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Crystal and Molecular Structure of 3,8-Di-*t*-butyl-5,6-diphenyl-1-thioxo-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene

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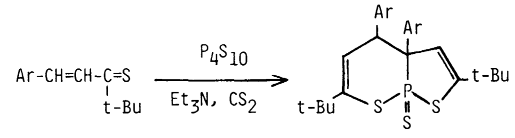
The crystal and molecular structures of the title compound were determined by means of X-ray diffraction. Crystal data: $C_{26}H_{31}S_3P$, M_r=470.68, orthorhombic, a=17.116(4), b=19.798(4), c=14.898(3) Å, V=5048.4 Å^3 (21 °C), space group Pbca, D_m=1.23, D_x=1.239 g cm^{-3}, Z=8, μ=3.58 cm^{-1} (Mo $K\alpha$). The structure was solved by the direct method and refined by the full-matrix least-squares method to R=0.083 for 3318 observed reflections. The bicyclo skeleton is so highly strained that abnormal bond distances [P–C of 1.895(5) and C–C of 1.594(6) Å] were observed. Conformation of six-membered ring is a boat-form.

Previously, we found that treatment of α,β-unsaturated thioketones (**1**) with P_4S_{10} gave 1-thioxo-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-dienes (**2**).[1,2] They possess a characteristic heterocyclic skeleton, and are useful starting materials of the synthesis of various new heterocycles. The X-ray analysis of the title compound (**3**) has been performed to confirm its exact structure, since the arrangement of phosphorus and sulfur atoms in the molecule are difficult to elucidate by spectroscopic methods (IR, ^{1}H-, and ^{13}C-NMR spectra).



1 **2**

3 : Ar = Ph

Experimental

The synthesis of the compound was described previously.[1] Crystals were obtained from chloroform as colorless hexagonal platelets with a well-developed(010) cleavage plane.

After determining preliminary cell parameters and space group from Weissenberg photographs, a crystal with dimensions of 0.35×0.40×0.50 mm was mounted with the c axis parallel to the ϕ-axis on a Hilger & Watts diffractometer. Lattice parameters were determined by a least-aquares procedure with setting angles of 12 reflections with 20.9°<θ<25.9° (Zr-filtered Mo $K\alpha$ radiation, λ=0.7107 Å). The intensities were recorded with a θ-2θ step scan mode at every 0.02° of θ step up to $2\theta \leq 55°$. The scan width of θ was 0.8° for all the reflections. Counting time was 1 s count at each 40 steps of 0.04° in 2θ, background count of 5 s at each end of the scan range. Three standard reflections, (040, 021, and 210) monitored every 50 measurements, showed changes within ±3% of $|F|$'s throughout the data collection. Of the 6408 independent reflections measured, 3320 with $F_o \geq 3\sigma(F)$ were used for further calculations. Lorentz and polarization corrections were applied as usual, but the absorption correction was not made. Density was observed by the flotation method with K_2HgI_4 aqueous solution.

Crystal Data: $C_{26}H_{31}S_3P$, M_r=470.68, orthorhombic, a=17.116(4), b=19.798(4), c=14.898(3) Å, V=5048.4 Å^3 (21 °C); absent spectra: *0kl k* odd, *h0l l* odd, *hk0 h* odd; Space group Pbca; D_m=1.23, D_x=1.239 g cm^{-3}; Z=8; μ=3.58 cm^{-1} (Mo $K\alpha$).

Solution and Refinement of the Structure

The structure was solved by the direct method.[3] After several cycles of block-diagonal least-squares refinement, 19 H atoms were located on a difference Fourier map. The next cycles with anisotropic non-H atoms and isotropic 19 H atoms reduced R to 0.090. Then, difference Fourier map revealed the remaining 12 H atoms. The final refinement was carried out with the full-matrix least-squares with the anisotropic thermal parameters for non-H atoms, a fixed isotropic thermal parameter for H atoms, B=4.0 Å^2, and anomalous dispersion corrections for S and P atoms. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$, where $w=[\sigma^2(F_o)]^{-1}$ and $\sigma(F_o)$ is the standard deviation in the observed amplitudes based on counting statistics.

In the final cycle, the maximum parameter shft/error was less than 0.5. Final R and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$ were 0.083 and 0.038, respectively, where two reflections (040 and 021) were given zero weight because they were seriously affected by extinction. A final difference synthesis showed no significant feature. The atomic scattering factors with anomalous corrections were adopted from "International Tables for X-ray Crystallography."[4] All the computations were performed on a HITAC M-200H computer at the Compurter Center of Tokyo University with the *UNICS* program system.[5]

Discussion

The final atomic coordinates and equivalent temperature parameters are listed in Table 1. The numbering scheme is given in Fig. 1 with the bond distances, and Table 2 shows the bond angles.[6] Figure 2 gives the stereoscopic view of the molecule drawn by *ORTEP*.[7]

The bicyclo skeleton has a shallow envelope thiaphosphacyclopentene ring and a boat-form thiaphosphacyclohexene ring, which are cis-fused together with the bridging P–C(4) bond that is the side of the boat of the six-membered ring.

The molecule possesses three stereochemically char-

Table 1. The final fractional coordinates and equivalent isotropic thermal parameters
Estimated standard deviations are given in parentheses. The equivalent isotropic thermal parameters for non-hydrogen atoms are calculated using the expression: $B_{eq}=4/3\sum_i\sum_j \mathbf{a}_i\mathbf{a}_j\beta_{ij}$, where the $\mathbf{a}_i$'s are the unit cell edges in direct space. The isotropic thermal parameter of hydrogen atoms is fixed, $B=4.0$ Å^2.

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z
P	0.10993(7)	0.37035(7)	0.30978(9)	3.35(8)	H(2)	0.158(3)	0.343(3)	0.566(3)
S(1)	0.18690(8)	0.43856(7)	0.37048(9)	3.73(8)	H(3)	0.059(3)	0.430(2)	0.488(3)
S(2)	0.16903(8)	0.27822(7)	0.29822(9)	4.23(9)	H(32)	−0.062(3)	0.435(2)	0.556(3)
S(3)	0.07438(8)	0.40783(8)	0.19788(9)	5.4(1)	H(33)	−0.148(3)	0.406(2)	0.665(3)
C(1)	0.2085(3)	0.3920(2)	0.4710(3)	2.9(3)	H(34)	−0.130(3)	0.297(2)	0.739(3)
C(2)	0.1492(3)	0.3649(2)	0.5157(3)	2.9(3)	H(35)	−0.028(3)	0.230(2)	0.705(3)
C(3)	0.0639(3)	0.3775(2)	0.4924(3)	2.7(3)	H(36)	0.057(3)	0.266(3)	0.596(3)
C(4)	0.0376(3)	0.3443(2)	0.3997(3)	2.7(3)	H(42)	−0.098(3)	0.280(2)	0.384(3)
C(5)	0.0442(3)	0.2688(2)	0.4062(3)	2.9(3)	H(43)	−0.224(3)	0.317(3)	0.354(3)
C(6)	0.1006(3)	0.2345(2)	0.3694(3)	3.0(3)	H(44)	−0.244(3)	0.440(3)	0.339(3)
C(7)	0.2950(3)	0.3875(3)	0.4946(4)	3.6(3)	H(45)	−0.135(3)	0.510(2)	0.347(3)
C(8)	0.3301(4)	0.4579(4)	0.4963(6)	7.4(5)	H(46)	−0.012(3)	0.472(2)	0.369(3)
C(9)	0.3384(4)	0.3442(5)	0.4268(6)	7.9(6)	H(5)	0.003(3)	0.249(3)	0.445(3)
C(10)	0.3055(4)	0.3559(5)	0.5858(6)	8.5(6)	H(81)	0.387(3)	0.457(3)	0.507(3)
C(11)	0.1202(3)	0.1594(3)	0.3842(3)	3.6(3)	H(82)	0.298(3)	0.475(3)	0.551(3)
C(12)	0.0500(4)	0.1237(3)	0.4251(5)	5.8(4)	H(83)	0.331(3)	0.472(3)	0.433(3)
C(13)	0.1431(4)	0.1250(3)	0.2957(5)	6.7(5)	H(91)	0.339(4)	0.367(3)	0.373(3)
C(14)	0.1892(4)	0.1556(3)	0.4498(5)	5.6(4)	H(92)	0.322(3)	0.300(3)	0.447(4)
C(31)	0.0089(3)	0.3553(2)	0.5673(3)	2.5(3)	H(93)	0.393(3)	0.348(3)	0.442(3)
C(32)	−0.0533(3)	0.3961(3)	0.5905(3)	3.5(3)	H(101)	0.360(3)	0.365(3)	0.606(3)
C(33)	−0.1056(3)	0.3758(3)	0.6561(4)	4.4(4)	H(102)	0.287(3)	0.315(3)	0.592(4)
C(34)	−0.0977(3)	0.3145(3)	0.6974(4)	4.5(4)	H(103)	0.280(3)	0.389(3)	0.632(3)
C(35)	−0.0354(3)	0.2730(3)	0.6759(3)	3.6(3)	H(121)	0.060(3)	0.076(2)	0.433(3)
C(36)	0.0180(3)	0.2933(3)	0.6111(3)	3.2(3)	H(122)	0.000(3)	0.130(3)	0.380(3)
C(41)	−0.0434(3)	0.3699(2)	0.3761(3)	3.0(3)	H(123)	0.033(3)	0.140(3)	0.492(3)
C(42)	−0.1063(3)	0.3269(3)	0.3705(3)	3.5(3)	H(131)	0.152(3)	0.075(2)	0.315(3)
C(43)	−0.1811(4)	0.3514(3)	0.3555(4)	4.8(4)	H(132)	0.193(3)	0.143(3)	0.267(4)
C(44)	−0.1942(3)	0.4195(4)	0.3465(4)	5.1(4)	H(133)	0.085(3)	0.120(2)	0.264(3)
C(45)	−0.1315(4)	0.4631(3)	0.3507(4)	4.8(4)	H(141)	0.241(3)	0.184(3)	0.428(3)
C(46)	−0.0561(3)	0.4386(3)	0.3654(4)	4.0(3)	H(142)	0.208(3)	0.108(2)	0.469(3)
					H(143)	0.171(3)	0.175(3)	0.512(3)

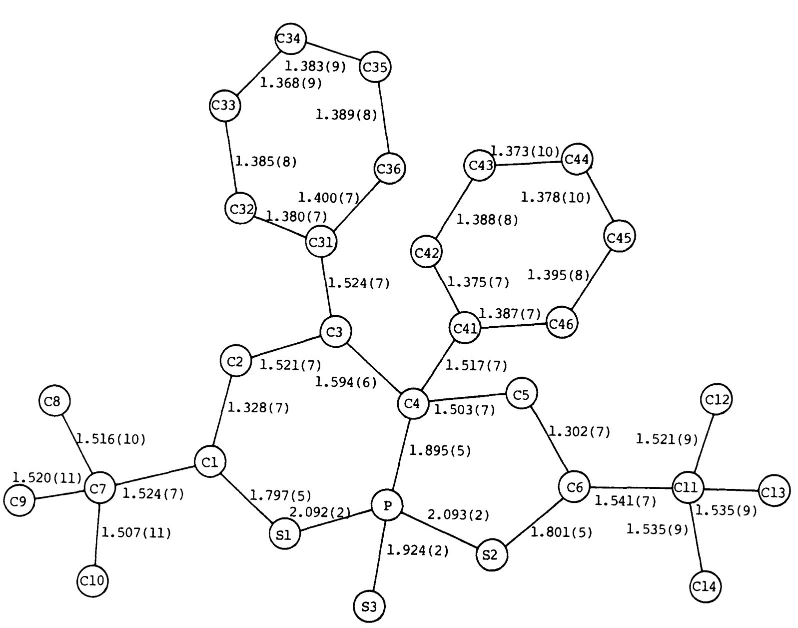


Fig. 1. Atom numbering and bond distaces (Å) of **3**. E.s.d.'s are in parentheses.

acteristic features. (i) The conformation of six-membered ring is a boat-form, as mentioned above. (ii) Several abnormal bond distances and bond angles are observed about the bridgehead P and C(4) atoms. The C(3)–C(4) bond distance of 1.594(6) Å is apparently longer than the commonly accepted C–C bond distance, and the observed P–C(4) bond distance of 1.895(5) Å is longer than the average P–C bond distance of 1.832(7) Å in 4-*t*-butyl-5-cyano-2-phenyl-1-thioxo-7-thia-1-phosphabicyclo[2.2.1]hept-2-ene,[2] which was synthesized by using **3** as the starting material.[1] (iii) Though C(3) is a chiral atom, the conformational isomer has not been found in the present study.

These features can be elucidated by positing the existence of two double bonds in the ring system and the four bulky substituents, especially two neighboring phenyl groups. *cis*-8-Azabicyclo[4.3.0]non-3-ene methiodide[8] possesses a boat-form cyclohexene ring, which consists of six ring carbon atoms with no substituents except for hydrogen atoms. It has a similar bicyclo skeleton to that of **3** and has no abnormal bond distances in the ring system. So, if both bridgehead atoms are tetrahedrally bonded, the most stable conformation of *cis*-fused bicyclo[4.3.0]non-3-ene ring must be a boat-form. In the case of the present compound (**3**), moreover, the second ethylenic group in the five-membered ring, makes the *trans*-fusing of two rings impossible. The elongation of P–C(4) and C(3)–C(4) bonds are due to the strain caused by the neighboring phenyl groups: such a situation is often observed in fused ring systems with bulky substituents.[9] The phenyl group attached to the C(3) takes a position eclipsed to the H(2), while it is staggered (gauche) to the other phenyl group attached to

TABLE 2. THE BOND ANGLES WITH THEIR E.S.D.'S IN PARENTHESES

Bond angle	$\phi/°$	Bond angle	$\phi/°$
S(1)-P-S(2)	107.08(8)	C(1)-C(7)-C(10)	110.4(5)
S(1)-P-S(3)	108.95(9)	C(8)-C(7)-C(9)	109.6(6)
S(1)-P-C(4)	106.3(2)	C(8)-C(7)-C(10)	108.6(6)
S(2)-P-S(3)	114.70(9)	C(9)-C(7)-C(10)	107.8(6)
S(2)-P-C(4)	97.9(2)	C(6)-C(11)-C(12)	109.5(5)
S(3)-P-C(4)	120.7(2)	C(6)-C(11)-C(13)	111.1(5)
P-S(1)-C(1)	99.2(2)	C(6)-C(11)-C(14)	107.8(4)
S(1)-C(1)-C(2)	117.9(4)	C(12)-C(11)-C(13)	109.9(5)
S(1)-C(1)-C(7)	115.0(3)	C(12)-C(11)-C(14)	109.3(5)
C(7)-C(1)-C(2)	127.1(5)	C(13)-C(11)-C(14)	109.1(5)
C(1)-C(2)-C(3)	123.6(5)	C(3)-C(31)-C(32)	119.5(4)
C(2)-C(3)-C(4)	113.7(4)	C(3)-C(31)-C(36)	121.7(4)
C(2)-C(3)-C(31)	112.2(4)	C(31)-C(32)-C(33)	120.4(5)
C(4)-C(3)-C(31)	110.0(4)	C(32)-C(33)-C(34)	120.7(6)
C(3)-C(4)-P	108.4(3)	C(33)-C(34)-C(35)	119.9(6)
C(3)-C(4)-C(41)	108.8(4)	C(34)-C(35)-C(36)	119.8(5)
P-C(4)-C(41)	110.0(3)	C(35)-C(36)-C(31)	120.3(5)
C(3)-C(4)-C(5)	109.4(4)	C(36)-C(31)-C(32)	118.8(5)
P-C(4)-C(3)	108.4(3)	C(4)-C(41)-C(42)	121.5(4)
P-C(4)-C(5)	105.5(3)	C(4)-C(41)-C(46)	119.9(4)
C(4)-C(5)-C(6)	123.2(5)	C(41)-C(42)-C(43)	121.0(5)
C(5)-C(6)-S(2)	118.7(4)	C(42)-C(43)-C(44)	120.6(6)
C(5)-C(6)-C(11)	127.2(5)	C(43)-C(44)-C(45)	119.0(7)
C(11)-C(6)-S(2)	114.0(3)	C(44)-C(45)-C(46)	120.6(6)
P-S(2)-C(6)	93.2(2)	C(45)-C(46)-C(41)	120.3(5)
C(1)-C(7)-C(8)	109.5(5)	C(46)-C(41)-C(42)	118.5(5)
C(1)-C(7)-C(9)	110.8(5)		

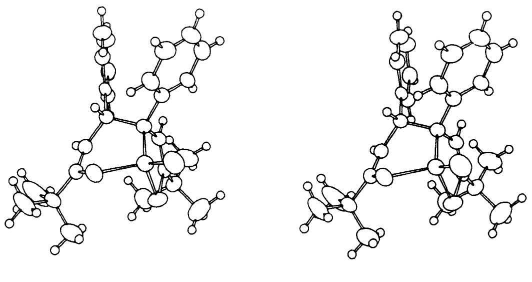


Fig. 2. Stereoscopic view of molecule **3**. The thermal ellipsoids for non-H atoms are at the 50 % probability level, while H atoms are represented by spheres of arbitrary radius.

TABLE 3. TORSION ANGLES ABOUT SIX-MEMBERED RING

Bond	Angle $\theta/°$
P-S(1)-C(1)-C(2)	46.5
S(1)-C(1)-C(2)-C(3)	7.0
C(1)-C(2)-C(3)-C(4)	68.9
C(2)-C(3)-C(4)-P	50.9
C(3)-C(4)-P-S(1)	5.0
C(4)-P-S(1)-C(1)	47.6
C(31)-C(3)-C(4)-C(41)	62.7
C(41)-C(4)-C(3)-H(3)	54.2
C(31)-C(3)-C(2)-H(2)	5.5

TABLE 4. DEVIATIONS OF ATOMS FROM LEAST-SQUARES PLANES (l/Å)

Plane E1: $0.0496X-0.8442Y-0.5337Z+10.1282=0$			
S (1)	0.01	C (3)	−0.04
C (1)	0.01	C (7)	−0.03
C (2)	0.06		
Plane E2: $-0.5988X-0.1855Y-0.7791Z+6.2238=0$			
S (2)	0.01	C (6)	0.04
C (4)	−0.07	C (11)	−0.05
C (5)	0.07	P*	0.14
Plane P1: $-0.5585X-0.4365Y-0.7054Z+9.1227=0$			
C (31)	0.005	C (35)	−0.001
C (32)	0.003	C (36)	−0.006
C (33)	−0.011	C (3)*	0.075
Plane P2: $0.1363X-0.0855Y-0.9870Z+6.2504=0$			
C (41)	−0.007	C (45)	0.003
C (42)	0.001	C (46)	0.005
C (43)	0.006	C (4)*	−0.122
C (44)	−0.008		

Average e.s.d.'s are 0.04 Å for Planes E1 and E2, and 0.007 Å for Planes P1 and P2. Orthogonal coordinates X, Y, and Z (Å) are parallel to the crystal axes a, b and c.

Atoms marked with asterisk were excluded from the calculations.

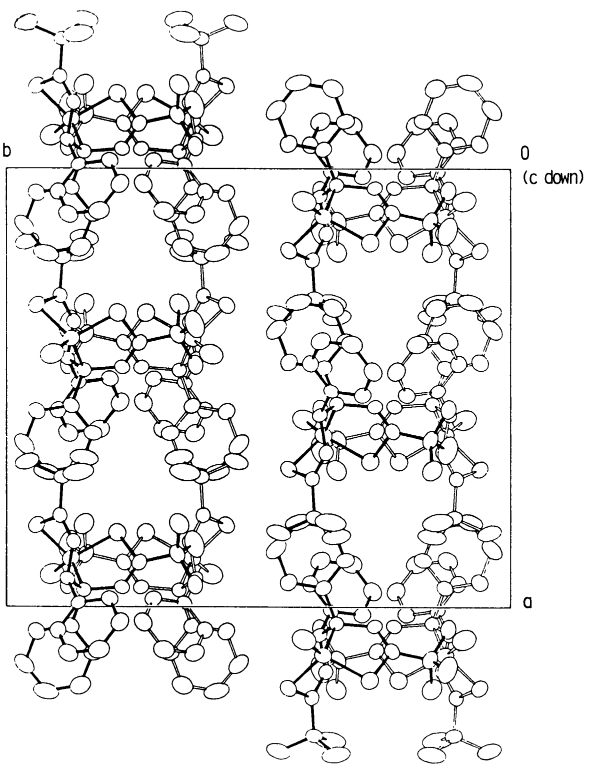


Fig. 3. Crystal structure of **3** projected along the *c* axis. The thermal ellipsoids for non-H atoms are at the 50% probability level. H atoms are omitted.

the C(4). Since this stereochemical feature gives the minimum Pitzer strain, the formation of a conformational isomer about C(3) must be difficult. Several torsion angles related to the six-membered ring are listed in Table 3.

The two ethylenic groups and the two phenyl groups each form fairly good planes. Table 4 gives their least-squares planes with deviations of atoms from them. The dihedral angles between the planes are as follows: E1-P1, 44.2°; E2-P2, 45.3°, and P1-P2, 48.9°.

The crystal structure of **3** is shown in Fig. 3.⁷⁾ There are no special interactions between the molecules, since all the intermolecular atomic distances are considered to be van der Waals contacts.

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