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MOLECULAR STRUCTURE OF P-SUBSTITUTED 1,3,5-TRIAZA-7-PHOSPHAADAMANTANES: VIBRATION SPECTRA AND CRYSTAL STRUCTURE ANALYSES

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MOLECULAR STRUCTURE OF P-SUBSTITUTED 1,3,5-TRIAZA-7-PHOSPHAADAMANTANES: VIBRATION SPECTRA AND CRYSTAL STRUCTURE ANALYSES

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Homologs: 1,3,5-triaza-7-phosphaadamantane-7-oxide and 1,3,5-triaza-7-phosphaadamantane-7-sulfide have been characterized by IR and Raman spectroscopy and by crystal structure analyses. The spectra and crystal structures are interpreted in comparison with the parent compound, 1,3,5-triaza-7-phosphaadamantane. The effects of the change in coordination as the result of addition of a substituent at the phosphorus atom and the influence of the character of the respective substituents on the bonding geometry of the phosphorus atom are also examined.

INTRODUCTION

Preparative procedures have been reported¹⁻⁴ for each of the homologous series: 1,3,5-triaza-7-phosphaadamantane, **1**, 1,3,5-triaza-7-phosphaadamantane-7-oxide, **2**, and 1,3,5-triaza-7-phosphaadamantane-7-sulfide, **3**. Homologs **1** and **2** have been characterized as being nitrogen oriented in their chemistry⁵ and thus as resembling hexamethylenetetramine.

Some interesting differences in chemical properties have been reported for these homologs. The oxide, **2**, has been found to be stable in hot formalin whereas **1** has been found to decompose under similar conditions.⁵ Preparation of 1-methyl-1-azonia-3,5-diaza-7-phosphaadamantane-7-sulfide iodide **4** has been accomplished both by the reaction of **3** with methyl iodide in benzene and by the reaction of 1-methyl-1-azonia-3,5-diaza-7-phosphaadamantane iodide, **5** with sulfur in benzene.³ Attempts to prepare 1-methyl-1-azonia-3,5-diaza-7-phosphaadamantane-7-oxide iodide, **6**, from **5** by oxidation with peroxides were not successful;³ **6** could, however, be easily prepared by reaction of **2** with methyl iodide.^{1,2}

In view of the differences in chemical reactivity displayed by homologs **1-3** and their quaternary

ammonium salts, we felt that additional characterization of their physical and chemical properties would be of interest. The ¹H nmr spectra of **1**, **2**, **5** and **6**¹ and ³¹P nmr chemical shifts for **1**,^{2,3} **2**,^{2,3} **3**,^{2,4} **4**,² **5**,^{2,3} and **6**² have been reported as have ir and Raman spectra and a crystal structure analysis⁴ for **1**. We wish to report ir and Raman spectra and crystal structure analyses for **2** and **3**.

EXPERIMENTAL

The methods of preparation of **2** and **3** used were reported earlier² as were the instrumentation and techniques used to measure the vibration spectra.⁴

High quality single crystals of **2** were obtained by slow evaporation of a methanol solution at room temperature; those for **3** were similarly obtained from a 3:2 dichloromethane:ethanol solution. Crystals of **2** and **3** were found to display Cm space-group symmetry with Z = 2 (one half molecule per asymmetric unit) and similar lattice parameters, Table I. The tabulated lattice parameters were obtained by least-squares refinement⁶ with automatically centered 2θ values obtained from the cooled crystal (T ≈ -120°C) used for intensity data collection. For **2**, the refinement was effected with 27 reflections in the angular range 35.4° < 2θ < 78.1° and, for **3**, 32 reflections in the angular range 35.0° < 2θ < 73.9° were utilized.

High resolution intensity data were collected for each crystal maintained at ca. -120°C (Syntex LT-1 low temperature device) with a Syntex P1 autodiffractometer (monochromatized Mo K_α radiation) operating in an ω-scan mode.

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TABLE I
Crystallographic Data

Space-group	2 Cm	3 Cm
<i>a</i>	7.220(7) Å	7.704(1)
<i>b</i>	9.279(8)	9.326(2)
<i>c</i>	5.897(4)	6.048(1)
β	113.24(5)°	107.30(1)
R	0.031	0.028
R _w	0.043	0.036
No. Variables refined	83	83
No. contributing reflections	1558	1757
No. unique reflns. measured	1565	1775
Sin θ/λ (max)	0.995	0.995

The scan rate was allowed to vary as a function of maximum peak intensity from 2.0 to 24.0 deg min⁻¹; the scan range was 0.75 deg and background radiation was measured on each side of the reflection center ($\Delta\omega = 1.0$ deg) for one half the total scan time. Three reference reflections, measured periodically for each crystal, displayed neither systematic nor significant variations in their intensities. The data were corrected for Lorentz and polarization effects; absorption corrections were not considered to be necessary.

The initial structural model for **2** was derived by application of the heavy atom technique; coordinates for the hydrogen atoms were subsequently obtained from difference Fourier maps. Refinement of all appropriate fractional atomic coordinates, anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms along with one scale factor was effected

TABLE II

Fractional atomic coordinates with estimated standard deviations

Atom	10 ⁴ <i>x</i>	10 ⁴ <i>y</i>	10 ⁴ <i>z</i>
a) 2			
P	0	5000	0
O	-2018 (2)	5000	-2030 (3)
C (11)	156 (2)	5000	3147 (3)
N (11)	2275 (2)	5000	4913 (2)
C (12)	1660 (1)	6503 (1)	145 (2)
N (12)	3601 (1)	6326 (1)	2262 (1)
C (21)	3337 (1)	6279 (1)	4606 (2)
C (22)	4617 (2)	5000	2043 (2)
b) 3			
P	0	-5000	0
S	2369 (1)	-5000	2371 (1)
C (11)	-18 (2)	-5000	-3046 (3)
N (11)	-1911 (2)	-5000	-4580 (2)
C (12)	-1525 (1)	-6510 (1)	-22 (2)
N (12)	-3242 (1)	-6329 (1)	-1920 (2)
C (21)	-2903 (1)	-6287 (1)	-4197 (2)
C (22)	-4189 (2)	-5000	-1625 (3)

TABLE III
Anisotropic temperature factors

Atom	10 ² U ₁₁	10 ² U ₂₂	10 ² U ₃₃	10 ² U ₁₂	10 ² U ₁₃	10 ² U ₂₃
a) 2						
P	1.1	1.9	1.4	0.0	0.2	0.0
O	1.5	4.0	2.3	0.0	-0.4	0.0
C (11)	1.4	1.8	1.9	0.0	0.9	0.0
N (11)	1.6	1.5	1.3	0.0	0.7	0.0
C (12)	1.9	1.6	1.6	0.2	0.7	0.3
N (12)	1.5	1.4	1.5	-0.1	0.7	-0.0
C (21)	1.7	1.5	1.4	-0.2	0.6	-0.3
C (22)	1.3	1.6	1.8	0.0	0.8	0.0
b) 3						
P	1.3	1.2	1.2	0.0	0.4	0.0
S	1.4	2.1	1.7	0.0	0.1	0.0
C (11)	1.6	1.8	1.5	0.0	0.7	0.0
N (11)	1.7	1.6	1.3	0.0	0.4	0.0
C (12)	1.8	1.3	1.6	-0.1	0.5	0.2
N (12)	1.5	1.4	1.7	-0.2	0.5	0.0
C (21)	1.9	1.6	1.6	-0.2	0.5	-0.3
C (22)	1.4	1.8	2.0	0.0	0.7	0.0

by block-diagonal least-squares techniques. The conventional R values resulting from the refinement, the number of data contributing to it and the number of parameters refined are among the data in Table I. The fractional coordinates from **2**, with an appropriate lengthening of the vector from the phosphorus atom to the exocyclic substituent, were used as the starting model for the structure of **3**. The latter structural model was refined in the same manner as that for **2**, Table I

TABLE IV

Fractional Atomic Coordinates (with Estimated Standard Deviations) and Isotropic Temperature Factors for Hydrogen Atoms.^a

Atom	10 ⁴ <i>x</i>	10 ⁴ <i>y</i>	10 ⁴ <i>z</i>	10 ² U
a) 2				
H (111)	-523 (34)	5832 (25)	3433 (42)	1.7
H (121)	1054 (31)	7350 (25)	263 (39)	1.3
H (122)	1914 (35)	6567 (24)	-1409 (43)	1.9
H (211)	2441 (38)	7141 (26)	4609 (44)	2.2
H (212)	4634 (32)	6233 (29)	5899 (39)	2.6
H (221)	5874 (50)	5000	3403 (61)	2.1
H (222)	4574 (52)	5000	177 (74)	2.6
b) 3				
H (111)	662 (33)	-5883 (27)	-3287 (45)	2.3
H (121)	-1736 (34)	-6520 (24)	1609 (42)	2.1
H (122)	-866 (27)	-7410 (23)	-170 (38)	1.3
H (211)	-2207 (31)	-7153 (22)	-4344 (38)	1.5
H (212)	-4048 (34)	-6340 (24)	-5341 (40)	1.6
H (221)	-4333 (43)	-5000	-100 (54)	1.2
H (222)	-5373 (44)	-5000	-2690 (54)	1.2

^a The first two numbers of the hydrogen atom labels correspond to the labels of the carbon atom to which they are bonded.

also contains a similar summary for the results of the refinement. The fractional atomic coordinates of the nonhydrogen atoms of the two structures are presented in Table II, the anisotropic temperature factors in Table III and the fractional atomic coordinates and isotropic temperature factors for the hydrogen atoms in Table IV. A list of calculated and observed structure factors is available.⁷

RESULTS AND DISCUSSION

The ir and Raman spectra of **2** and **3** are tabulated, with their assignments, in Table V. As expected, in view of their similar chemical structure and isomorphous crystal structures, their solid state spectra are very similar and, in many regions, nearly identical. The solution (aqueous) Raman spectra are also very similar to their solid phase counterparts so that one may infer that the structure observed in the crystal

is representative of that in solution as well. The spectra are also very similar to those of the mother compound, **1**, the assignment of which has been discussed in some detail.⁴ As for **1**, the vibration spectra of **2** and **3** are consistent with C_{3v} symmetry.

There are a few noteworthy differences among the vibration spectra of homologs **1–3**. These can be assigned to the different substituents at the phosphorus atom and their interaction with the vibrations of the skeleton of the molecule. For example, the P=O valence vibration at 1167 cm^{-1} (ir) falls within the region considered to be characteristic for this functional group. It also coincides with one of the CNC valence vibrations (1183 cm^{-1} in the spectrum of **1** and 1159 cm^{-1} for that of **3**). The high intensity of the ir/Raman pair in this region and the degree of depolarization of the Raman line clearly arise largely

TABLE V
Ir and Raman spectra of **2** and **3**

2			3		
RE (Int) solid	RE aq. soln.	ir solid	RE solid	ir solid	Assignment
289 m	297 w, br, dp	279 s-m	265 m	279 w	δ PCN
393 s	391 s-m, dp	389 w	350 vs	342 w	δ PCN } + δ OPC + δ SPC
423 s	415 s-m, p	415 w	385 m	381 m	
543 w-m	546 m, p	541 w-m	532 w-m	542 w	δ PCN (δ CNC)
578 w	589 w, br, dp	576 m, br	585 w	577 s-m	
583 w				629 s, br	ν S=P
662 vs	669 vs, p	658 vw	636 s-m	640 sh	ν PCN (puls.)
733 w	745 m, p	729 w	740 vw	722 }	ν PCN ν (CNC)
743 w-m		739 w-m		732 }	
783 w-m	788 w-m, br	778 w-m	777 m	770 m	ρ CH ₂
795 sh		800 sh	800 vw	791 }	
		805 s		801 }	
901 vw	898 w, dp	905 s	900 vw	892 s-m	δ CNC (+ ρ CH ₂)
945 m	943 s-m, p	945 w-m	947 w-m	939 s	
965 vw	972 vvw, dp	972 vs	970 vw	959 vs, br	δ_s CNC (+ δ PCN)
1000 w-m	1006 m, p	1004 s	1009 w-m	1001 s	ν CNC
1029 w-m	1033 w, p	1033 vw	1032 vw	1028 w-m	δ, ρ CH ₂
1095 w-m		1098 m	1095 vw	1091 s-m	ν CNC
			—	1159 vw	ν P=O
1163 m	1148 s-m, br, p	1167 vs		1230 s-m	ν CNC (+ δ CH ₂)
1233 w		1236 s-m	1233 w	1268 sh	
		1251 w	1278 vw, br	1275 s	δ_{as}, δ_s CH ₂
1283 w-m	1281 vw, dp	1285 vs	1278 vw, br		
1353 w-m	1341 w-m, dp	1346 w-m	1350 vw		
1373 w-m		1372 w	1370 vw	1365 w-m, br	
1383 w-m		1383 sh			
	1413 w-m, dp	1409 m	1441	1406 s-m	
1438 w-m		1440 w-m	1443 w	1439 m	
			1459 vw		

^a s = strong, m = medium, w = weak, br = broad, sh = shoulder, v = very, p = polarized, dp = depolarized.

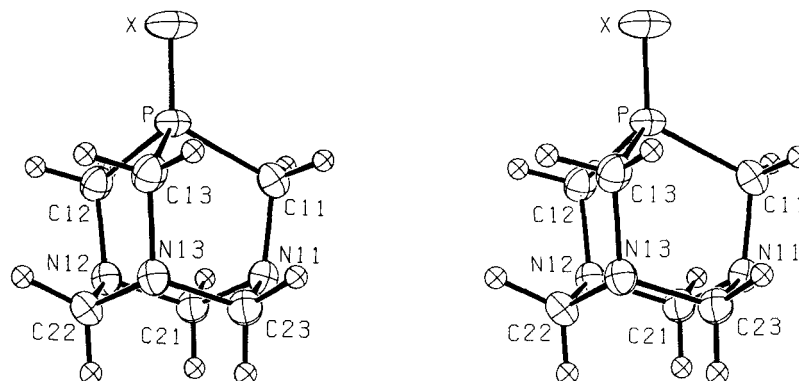


FIGURE 1 Stereoscopic projection of a molecular model for **2** ($X = O$) and **3** ($X = S$). The refined atomic coordinates for **2** were used for the drawing.⁸ The ellipsoids for the nonhydrogen atoms are representative of the refined thermal parameters; hydrogen atoms are depicted with arbitrary isotropic temperature factors. The labeling scheme depicted therein is applicable to the atoms of **2** and **3**.

from the $P=O$ vibration. The corresponding $P=S$ vibration produces an intense and relatively broad ir absorption band at 629 cm^{-1} . The absorption from this vibration in the Raman spectrum cannot be separated from the PNC valence vibration at 636 cm^{-1} ; the latter vibration may be referred to as a close neighborhood induced “pulsation”.

TABLE VI

Bond distances and angles (with estimated standard deviations) between nonhydrogen atoms

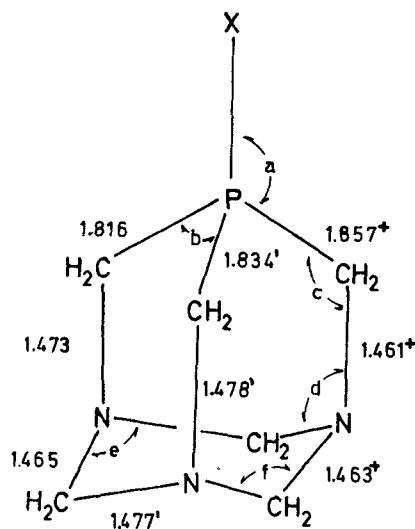
	2 ($X=O$)	3 ($X=S$)
P–X	1.476 (2) Å	1.9572 (4)
P–C (11)	1.814 (2)	1.838 (2)
P–C (12)	1.819 (2)	1.831 (1)
C (11)–N (11)	1.473 (2)	1.478 (2)
C (12)–N (12)	1.473 (2)	1.481 (1)
N (11)–C (21)	1.468 (2)	1.478 (2)
N (12)–C (21)	1.463 (2)	1.476 (2)
N (12)–C (22)	1.464 (2)	1.476 (1)
X–P–C (11)	118.2 (1)°	117.5 (1)
X–P–C (12)	117.4 (1)	117.5 (1)
C (11)–P–C (12)	100.3 (1)	100.3 (1)
C (12)–P–C (13)	100.2 (1)	100.5 (1)
P–C (11)–N (11)	110.6 (1)	110.0 (1)
P–C (12)–N (12)	110.1 (1)	110.0 (1)
C (11)–N (11)–C (21)	111.2 (1)	111.2 (1)
C (31)–N (11)–C (23)	108.5 (1)	108.7 (1)
N (11)–C (21)–N (12)	114.2 (1)	114.2 (1)
C (12)–N (12)–C (21)	111.6 (1)	111.2 (1)
C (11)–N (11)–C (22)	111.2 (1)	111.2 (1)
N (12)–C (22)–N (13)	114.4 (1)	114.3 (1)
C (21)–N (12)–C (22)	108.3 (1)	108.8 (1)

A stereoscopic projection⁸ representing a suitable molecular model for both **2** and **3** is presented in Figure 1; the applicable labelling scheme is displayed therein. All bond distances and bond angles between nonhydrogen atoms are contained in Table VI.

In the crystal, molecules of **2** and **3** display exact (crystallographic) mirror symmetry and, as indicated by the close similarity in appropriate symmetry independent bond distances and bond angles, both also display a good approximation to C_{3v} symmetry.

Just as substituent effects are observed in the ir and Raman spectra, significant differences in bonding geometry are detectable by comparison of the crystal structures of the homologs. The observed structural differences can be traced to two sources: to the presence of an additional substituent on the phosphorus atom (**2** and **3** relative to **1**), and to differences in the substituents (**2** relative to **3**). To facilitate assessing these differences, the average values for chemically equivalent bond distances and angles for **1**–**3** are presented in Figure 2. As expected, the homologs display the largest differences in bonding geometry in the bonds that involve the phosphorus atom and the carbon atoms (C_α) bonded to it.

The introduction of substituent X on the phosphorus atom is accompanied by an opening of the $C_\alpha PC'_\alpha$ bond angle by 4° and a decrease in the $PC_\alpha N$ bond angle by the same magnitude. Since **2** and **3** display identical $C_\alpha PC'_\alpha$ and $PC_\alpha N$ bond angles, the changes in their values relative to those in **1** most likely reflect a change in hybridization of the phosphorus atom. Such a change is not unexpected since the coordination number of phosphorus in **1** is different from that in **2** and **3**.



Angles (°)	<u>2</u>	<u>3'</u>	<u>1</u> + <u>4</u>
a	117.8	117.5	
b	100.2	100.2	96.1
c	110.3	110.0	114.1
d	111.3	111.2	111.0
e	108.4	108.7	108.3
f	114.3	114.2	114.4

FIGURE 2 Averaged distances and angles for chemically equivalent bonds in homologs 1,⁴ 2 and 3.

There are also clearly significant differences in the $P-C_{\alpha}$ bond lengths among the three homologs. Unlike the differences in bond angles, the length of these bonds clearly depends on the nature of substituent X. The greatest change relative to 1 is that in the oxide, 0.041 Å; the analogous difference for 3 is 0.023 Å. In both cases the $P-C_{\alpha}$ bond is shorter for the substituted phosphadamantane cage. The differences in the magnitude of the change may be an effect of differences in the electronic structure of the substituent (e.g., the presence of low lying empty d orbitals on the sulfur atom) or it may reflect the different electronegativity of the respective substituent. We believe a good case can be made for the latter cause.

A correlation between the $P-C_{\alpha}$ bond length and the electronegativity of the X-substituent can be explained in terms of the concept of an ionic resonance energy contribution to normally covalent bonds

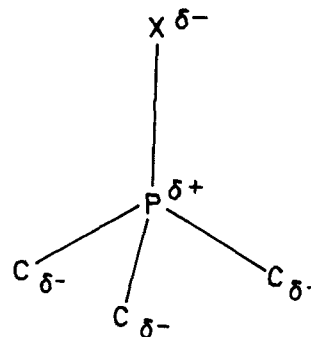


FIGURE 3 A schematic representation of the charge distribution responsible for ionic resonance stabilization energy in nominally covalent bonds.

between heteroatoms.^{9,10} A schematic representation of the ionic contribution to such bonds with the phosphorus atom, Figure 3, may be used to explore this concept. The charge distribution depends on the respective electronegativities of the atoms involved. The applicable electronegativity series in this case is $O \gg S \approx C > P$.¹¹ Thus the oxygen substituent in 2 induces a significantly greater δ^+ charge on the central phosphorus atom than does the sulfur atom in 3. Consequently there is greater ionic stabilization of the $P-C_{\alpha}$ bond in 2 than in 3 and, as would be expected, the $P-C_{\alpha}$ bonds are shorter in the oxide.

The suitability of this mechanism for explaining the differences in the $P-C_{\alpha}$ bond lengths between 2 and 3 is further substantiated by the observation that it is also applicable to the $P-X$ bond when the remaining α substituents differ in electronegativity from a CH_2 moiety. There are reported crystal structure analyses in which these atoms are oxygen atoms and in which the X atom is oxygen¹² or sulfur.¹³ In each case the $P=O$ bond length (1.445 (2) Å) and the $P=S$ bond length (1.933 (2) Å) are shorter than in 2 and 3, respectively. Clearly this observation is consistent with an increased δ^+ charge on the central P atom.

In view of the above discussion, we believe that the differences in bonding geometry we have found for the homologs 1-3 are traceable to hybridization differences between the parent, 1, and the substituted homologs, 2 and 3 and to differences in the electronegativity of the substituent atoms. While the changes in bond angles appear to result almost exclusively from the change in hybridization, the changes in bond distances most likely reflect both this change and the electronegativity of the substituents.

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