modes involved in uranate absorption bands at <500 cm^{-1}, and no further consideration of this energy range will be given here.

Zachariasen[25] found that the unit cell of α-UO_3 contained one uranium and three oxygen atoms with $\mathrm{U{-}2O_I} = 2.08$ A and $\mathrm{U{-}6O_{II}} = 2.39$ A. The site symmetry of the uranium atom was given as D_{3d} with infinite $\mathrm{U{-}O_I{-}U{-}O_I}$ chains along the z axis. The same type of chain between layers containing $\mathrm{U{-}O_{II}}$ bonds has been identified in α-U_3O_8, and the $\mathrm{U{-}O_I}$ bond distance has been reported to be 2.07 A.[26] Thus, neither of these structures exhibits uranyl groups. Tsuboi and co-workers[24] have interpreted the 700-cm^{-1} band in α-UO_3 as the fundamental asymmetric $\mathrm{U{-}O_I}$ stretching mode and have ascribed the three higher frequencies (770, 890, and 935 cm^{-1}) to combinations of lower energy fundamentals. The assignment of the 700-cm^{-1} band is consistent with the observation of a strong absorption in U_3O_8 near the same energy which must also be due, at least in part, to a similar stretching mode. However, the group theoretical analysis of the D_{3d} symmetry in the paper on α-UO_3 is incorrect (see ref 13), so the validity of the assignments in the case of the bands at 770, 890, and 935 cm^{-1} is questionable. The assignments are not, however, unreasonable, particularly for the latter two frequencies.

It appears that the 760-cm^{-1} band in the polyuranate, occurring as it does so near the energy of the band ascribed to the $\mathrm{U{-}O_I{-}U{-}O_I}$ stretch in U_3O_8, should be similarly interpreted. The fact that it is shifted to a somewhat higher frequency is consistent with the X-ray results which show that the c axis in the polyuranate is slightly shorter than that in U_3O_8.

The intensity and sharpness of the 880-cm^{-1} band in the polyuranate argues against its being a combination frequency; however, both its intensity and frequency are consistent with its interpretation as a fundamental uranyl ($\mathrm{O_I{-}U{-}O_I}$) asymmetric stretching mode. The corresponding $\mathrm{U{-}O_I}$ bond length ($R_{\mathrm{U-O_I}}$), obtained from the expression[13]

$$R_{\mathrm{U-O_I}}\ (\mathrm{A}) = 53.3\nu_{\mathrm{A}}^{-2/3} + 1.17$$

where ν_{A} is the assumed asymmetric stretching frequency (cm^{-1}), is 1.75 A. We suggest, therefore, that there are at least two different types of $\mathrm{U{-}O_I}$ sites in the polyuranate. Following this interpretation, one site is associated with the $\mathrm{U{-}O_I{-}U{-}O_I}$ chain, which we assume holds the layers containing $\mathrm{U{-}O_{II}}$ groups together; the corresponding $\mathrm{U{-}O_I}$ distance is probably near that in α-UO_3 and U_3O_8, ~2.06 A. A second site, presumably associated with the presence of Na_2O in the lattice, seems more reasonably interpreted in terms of a uranyl-type bond of length ~1.75 A. Such a structure implies that the unit cell should be large, as is indeed consistent with the X-ray diffraction results.

Acknowledgment.—We wish to thank Elizabeth Gebert for technical assistance and helpful discussions with respect to the X-ray diffraction results.

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(25) W. H. Zachariasen, *Acta Cryst.*, **1**, 265 (1948).

(26) B. O. Loopstra, *ibid.*, **17**, 651 (1964).

CONTRIBUTION FROM THE CHEMISTRY DIVISION, NAVAL ORDNANCE LABORATORY,
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2,6-Diazidohexaphenylcyclophosphonitrile Tetramer[1]

BY CLAY M. SHARTS, ANDREW J. BILBO, AND DAVID R. GENTRY[2]

Received June 18, 1966

Reaction of 2,6-dichlorohexaphenylcyclophosphonitrile tetramer with lithium azide in refluxing acetonitrile gave *cis*- and *trans*-2,6-diazidohexaphenylcyclophosphonitrile tetramer (*cis*-II and *trans*-II). Structures were assigned the two isomers of II on the basis of observed dipole moments: for *cis*-II, mp 147.5–148.0°, dipole moment 3.7 D.; for *trans*-II, mp 206–208°, dipole moment 0.2 D. In refluxing acetonitrile an azide ion catalyzed equilibrium exists with $K_{\mathrm{eq}} = 2.6$ for the reaction *cis*-II = *trans*-II, $\Delta G_{355} = 0.67$ kcal/mole. In a kinetic study carried out with a thermal balance, it was found that *cis*-II and *trans*-II both decompose above 200° by first-order kinetics with activation energies of 34.2 and 37.5 kcal/mole, respectively. In chemical reactions with triphenylphosphine and heptafluoropropyldiphenylphosphine, *trans*-II underwent the expected reactions at each azide group to eliminate 2 moles of nitrogen and to add 2 moles of phosphine linked by N=P bonds to give *trans*-2,6-bis(triphenylphosphazido)hexaphenylcyclophosphonitrile tetramer and *trans*-2,6-bis(heptafluoropropyldiphenylphosphazido)hexaphenylcyclophosphonitrile tetramer. Similarly, *cis*-II and triphenylphosphine gave *cis*-2,6-bis(triphenylphosphazido)hexaphenylcyclophosphonitrile tetramer. Reaction of *cis*-II with 1,4-bis(diphenylphosphino)butane did not lead to the expected 1:1 polymer but gave instead the cyclic 1:1 addition product *cis*-2,6-[P,P-butanobis(diphenylphosphazido)]hexaphenylcyclophosphonitrile tetramer.

The work reported here was prompted by the recent synthesis of 2,6-dichlorohexaphenylcyclophosphonitrile tetramer (I) reported by Herring and Douglas.[3] The goal was to convert the dichloride I

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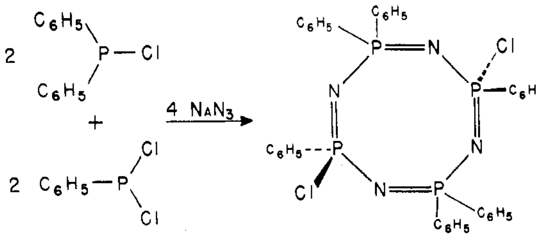
[1] Presented to the First Western Regional Meeting of the American Chemical Society, Los Angeles, Calif., Nov 19, 1965.

[2] Inquiries should be directed to either C. M. Sharts at San Diego State College, San Diego, Calif., or A. J. Bilbo, Code 442, at Naval Ordnance Laboratory, Corona, Calif.

[3] D. L. Herring and C. M. Douglas, *Inorg. Chem.*, **4**, 1012 (1965).



I

into the corresponding diazide derivative of I and to use the diazide derivative as a polymer intermediate for polymerization with appropriate bisphosphines. This report summarizes the work carried out preparatory to polymerization studies.

Experimental Section

Melting points are corrected and were observed on a Fisher-Johns block. Qualitative infrared spectra were observed with Beckman IR-5 and IR-5A spectrophotometers. Quantitative infrared spectra were observed on a Perkin-Elmer Model 621 grating infrared spectrophotometer. Thermal decompositions were followed with a Stanton Model H.T. thermal balance. Molecular weights were measured with a Mechrolab Model 30 osmometer. Dielectric constant measurements for dipole moments were made with a W.T.W. Dipolmeter, Type DM 01, using a Type DFL-1 liquid cell. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories.

2,6-Diazidohexaphenylcyclophosphonitrile Tetramer.—The *cis* and *trans* isomers of the title compound, hereafter referred to as *cis*-II and *trans*-II, were prepared by heating for 3 days under reflux a mixture of 0.80 g (0.0011 mole) of 2,6-dichlorohexaphenylcyclophosphonitrile tetramer[3] and 2.0 g (0.41 mole) of lithium azide in 50 ml of anhydrous acetonitrile. The hot reaction solution was filtered to remove insoluble excess lithium azide and the lithium chloride formed in the reaction. The volume of the hot filtrate was reduced to 25 ml by distillation. From the cooled solution was obtained 0.20 g of solid, mp 204–206°, assigned as *trans*-II. Second and third crops of crystals from the mother liquor melted at 203–204° and 202–204°, respectively. Treatment of the filtered lithium azide and lithium chloride with water left a precipitate of an additional 0.10 g of *trans*-II, mp 198–204°. Repeated crystallizations of *trans*-II gave an analytical sample, mp 206–208°.

Anal. Calcd for $C_{36}H_{30}N_{10}P_4$: C, 59.51; H, 4.16; N, 19.28; P, 17.05. Found: C, 59.79, 59.66; H, 4.33, 4.22; N, 18.90, 19.44; P, 17.10, 17.25.

From the mother liquors of the crystallizations of high-melting *trans*-II was obtained 0.12 g of another compound assigned as *cis*-II melting over the broad range of 122–133°. This material had a very clean, sharp infrared spectrum that differed in only three or four absorption bands from the spectrum of *trans*-II. Comparison of Figures 1 and 2 shows that the major difference in the infrared spectra of *trans*-II and the low-melting *cis*-II is that *trans*-II has a strong band at 793 cm^{-1} (12.61 μ) which is absent in *cis*-II and that *cis*-II has a band at 899 cm^{-1} (11.13 μ) which is absent in the spectrum of *trans*-II.

Recrystallization of *cis*-II gave material melting at 131–133°. No higher melting *cis*-II could be obtained by repeated recrystallizations. However, two kinds of crystals could be seen in the crystallized *cis*-II: higher melting, small needles found to be *trans*-II and larger, well-formed rhombic crystals which were *cis*-II.

Hand selection of the larger, well-formed crystals of *cis*-II from the material melting at 131–133° gave a material that could be recrystallized from acetonitrile to a purity indicated by mp 147.5–148.0°. The *cis*-II melting at 131–133° gave a satisfactory analysis which confirmed that the major impurity of *cis*-II was *trans*-II. A sample of *cis*-II, mp 147.5–148.0°, was analyzed.

Anal. Calcd for $C_{36}H_{30}N_{10}P_4$: C, 59.51; H, 4.16; N, 19.28; P, 17.05. Found: C, 59.10; H, 4.14; N, 19.29; P, 17.31.

A larger scale run starting with 20 g of impure 2,6-dichlorohexaphenylcyclophosphonitrile tetramer and 20 g of lithium azide gave 13.1 g (65%) of *trans*-II and 1.2 g (6%) of *cis*-II.

Dipole Moments of *cis*- and *trans*-2,6-Diazidohexaphenylcyclophosphonitrile Tetramer.—The dipole moments of *cis*-II and *trans*-II were measured in benzene solution at 25.20 ± 0.20 and 25.15 ± 0.05°, respectively. The experimental data are tabulated in Table I.

Table I

C, concn, mole fraction	ϵ, dielectric constant	d, density (cor), g/ml	n, refractive index	P_2, polarization
cis Isomer, Mp 147.5–148.0°				
0.000 (pure benzene)	2.2725	0.8734	1.4981	26.635 (P_1)
0.001164	2.3008	0.8782	1.4995	479.38
0.002056	2.3147	0.8793	1.5004	487.24
0.003341	2.3128	0.8811	1.5016	354.98
0.003877	2.3563	0.8819	1.5023	497.88
0.006412	2.3909	0.8858	1.5050	460.67
$P_{2,\infty}$ = 480; R_2 = 200; μ = 3.7 ± 0.3 D.				
trans Isomer, Mp 206–208°				
0.0 (pure benzene)	2.2725	0.8722	1.4979	26.672 (P_1)
0.0004904	2.2725	0.8700	1.4988	365.16
0.0008252	2.2778	0.8706	1.4991	468.99
0.001199	2.2814	0.8712	1.4993	406.15
0.002147	2.2832	0.8692	1.5006	433.28

$P_{2,\infty}$ = 393.5 (least-squares plot); R_2 = 392.7 (least-squares plot); μ = 0.2 ± 1.0 D.

Equilibrium between the *cis* and *trans* Isomers of 2,6-Diazidohexaphenylcyclophosphonitrile Tetramer.—A mixture of 127.0 mg (0.175 mole) of *trans*-II and 551.5 mg (11.3 mmoles) of lithium azide was heated under reflux with 15 ml of anhydrous acetonitrile for 1 week. Solid II amounting to 114.4 mg was recovered and analyzed by infrared spectrophotometry using absorption at 793 cm^{-1}. Determination of the amount of *trans*-II in the sample was made using a standard curve of absorption at 793 cm^{-1} *vs.* per cent *trans*-II in the sample. The recovered II was determined to be 71% (70.6 ± 1.5%) *trans*-II and 29% *cis*-II.

In a similar experiment, from 104.6 mg (0.146 mmole) of *cis*-II was recovered 83.3 mg (0.115 mmole) of solid II which was found to be 73% (72.8 ± 1.5%) *trans*-II and 27% *cis*-II.

The equilibrium position between *cis*-II and *trans*-II is taken as 72% *trans*-II and 28% *cis*-II. From this $K_{eq} = 72/28 = 2.6$ for the reaction *cis*-II = *trans*-II. From the relationship $\Delta G = -RT \ln K$, the free energy at 355°K (the boiling point of acetonitrile) is calculated as 0.67 kcal/mole.

Kinetics of Thermal Decomposition of *cis*- and *trans*-2,6-Diazidohexaphenylcyclophosphonitrile Tetramer (*cis*-II and *trans*-II).—The rate at which *cis*-II and *trans*-II were thermally decomposed to give a product of known elemental composition and unknown structure and 2 moles of nitrogen was measured. Samples (0.10–0.30 g, 0.15–0.41 mmole) of *cis*-II and *trans*-II were heated at constant temperature over the range of temperatures 200–260° and the weight of the sample followed continuously. The data for a typical run are shown in Figure 3, in which the weight loss of a sample of *trans*-II, heated at 240°, is shown plotted against time. The raw data from thermal balance runs were replotted using the natural logarithm of the amount of diazide remaining *vs.* time. Figure 4 shows a typical plot. Except for the initial 2 or 3 min, for each run a straight-line plot was obtained for over 2 half-lives. The slope of the line was taken to give the rate constants which are summarized below.

Original graphical plots are available in the thesis from which

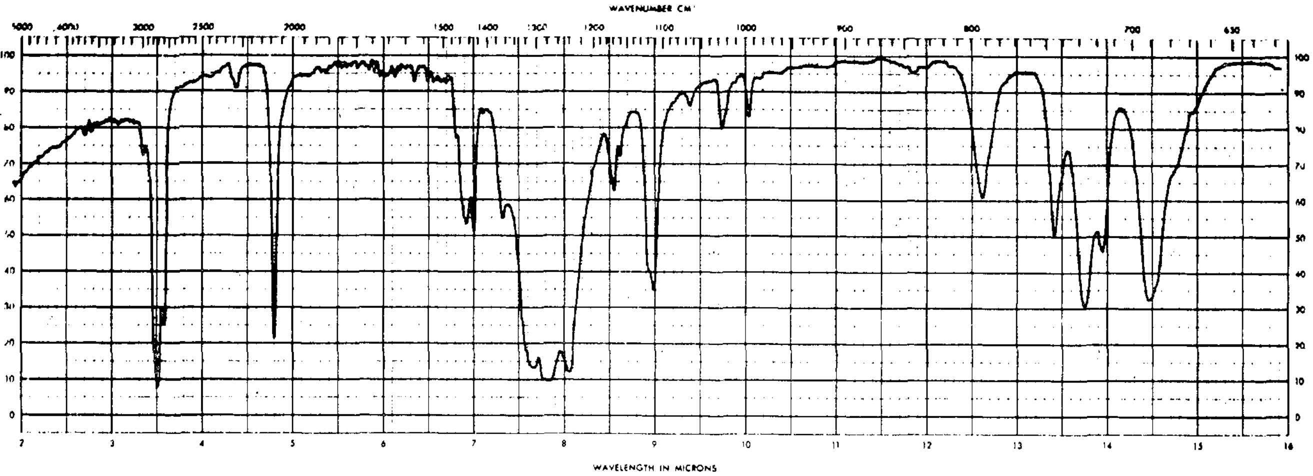


Figure 1.—Infrared spectrum of *trans*-2,6-diazidohexaphenylcyclophosphonitrile tetramer.

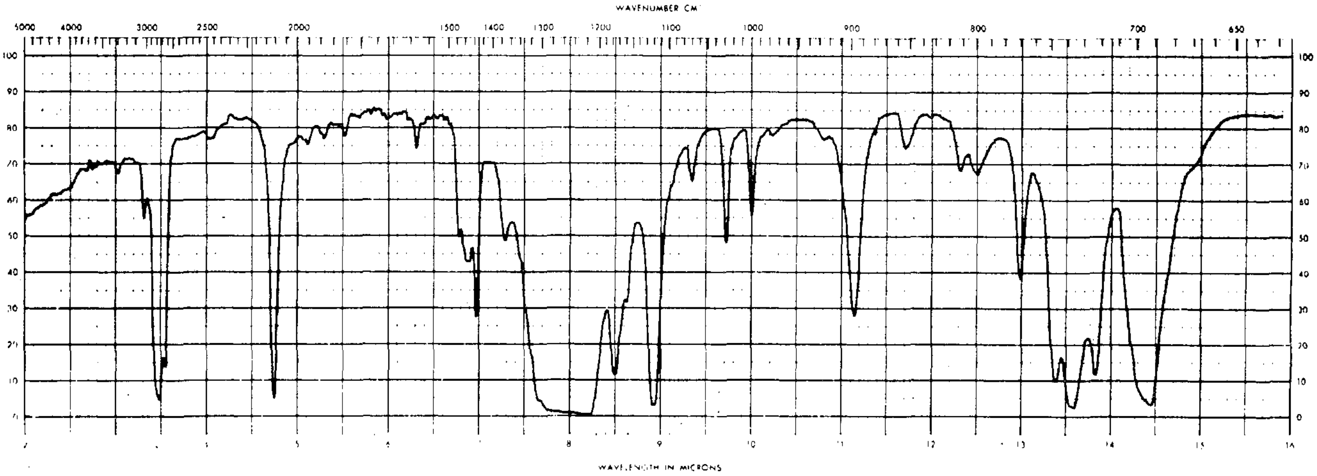


Figure 2.—Infrared spectrum of *cis*-2,6-diazidohexaphenylcyclophosphonitrile tetramer.

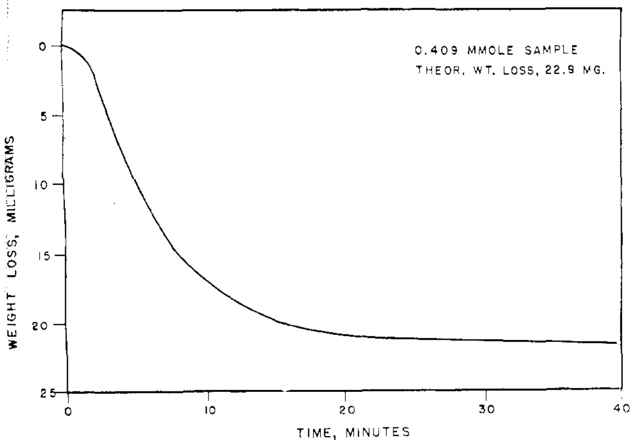


Figure 3.—Thermal gravimetric analysis of 0.409-mmole sample of *trans*-2,6-diazidohexaphenylcyclophosphonitrile tetramer at 240°.

this experimental work is extracted.[4] In all cases the slopes of lines were obtained by a least-squares plot of the experimental data (Table II).

The natural logarithms of the first-order rate constants for decomposition of *cis*-II and *trans*-II were plotted against $1/T$ for each isomer. In Figure 5 the least-squares plot for *trans*-II is shown which gives an activation energy for decomposition of *trans*-II of 37.5 kcal/mole. A similar least-squares plot in

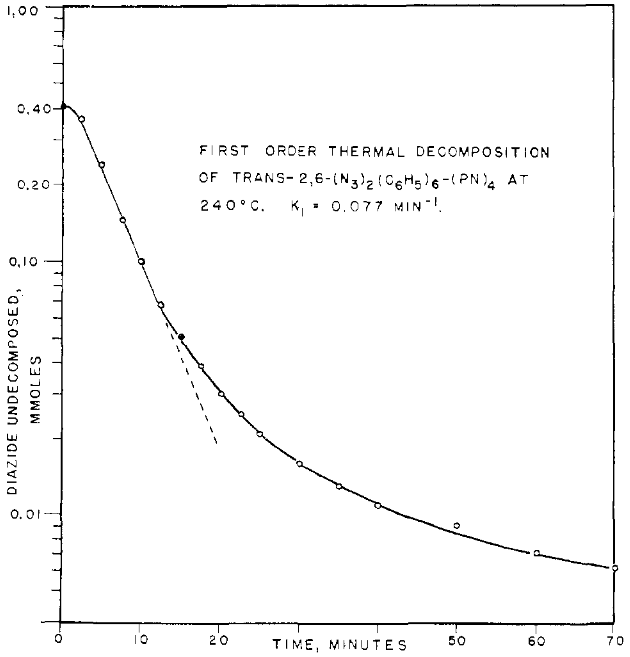


Figure 4.—First-order thermal decomposition of *trans*-2,6-diazidohexaphenylcyclophosphonitrile tetramer at 240°.

Figure 6 for *cis*-II gives a value of 34.2 kcal/mole for the activation energy for thermal decomposition of *cis*-II.

For *trans*-II the first-order plots held only over 75–80% reac-

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(4) R. Gentry, Master's Thesis, San Diego State College, San Diego, Calif., 1966.

TABLE II

Thermal Decomposition of *cis*-II

Sample size, mmole	Temp, °C	Rate const, min^{-1}
0.274	220	0.0260
0.213	230	0.0550
0.272	240	0.0982

Thermal Decomposition of *trans*-II

Sample size, mmole	Temp, °C	1° rate const, min^{-1}	2° rate const, mmole^{-1} min^{-1}
0.351	200	0.010	0.0558
0.314	220	0.0368	0.35
0.352	230	0.0782	. . .
0.410	240	0.177	2.92
0.312	240	0.159	2.6
0.351	243	0.174	. . .
0.326	250	0.552	6.7
0.144	260	0.644	. . .

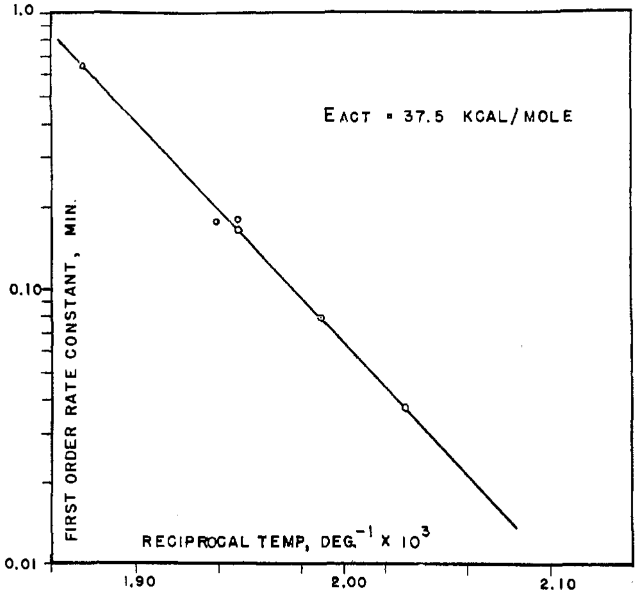


Figure 5.—Activation energy determination for first-order thermal decomposition of 2,6-diazidohexaphenylcyclophosphonitrile tetramer.

tion (see Figure 4). After a short transition the decomposition became second order as shown in Figure 7, in which the reciprocal of *trans*-II remaining from decomposition is plotted *vs.* time. Similar plots available in the thesis[4] from which these data are extracted give the second-order constants tabulated above.

In order to verify that the decompositions occurred by loss of two nitrogen molecules *and only* by loss of two nitrogen molecules, the residues from several thermal decompositions carried to 100% decomposition were submitted to elemental analysis. In addition to the elemental analyses tabulated in Table III, the infrared spectrum of each residue showed the residue to be free of 2100-cm^{-1} azide absorption

TABLE III

ELEMENTAL ANALYSIS OF RESIDUES FROM THERMAL DECOMPOSITION

	% C	% H	% N	% P
Anal of starting diazide	59.51	4.16	19.28	17.05
Theoret anal for 100% less 2N$_2$	64.47	4.52	12.52	18.49
Residue 200° run	63.23	4.58	13.08	18.19
Residue 220° run	64.13	4.63	12.59	18.53
Residue 240° run	64.21	4.38	12.58	18.44

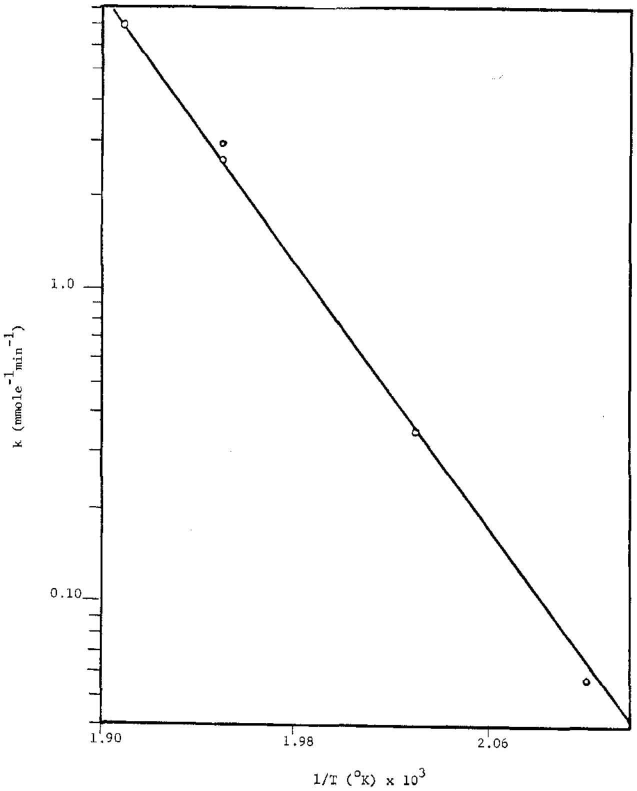


Figure 6.—Activation energy determination for second-order thermal decomposition of *trans*-2,6-diazidohexaphenylcyclophosphonitrile tetramer.

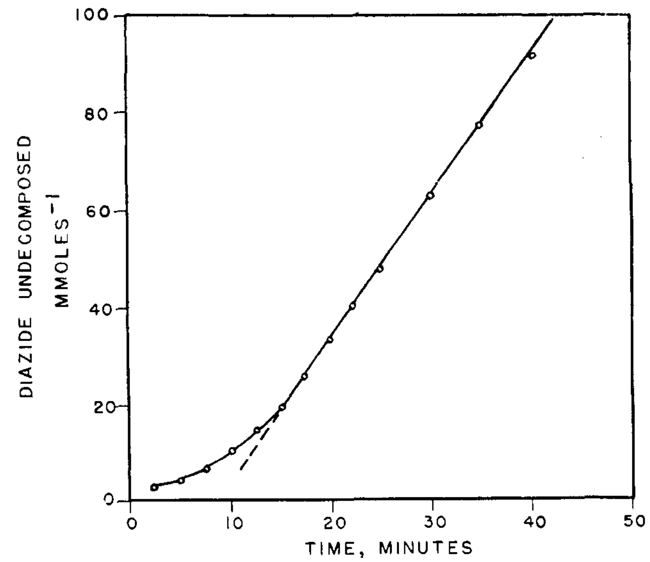


Figure 7.—Second-order thermal decomposition of *trans*-2,6-diazidohexaphenylcyclophosphonitrile tetramer at 240°. K_2 = 2.9 min^{-1} mmole^{-1}.

Reaction of Triphenylphosphine with *trans*-2,6-Diazidohexaphenylcyclophosphonitrile Tetramer.—An intimate mixture of 0.156 g (0.214 mmole) of *trans*-II and 0.130 g (0.496 mmole) of triphenylphosphine was heated at 135–140° for 1 hr in an evacuated tube which was connected to a calibrated vacuum line. A nearly quantitative evolution of nitrogen occurred at 135–140°. The reaction tube was heated at 170° for a short period to drive the reaction to completion.

Nitrogen measurement was: calculated for 0.214 mmole of *trans*-II, 9.60 ml; found, 9.59 ml (99.8%).

When recrystallized once from benzene the light tan product melted at 237–240°; after additional crystallizations, at 240–241°.

The infrared spectrum of the product did not have an absorption at 2100 cm^{-1} confirming that the azide group had undergone reaction.

Anal. Calcd for $C_{72}H_{60}P_6N_6$: C, 72.35; H, 5.06; P, 15.55; N, 7.03. Found: C, 70.58; H, 4.93; P, 15.30; N, 7.25.

Reaction of Heptafluoropropyldiphenylphosphine with *trans*-2,6-Diazidohexaphenylcyclophosphonitrile Tetramer.—In an evacuated tube open to the vacuum line and gas measurement system, a mixture of 0.3661 g (1.055 mmole) of heptafluoropropyldiphenylphosphine[5] and 0.3644 g (0.502 mmole) of *trans*-II was heated at 80–150° for 24 hr. A water condenser fitted to the upper portion of the reaction tube prevented the liquid phosphine, bp 94–95° (1 mm), from escaping. As gas evolution proceeded, the nitrogen pressure in the tube increased sufficiently to raise the boiling point of the phosphine so that higher temperatures could be utilized. Heating at 150° for 24 hr and at 200° for 24 hr did not give a quantitative yield of nitrogen.

Nitrogen measurement was: calculated for 0.502 mmole of *trans*-II, 22.5 ml STP; found, 17.7 ml (78.9%). The initially obtained product was a dark, glassy material. After recrystallizations from benzene–hexane a white solid melting over a range was obtained. Repeated recrystallizations gave a material melting at 104–106° and softening at 90–95°.

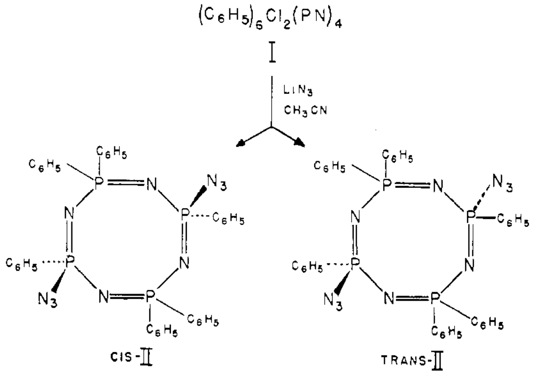
Anal. Calcd for $C_{66}H_{50}F_{14}P_6N_6$: C, 55.87; H, 3.79; F, 20.02; P, 13.99; N, 6.33. Found: C, 57.48; H, 3.65; F, 19.29; P, 13.48; N, 6.09.

Reaction of 1,4-Bis(diphenylphosphino)butane and *cis*-2,6-Diazidohexaphenylcyclophosphonitrile Tetramer.—Equimolar amounts of 1,4-bis(diphenylphosphino)butane[5] (0.104 g, 0.245 mole) and *cis*-II (0.178.4 g, 0.245 mole) were dissolved in 15 ml of carefully purified chlorobenzene and the solution was heated under reflux for 1 week. Chlorobenzene was distilled off to give 1–2 ml of solution. On cooling, white crystals formed in the solution. When recrystallized from benzene and dried at 1 mm and 56°, the crystals melted at 314–317° and amounted to 0.21 g (78%).

Anal. Calcd for $C_{64}H_{58}N_6P_6$: C, 70.06; H, 5.33; N, 7.66; P, 16.96; mol wt, 1097. Found: C, 70.46; H, 5.36; N, 8.30; P, 17.60; mol wt, 1050.

Results and Discussion

The reaction of 2,6-dichlorohexaphenylcyclophosphonitrile tetramer (I)[6] with lithium azide suspended in acetonitrile gave two isomers of 2,6-diazidohexaphenylcyclophosphonitrile tetramer (II), melting at 204–206 and 147.5–148.0°, respectively. The high-melting isomer had a dipole moment of 0.2 ± 0.3 D. and was assigned a *trans* structure. The low-melting isomer had a dipole moment of 3.7 ± 0.3 D. and was assigned as the *cis* isomer of II. Isomers *cis*-II and *trans*-II can be differentiated by characteristic absorptions as shown in Figures 1 and 2. *cis*-II has a strong unique absorption at 899 cm^{-1} absent in *trans*-II, while *trans*-II has a strong band at 793 cm^{-1} absent in *cis*-II. These infrared differences made possible the determination of the composition of mixtures of *cis*-II and *trans*-II.



cis-II   trans-II

Isolation and purification by crystallization of *trans*-II were very easy. In contrast *cis*-II was difficult to purify. Problems encountered in attempting to purify *cis*-II led to the discovery that isomerization of each isomer is catalyzed by azide ion and that in the presence of azide ion an equilibrium composition can be achieved.

Pure *cis*-II and pure *trans*-II were each heated with lithium azide in refluxing acetonitrile. For each of the reactions all of the diazide II was recovered and analyzed. It was found by quantitative infrared analysis that both *cis*-II and *trans*-II were isomerized to the same mixture of isomers within experimental error, 72% *trans*-II and 28% *cis*-II. For the reaction *trans*-II = *cis*-II the equilibrium constant is 2.6 and the free energy of reaction at 355°K is 0.67 kcal/mole.

For proposed reactions with *cis*-II and *trans*-II it was considered important to know the temperatures at which decomposition could be expected.

When either of the diazides, *cis*-II or *trans*-II, was heated above 200° either in a solution or in the melted phase, smooth evolution of nitrogen occurred. Below 160° no significant decomposition occurred over 24 hr. Each of the isomeric diazides was decomposed in a thermal balance in a series of isothermal kinetic runs over the temperature range of 200–260°. It was found that both *cis*-II and *trans*-II underwent thermal decomposition by first-order kinetics for at least 75–80% decomposition. Experimental data for a single run are plotted in Figures 3 and 4. From rate constants at different temperatures the activation energies for decomposition were determined as 34.2 kcal/mole for *cis*-II and 37.5 kcal/mole for *trans*-II. Experimentally, *trans*-II decomposes faster than *cis*-II at a specific temperature. Since the activation energy for decomposition of *trans*-II is greater than for *cis*-II, the preexponential factor for *cis*-II must be significantly larger. Stated another way, the entropy of activation for *cis*-II must be significantly greater than for *trans*-II.

An unexpected and unexplained observation was that over the last 10–15% of decomposition *trans*-II decomposed by second-order kinetics as shown in Figure 7. The activation energy for second-order decomposition is 49.8 kcal/mole. Analysis of the thermal decomposition products of *cis*-II and *trans*-II confirmed the thermal gravimetric results of the loss of exactly two molecules of nitrogen per molecule of diazide II decomposed. No structures were established for the decomposition products but one can speculate as shown.

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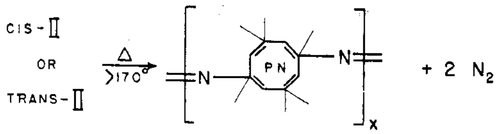
(5) C. M. Sharts, *Inorg. Chem.*, in press.

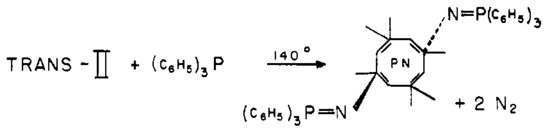
(6) This is most likely the *trans* isomer; private communication.



The energies of activation for thermal decomposition of *cis*-II and *trans*-II are consistent with the activation energies determined for decomposition of various organic azides as given by Appl and Huisgen.[7] The activation energies in kcal/mole for several azides are: ethyl azide, 39.7 and 39.0; phenyl azide, 34.7; *m*-nitrophenyl azide, 35.4; *m*-methylphenyl azide, 35.0; *m*-methoxyphenyl azide, 34.7.[7]

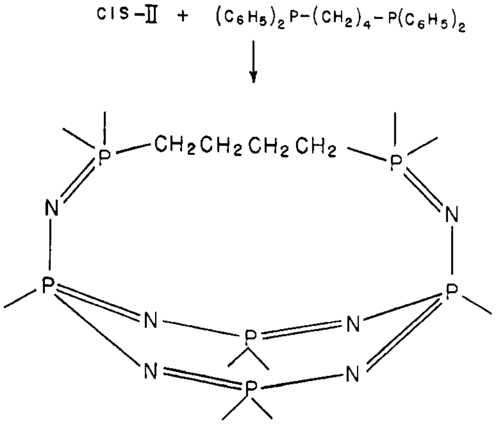
Compounds *cis*-II and *trans*-II were prepared as polymer intermediates for polymerization with bisphosphines. To confirm that the azido groups underwent reactions as expected,[8] reactions of both *cis*-II and *trans*-II were carried out with phosphines.

A smooth reaction with evolution of 2 moles of nitrogen was found to occur between 1 mole of *trans*-II and 2 moles of triphenylphosphine at 132° in the melted phase or in chlorobenzene solution. All properties determined for the product were consistent with the structure *trans*-2,6-bis(triphenylphosphazido)-hexaphenylcyclophosphonitrile tetramer as shown below. When *trans*-II was similarly heated at 132° by itself or in chlorobenzene solution, no nitrogen was evolved and *trans*-II was recovered unchanged. From this and kinetic data, then, it can be deduced that displacement of nitrogen from the azide groups of *trans*-II to give the phosphorus–nitrogen double bond is a concerted process. An azine intermediate does not occur.



Heptafluoropropyldiphenylphosphine was prepared by the procedure reported separately[5] as a potential compound for end-capping azide-terminated polymers synthesized by polymerizing II with bisphosphines. Reaction between *trans*-II and heptafluoropropyldiphenylphosphine occurred in a slurry at 140° with the expected nitrogen evolution. The product was assigned a structure similar to the structure for the triphenylphosphine adduct shown above and is believed to be *trans*-2,6-bis(heptafluoropropyldiphenylphosphazido)hexaphenylcyclophosphonitrile tetramer.

The difficulty encountered in obtaining pure *cis*-II greatly limited the study of reactions of *cis*-II with phosphines. It was shown by vacuum line techniques that 2 moles of triphenylphosphine underwent reaction at 130° with 1 mole of *cis*-II to generate 2 moles of nitrogen. An extremely interesting reaction occurred in the attempted polymerization of *cis*-II with 1,4-bis(diphenylphosphino)butane. A polymer had been expected with alternating *cis*-II and 1,4-bis(diphenylphosphino)butane units held together by phosphorus–nitrogen double bonds. Instead, a 1:1 adduct was obtained which was assigned the bridge structure *cis*-2,6-[P,P-butanobis(diphenylphosphazido)]hexaphenylcyclophosphonitrile tetramer, as illustrated below, consistent with observed properties of the compound. In contrast with the behavior of *cis*-II, *trans*-II undergoes polymerization with 1,4-bis(diphenylphosphino)butane.



Polymerization studies between either *cis*-II or *trans*-II and substituted diphosphines are in progress and will be reported separately at a later time. Additional studies on the decomposition of *cis*-II and *trans*-II in selected solvents are in progress.

Acknowledgment.—This investigation was supported in part by the Bureau of Naval Weapons, Department of the Navy. We are indebted to Mrs. C. M. Douglas and Mr. D. L. Herring for providing samples of 2,6-dichlorohexaphenylcyclophosphonitrile tetramer.

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(7) M. Appl and R. Huisgen, *Chem. Ber.*, **92**, 2961 (1959).

(8) D. L. Herring, *J. Org. Chem.*, **26**, 3998 (1961).