accompanied this loss of intensity. Several measurements on other reflections indicated that the decrease in intensity was approximately uniform over the entire sphere of data. The data-processing program[11] has applied a correction to the intensities, assuming a linear decrease in intensity with time. Out of a possible 2795 reflections with $2\theta < 130°$, 2442 were considered to be above background. No absorption or extinction corrections were applied to the data; the maximum and minimum transmission coefficients were estimated to be 0.45 and 0.33.

Structure Determination

The structure determination was carried out on the data collected by film methods.[9] Although the number of molecules in the unit cell led us to favor the centric space group Pnma, rather than the acentric Pn2$_1$a, the latter group had to be considered a possibility. Various statistical tests, which are part of a program[12] which puts intensities on an absolute scale and calculates normalized structure factors (E's), indicated a centric space group. The final proof came in the fact that the structure refined successfully in Pnma.

An extensive study of the three-dimensional Patterson map failed to provide us with the orientation of the ring by identification of a triangle of P–P vectors. Accordingly, since the statistical tests had indicated a centric space group, the symbolic addition procedure[13] was applied. The calculations were performed using programs developed by Fleischer and coworkers.[12] The first set of starting reflections did not give chemically reasonable E maps with three different sign combinations. Then, two of the six starting reflections which had led to a relatively large number of inconsistencies were replaced. The third sign combination[14] from the new group of six reflections with assigned letter symbols gave a more chemically reasonable E map. A total of 406 reflections was used to calculate this map. The reflections used in this procedure are given in Table I.

The E map showed two major peaks on the mirror plane at $y = {}^1/_4$ and two major peaks about 1.35 Å from this mirror plane. Inasmuch as the trimeric phospho-

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[9] C. W. Allen, I. C. Paul, and T. Moeller, *J. Am. Chem. Soc.*, **89**, 6361 (1967).

[10] T. Moeller and F. Tsang, *Chem. Ind.* (London), 361 (1962).

[11] F. R. Ahmed, S. R Hall, M. E. Pippy, and C. P. Saunderson, "NRC Crystallographic Programs for the IBM/360 System," National Research Council, Ottawa, Canada, 1967, NRC-2A.

[12] We used a package of programs written by E. B. Fleischer, A. Stone, and R. Dewar of the University of Chicago. One of the programs, FAME, incorporates statistical tests and calculates normalized structure factors. Another program, MAGIC, determines signs by the Karle–Hauptman Σ_2 relationship from a basic set of reflections which are given letter symbols.

[13] An authoritative description and review of this method is given by J. Karle and I. L. Karle, *Acta Cryst.*, **21**, 849 (1966).

[14] For a given set of symbols, the sign combinations are listed in order of increasing number of inconsistencies, *i.e.*, when a reflection acquires opposite signs by different combinations of the starting reflections. In our experience, it is quite possible for the third or fourth sign combination in this list to turn out to be the correct one.

TABLE I

SIGN-DETERMINING REFLECTIONS

h	k	l	E	Sign
3	4	2	3.40	+ to determine origin
6	5	4	3.13	+
5	5	9	4.42	−
1	6	9	3.18	+ to determine origin
3	1	2	3.86	+ to determine origin
10	5	3	3.78	−

TABLE II

Final Atomic Coordinates in Fractions of the Unit Cell Edge with Standard Deviations in Parentheses[a]

	x	y	z
P(1)	−0.0031 (1)	0.2500	0.0446 (1)
N(2)	0.0461 (3)	0.1413 (4)	0.0727 (3)
P(3)	0.1438 (1)	0.1428 (1)	0.1043 (1)
N(4)	0.1943 (5)	0.2500	0.1170 (6)
F(5)	0.1493 (3)	0.0754 (4)	0.1799 (2)
F(6)	0.2040 (3)	0.0712 (3)	0.0528 (2)
C(7)	−0.0124 (5)	0.2500	−0.0629 (5)
C(8)	−0.0150 (5)	0.1547 (6)	−0.1032 (4)
C(9)	−0.0236 (6)	0.1543 (8)	−0.1868 (5)
C(10)	−0.0274 (8)	0.2500	−0.2254 (7)
C(11)	−0.1141 (6)	0.2500	0.0848 (5)
C(12)	−0.1590 (6)	0.1552 (7)	0.0998 (6)
C(13)	−0.2467 (6)	0.1573 (8)	0.1298 (6)
C(14)	−0.2883 (9)	0.2500	0.1448 (9)
P(15)	0.4440 (2)	0.2500	0.0133 (1)
N(16)	0.4356 (4)	0.1408 (4)	0.0643 (3)
P(17)	0.4431 (1)	0.1424 (2)	0.1561 (1)
N(18)	0.4514 (6)	0.2500	0.2023 (4)
F(19)	0.3658 (3)	0.0768 (4)	0.1929 (2)
F(20)	0.5213 (3)	0.0710 (4)	0.1834 (3)
C(21)	0.5519 (5)	0.2500	−0.0377 (5)
C(22)	0.5922 (5)	0.1553 (6)	−0.0555 (5)
C(23)	0.6768 (6)	0.1553 (8)	−0.0911 (6)
C(24)	0.7185 (8)	0.2500	−0.1075 (7)
C(25)	0.3568 (6)	0.2500	−0.0611 (5)
C(26)	0.3252 (6)	0.1539 (7)	−0.0909 (5)
C(27)	0.2589 (6)	0.1557 (7)	−0.1504 (6)
C(28)	0.2272 (8)	0.2500	−0.1781 (8)

Final Coordinates and Isotropic Temperature Factors for Hydrogen Atoms[b]

	x	y	z	B_θ, Å^2
H(8)	−0.015 (4)	0.084 (5)	−0.069 (4)	4 (2)
H(9)	−0.025 (6)	0.070 (7)	−0.233 (5)	9 (2)
H(10)	−0.036 (6)	0.250	−0.284 (6)	3 (2)
H(12)	−0.139 (5)	0.086 (7)	0.088 (5)	6 (2)
H(13)	−0.279 (5)	0.081 (6)	0.146 (4)	5 (2)
H(14)	−0.332 (10)	0.250	0.179 (9)	11 (2)
H(22)	0.564 (5)	0.077 (6)	−0.023 (4)	7 (2)
H(23)	0.707 (6)	0.081 (7)	−0.123 (5)	11 (3)
H(24)	0.778 (6)	0.250	−0.141 (5)	4 (2)
H(26)	0.352 (5)	0.078 (6)	−0.072 (5)	7 (2)
H(27)	0.217 (5)	0.075 (7)	−0.163 (5)	7 (2)
H(28)	0.186 (7)	0.250	−0.206 (6)	4 (3)

[a] Origin as in "International Tables for X-Ray Crystallography," Vol. I, p 151. [b] Hydrogen atoms are given the number of the atom to which they are bonded.

nitrilic fluoride,[15] chloride,[16] and bromide[17] crystallize in Pnma (or its equivalent by rotation of axes) and are bisected by a crystallographic mirror plane perpendicular to the plane of the ring, we considered this E map as providing a promising model for solution of the structure. Such a solution would require two independent half-molecules in the asymmetric unit and might partially explain the complexity of the Patterson map. The R factor, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, from a structure factor calculation on the four phosphorus atoms was 0.50. A Fourier map based on the signs of the phosphorus atoms allowed the positions of all of the remaining atoms, other than hydrogen, to be determined.

The refinement described in this paper was carried out with the counter data. All reflections were given unit weight and the quantity minimized was $\Sigma w||F_o| - |F_c||^2$. After four cycles of full-matrix least-squares refinement[18] varying positional and isotropic thermal parameters, the R factor was 0.14. The thermal motion of the atoms was then treated anisotropically. Owing to limitations of computer capacity, the two independent molecules were refined separately in alternate cycles. Four partial cycles of anisotropic refinement gave an R factor of 0.074. A difference map enabled us to identify the positions of the 12 crystallographically independent hydrogen atoms. While there were no other peaks on this map larger than those representing hydrogen atoms, there were a few peaks of approximately the same height; these could not be correlated with any structural feature. Refinement of positional and isotropic thermal parameters for the hydrogen atoms together with positional and anisotropic thermal parameters for the other atoms gave a final R factor of 0.059 on all observed data. In the final cycles of refinement, the largest ratio of shifts to standard deviations was 0.5. The final positional and anisotropic thermal parameters are listed in Tables II and III. Table IV contains the observed and final calculated structure amplitudes. Unobserved reflections were not included in the least-squares refinements, but the structure factors of all the unobserved reflections were calculated and no inconsistencies were found.

The weighted R factor

$$R_w = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2}$$

was 0.129 at the conclusion of the isotropic refinement and 0.071 after refinement of the anisotropic temperature factors. If the test proposed by Hamilton[19] is adopted, the results of the anisotropic refinement can be accepted at the 0.995% confidence level.

The scattering curves for neutral P, N, F, C, and H were taken from ref 20. Corrections for anomalous dispersion were neglected since the terms are quite small.[21]

Results and Discussion

Schematic drawings of the molecular structure are shown in Figure 1. The atom numbering used in the

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(15) M. W. Dougill, *J. Chem. Soc.*, 3211 (1963).

(16) A. Wilson and D. F. Carroll, *ibid.*, 2548 (1960).

(17) E. Giglio and R. Puliti, *Acta Cryst.*, **22**, 304 (1967).

(18) We used a modified version of a program written by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, "I. U. C. World List of Crystallographic Computer Programs," International Union of Crystallography, 1962, no. 384.

(19) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

(20) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 201–207.

(21) $\Delta f' = 0.2$ and $\Delta f'' = 0.5$ for phosphorus with Cu Kα radiation: D. H. Templeton, ref 20, pp 213–216.

TABLE III[a]

FINAL ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) EXPRESSED AS EXP$[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
P(1)	43 (1)	63 (2)	42 (1)	. . .[b]	−15 (2)	. . .
N(2)	48 (2)	68 (4)	59 (2)	5 (5)	−16 (4)	−4 (5)
P(3)	46 (1)	80 (1)	46 (1)	12 (2)	−4 (1)	19 (2)
N(4)	48 (4)	97 (6)	55 (4)	. . .	−17 (6)	. . .
F(5)	81 (2)	136 (4)	67 (2)	−8 (6)	−42 (4)	81 (5)
F(6)	74 (2)	107 (3)	74 (2)	45 (5)	22 (4)	−13 (5)
C(7)	41 (4)	84 (7)	43 (4)	. . .	3 (6)	. . .
C(8)	78 (4)	88 (6)	52 (3)	−31 (8)	−5 (6)	−16 (7)
C(9)	85 (5)	149 (9)	52 (4)	−28 (12)	−11 (7)	−63 (10)
C(10)	79 (7)	198 (17)	36 (5)	. . .	−25 (9)	. . .
C(11)	50 (5)	94 (8)	35 (3)	. . .	−5 (6)	. . .
C(12)	69 (5)	97 (7)	96 (5)	−12 (10)	31 (8)	−7 (10)
C(13)	64 (5)	134 (9)	124 (7)	−15 (11)	46 (9)	29 (13)
C(14)	60 (7)	153 (14)	78 (7)	. . .	13 (11)	. . .
P(15)	57 (1)	69 (2)	30 (1)	. . .	−3 (2)	. . .
N(16)	76 (3)	78 (4)	37 (2)	−3 (6)	1 (4)	26 (5)
P(17)	64 (1)	106 (2)	39 (1)	−11 (2)	−7 (1)	35 (2)
N(18)	86 (5)	130 (8)	29 (3)	. . .	−10 (6)	. . .
F(19)	100 (3)	166 (5)	61 (2)	−72 (7)	17 (4)	61 (5)
F(20)	100 (3)	132 (4)	72 (2)	38 (6)	−34 (4)	60 (5)
C(21)	49 (4)	76 (6)	30 (3)	. . .	−19 (6)	. . .
C(22)	70 (4)	91 (6)	73 (4)	27 (9)	25 (7)	16 (8)
C(23)	71 (5)	129 (8)	88 (5)	48 (11)	25 (8)	−27 (11)
C(24)	52 (6)	185 (16)	52 (5)	. . .	−6 (9)	. . .
C(25)	56 (5)	103 (8)	30 (3)	. . .	−10 (6)	. . .
C(26)	94 (5)	127 (8)	57 (4)	−51 (11)	−44 (7)	35 (9)
C(27)	103 (6)	168 (11)	83 (5)	−61 (14)	−80 (10)	46 (12)
C(28)	50 (6)	274 (24)	54 (6)	. . .	−6 (10)	. . .

[a] Estimated standard deviations are given in parentheses. [b] Dots indicate that this parameter is zero by virtue of the site symmetry of the atom.

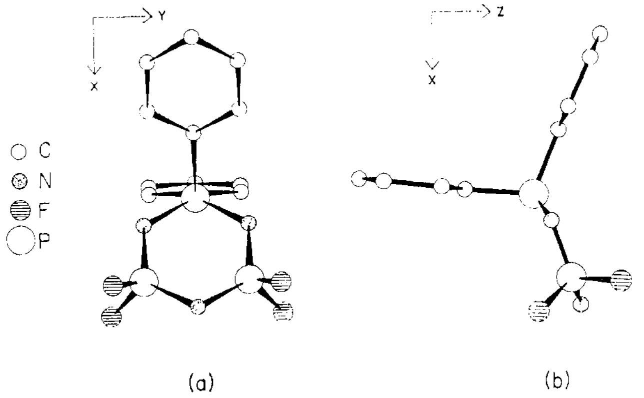

Figure 1.—View of a single molecule: (a) down the *c* axis; (b) down the *b* axis. In (a) there is a crystallographic mirror plane normal to the *y* direction.

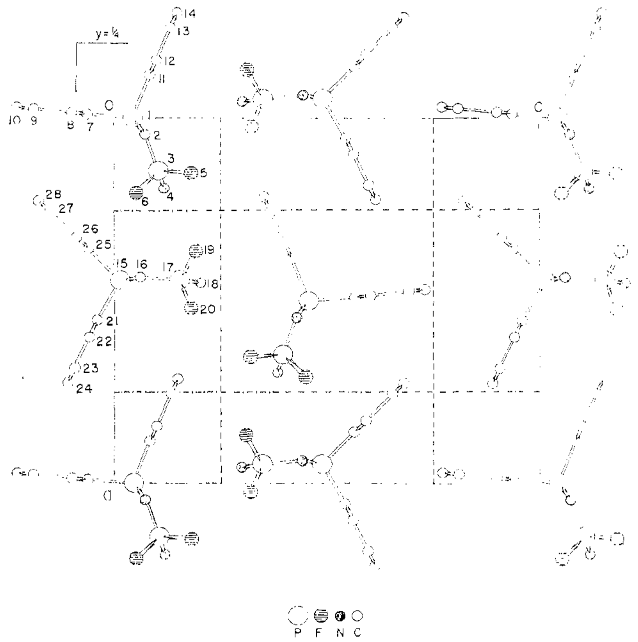

Figure 2.—View of part of the unit cell projected onto the *ac* plane. Only the atoms lying between $y = 0$ and $y = {}^1/_4$ are shown. The atom numbering used in the analysis and in Table II is given.

present analysis is shown in Figure 2. In each of the independent molecules, the crystallographic mirror plane at $y = {}^1/_4$ bisects the phosphorus atom bearing the phenyl groups, the opposite nitrogen atom, and the phenyl rings (through the phosphorus-substituted carbon atom and the *para* carbon atom). Five atoms of the phosphorus–nitrogen ring are approximately planar (Table V), while the phenyl-substituted phosphorus atom is an average distance of 0.203 Å from this plane. The deviation of the nitrogen atom, opposite the phenyl-substituted phosphorus atom, from the other four atoms in the ring is, however, significant (0.06 Å). This represents a new conformation for an isolated six-membered ring although a somewhat similar geometry has been found in fused-ring systems in the carbocyclic series (*e.g.*, in 4-bromoestrone[22,23]) and proposed in several other fused-ring systems on the basis of models

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(22) D. A. Norton, G. Kartha, and C. T. Lu, *Acta Cryst.*, **16**, 89 (1963).
(23) H. J. Geise, C. Altona, and C. Romers, *Tetrahedron*, **23**, 439 (1967).

and infrared data.[24] The plane through the three phosphorus atoms makes an average angle of 5° 45′ with the plane through the three nitrogen atoms. In several conformations, including the ideal "chair," these planes would be parallel.

In contrast to the fluoride derivative, the 1,1-diphenylphosphonitrilic chloride trimer exists in a "slight chair" conformation.[8] Some comparisons of ring conformations in a number of phosphonitrilic trimers[8,15–17,25–27] are collected in Table VI.

Although the $(NPF_2)_3$ molecule is definitely planar, most of the other "aromatic" phosphonitrilic compounds deviate from planarity to a greater or lesser extent. The $(NHPO_2)_3^{3-}$ anion,[27] while representative of an essentially different bonding system, is included as an example of an almost ideal "chair" conformation. The $(NPCl_2)_3$ and $N_3P_3Cl_4(C_6H_5)_2$ molecules can be described as "slight chairs," whereas the $N_3P_3Cl_2(C_6H_5)_4$ and $N_3P_3F_4(C_6H_5)_2$ molecules can be described as "slight boats." The former compound, however, does not have a planar set of four "central atoms," while in the present study the deviation of nitrogen atoms from this plane is much smaller than that of the phosphorus.

Table VII contains the dihedral angles[28] within the phosphonitrilic ring in the molecules described above. These angles offer the best detailed description of the conformations of the rings in the various compounds and allow distinctions to be made in the N_3P_3 series. The greater deviation from planarity in going from fluorine to bromine as substituent on the phosphorus atoms is apparent. The relatively close similarity in conformation between the two independent molecules in the present study and also in the crystal structure of $N_3P_3Cl_2(C_6H_5)_4$[25] is also indicated in this table.

The observed bond lengths, uncorrected for the effects of thermal vibration, and angles for the 1,1-$N_3P_3F_4(C_6H_5)_2$ molecules are summarized in Table VIII. There are three sets of different phosphorus–nitrogen bond lengths, as was found in the case of the 1,1-$N_3P_3Cl_4(C_6H_5)_2$ molecule.[8] For the chloride compound, the lengths are 1.555 (5), 1.578 (5), and 1.615 (5) Å; for the fluoride, they are 1.539 (5), 1.558 (4), and 1.618 (5) Å. In the parent phosphonitrilic halides, the nitrogen lone pair is considered to donate electrons to favorable phosphorus d orbitals, giving rise to a π' system.[29] Replacement of a fluorine atom by a phenyl group causes an expansion in the size of the d orbital of the phosphorus atom and reduces the efficiency of overlap with the orbitals of the nitrogen atom. This change would affect both the σ and π systems (including the delocalization of the lone pair of electrons on the nitrogen atom). The fluorine atoms on the remaining two phosphorus atoms tend to pull the lone pair and σ-bonding electrons of the nitrogen atoms close to these phosphorus atoms. The competing influences of each of the three phosphorus atoms for the lone-pair electrons on the two adjacent nitrogen atoms (Figure 3) might be expected to result in increasing double-bond character in the order P(1)–N(2), P(3)–N(4), P(3)–N(2). The observed bond lengths correlate well with this range of expected double-bond character.

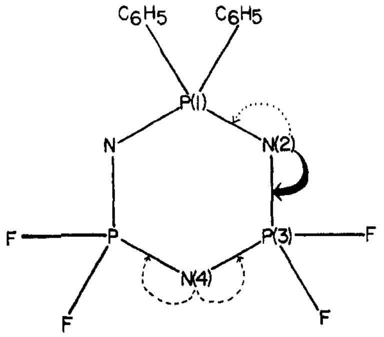

Figure 3.—Drawing of molecule showing donation of lone-pair electrons on N(2) and N(4) among the three nonequivalent N–P bonds. The heavy arrow indicates greatest donation of electrons, the dashed arrow intermediate donation, and the dotted arrow the smallest donation.

The endocyclic angle at P(1) is significantly less than 120° on account of the substantial deviation of P(1) from the plane of the ring. The endocyclic angles are similar in the $N_3P_3F_4(C_6H_5)_2$ and $N_3P_3Cl_4(C_6H_5)_2$ molecules (the N–P$(C_6H_5)_2$–N angles being in surprisingly good agreement considering the differences in conformation between the two rings), but there are changes in the exocyclic bond angles. The Cl–P–Cl angle is 100.3° whereas the F–P–F angle is 96.9°. The C–P–C angle is 104° in the chloride derivative and 107.9° in the fluoride derivative. The phosphorus–carbon and phosphorus–fluorine bond lengths are the normally observed values.[30]

A number of interesting structural differences are thus apparent from a comparison of the 1,1-diphenylphosphonitrilic chloride and fluoride trimers. These differences probably arise from the greater electronegativity of fluorine causing a relative contraction of the d orbitals of the phosphorus atoms. The two P–N distances involving the fluorine-substituted phosphorus atom appear somewhat shorter than the corresponding lengths in the chloride compound, as might be expected from a more efficient overlap with the orbitals of the nitrogen atoms. The C–P–C bond angle is closer to the tetrahedral angle in the fluoride derivative, reflecting a smaller d orbital contribution at this center since the π electrons are drawn more toward the halide-substituted phosphorus atoms than in the corresponding chloride compound. The greater tendency toward planarity of the nitrogen atoms and the phosphorus atoms bearing the fluorine atoms in the fluoride trimer results from an increased

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(24) E. M. Philbin and T. S. Wheeler, *Proc. Chem. Soc.*, 167 (1958).

(25) N. V. Mani, F. R. Ahmed, and W. H. Barnes, *Acta Cryst.*, **21**, 375 (1966).

(26) L. A. Siegel and J. H. van den Hende, *J. Chem. Soc.*, *A*, 817 (1967).

(27) R. Olthof, T. Migchelsen, and A. Vos, *Acta Cryst.*, **19**, 596 (1965).

(28) See, *e.g.*, E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, p 6.

(29) D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 4118 (1962).

(30) L. E. Sutton in "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 18, The Chemical Society, London, 1965, pp S 9s, S 22s.

TABLE IV

FINAL LIST OF h, k, l, $|F_o|$, AND F_c FOR THE OBSERVED REFLECTIONS

k	l	$\|F_{obs}\|$	F_{calc}
[illegible]	[illegible]	[illegible]	[illegible]

TABLE IV (*Continued*)

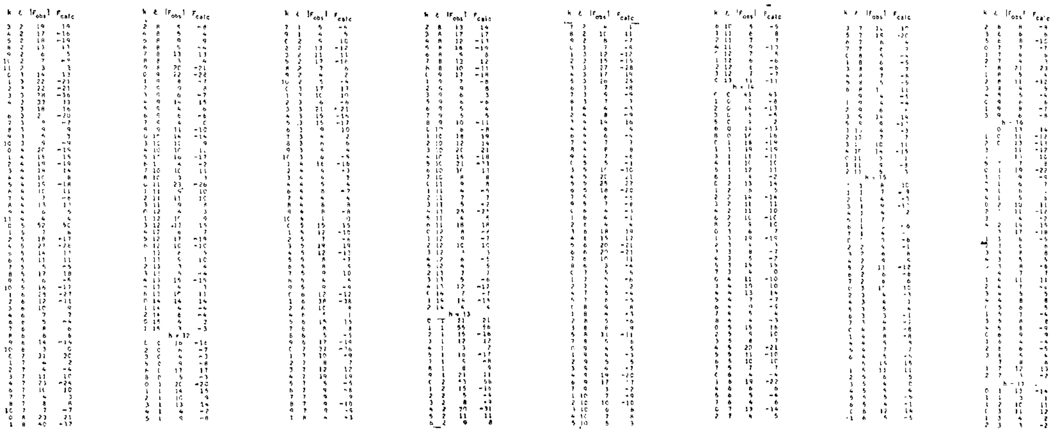

TABLE V

DETAILS OF BEST PLANES THROUGH VARIOUS GROUPS OF ATOMS WHICH ARE GIVEN WEIGHTS, WHERE $w = 1/\sigma^2$ (σ FROM LEAST-SQUARES)[a]

P(1)	*0.000*	0.213	0.192	0.202	P(15)	*0.000*	0.210	0.185	0.203
P(3)	*0.000*	−0.038	*0.000*	*−0.002*	P(17)	*0.000*	−0.044	*0.000*	*−0.004*
P(3′)[b]	*0.000*	−0.038	*0.000*	*−0.002*	P(17′)	*0.000*	−0.044	*0.000*	*−0.004*
N(2)	−0.124	*0.000*	*0.000*	*0.006*	N(16)	0.119	*0.000*	*0.000*	*0.010*
N(2′)	−0.124	*0.000*	*0.000*	*0.006*	N(16′)	0.119	*0.000*	*0.000*	*0.010*
N(4)	0.119	*0.000*	0.057	*0.052*	N(18)	−0.127	*0.000*	0.067	*0.056*
F(5)	−1.115			−1.163	F(19)	1.144			−1.197
F(6)	1.154			1.110	F(20)	−1.159			1.113
C(7)	1.575			1.846	C(21)	−1.592			1.864
C(11)	−1.297			−0.987	C(25)	1.295			−1.023
				$\chi^2 = 32.7$					$\chi^2 = <59.0$
				$P = <0.005$[c]					$P = <0.005$

[a] The atoms included in the plane are given in italic type. The results of a χ^2 test are also listed, along with the probability (P) that the deviations describe a normal distribution. [b] Atoms related to another by the mirror reflection are designated by primes. [c] The acceptance level for the points being planar.

TABLE VI

COMPARISON OF RING CONFORMATIONS AMONG VARIOUS $(NP)_3$ DERIVATIVES[a]

	$(NPF_2)_3$	$(NPCl_2)_3$	$(NPBr_2)_3$	$(NP)_3F_4(C_6H_5)_2$		$(NP)_3Cl_4(C_6H_5)_2$	$(NP)_3Cl_2(C_6H_5)_4$		$(NH\text{-}PO_2)_3^{3-}$ [e]	$N_3P_3(O_2C_6H_4)_3$	
Ref	15	16	17	Present work		8	25		27	26	
Space group	Pnma	Pnma	Pnma[b]	Pnma		$P2_1/n$	C2/c		$P2_1/n$	$P6_3$	
				I	II		I	II		I	II
Angle between two planes defined by 3 P and 3 N atoms	0° 56′	3° 58′	4° 39′	6° 2′	5° 28′	2° 38′	5° 2′	6° 44′	4° 6′	0°	0°
Dev of 3 N from plane through 3 P, Å	0.01	0.01	0.03	0.12	0.13	0.02	0.11	0.11	0.39	0.06	0.10
	0.01	0.01	0.21	−0.12	−0.12	0.11	−0.13	−0.16	0.45	0.06	0.10
	−0.02	0.09	0.21	−0.12	−0.12	0.13	−0.01	−0.02	0.44	0.06	0.10
Av esd of best plane through 4 atoms,[c] Å	...[d]	...	...	...	...	0.02	0.03	0.03	0.01	...	...
Dev of apical P and N atoms from above plane, Å	P 0.00	0.02	0.32	0.19	0.19	0.10	0.10	0.06	0.64	0.10	0.15
	N 0.00	−0.10	−0.12	0.06	0.07	−0.17	0.08	0.14	−0.60	−0.09	−0.15
Literature description	Planar	Slight chair	Slight chair	Slight boat		Slight chair	Slight boat		Chair	Slight chair	

[a] A great deal of the information in this table was calculated by us from the data presented in the original papers. [b] In ref 17 the space group is described as Pcmn. [c] Where the molecules have a crystallographic mirror plane, there is an exact plane through the four ring atoms which do not lie on the mirror plane; in such cases this plane is chosen. In molecules which do not have C_s crystallographic symmetry, the group of four "central" atoms with the lowest average distance from the best plane through these atoms was chosen for description of ring shape. [d] This indicates that four atoms are planar by symmetry. [e] This compound is clearly not analogous to this general group of phosphonitrilic compounds and is included mainly as an example of an $(NP)_3$ compound which resembles the carbocyclic "chair" conformation.

rigidity of the phosphorus–nitrogen bonds due to the increase in double-bond character.

The molecular packing diagram viewed along the *b* axis is shown in Figure 2, and a stereopicture of the structure along the *c* axis is shown in Figure 4. The intermolecular contacts are listed in Table IX. The F----F intermolecular contacts are greater than the sum of the van der Waals radii, 2.70 Å,[31] and are of the order

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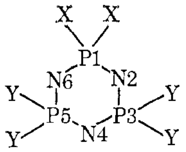
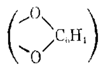
(31) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

Table VII

Dihedral Angles[a–c] (deg) in Phosphonitrilic Ring Systems



	$(NPF_2)_3$	$(NPCl_2)_3$	$(NPBr_2)_3$	$(NP)_3F_4(C_6H_5)_2$		$(NP)_3Cl_4(C_6H_5)_2$	$(NP)_3Cl_2(C_6H_5)_4$		$(NHPO_2)_3^{3-}$	$N_3P_3(O_2C_6H_4)_3$	
X	F	Cl	Br	C_6H_5		C_6H_5	Cl				
Y	F	Cl	Br	F		Cl	C_6H_5				
				I	II		I	II		I	II
N(6)P(1)–N(2)P(3)[d]	−1.5	1.7	−26.0	−15.0	−14.5	−6.9	−4.0	−2.4	47.5	0.0	0.0
P(1)N(2)–P(3)N(4)	0.4	−5.0	17.9	5.5	4.8	5.4	9.8	8.1	−47.9	4.0	6.4
N(2)P(3)–N(4)P(5)	0.8	8.2	−10.9	4.9	5.7	−9.2	−3.3	−2.9	49.9	0.0	0.0
P(3)N(4)–P(5)N(6)	−0.8	−8.2	10.9	−4.9	−5.7	14.7	−6.2	−7.7	−50.8	4.0	6.4
N(4)P(5)–N(6)P(1)	−0.4	5.0	−17.9	−5.5	−4.8	−15.3	11.0	13.8	48.6	0.0	0.0
P(5)N(6)–P(1)N(2)	1.5	−1.7	26.0	15.0	14.5	11.8	−6.4	−9.3	−48.2	4.0	6.4

[a] All of these angles were calculated by us from the data presented in the original papers (for references see Table VI). [b] The angle AB–CD is taken as positive if, when viewed along the B–C bond, atom D has to be rotated counterclockwise to eclipse atom A. [c] In the molecules which have C_s molecular symmetry the sign convention for the dihedral angles is arbitrary, as bonds related by reflection will have dihedral angles with equal magnitude but opposite sign. [d] The numbering system used in this table is dictated by the substituent pattern and does not, in general, correspond to that used in the original paper.

Table VIII

Bond Lengths (Å) and Angles (deg)[a]

Bonds

P(1)–N(2)	1.617 (5)	P(15)–N(16)	1.619 (5)
P(1)–C(7)	1.802 (9)	P(15)–C(21)	1.810 (8)
P(1)–C(11)	1.776 (9)	P(15)–C(25)	1.793 (9)
N(2)–P(3)	1.539 (5)	N(16)–P(17)	1.539 (5)
P(3)–N(4)	1.555 (4)	P(17)–N(18)	1.561 (4)
P(3)–F(5)	1.523 (5)	P(17)–F(19)	1.538 (5)
P(3)–F(6)	1.530 (4)	P(17)–F(20)	1.533 (5)
C(7)–C(8)	1.375 (8)	C(21)–C(22)	1.364 (8)
C(8)–C(9)	1.403 (11)	C(22)–C(23)	1.386 (11)
C(9)–C(10)	1.365 (11)	C(23)–C(24)	1.368 (11)
C(11)–C(12)	1.387 (10)	C(25)–C(26)	1.387 (10)
C(12)–C(13)	1.392 (11)	C(26)–C(27)	1.398 (13)
C(13)–C(14)	1.341 (11)	C(27)–C(28)	1.355 (12)

Angles

N(2)–P(1)–N(2′)	115.2 (3)	N(16)–P(15)–N(16′)	115.8 (3)
C(7)–P(1)–C(11)	107.9 (3)	C(21)–P(15)–C(25)	107.9 (2)
N(2)–P(1)–C(7)	108.9 (3)	N(16)–P(15)–C(21)	108.4 (3)
N(2)–P(1)–C(11)	107.9 (3)	N(16)–P(15)–C(25)	108.1 (3)
P(1)–N(2)–P(3)	120.8 (2)	P(15)–N(16)–P(17)	120.6 (2)
N(2)–P(3)–N(4)	120.6 (3)	N(16)–P(17)–N(18)	120.7 (3)
N(2)–P(3)–F(5)	109.2 (3)	N(16)–P(17)–F(19)	109.8 (3)
N(2)–P(3)–F(6)	110.2 (3)	N(16)–P(17)–F(20)	110.1 (3)
N(4)–P(3)–F(5)	110.0 (3)	N(18)–P(17)–F(19)	108.9 (3)
N(4)–P(3)–F(6)	107.8 (2)	N(18)–P(17)–F(20)	107.4 (3)
F(5)–P(3)–F(6)	96.3 (2)	F(19)–P(17)–F(20)	97.4 (3)
P(3)–N(4)–P(3′)	120.1 (2)	P(17)–N(18)–P(17′)	119.9 (1)
P(1)–C(7)–C(8)	119.4 (3)	P(15)–C(21)–C(22)	119.3 (3)
C(8)–C(7)–C(8′)	121.2 (6)	C(22)–C(21)–C(22′)	121.4 (6)
C(7)–C(8)–C(9)	119.6 (4)	C(21)–C(22)–C(23)	119.3 (4)
C(8)–C(9)–C(10)	118.1 (6)	C(22)–C(23)–C(24)	119.6 (5)
C(9)–C(10)–C(9′)	123.4 (8)	C(23)–C(24)–C(23′)	120.8 (7)
P(1)–C(11)–C(12)	120.7 (5)	P(15)–C(25)–C(26)	119.5 (4)
C(12)–C(11)–C(12′)	118.4 (6)	C(26)–C(25)–C(26′)	121.0 (6)
C(11)–C(12)–C(13)	119.7 (5)	C(25)–C(26)–C(27)	118.6 (5)
C(12)–C(13)–C(14)	120.8 (8)	C(26)–C(27)–C(28)	120.0 (6)
C(13)–C(14)–C(13′)	120.5 (7)	C(27)–C(28)–C(27′)	121.8 (9)

[a] The C–H lengths range from 0.8 to 1.3 Å with a typical esd of 0.1 Å; the C–C–H angles range from 113 to 127° with a typical esd of 5°.

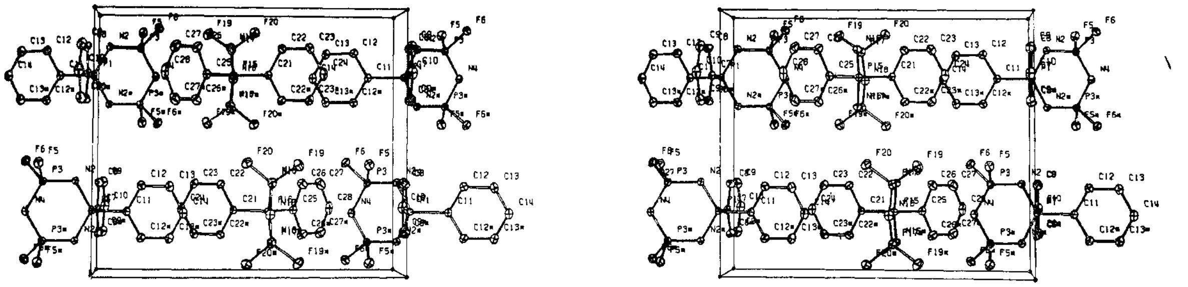


Figure 4.—A stereoscopic view of the contents of half a unit cell viewed along the $+z$ direction. The origin is at the near top left-hand corner, the $+x$ direction is horizontally toward the right, and the $+y$ direction is vertically downward. The contents of the cell from $-c/4$ to $+c/4$ are shown.

TABLE IX[a]

INTERMOLECULAR CONTACTS (Å) LESS THAN 3.70 Å

F(6)···N(16)	3.54	F(19)···C(12)^{II}	3.62
P(3)···F(19)	3.70	F(19)···C(13)^{II}	3.55
N(4)···F(19)	3.58	F(20)···F(5)^{II}	2.97
F(5)···F(19)	3.21	N(18)···C(11)^{II}	3.69
F(6)···F(19)	3.35	C(24)···C(28)^{III}	3.59
F(6)···C(26)	3.17	F(20')···C(9)^{IV}	3.57
F(6)···C(27)	3.65	F(5')···C(9)^{V}	3.43
F(20)···C(14)^{I}	3.66	F(6')···C(23)^{VI}	3.41
F(5)···C(13)^{II}	3.68	F(19')···C(23)^{VI}	3.43

[a] The Roman numeral superscripts refer to atoms related to those listed in Table II by the transformations: (I) $1 + x, y, z$; (II) $^1/_2 + x, y, ^1/_2 - z$; (III) $^1/_2 + x, y, -^1/_2 - z$; (IV) $^1/_2 - x, ^1/_2 + y, ^1/_2 + z$; (V) $-x, ^1/_2 + y, -z$; (VI) $1 - x, ^1/_2 + y, -z$.

of magnitude of those found in trimeric[15] and tetrameric[7] phosphonitrilic fluorides. There is no evidence for C–H---F hydrogen bonding. The sum of the van der Waals radii[28] for $>$CH and F is 3.35 Å, much shorter than the distance between the atoms F(20) and C(13)^{I} (Table IX) which might appear from Figure 4 to be reasonably placed for hydrogen bonding.

The present structure adds to the number of phosphonitrilic compounds which crystallize in Pnma, with a similar packing arrangement. The cell parameters normal to the mirror plane in the four crystals lie in the range 12.19 (for $(NPF_2)_3$) to 13.36 Å (for $(NPBr_2)_3$).

The symmetry requirements of Pnma may be responsible for another major contrast between the molecular conformations of the species $N_3P_3F_4(C_6H_5)_2$ and $N_3P_3Cl_4(C_6H_5)_2$. The angle of rotation of the two phenyl rings with the plane through the phosphorus atom bearing the phenyl groups, the opposite nitrogen atom, and the two carbon atoms bonded to the phosphorus atom is 90° in the fluoride compound. In the chloride compound the corresponding angles are 46° 50′ and 56° 50′. While there is no evidence for large-scale rotational disorder about the P–C bonds in $N_3P_3F_4(C_6H_5)_2$, inspection of the thermal ellipsoids (Figure 4) indicates that the principal molecular motion involves oscillation of the phenyl rings about the P–C bonds. This motion has a definite effect on the C–C bond lengths in the phenyl rings. The average C–C length is 1.377 ± 0.018 Å, compared to the value of 1.394 Å, usually found in phenyl rings.[32] The bonds which do not lie in a plane perpendicular to the b axis are most affected. Similar effects have been noted in other phenyl-substituted phosphonitrilic derivatives.[8,25] This thermal motion is probably mainly responsible for the larger internal deviation in the C–C lengths than those found from the least-squares refinements. As thermal motion will be less important in the phosphonitrilic ring, we believe that the standard deviations reported for this portion of the molecule are reasonably valid.

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(32) Reference 30, p S 16s.