CONTRIBUTION FROM W. A. NOYES CHEMICAL LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

The Crystal and Molecular Structure of Trimeric Phosphonitrilic Isothiocyanate[1]

BY J. BRIAN FAUGHT,[2] THERALD MOELLER, AND IAIN C. PAUL[3]

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The crystal structure of trimeric phosphonitrilic isothiocyanate, $N_3P_3(NCS)_6$, has been determined by three-dimensional single-crystal X-ray studies. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.79$ (3), $b = 8.02$ (2), $c = 10.31$ (1) Å, $\alpha = 96°\ 0'$ (30′), $\beta = 99°\ 4'$ (30′), $\gamma = 97°\ 28'$ (30′), and two molecules per unit cell. The calculated density is 1.70 (2) g cm^{-3}; the experimental density is 1.62 (8) g cm^{-3}. The structure was solved from 1246 independent nonzero reflections collected on film by the Weissenberg technique and refined to a conventional R factor of 0.12. The nitrogen atoms of two isothiocyanate groups are bonded to each phosphorus atom in the six-membered phosphorus–nitrogen ring. Five of the atoms of the phosphonitrilic ring are planar, with the sixth atom, a nitrogen, 0.15 Å out of the plane. The average P–N bond length in the ring is 1.58 Å with a root-mean-square deviation of 0.05 Å; the average P–N (exocyclic) bond length is 1.63 ± 0.01 Å.

Introduction

Timeric phosphonitrilic isothiocyanate was first prepared by Audrieth and coworkers.[4,5] The isothiocyanate structure as opposed to the thiocyanate structure was assigned on the basis of the infrared spectrum.[4] Stahlberg and Steger[6] made a detailed study of the Raman spectrum of this compound in solution and also concluded that the structural unit in this compound is the isothiocyanate. They interpreted the spectrum in terms of D_{3h} molecular symmetry.

Crystal and molecular structures have been reported for several other trimeric compounds, including the fluoride,[7] chloride,[8,9] and bromide,[10] but no pseudohalide structure has been determined. This paper reports the results of a three-dimensional X-ray analysis on the structure of trimeric phosphonitrilic isothiocyanate.

Experimental Section

Crystal Data and Data Collection.—Material suitable for single-crystal studies was prepared from a solution of trimeric phosphonitrilic isothiocyanate in *n*-heptane at 0°. A preliminary examination of a typical crystal using precession photographs indicated that it belonged to the triclinic system. No systematic absences could be detected, and only C_i diffraction symmetry was noted.

The unit cell dimensions, as measured from photographs taken on a 60-mm Buerger precession camera, equipped with a Polaroid cassette, using Zr-filtered Mo Kα radiation (λ 0.7107 Å) at 25°, are as follows: $a = 11.79$ (3), $b = 8.02$ (2), $c = 10.31$ (1) Å, $\alpha = 96°\ 0'$ (30′), $\beta = 99°\ 4'$ (30′), $\gamma = 97°\ 28'$ (30′). The standard deviations result from a number of measurements of the reciprocal lattice dimensions. The density measured by flotation in a bromobenzene–iodobenzene mixture is 1.62 (8) g/cm^3, compared with the calculated value of 1.70 (2) g/cm^3 assuming two molecules of $N_3P_3(NCS)_6$ (mol wt 483.43) in a unit cell of volume 947 Å^3. The crystals are quite soluble in the liquids that we tried to use for a density determination. The above value was obtained by partially saturating the solvent mixture and carrying out the determination as rapidly as possible. $F(000)$ is 480, and the linear absorption coefficient for Cu Kα radiation is 88.6 cm^{-1}. The possible space groups are P1 or $P\bar{1}$.

The crystal selected for data collection had the dimensions 0.33 mm (along the *a* axis) and approximately 0.20 and 0.35 mm along the *b* and *c* axes, respectively. The crystal was mounted in a 0.5-mm, thin-walled capillary which was sealed at both ends, as the crystals decompose after prolonged exposure to the atmosphere. Multiple-film, equiinclination Weissenberg photographs were taken with Ni-filtered Cu Kα radiation in a cold room maintained at 4 ± 2°. For the levels 1*kl* through 9*kl*, two exposures were necessary to record all the symmetry-nonequivalent data on the upper portion of the film. A total of 1246 independent nonzero intensities were estimated by visual comparison of the reflections on the upper portion of the films with a series of standard spots prepared from a specimen crystal. Lorentz, polarization, and spot-shape[11] corrections were applied to the data. Intralevel scaling was accomplished by comparison of common reflections. The levels 0*kl* to 9*kl* were initially scaled together according to the exposure time. An absorption correction was applied to the data using the program GNABS.[12] The minimum and maximum transmission factors were calculated to be 0.115 and 0.312, respectively.

Structure Determination

The results of some statistical tests which are part of the program FAME[13] suggested that the crystal belongs to the centric space group $P\bar{1}$. Since there are several moderately heavy atoms in this molecule (phosphorus and sulfur), it did not seem likely that the heavy-atom approach to the solution would be straightforward; so the symbolic addition method[14] was used. The reflections used to initiate the symbolic addition

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[1] Supported in part by NIH Grants GM 11996 and GM 12470.

[2] Gulf Oil Corp. Fellow in Chemistry, 1968–1969.

[3] Alfred P. Sloan Research Fellow.

[4] R. J. A. Otto and L. F. Audrieth, *J. Amer. Chem. Soc.*, **80**, 5894 (1958).

[5] G. Tesi, R. J. A. Otto, F. G. Sherif, and L. F. Audrieth, *ibid.*, **82**, 528 (1960).

[6] R. Stahlberg and E. Steger, *Spectrochim. Acta, Part A*, **23**, 2185 (1967).

[7] M. W. Dougill, *J. Chem. Soc.*, 3211 (1963).

[8] A. Wilson and D. F. Carroll, *ibid.*, 2548 (1960).

[9] E. Giglio, *Ric. Sci.*, **30**, 721 (1960); F. Pompa and A. Ripamonti, *ibid.*, **29**, 1516 (1959).

[10] E. Giglio and R. Puliti, *Acta Crystallogr.*, **22**, 304 (1967).

[11] D. C. Phillips, *ibid.*, **7**, 746 (1954).

[12] For absorption corrections, we used a local modification of a program, GNABS, suitable for a crystal bounded by plane faces. The program was written by C. W. Burnham, Geophysical Laboratory, Carnegie Institute, Washington, D. C.

[13] For the symbolic addition method, we used a package of programs containing FAME and MAGIC written by E. B. Fleischer, A. L. Stone, and R. B. K. Dewar of the University of Chicago. FAME calculates normalized structure amplitudes, *E*'s, and MAGIC determines the signs of the *E*'s using the Karle–Hauptman Σ_2 relationship and carries out the symbolic addition procedure. The phased *E*'s are used as coefficients in the Fourier synthesis

[14] J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

TABLE I
SIGN-DETERMINING SYMBOL ASSIGNMENTS

Symbol	h	k	l	E	Sign
A	3	0	−2	2.40	+
B	4	3	4	2.88	−
C	2	4	−1	2.45	+ (to determine origin)
D	0	1	−3	3.53	+ (to determine origin)
E	3	6	−1	3.69	+
F	3	1	−8	2.96	−
G	3	−5	1	2.66	+ (to determine origin)
H	0	6	−2	2.86	−

procedure (shown in Table I) were chosen from the group of 25 reflections with largest normalized structure amplitudes (E)[14] with proper regard to their parity and because of the large number of interactions with other reflections. From these starting reflections, other reflections were generated and their signs computed. The sign combination with all the starting symbols having plus signs did not produce any contradictions in the symbol equivalences among the 274 reflections with $E > 1.40$. This assignment often occurs in the triclinic case and is trivial. The sign combination with the next lowest number of contradictions (24% of the symbol equivalences) gave a solution to the problem.

An E map calculated from 248 of the 274 reflections with $E > 1.40$ could be readily interpreted in terms of three phosphorus atoms forming an equilateral triangle. This map also contained four other large peaks which were in reasonable positions for sulfur atoms. With this skeletal arrangement of atoms as a basic model, the positions of all other atoms could be identified from the E map.

From a structure factor calculation based on all 24 atoms and setting all isotropic thermal parameters to 3.0 Å^2, R was found to be 0.37, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. After adjustment of interlevel scale factors, full-matrix least-squares refinement of the positional parameters and the isotropic thermal parameters was carried out using the UCLA-LS program.[15] All reflections were given unit weight, and the quantity $\Sigma w(|F_o| - |F_c|)^2$ was minimized. After six cycles of refinement on observed data only, the R factor was 0.18. The interlevel scale factors were then adjusted such that $\Sigma F_o = \Sigma F_c$ for each level, and the refinement was continued with anisotropic thermal parameters for all atoms. A Hughes-type weighting scheme[16] was used in this part of the refinement, with $\sqrt{w} = |F_o|/30.0$ when $|F_o| \leq 30.0$, and $\sqrt{w} = 30.0/|F_o|$ when $|F_o| > 30.0$ where $4F_{\min}$ is approximately 30.0. Because of storage limitations, only 12 atoms were refined anisotropically at one time. After four cycles of anisotropic refinement, $R = 0.12$ on the 1246 observed reflections and $R_2 = 0.12$, where

$$R_2 = \left[\frac{\Sigma w||F_o| - |F_c||^2}{\Sigma w|F_o|^2}\right]^{1/2}$$

During the final cycle of refinement, the greatest parameter shift was less than 0.2σ.

The scattering curves for neutral P, N, C, and S atoms were taken from the compilation in ref 17. Corrections for anomalous dispersion were neglected for the P and S atoms, because the terms are sufficiently small[18] to be of little importance in the present analysis.

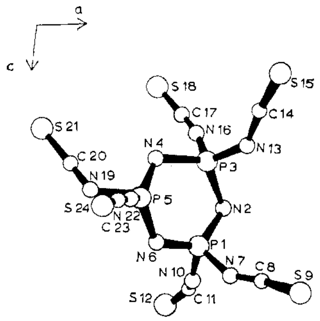

Figure 1.—View of a single molecule perpendicular to the a–c plane.

The final difference map was quite smooth, with the highest peaks having numerical values of ±15 where a typical carbon atom in an F_o map had a peak value of 65 on the same scale. None of the calculated structure amplitudes for the unobserved reflections was sufficiently large that one would expect any of these reflections to be measurable on the films.

Results and Discussion

A drawing of the molecule of trimeric phosphonitrilic isothiocyanate viewed perpendicular to the a–c plane is shown in Figure 1. The atom notation is indicated in this drawing.

TABLE II
FINAL ATOMIC COORDINATES OF TRIMERIC PHOSPHONITRILIC ISOTHIOCYANATE[a]

Atom	x	y	z
P(1)	0.8163 (5)	0.0847 (7)	1.0127 (6)
N(2)	0.8750 (15)	0.0200 (25)	0.8923 (18)
P(3)	0.8069 (5)	0.0347 (7)	0.7440 (6)
N(4)	0.7004 (15)	0.1311 (23)	0.7313 (17)
P(5)	0.6368 (5)	0.1801 (7)	0.8450 (6)
N(6)	0.7017 (16)	0.1543 (22)	0.9923 (17)
N(7)	0.9110 (18)	0.2313 (24)	1.1060 (18)
C(8)	0.9973 (20)	0.3327 (29)	1.1335 (20)
S(9)	1.1037 (6)	0.4664 (9)	1.1667 (8)
N(10)	0.8088 (22)	−0.0602 (31)	1.1154 (24)
C(11)	0.7914 (20)	−0.1929 (35)	1.1378 (22)
S(12)	0.7796 (8)	−0.3779 (11)	1.1828 (9)
N(13)	0.9053 (18)	0.1191 (28)	0.6679 (21)
C(14)	0.9280 (20)	0.1844 (32)	0.5856 (31)
S(15)	0.9783 (9)	0.2692 (16)	0.4675 (10)
N(16)	0.7773 (17)	−0.1530 (23)	0.6608 (19)
C(17)	0.7231 (23)	−0.2581 (36)	0.5996 (28)
S(18)	0.6528 (11)	−0.4187 (15)	0.5007 (11)
N(19)	0.5014 (16)	0.0895 (22)	0.8212 (18)
C(20)	0.4395 (24)	0.0110 (33)	0.7343 (27)
S(21)	0.3464 (8)	−0.1047 (12)	0.6182 (9)
N(22)	0.6201 (19)	0.3779 (25)	0.8465 (21)
C(23)	0.5854 (18)	0.5020 (30)	0.8519 (19)
S(24)	0.5389 (8)	0.6773 (9)	0.8704 (8)

[a] The coordinates are given in fractions of the unit cell edges with the standard deviations in parentheses.

Table II contains a list of the final fractional coordinates of the atoms, and the final anisotropic thermal

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[15] Using a local modification of the program written by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, "I. U. C. World List of Crystallographic Programs," International Union of Crystallography, 1962, No. 384.

[16] E. W. Hughes, *J. Amer. Chem. Soc.*, **63**, 1737 (1941).

[17] J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 201–207.

[18] D. H. Templeton, ref 17, pp 213–216.

TABLE III

FINAL ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) FOR TRIMERIC PHOSPHONITRILIC ISOTHIOCYANATE[a]

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
P(1)	58 (7)	109 (11)	83 (8)	−10 (12)	10 (11)	27 (15)
N(2)	38 (18)	277 (48)	84 (27)	99 (45)	−22 (34)	−87 (56)
P(3)	51 (6)	115 (11)	80 (8)	5 (12)	36 (10)	9 (15)
N(4)	54 (19)	223 (43)	73 (23)	144 (45)	43 (32)	43 (49)
P(5)	36 (6)	99 (11)	88 (8)	33 (11)	14 (11)	1 (14)
N(6)	60 (20)	172 (39)	76 (24)	42 (43)	−24 (33)	−128 (48)
N(7)	83 (21)	152 (40)	88 (25)	−74 (48)	8 (36)	−26 (50)
C(8)	55 (24)	137 (45)	74 (28)	25 (57)	12 (38)	−43 (56)
S(9)	89 (8)	198 (15)	186 (11)	−105 (17)	−45 (14)	100 (20)
N(10)	172 (32)	161 (50)	189 (40)	−47 (60)	18 (52)	276 (76)
C(11)	59 (24)	220 (64)	75 (31)	48 (59)	−51 (41)	−87 (74)
S(12)	179 (12)	246 (19)	211 (14)	26 (22)	29 (19)	258 (26)
N(13)	75 (23)	242 (51)	101 (28)	−9 (49)	97 (40)	105 (60)
C(14)	38 (24)	205 (58)	162 (44)	−23 (54)	28 (51)	31 (81)
S(15)	170 (12)	639 (36)	180 (13)	54 (32)	193 (21)	300 (35)
N(16)	71 (21)	93 (38)	110 (27)	−45 (43)	−35 (36)	−38 (49)
C(17)	78 (29)	193 (62)	146 (39)	−48 (65)	55 (51)	7 (79)
S(18)	256 (16)	479 (31)	233 (16)	−473 (38)	111 (26)	−329 (37)
N(19)	60 (18)	126 (36)	61 (23)	−56 (40)	−28 (31)	−67 (46)
C(20)	101 (31)	204 (60)	122 (38)	109 (69)	130 (57)	73 (79)
S(21)	156 (11)	351 (22)	171 (13)	−63 (24)	−149 (19)	−52 (27)
N(22)	129 (26)	71 (38)	158 (32)	94 (48)	50 (42)	−6 (52)
C(23)	50 (21)	123 (47)	52 (26)	−22 (47)	29 (35)	8 (53)
S(24)	168 (10)	145 (14)	204 (12)	201 (18)	127 (17)	117 (20)

[a] The form of the expression is $\exp\{-[b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl]\}$. Estimated standard deviations are in parentheses.

parameters are listed in Table III. Table IV is a listing of the observed and calculated structure factors. The bond lengths and angles are presented in Table V. The estimated standard deviations in the bond lengths and angles are calculated from the standard deviations of the positional parameters. The position of the molecule in the unit cell is shown in the packing diagram in Figure 2, along with some intermolecular S---S contacts.

All the atoms of trimeric phosphonitrilic isothiocyanate are crystallographically independent. The P–N bond lengths in the ring vary from 1.52 to 1.64 Å, with a mean bond length of 1.58 Å and a root-mean-square deviation of 0.05 Å; the standard deviation calculated from least squares for an individual bond length is ±0.02 Å. Although there is a considerable discrepancy between the internal consistency of these lengths and the least-squares esd, there is no chemical reason to expect differences in the P–N bond lengths. Trimeric phosphonitrilic isothiocyanate melts at 41–42°;[4,5] hence the X-ray analysis was carried out within 40° of the melting point, and the results may be greatly affected by thermal motion (see later).

TABLE IV

FINAL LIST OF h, k, l, F_o, AND F_c

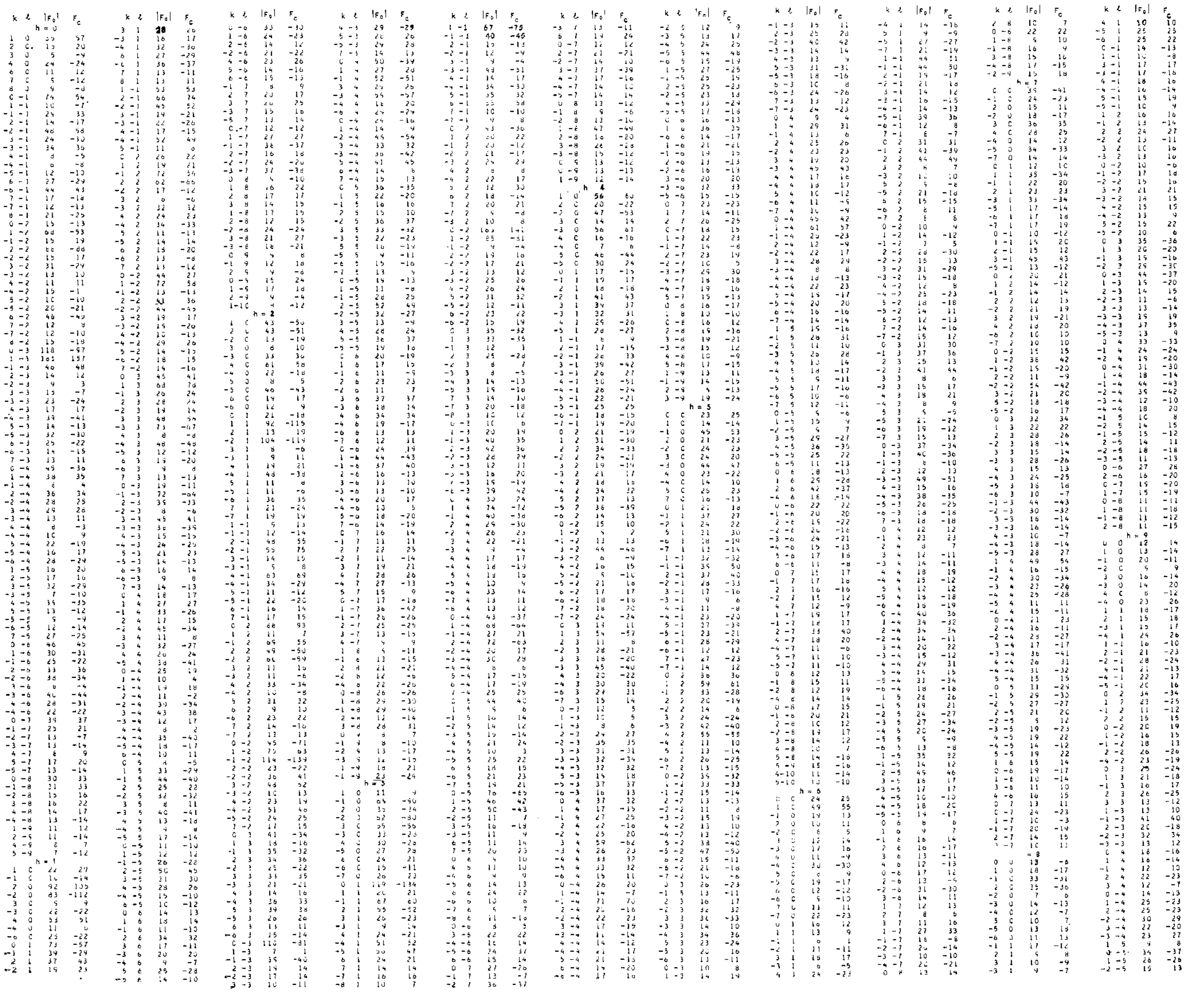


TABLE V

BOND LENGTHS AND BOND ANGLES FOR TRIMERIC PHOSPHONITRILIC ISOTHIOCYANATE[a]

Bond Lengths, Å

P(1)–N(2)	1.59 (2)	P(3)–N(13)	1.62 (2)
N(2)–P(3)	1.63 (2)	N(13)–C(14)	1.09 (4)
P(3)–N(4)	1.55 (2)	C(14)–S(15)	1.61 (3)
N(4)–P(5)	1.53 (2)	P(3)–N(16)	1.62 (2)
P(5)–N(6)	1.64 (2)	N(16)–C(17)	1.08 (3)
N(6)–P(1)	1.52 (2)	C(17)–S(18)	1.60 (3)
P(1)–N(7)	1.62 (2)	P(5)–N(19)	1.64 (2)
N(7)–C(8)	1.19 (3)	N(19)–C(20)	1.13 (3)
C(8)–S(9)	1.51 (2)	C(20)–S(21)	1.61 (3)
P(1)–N(10)	1.65 (2)	P(5)–N(22)	1.62 (2)
N(10)–C(11)	1.11 (3)	N(22)–C(23)	1.12 (3)
C(11)–S(12)	1.60 (3)	C(23)–S(24)	1.58 (2)

Average Bond Lengths, Å

P–N(*endo*)	1.58 ± 0.05	N–C	1.12 ± 0.04
P–N(*exo*)	1.63 ± 0.01	C–S	1.59 ± 0.04

Bond Angles, Deg

N(2)–P(1)–N(6)	122 (1)	N(6)–P(5)–N(22)	108 (1)
N(2)–P(3)–N(4)	118 (1)	N(7)–P(1)–N(10)	100 (1)
N(4)–P(5)–N(6)	115 (1)	N(13)–P(3)–N(16)	100 (1)
P(1)–N(2)–P(3)	117 (1)	N(19)–P(5)–N(22)	101 (1)
P(3)–N(4)–P(5)	125 (1)	P(1)–N(7)–C(8)	156 (1)
P(5)–N(6)–P(1)	122 (1)	P(1)–N(10)–C(11)	152 (2)
N(2)–P(1)–N(7)	107 (1)	P(3)–N(13)–C(14)	149 (2)
N(2)–P(1)–N(10)	110 (1)	P(3)–N(16)–C(17)	156 (2)
N(6)–P(1)–N(7)	107 (1)	P(5)–N(19)–C(20)	135 (2)
N(6)–P(1)–N(10)	109 (1)	P(5)–N(22)–C(23)	165 (2)
N(2)–P(3)–N(13)	105 (1)	N(7)–C(8)–S(9)	178 (2)
N(2)–P(3)–N(16)	109 (1)	N(10)–C(11)–S(12)	173 (3)
N(4)–P(3)–N(13)	111 (1)	N(13)–C(14)–S(15)	172 (2)
N(4)–P(3)–N(16)	112 (1)	N(16)–C(17)–S(18)	174 (2)
N(4)–P(5)–N(19)	114 (1)	N(19)–C(20)–S(21)	176 (1)
N(4)–P(5)–N(22)	109 (1)	N(22)–C(23)–S(24)	176 (1)
N(6)–P(5)–N(19)	110 (1)		

Average Bond Angles, Deg

N(*endo*)–P–N(*endo*)	119 ± 3	N(*exo*)–P–N(*exo*)	100 ± 1
P–N(*endo*)–P	121 ± 4	P–N–C	152 ± 10
N(*endo*)–P–N(*exo*)	109 ± 2	N–C–S	175 ± 2

[a] Standard deviations are in parentheses.

The angles in the P–N ring also vary over a wide range of values with a mean value of 121.0° and an rms deviation of 4.0° for the P–N–P angles and a mean of 118.5° and an rms deviation of 3.4° for the N–P–N angles.

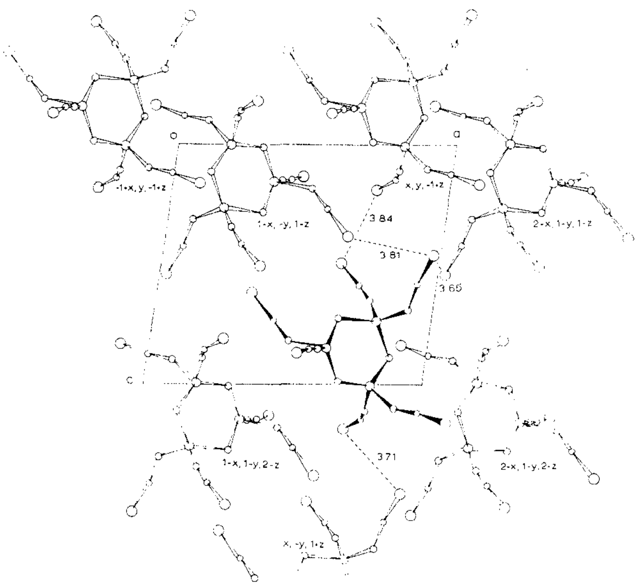


Figure 2.—Packing diagram of trimeric phosphonitrilic isothiocyanate. The molecule with the dark bonds corresponds to the coordinates listed in Table II. Some sulfur–sulfur intermolecular contacts are shown.

TABLE VI

COMPARISON OF CARBON–SULFUR BOND LENGTHS CORRECTED FOR THERMAL MOTION USING THE RIDING MODEL OF BUSING AND LEVY[a]

Bond	Uncor	Riding model	Bond	Uncor	Riding Model
C(8)–S(9)	1.51	1.55	C(17)–S(18)	1.60	1.70
C(11)–S(12)	1.60	1.65	C(20)–S(21)	1.61	1.67
C(14)–S(15)	1.61	1.68	C(23)–S(24)	1.58	1.63

[a] See ref 20.

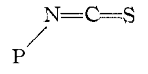
The phosphorus to nitrogen (isothiocyanate) bond is shorter (1.62–1.65 Å) than expected and, in particular, is considerably shorter than the presumed single P–N bond length of 1.77 (2) Å found in the species $NaPO_3NH_3$.[19] The average N–C bond length of 1.12 ± 0.04 Å and the average C–S bond length of 1.59 ± 0.04 Å are short, but they are in the range of values found for other isothiocyanate structures. Thermal corrections[20] were applied to the C–S bonds because of the large thermal parameters associated with the sulfur atoms. These results are summarized in Table VI. These corrections were made using anisotropic thermal parameters calculated from film data collected about a single axis, and consequently only the order of magnitude of the correction is worth noting. The large corrections to the terminal C═S bonds are not surprising in that the analysis was carried out near the melting point of the crystal. No correction to the other bonds was attempted.

The average P–N–C angle is 152 ± 10°, with four of these angles in the range 149–156° and one significantly smaller (135°) and one significantly larger (165°). R–N–C angles ranging from 130 to 180° have been reported. The average N–C–S angle is 175 ± 2°.

The isothiocyanate group attached to the phosphorus atom can be described by a resonance hybrid of structures I and II. Contributions from structure I would

$$\mathrm{P{-}N^{+}{\equiv}C{-}S^{-}}$$

I



$$\mathrm{P{-}N{=}C{=}S}$$

II

$$\mathrm{P^{-}{=}N^{+}{=}C{=}S}$$

III

account for the short C–N bond, while a resonance hybrid would lead to P–N–C angles intermediate between 120 and 180°. The shortness of the P–N (isothiocyanate) bond can be accounted for by the donation of the lone-pair electrons on the nitrogen atom into a 3d orbital of favorable symmetry on the phosphorus atom. The postulate of lone-pair donation into the 3d orbitals of the phosphorus atom from an exocyclic nitrogen atom is not new. It has been offered in the cases of $N_4P_4(N(CH_3)_2)_8$,[21] $N_6P_6(N(CH_3)_2)_{12}$,[22] and

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(19) D. W. J. Cruickshank, *Acta Crystallogr.*, **17**, 671 (1964).

(20) W. R. Busing and H. A. Levy, *ibid.*, **17**, 142 (1964).

(21) G. J. Bullen, *J. Chem. Soc.*, 3193 (1962).

(22) A. J. Wagner and A. Vos, *Acta Crystallogr., Sect. B*, **24**, 1423 (1968).

TABLE VII
DETAILS OF THE BEST PLANES FOR TRIMERIC PHOSPHONITRILIC ISOTHIOCYANATE[a]

Atom	Dev from the plane				
P(1)	−0.03	*−0.00*	*−0.01*	*−0.01*	*−0.01*
N(2)	*−0.04*	*−0.02*	−0.05	*0.06*	*−0.02*
P(3)	*0.00*	*0.00*	*0.01*	0.13	*0.01*
N(4)	−0.14	−0.15	*−0.09*	*−0.06*	*−0.13*
P(5)	*0.00*	*−0.01*	0.07	*0.01*	*0.00*
N(6)	*0.04*	*0.06*	*0.10*	0.02	*0.06*
Parameter	**Value**				
χ^2	10.35	13.44	61.04	19.84	71.37
P^b	<0.005	<0.005	<0.005	<0.005	<0.005
χ^{*2}	2.59	3.36	15.26	4.96	17.84
P	0.100	0.100	<0.005	0.025	<0.005

[a] The distances involving atoms included in the plane calculations are italicized. The results of the χ^2 test are also listed, along with the probability (P) that the deviations describe a normal distribution. In the calculation of χ^2, the atoms are given weights, where $w = 1/\sigma^2$. In the case of χ^{*2}, the weights were calculated using σ^*, where $\sigma^* = 2\sigma$ from the least-squares refinement. [b] The acceptance level for the points being planar.

$N_3P_3Cl_2(NH\text{-}i\text{-}C_3H_7)_4 \cdot HCl$.[23] In these cases, the short P–N bond was accompanied by P–N–C angles in the range 119–125°. In the present case, the average value of the P–N–C angle is 152°, suggesting some contribution from an "allylic"-type structure (III).

The results of the best-planes calculations through various sets of atoms and some torsion angle calculations[24,25] are presented in Tables VII and VIII, respectively. The atoms P(1), N(2), P(3), P(5), and N(6) can be considered to form a plane with N(4) out of the plane by 0.15 Å. The trimeric phosphonitrilic isothiocyanate is the first uniformly hexasubstituted trimeric species studied to date which has this conformation. The torsion angles demonstrate the deviation of the ring from planarity. A recent redetermination of the structure of trimeric phosphonitrilic bromide[26] shows that the phosphonitrilic ring in this molecule is much more planar than had been previously assumed.[10]

The endocyclic bond lengths and angles obtained for the phosphonitrilic isothiocyanate trimer are consistent with the parameter–electronegativity plots for uniformly substituted phosphonitrilic trimers given by Ahmed and coworkers[25] only if one uses the value 3.0 for the electronegativity of a nitrogen atom[27] rather than the value 4.17 calculated by Huheey[28] for the isothiocyanate group.

There are no unexpectedly short intermolecular contacts. The shortest S---S distance is 3.65 Å (Figure 2), while the shortest S---N, N---N, N---C, C---C, and C---S distances are 3.36 Å between S(9) and N(22) [2 − x, 1 − y, 2 − z], 3.43 Å between N(2) and N(7) [2 − x, −y, 2 − z], 3.38 Å between N(2) and C(8) [2 − x, −y, 2 − z], 3.61 Å between C(11) and C(20) [1 − x, −y, 2 − z], and 3.40 Å between C(20) and S(24) [x, −1 + y, z], respectively.

TABLE VIII
TORSION ANGLES[a,b] (IN DEGREES) IN SOME HEXASUBSTITUTED TRIMERIC PHOSPHONITRILIC RING SYSTEMS

Compound	$(NPF_2)_3$	$[NP(C_6H_5)_2]_3$	$[NP(NCS)_2]_3$	$(NPCl_2)_3$	$(NPBr_2)_3$[c]	
N(6)P(1)–N(2)P(3)	−1.5	−4.4	−1.0	1.7	−26.0	−6.7
P(1)N(2)–P(3)N(4)	0.4	2.7	−7.9	5.0	17.9	6.3
N(2)P(3)–N(4)P(5)	0.8	−2.4	14.3	8.2	−10.9	−5.5
P(3)N(4)–P(5)N(6)	−0.8	4.5	−10.5	−8.2	10.9	5.5
N(4)P(5)–N(6)P(1)	−0.4	−6.4	0.6	5.0	−17.9	−6.3
P(5)N(6)–P(1)N(2)	1.5	5.4	4.7	−1.7	26.0	6.7
Lit. description	Planar	Slight chair		Slight chair	Slight chair	

[a] The torsion angles for the fluoride, chloride, and bromide were obtained from ref 24. The angles for the hexaphenyl compound were calculated by us from the data presented in ref 25. [b] The angle AB–CD is taken as positive if, when viewed along the B–C bond, atom A has to be rotated clockwise to eclipse atom D. [c] The first set of values for $(NPBr_2)_3$ are those based on the results of Giglio and Puliti,[10] while the second set of values are those found in a very recent and more nearly accurate analysis by Wagner and coworkers.[26]

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