

The Crystal and Molecular Structure of an Unusual<sup>4,9</sup> Heterocycle,<sup>6,2</sup>  
2-Thia-1,3,5-triaza-7-phosphaadamantane 2,2-Dioxide<sup>5,1</sup>

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The crystal and molecular structure of 2-thia-1,3,5-triaza-7-phosphaadamantane 2,2-dioxide ( $C_5H_{10}SPO_2N_3$ ) has been determined by single crystal x-ray diffraction techniques. The compound crystallizes in the space group  $P2_1/c$  with four formula weights per unit cell of dimensions  $a = 6.129$  (1) Å,  $b = 12.440$  (2) Å,  $c = 14.028$  (2) Å,  $\beta = 127.31$  (1)°. The structure was solved by direct methods and refined to a final value of  $R = 0.079$ .

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#### Introduction.

Many of the successful flame retardant finishes are based upon phosphorus-nitrogen polymers or upon sulfur-nitrogen products such as ammonium sulfate and ammonium sulfamate. The phosphorus, nitrogen, sulfur compound, 2-thia-1,3,5-triaza-7-phosphaadamantane 2,2-dioxide (1), and other related compounds have recently been synthesized in an effort to discover new flame retardant monomers (1).

Such multi-basic, non-chelating cage compounds also form complexes with low-valent metal carbonyls. A similar triaza-phosphaadamantane compound has recently been complexed with metal pentacarbonyls where the central metal ion is Cr, W, or Mo. In the molybdenum pentacarbonyl complex, an x-ray diffraction study (2) has shown

that the ligand binds to the metal through its phosphorus rather than one of the nitrogens. Finally, the structure of a heterocycle which contains carbon, nitrogen, phosphorus and sulfur, all as ring atoms, in the same ring, is itself of intrinsic interest.

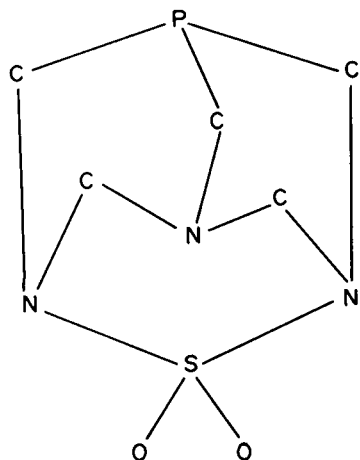


Figure 1

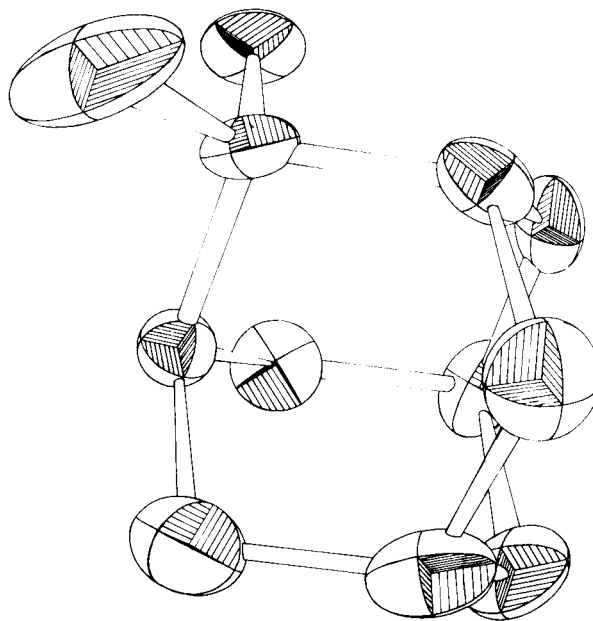


Figure 2 ORTEP drawing of the molecule.

Table I  
Fractional Coordinates and Anisotropic Thermal Parameters (a)  
(Standard Deviations in parenthesis)

Atom	X	Y	Z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
S	.6434 (6)	.4874 (2)	.7503 (2)	.0390 (5)	.0028 (1)	.0052 (3)	.0024 (4)	.0079 (6)	.0003 (1)
O1	.721 (1)	.5417 (6)	.8557 (7)	.067 (3)	.0043 (5)	.007 (1)	.003 (1)	.011 (2)	-.002 (1)
O2	.436 (1)	.5323 (6)	.6368 (7)	.046 (3)	.0060 (6)	.006 (1)	.009 (1)	.007 (2)	.004 (1)
P	.7369 (8)	.2774 (3)	.6300 (3)	.055 (1)	.0084 (3)	.0081 (4)	.0005 (6)	.0136 (8)	-.0037 (2)
N3	.0367 (9)	.3037 (6)	.8766 (8)	.041 (2)	.0049 (6)	.004 (1)	.004 (1)	.006 (1)	.001 (1)
N2	.9251 (9)	.4716 (6)	.7612 (8)	.033 (2)	.0055 (6)	.004 (1)	-.002 (1)	.006 (1)	.001 (1)
N1	.5517 (9)	.3659 (6)	.7559 (8)	.032 (2)	.0637 (5)	.006 (1)	-.001 (1)	.010 (2)	-.004 (1)
C1	.461 (1)	.303 (1)	.647 (1)	.046 (2)	.006 (1)	.007 (1)	-.009 (2)	.008 (2)	.002 (1)
C2	.865 (1)	.415 (1)	.654 (1)	.040 (4)	.012 (1)	.006 (1)	-.003 (2)	.012 (1)	.001 (1)
C3	.997 (1)	.2321 (8)	.784 (1)	.059 (4)	.004 (1)	.010 (1)	.008 (1)	.015 (1)	.000 (1)
C4	.133 (1)	.4066 (9)	.873 (1)	.031 (4)	.007 (1)	.005 (1)	.000 (2)	.006 (1)	.000 (1)
C5	.788 (1)	.3123 (8)	.869 (1)	.045 (4)	.005 (1)	.006 (1)	.000 (2)	.011 (1)	.001 (1)

(a) Anisotropic temperature factors are of the form:  $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$ .

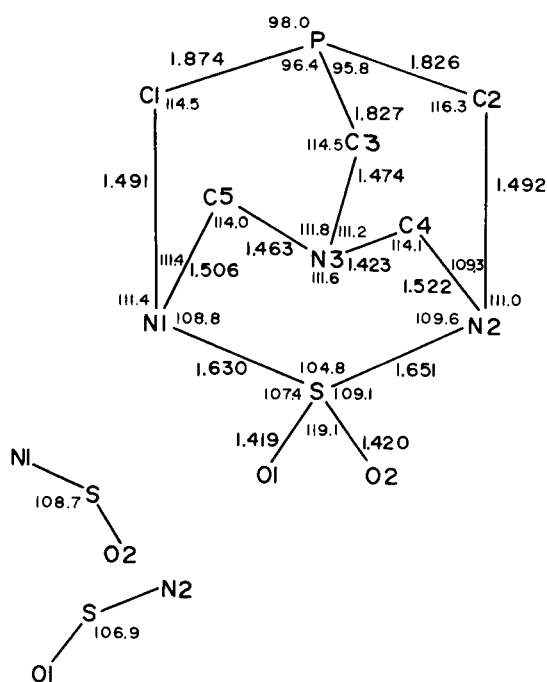


Figure 3 Schematic drawing of the molecule with bond angles and bond distances shown.

## EXPERIMENTAL

Crystals of the compound were kindly supplied by D. J. Daigle, Southern Regional Research Center in New Orleans, La. A single plate-like crystal having its longest dimension no greater than 0.25 mm was selected for data taking. The symmetry and cell dimensions of this crystal were determined on a General Electric XRD-5 diffractometer using Cu-K $\alpha$  radiation. Polar plots of the reciprocal

Table II  
Calculated Hydrogen Positions  
Refined Isotropic Temperature Factors

Atom	X	Y	Z	$\beta_{iso}$
H8	.3819	.2322	.6484	5.86
H8*	.3044	.3442	.5735	5.59
H9	.8328	.3550	.9403	2.96
H9*	.7297	.2381	.8741	4.00
H10	.1784	.2259	.7969	5.11
H10*	.9454	.1587	.7939	5.68
H11	.1873	.4488	.9461	4.14
H11*	.3038	.3965	.8781	4.10
H12	.7223	.4588	.5803	4.16
H12*	.0368	.4139	.6597	3.40

lattice revealed  $2/m$  symmetry with extinctions:  $l = 2n + 1$  for the  $(h0l)$  projection and  $k = 2n + 1$  for the  $(0k0)$  line, uniquely characterizing the monoclinic space group as  $P2_1/c$ . Lattice constants were determined through a least squares procedure using 24 reflections at high  $2\theta$  values (greater than  $65^\circ$ ) where the  $K\alpha_1$ - $K\alpha_2$  doublet is resolvable. These measurements were done under fine conditions ( $1^\circ$  take-off angle and  $0.05^\circ$  slit). The resultant lattice constants and their estimated standard deviations are:  $a = 6.129$  (1) Å;  $b = 12.440$  (2) Å;  $c = 14.028$  (2) Å;  $\beta = 127.31$  ( $1^\circ$ ).

The calculated density of 1.62 g/cc, assuming four molecules per unit cell, was accepted as reasonable and subsequently confirmed by the complete structure determination.

Three dimensional intensity data were collected on a G. E. XRD-490 automated diffractometer by the stationary crystal, stationary counter method using Cu-K $\alpha$  radiation and balanced nickel and cobalt filters. A total of 1377 unique intensities were measured to a two theta limit of  $140^\circ$  ( $d = .820$  Å). Of these, 1130 (83%) were considered statistically significant by the criterion:

$$(I_{Ni} - 2\delta(I_{Ni})) - (I_{Co} + 2\delta(I_{Co})) > 90$$

where the sigmas were based entirely on counting statistics with a

Table III

Maximum Estimated Standard Deviations (esd) in the Molecular Parameters

	Distances (Å)	Angles	(Degrees)
P-C	0.016	CPC	0.5
N-C	0.020	PCN	0.5
N-S	0.012	CNC	0.6
S-O	0.010	NCN	0.9
		NSN	0.6
		NSO	0.5
		OSO	0.5

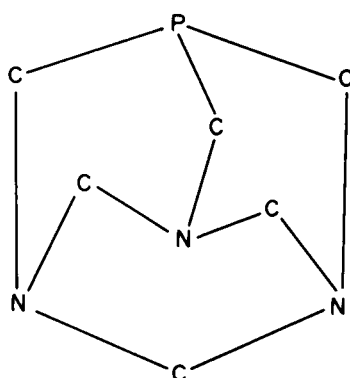


Figure 4

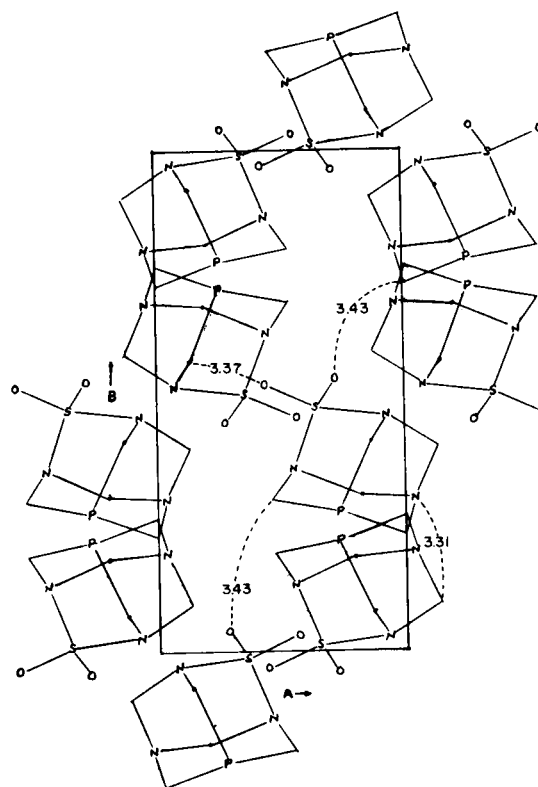


Figure 5 Projection of the contents of the unit cell down the c-axis. Close contact distances less than 3.5 Å are shown.

ten second counting time being used. The intensities were corrected for  $\alpha_1$ - $\alpha_2$  splitting as a function of two-theta and for absorption as a function of phi with a spread of less than 15% over the entire range of phi. Lorentz-polarization corrections were made and the intensities were reduced to structure amplitudes in the usual manner.

#### Structure Determination.

The structure was solved by direct methods using the program FAZC (3). Normalized structure factor magnitudes,  $|E|$ 's, were calculated and scaled with a K-curve (4). Using all data with  $|E| > 1.45$  (217 E's), an origin was chosen and an additional two reflections were then permuted through all four possibilities. An E-map calculated from the permutation with the highest con-

sistency index and the largest number of phased reflections contained 12 peaks arranged in a chemically reasonable manner. The proper scattering factors, based on a comparison of this structure to that anticipated, were assigned to all peaks. After five cycles of isotropic least squares refinement (5) had reduced the residual from an initial value  $R = 0.45$  to a value of  $R = 0.174$  another Fourier map was run. Based on this, the four larger atoms (P,S,O-1, O-2) were assigned anisotropic temperature factors, the scattering factor curves for P,S were corrected for anomalous dispersion, the structure refined to a value of  $R = 0.109$ . The remaining ring atoms were converted to anisotropic temperature factors with the resultant structure refining to a value of  $R = 0.084$ . Addition of

Table IV

Comparison of This Compound to PTA

	This Compound	PTA
P-C	$1.84 \pm .02 \text{ \AA}$	$1.84 \pm .02_0 \text{ \AA}$
P...C-N	$1.49 \pm .01_0$	$1.49 \pm .01_4$
N...C-N	$1.48 \pm .03_5$	$1.46 \pm .01_1$
CPC	$97 \pm 0.8^\circ$	$98 \pm 1^\circ$
PCN	$115 \pm 0.9^\circ$	$112 \pm 1^\circ$
CNC	$111 \pm 1.0^\circ$	$110 \pm 2^\circ$
NCN	$114 \pm 0.2^\circ$	$114 \pm 1^\circ$

the missing ten methylene hydrogens (calculated on the basis of the anticipated geometry and a C-H distance of 1.0 Å) led to  $R = 0.08_1$ . Final refinements, with all of the ring atoms anisotropic; and the hydrogen atoms with fixed coordinates, but with the temperature factors allowed to vary isotropically, led to a value of  $R = 0.07_8$ . A difference Fourier map at this stage showed, at most, only very diffuse regions with  $\rho = 0.3 \text{ e}/\text{Å}^3$  or less. Refinement was thus considered as completed.

#### Results and Discussion.

The least squares coordinates and anisotropic temperature factors for the non-hydrogen atoms together with the estimated standard deviation (esd) for each parameter are summarized in Table I. The final calculated hydrogen coordinates and their isotropic temperature factors are listed in Table II. Figure 2 shows an ORTEP drawing of molecule while Figure 3 gives a schematic drawing with the various bond distances and bond angles indicated on the figure. To summarize, the *maximum* esd values for these various distances and angles, excluding hydrogens, are given in Table III.

The trigonal symmetry observed in the analogous phosphotriazaadamantane (PTA) ligand (Figure 4) is destroyed by this substitution of the  $-\text{SO}_2$  group for the  $-\text{CH}_2$  found in the PTA complex. However, this compound closely approximates the anticipated bilateral symmetry as is evident by comparing the crystallographically-independent parameters. Furthermore, with the exception of differences resulting in the immediate environment of this  $-\text{SO}_2$  group both this ring system and the PTA complex are remarkably similar attesting to the rigidity of the adamantane-like ring. Table IV shows this similarity.

Sterically, this compound, in the vicinity of the phosphorus and attached methylene groups is very similar to PTA. Both would thus sweep out similar cone angles (as defined by Tolman (6) in metal complexes. Based upon the calculations for the  $\text{Mo}(\text{CO})_5$  PTA (2), this angle should be near  $102^\circ$  and about  $12^\circ$  smaller than the similarly defined cone angle for trimethylphosphine (7). All three ligands, however, sweep out relatively small cone angles compared to the larger ligands such as  $\text{PPh}_3$ ,  $\text{PPh}_2\text{Me}$ ,  $\text{P}(\text{n-Bu})_3$ , etc. The electronic properties of PTA and  $\text{PMe}_3$  as inferred from  $\nu(\text{C})$  and force constant calculations are fairly similar (8). This compound should also have analogous electronic properties (9). The admixture of steric and electronic properties is important in  $^{31}\text{P}$  nmr correlations (10). Hence this compound and the PTA ligand, both of which are easily handled solids, are suitable alternatives to  $\text{P}(\text{CH}_3)_3$  in studies requiring a range of ligands of varying steric and electronic properties.

The  $-\text{SO}_2$  group inserted in the end opposite the phosphorus has molecular parameters in line with those found in analogous compounds. Thus the S-O distance of 1.41 Å is well within the range 1.37-1.47 Å quoted (11-13) in other such systems. The S-N distance of  $1.64 \pm 0.1$  Å also lies within the range 1.60-1.69 Å found in other moieties (11-14) containing an S-N bond.

Finally, there are no significant close contacts between the molecules. Figure 5, which is a projection of the contents of the unit-cell down the c-axis, lists the three contact distances less than 3.50 Å within the unit cell.

#### Acknowledgments.

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$$R = \frac{\sum w [|kF_o| - |F_c|]}{\sum w |kF_o|}$$
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