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Crystal and Molecular Structure of 1,5-Bis(*p*-chlorophenyl)-2,4-diaza-1,3,5-trithiapenta-2,3-diene, $(p\text{-}ClC_6H_4)_2S_3N_2$

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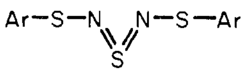
The structure of the title compound obtained from the reaction of *p*-chlorophenylmagnesium bromide with tetrasulfur tetranitride has been determined from data obtained on an automatic diffractometer. Crystals are monoclinic with space group $P2_1/c$, $Z = 4$, $a = 3.972$ (3) Å, $b = 19.531$ (8) Å, $c = 19.37$ (2) Å, and $\beta = 109.7$ (2)°. Calculated and observed densities are 1.63 and 1.60 ± 0.03 g cm^{-3}, respectively. A full-matrix least-squares refinement on 964 unique positive reflections led to a conventional R of 0.054. The nearly planar structure is of the linear thiodiimide type with cis,cis geometry around the central N_2S unit. The outer and inner N-S bonds average 1.660 (13) and 1.550 (12) Å, respectively.

Although tetrasulfur tetranitride is quite reactive toward nucleophiles, very little is known of the mechanisms of these reactions. The products differ considerably from one nucleophile to another. Thus, benzylamine[1,2] leads to benzylidenimine tetrasulfide, ammonia[3] leads to $S_2N_2{\cdot}NH_3$, triphenylphosphine[4] leads to the cyclic $Ar_3PNS_3N_3$, and substituted diazomethanes[5] lead to the apparently linear $(Ar_3CN)_2S_3N_2$.

A possible mechanistic interpretation for some of these reactions put forward several years ago[6,7] suggested addition of the nucleophile across sulfur-nitrogen bonds followed by breakup of the adduct to give either two substituted S_2N_2 units (if symmetrical addition and cleavage occurred) as presumably found with ammonia[3] or substituted S_3N_2 and N_2S fragments (if unsymmetrical addition and cleavage occurred). The reaction[8] of aromatic Grignard reagents leading to a product of composition $Ar_2S_3N_2$ has been suggested[6,7] as a possible example of the latter, unsymmetrical, addition.

In view of the wide variety of structural types represented in the products of the reactions of nucleophiles with tetrasulfur tetranitride, the inability of the available physical data to distinguish between the proposed structure I and alternative cyclic structures II and III, and the recent interest in compounds containing alternating sulfur-nitrogen chains as photoconductors,[9,10] we have determined the structure of the product of the reaction of *p*-chlorophenylmagnesium bromide with tetrasulfur tetranitride by single-crystal X-ray diffraction.



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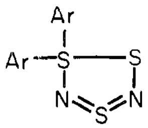

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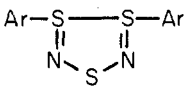

III

Experimental Section

Crystal Data. 1,5-Bis(*p*-chlorophenyl)-2,4-diaza-1,3,5-trithiapenta-2,3-diene, $C_{12}H_8Cl_2S_3N_2$, was prepared from tetrasulfur tetranitride and *p*-chlorophenylmagnesium bromide as previously described[8] and recrystallized from benzene-hexane solutions to give deep red flat needles of mp 159–160°, lit.[8] mp 160°.

Preliminary film data showed the crystals to be monoclinic with systematic absences on the $0k0$ axis of type $k = 2n + 1$ and in the $h0l$ layer of type $l = 2n + 1$ (observed on $0kl$ and $1kl$ Weissenberg films). These uniquely defined the space group as $P2_1/c$. Cell parameters were obtained by least-squares refinement to values of 2θ for 19 well-centered reflections collected at room temperature on a Syntex automatic diffractometer and were $a = 3.972$ (3) Å, $b = 19.531$ (8) Å, $c = 19.37$ (2) Å, and $\beta = 109.7$ (2)°; $d = 1.63$ g cm^{-3} and $Z = 4$. The density measured by flotation in bromobenzene-diiodomethane was 1.60 ± 0.03. The fairly large error in the determination resulted from high solubility of the crystal in this media.

Intensity data were collected to $2\theta = 45°$ on the above diffractometer using graphite-monochromatized Mo Kα radiation (λ 0.71069 Å) and a variable scan rate in the θ–2θ technique. Stationary counts on each side of the peak for half the scan time established background. Thus, the peak intensity is $N_{\mathbf{Pk}} = N_{\mathbf{T}} - N_{\mathbf{BG}_1} - N_{\mathbf{BG}_2}$ where $N_{\mathbf{T}}$ is the total peak count and $N_{\mathbf{BG}_1}$ and $N_{\mathbf{BG}_2}$ are background counts. σ_I's were derived from $\sqrt{\sigma_{\mathbf{Pk}}{}^2}$ where $\sigma_{\mathbf{Pk}} = \sqrt{N_{\mathbf{T}} + N_{\mathbf{BG}_1} + N_{\mathbf{BG}_2}}$. The orientation of the crystal was random but was such that the a axis (needle axis) was approximately (±2–3°) collinear with the spindle axis. The crystal used was an irregular chunk with maximum and minimum dimensions of 0.2 and 0.06 mm, respectively. The linear absorption coefficient was 18 cm^{-1}. The largest absorption corrections would be about ±10% and were ignored. After averaging of equivalent reflections,[11] 964 unique positive reflections remained, of which 340 had $1 > 3\sigma$ and were considered as "observed." After the data were corrected for Lorentz and polarization effects using the XRAY 67 program DATRDN (which allowed for monochromated intensity), these gave the structure factors for use in generating a three-dimensional Patterson function and for comparison with those calculated from model structures.[12]

Solution of the Structure. The positions of the three sulfur and two chlorine atoms were obtained from the Patterson function. During progressive refinement (CUDLS)[13] and electron density difference syntheses (SYMFOU)[13] the positions of the carbon and nitrogen atoms were obtained. Refinement of the positional parameters and isotropic temperature factors of these atoms led to $R = 0.11$.

The electron density difference map showed significant troughs and peaks (up to 1.5 e/Å^3) around the heavy atoms at this stage suggesting a need for anisotropic temperature factors for these atoms. With the addition of these parameters the unweighted discrepancy index immediately dropped to 0.07 with residuals in the electron density difference map of less than 0.5 e/Å^3. In view of the limited number of independent observed reflections, however, the subsequent full-matrix least-squares refinement using anisotropic temperature factors on the five heavy atoms was carried out with the components of the

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(1) Y. Sasaki and F. P. Olsen, *Can. J. Chem.*, 49, 271 (1971).

(2) J. Barrick, C. Calvo, and F. P. Olsen, *Chem. Commun.*, 1043 (1971).

(3) M. Becke-Goehring and R. Schwarz, *Z. Anorg. Allg. Chem.*, 296, 3 (1958).

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(7) M. Becke-Goehring and E. Fluck in "Developments in Inorganic Nitrogen Chemistry," C. B. Colburn, Ed., Elsevier, New York, N. Y., 1961, p 209.

(8) J. Weiss and H. Piechaczek, *Z. Naturforsch. B*, 18, 1139 (1963).

(9) B. Grushkin, U. S. Patent 3,615,409 (1971); *Chem. Abstr.*, 76, 40262 (1972).

(10) B. Grushkin, U. S. Patent 3,616,393 (1971); *Chem. Abstr.*, 76, 40283 (1972).

(11) Of the 150 pairs of equivalent reflections averaged, 100 differed by less than 1σ, 139 by less than 2σ, 147 by less than 3σ, and 149 by less than 4σ prior to averaging.

(12) Atomic scattering factors used were those quoted in "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p 202.

(13) Computer program CUDLS and GROUPLS were written locally by J. Stephens and SYMFOU was written by J. Rutherford.

aromatic rings replaced by rigid hexagons with carbon–carbon distances of 1.392 Å. Individual isotropic temperature factors were allowed to vary for each of the carbon atoms in these groups. The refinement was carried out using the computer program GROUPLS.[13]

In the final cycle of refinement the hydrogen atoms were included as part of these rigid rings with invariant isotropic temperature factors arbitrarily assigned[14] to be $U = 0.05$ Å^2 and a carbon–hydrogen distance of 0.980 Å. Their inclusion is justified because they are obviously part of the aromatic rings; their addition (without increasing the number of variables) resulted in a decrease of 0.01 in the unweighted value of R.

The weighting scheme used in the final stages of the refinement[15] was of the type

$$w = 1/[4.0 + 0.15|F_o| - 0.006|F_o|^2 + 10.0\sigma^2/|F_o|^2]$$

where the σ's were derived from counting statistics. This led to a final weighted R (R_w) of 0.063 for the 340 observed reflections (unweighted $R = 0.054$) where

$$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}$$

and

$$R_w = \frac{\sqrt{\Sigma w(|F_o| - |F_c|)^2}}{\Sigma w|F_o|^2}$$

The maximum shift per error in the final cycle of the refinement was 0.12. Observed and calculated structure factors for all reflections are listed[16,17] in Table I. The final positional isotropic and anisotropic thermal parameters and their estimated standard deviations are given in Tables II and III.

Results and Discussion

Figure 1 is a perspective view of the molecule looking down the x axis. The structure is of the open-chain thiodiimide type (I). The S_1–S_2 distance of 3.293 (8) Å is clearly incompatible with the 2.05–2.10 Å expected for a covalent bond between these two atoms. However, it is somewhat below the sum (generally[18] quoted as 3.70 Å) of van der Waals radii for two sulfur atoms. Sulfur–sulfur intramolecular distances of 3.00 Å have been taken previously[19] to indicate possible weak cross-ring bonding in S_8^{2+}; on the other hand, the intermolecular distance of 3.50 Å found[20] between S_6 molecules presumably does not represent bonding. The possibility that resonance structures similar to III may make some small contribution to bonding in I cannot be completely eliminated, but any such contributions must be quite small.

Table II. Positional and Isotropic Temperature Parameters for Light Atoms

Atoms	x/a	y/b	z/c	U,[14] Å^2
Group 1[a]	0.321 (2)	0.1189 (4)	0.3941 (5)	
C_1	0.113	0.1232	0.3204	0.035 (6)
C_2	0.109	0.1764	0.3680	0.052 (7)
C_3	0.317	0.1721	0.4418	0.047 (7)
C_4	0.529	0.1147	0.4679	0.054 (8)
C_5	0.532	0.0615	0.4203	0.046 (7)
C_6	0.324	0.0657	0.3465	0.039 (6)
H_2	0.961	0.2168	0.3497	*b*
H_3	0.315	0.2096	0.4753	*b*
H_5	0.681	0.0210	0.4386	*b*
H_6	0.327	0.0282	0.3130	*b*
Group 2[a]	0.802 (2)	0.1064 (5)	0.8934 (5)	
C_7	0.020	0.1150	0.9660	0.040 (7)
C_8	0.793	0.1676	0.9298	0.055 (7)
C_9	0.575	0.1590	0.8572	0.039 (6)
C_{10}	0.583	0.0978	0.8209	0.049 (7)
C_{11}	0.810	0.0453	0.8571	0.043 (7)
C_{12}	0.029	0.0538	0.9297	0.051 (7)
H_8	0.787	0.2106	0.9553	*b*
H_9	0.415	0.1960	0.8317	*b*
H_{11}	0.816	0.0022	0.8315	*b*
H_{12}	0.188	0.0168	0.9552	*b*
	Independent Light Atoms			
N_1	0.704 (5)	0.2024 (9)	0.2185 (9)	0.049 (5)
N_2	0.238 (5)	0.1989 (9)	0.077 (1)	0.060 (6)

[a] Group positions correspond to the geometric center of the hexagon. [b] U for all hydrogen atoms arbitrarily assigned to be invariant at 0.05 Å^2.

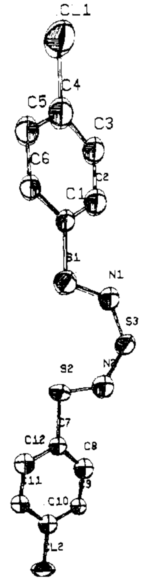

Figure 1. (p-$ClC_6H_4)_2S_3N_2$ looking down the x axis with y horizontal and z vertical.

The most obvious feature of the structure is the rather close approximation to planarity. The least-squares plane defined by C_1–C_6 differs from that defined by C_7–C_{12} by only 7.5°. The maximum deviation of any one carbon atom from a single plane fit to these 12 atoms is less than 0.11 Å, and only S_3 (0.47 Å) and N_1 (0.40 Å) lie more than 0.28 Å away from this plane. Indeed a single plane can be fit to the whole molecule with an average residual of 0.11 Å and a maximum residual of 0.24 Å (C_3).

The configuration is also such that the two aromatic rings are nearly collinear (*i.e.*, the projections of the lines from Cl_1 to S_1 and from Cl_2 to S_2 onto the molecular plane make an angle of 190°). The configuration adopted appears to be a compromise between having the rings linear and having S_3 lie near the plane defined by the two rings. Slight changes

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(14) All temperature factors reported herein are in Å^2 and were obtained from $U_{iso} = B_{iso}/8\pi^2$ and $U_{ij} = \beta_{ij}/2\pi^2 a_i^* a_j^*$ where the β_{ij}'s appear as the effect of temperature through $\exp[-(\beta_{11}h + 2\beta_{12}hk + \ldots)]$ in the structure factor expression and the a_i^*'s are the reciprocal lattice vectors. These units are chosen so that U = mean square thermal displacement directly.

(15) The function minimized in the full-matrix least-squares refinement was $\Sigma w(F_o - F_c)^2$. Unobserved reflections, measuring less than their calculated values, did not affect the refinement while those measuring greater than their calculated values did. In the last cycle, 183 unobserveds supplemented the 340 observeds in this manner.

(16) Table I, a listing of observed and calculated structure factors, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1353.

(17) The calculated values for the unobserved reflections were generally in reasonably good agreement with their observed values. All were within 5σ, with 5 of the 624 unobserved values between 4 and 5σ. These were higher angle reflections whose calculated structure factors were near zero.

(18) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, p 120.

(19) C. G. Davies, R. J. Gillespie, J. J. Park, and J. Passmore, *Inorg. Chem.*, 10, 2781 (1971).

(20) J. Donohue, A. Caron, and E. Goldisch, *J. Amer. Chem. Soc.*, 83, 3748 (1961).

Table III. Positional and Anisotropic Temperature Parameters[14] for Heavy Atoms

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S_1	0.864 (2)	0.1233 (3)	0.2272 (4)	0.084 (6)	0.053 (4)	0.039 (4)	0.007 (5)	0.008 (4)	−0.007 (3)
S_2	0.296 (2)	0.1178 (3)	0.0582 (3)	0.078 (7)	0.055 (4)	0.033 (5)	−0.001 (5)	−0.002 (4)	−0.007 (3)
S_3	0.435 (2)	0.2369 (3)	0.1509 (3)	0.124 (7)	0.043 (4)	0.039 (4)	0.001 (5)	−0.001 (4)	−0.004 (3)
Cl_1	0.806 (2)	0.1113 (3)	0.5585 (4)	0.094 (8)	0.076 (5)	0.038 (5)	0.009 (5)	−0.004 (4)	0.005 (3)
Cl_2	0.307 (2)	0.0888 (3)	0.7308 (3)	0.078 (6)	0.083 (5)	0.032 (4)	0.011 (5)	0.001 (4)	−0.003 (3)

in dihedral angles which would allow S_3 to move closer to the plane of the rest of the molecule would require greater deviation from linearity while a precisely linear structure would require S_3 to move further from the molecular plane. Alternatively, the dihedral angles could conceivably be dictated by the interatomic S_1-S_2 distance in turn reflecting some slight degree of overlap between the orbitals on these two atoms.

The geometry around the central double bonds is of the cis,cis type. This geometry would of course be required for any bonding between S_1 and S_2 and is of interest in connection with the structure of ditolylsulfur diimide reported recently.[21] Here, S_1 and S_2 are absent, and a cis,trans arrangement was observed around the central sulfur diimide unit. Cis,cis geometry would, however, in view of the small dihedral angles found for the five central atoms (C-N-S-N-C) in the latter, place the two aromatic rings in unacceptably close proximity. In I the closest approach between the ends is the S_1-S_2 distance; the aromatic rings are rotated well away from each other.

Table IV gives bond distances and angles. The average aromatic carbon-chlorine bond length of 1.730 (8) Å is typical, as is the average aromatic carbon-sulfur bond length of 1.747 (8) Å. If the four sulfur-nitrogen bonds are treated as equivalent, the average value is 1.605 (9) Å, but none of the four fall within 4.5σ of this value. The chemically equivalent, but crystallographically unique, S_1-N_1 and S_2-N_2 distances lie within 0.3σ of their average value of 1.660 (13) Å while the inner S_3-N_1 and S_3-N_2 distances, also crystallographically unique, differ from their average value of 1.550 (12) Å by less than 1σ. These two average values differ by 0.110 (18) Å or over 6σ. There are, therefore, two types of sulfur-nitrogen bonds in the compound.

The inner (short) distance is quite typical of a sulfur-nitrogen "double bond" length and is in good agreement with similar values of 1.53 and 1.56 Å reported[16] in ditolylsulfur diimide. The outer sulfur-nitrogen distance is short compared to the 1.76 Å found in sulfamic acid[22] but is quite typical of "normal" single-bond distances where some $d\pi$-$p\pi$ overlap is possible. For example, the N-S bond in heptasulfur imide has a length[23] of 1.69 Å.

The substantially greater bond angle around S_3 [124 (1)°] as compared to S_1 and S_2 [100 (1)°] is also suggestive of a higher oxidation state for S_3. The intramolecular S_1-S_3 and S_2-S_3 distances are 2.884 (9) and 2.877 (9) Å, respectively, and the rather large bond angles around N_1 [129 (2)°] and N_2 [126 (2)°] most likely reflect the fairly substantial van der Waals repulsions between these sulfur atoms.

Within the crystal lattice the orientations of the molecular planes are very nearly perpendicular to the xz plane (*i.e.*, parallel to the y axis). All coordinates for the atoms of any one molecule lie between $ny/4$ and $(n + 1)y/4$. The molecular plane is inclined in the x direction such that any one molecule traverses approximately three unit cells in x. The molecule is then repeated in a nearly linear fashion with a space of 3.288 (8) Å between chain ends (Cl_1-Cl_2 distance). Symmetry-related molecules are situated such that the S_3's fit one above and one below (in x) the gap between Cl_1 and Cl_2 although not centered (S_3-Cl_1 = 3.90 Å, S_3-Cl_2 = 3.84 Å for one; S_3-Cl_1 = 3.99 Å, S_3-Cl_2 = 4.73 Å for the other).

Table IV. Bond Lengths (Å) and Angles (deg) in $(p\text{-}ClC_6H_4)_2S_3N_2$[a]

Lengths

S_1-N_1	1.657 (18)	S_1-C_1	1.741 (10)[b]
S_2-N_2	1.662 (19)	S_2-C_7	1.753 (10)[b]
S_3-N_1	1.539 (16)	Cl_1-C_4	1.730 (11)[b]
S_3-N_2	1.561 (18)	Cl_2-C_{10}	1.729 (10)[b]

Angles

C_1-S_1-N_1	100 (1)	C_3-C_4-Cl_1	120 (1)
C_7-S_2-N_2	100 (1)	C_5-C_4-Cl_1	121 (1)
N_1-S_3-N_2	124 (1)	C_{12}-C_7-S_2	115 (1)
S_3-N_2-S_2	126 (2)	C_8-C_7-S_2	124 (1)
S_3-N_1-S_1	129 (2)	C_2-C_1-S_1	124 (1)
C_9-C_{10}-Cl_2	119 (1)	C_6-C_1-S_1	116 (1)
C_{11}-C_{10}-Cl_2	121 (1)		

[a] Estimated standard deviations in parentheses. [b] Errors in bond lengths to the members of the group were calculated assuming an uncertainty in the carbon position equivalent to the uncertainty in the *position* of the group. Errors in group orientation were not considered and these errors are therefore probably too low.

The quite short van der Waals contact distance for chlorine (usually[18] quoted as 3.60 Å) is quite comparable to the 3.293 Å found for the S_1-S_2 distance. Indeed, nonbonding repulsions between these two sets of atoms provide a reasonable explanation for their mutually short distances. Given the linear nature of the structure, any increase in the S_1-S_2 distance would require an even smaller Cl_1-Cl_2 distance and *vice versa.*

The slight rotation of the aromatic rings leads to intermolecular distances of approximately 3.5-3.6 Å between atoms of the aromatic rings in the next layer [C_1-C_6 = 3.52 Å, C_2-C_5 = 3.59 Å, C_3-C_4 = 3.52 Å, C_7-C_8 = 3.52 Å, C_9-C_{12} = 3.60 Å, C_{10}-C_{11} = 3.53 Å]. These contacts appear to determine the length of the x axis as well as to prevent further rotation to relieve Cl_1-Cl_2 or S_1-S_2 repulsions. Similar repulsions on the edges of the aromatic rings [C_2-C_8 = 3.65 Å, C_2-C_9 = 3.75 Å, C_3-C_8 = 3.70 and 3.72 Å, C_3-N_2 = 3.73 Å, C_5-Cl_1 = 3.71 Å, C_{11}-S_2 = 3.76 Å, C_{12}-C_{12} = 3.51 Å, C_{12}-S_2 = 3.63 Å] prevent further rotation in the y direction away from a collinear arrangement of the aromatic rings.

Registry No. 1,5-Bis-(*p*-chlorophenyl)-2,4-diaza-1,3,5-trithiapenta-2,3-diene, 38781-27-0.

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