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Crystal and Molecular Structure of 4-*t*-Butyl-5-cyano-2-phenyl-1-thioxo-7-thia-1-phosphabicyclo[2.2.1]hept-2-ene

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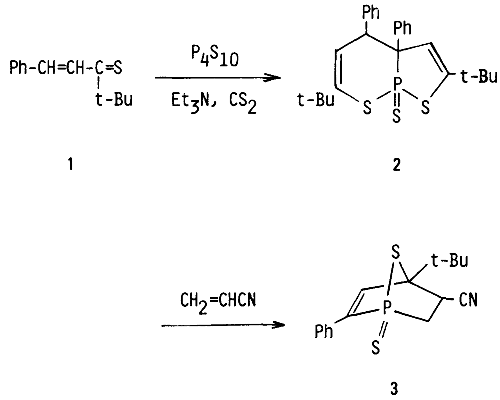
The crystal and molecular structures of the title compound were determined by means of X-ray diffraction. Crystal data: $C_{16}H_{18}NS_2P$, M_r=319.4, triclinic, a=12.731(2), b=13.143(1), c=12.483(1) Å, α=102.39(1), β=104.34(1), γ=117.96(1)°, V=1648.6 Å^3, space group $P\bar{1}$, D_m=1.30, D_x=1.287 g cm^{-3}, Z=4, μ=4.02 cm^{-1} (Mo $K\alpha$). The structure was solved by the direct method and refined by the block-diagonal least-squares method to R=0.082 for 4495 observed reflections. The bond distances and angles are in good agreement with the ordinary values except for the P–S–C bridged angle of 82.5°. An asymmetric unit contains two crystallographically independent molecules, which are rotational isomers along the P–C bond.

The title compound (**3**) was formed by the reaction of acrylonitrile and 3,8-di-*t*-butyl-5,6-diphenyl-1-thioxo-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene (**2**) prepared from 4,4-dimethyl-1-phenyl-1-pentene-3-thione (**1**).[1,2] Compound **3** has a unique norbornene-like skeleton in which one of the sulfur atoms bridges between phosphorus and carbon atoms. The present study was performed to confirm the structure and establish the total geometry of the molecule.



Experimental

The compound was prepared by the method described previously.[1] Colorless crystals were obtained by recrystallization from chloroform with a well-developed (112) face.

After determining preliminary cell constants and space group from Weissenberg photographs, a crytal with dimensions of 0.40×0.25×0.15 mm was mounted with the (112) face perpendicular to the ϕ axis on a Hilger & Watts diffractometer with Zr-filtered Mo$K\alpha$ radiation. Lattice constants were determined by a least-squares procedure for setting angles of 12 reflections with 16.5°<θ<21.4°. The intensities were recorded with an θ-2θ step scan mode at every 0.01° of θ step up to 2θ≦55°. The scan width of θ was 0.8° for all the reflections. Counting time was 1 s per step for peak measurements, and backgrounds were measured for 10 s at both ends of a scan.

Three standard reflections, monitored every 50 measurements, showed no significant change throughout the data collection. Of the 7545 independent reflections measured, 4495 with $F_o≧3\sigma(F)$ were used for further calculations. Lorentz and polarization corrections were applied but no absorption correction was made. No systematical absent spectra was observed. Density was determined by the flotation method with K_2HgI_4 aqueous solution.

Crystal Data: $C_{16}H_{18}NS_2P$, M_r=319.4, triclinic, a=12.731(2), b=13.143(1), c=12.483(1) Å, α=102.39(1), β=104.34(1), γ=117.96(1)°, V=1648.6 Å^3, space group $P\bar{1}$, D_m=1.30, D_x=1.287 g cm^{-3}, Z=4, μ=4.02 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, all the H atoms were located on the difference Fourier map. The final cycle was calculated with the anisotropic thermal parameters for non-H atoms, a fixed isotropic thermal parameter for H atoms, B=4.0 Å^2, and anomalous scattering factors for S and P atoms. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$, where $w=[\sigma^2(F)+0.0011|F_o|^2]^{-1}$. In the final cycle, the maximum parameter shift/error was less than 0.07. Final R and R_w were 0.082 and 0.084, respectively. A final difference Fourier synthesis showed no significant features. The atomic scattering factors were adopted from "International Tables for X-ray Crystallography."[4] All the computations were carried out on a HITAC M-200H computer at the Computer Center of Tokyo University with the *UNICS* program system.[5]

Results and Discussion

The asymmetric unit contains two crystallographically independent molecules, hereafter referred to as molecule A and molecule B. Table 1 lists the final fractional coordinates and the equivalent thermal parameters.[6] The bond distances with the numbering scheme of atoms are given in Fig. 1, and the bond angles in Table 2. The bond distances and angles including P and S atoms almost agree with the literature values[7] except for the P-S(2)-C(3) angle. Differences between corresponding bond distances and bond angles in molecules A and B are not so significant. Figure 2 shows an *ORTEP* drawing of molecule A.[8] Each of two five-membered rings takes an envelope conformation, commonly possessing the P-S(2)-C(3) bridge. A

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	B_{eq}/Å^2
Molecule A					Molecule B				
S(1)	0.6055(2)	0.4028(2)	0.4939(2)	6.3(1)	S(1)	1.0933(2)	0.3502(1)	−0.0343(2)	5.59(8)
S(2)	0.3256(2)	0.2740(2)	0.5516(1)	4.84(8)	S(2)	1.0084(1)	0.3933(1)	0.2047(1)	4.63(6)
P	0.5236(2)	0.3489(1)	0.5991(1)	4.09(7)	P	0.9594(1)	0.2978(1)	0.0264(1)	3.64(6)
N	0.5896(5)	0.4276(5)	1.0068(4)	5.2(2)	N	0.5170(4)	0.1198(4)	−0.0591(4)	5.2(2)
C(1)	0.5220(5)	0.2283(4)	0.6516(4)	3.1(2)	C(1)	0.8637(4)	0.1412(4)	0.0266(4)	3.1(2)
C(2)	0.4371(5)	0.1986(4)	0.7018(4)	3.1(2)	C(2)	0.8085(5)	0.1509(5)	0.1029(4)	3.4(2)
C(3)	0.3633(5)	0.2625(5)	0.7006(4)	3.5(2)	C(3)	0.8328(5)	0.2780(4)	0.1640(4)	3.6(2)
C(4)	0.4684(5)	0.4034(5)	0.7916(5)	4.1(3)	C(4)	0.7608(5)	0.3032(4)	0.0600(5)	3.5(2)
C(5)	0.5701(6)	0.4672(5)	0.7410(6)	5.0(3)	C(5)	0.8252(5)	0.3161(5)	−0.0308(5)	3.9(2)
C(61)	0.6063(5)	0.1817(5)	0.6489(4)	3.3(2)	C(61)	0.8329(5)	0.0254(4)	−0.0605(4)	3.2(2)
C(62)	0.7280(5)	0.2531(6)	0.6467(5)	4.6(3)	C(62)	0.9198(5)	0.0208(5)	−0.1077(5)	4.3(3)
C(63)	0.8059(6)	0.2062(7)	0.6488(6)	5.8(4)	C(63)	0.8880(6)	−0.0897(6)	−0.1879(5)	5.0(3)
C(64)	0.7643(7)	0.0900(7)	0.6507(6)	6.2(4)	C(64)	0.7688(7)	−0.1971(5)	−0.2259(6)	5.4(3)
C(65)	0.6440(6)	0.0182(6)	0.6507(5)	5.1(3)	C(65)	0.6809(6)	−0.1940(5)	−0.1800(6)	5.9(3)
C(66)	0.5649(5)	0.0641(5)	0.6508(5)	3.9(2)	C(66)	0.7115(5)	−0.0854(5)	−0.0990(5)	4.6(3)
C(7)	0.2364(5)	0.1938(6)	0.7207(5)	4.4(3)	C(7)	0.8030(6)	0.2964(6)	0.2788(5)	5.1(3)
C(71)	0.1526(6)	0.0569(6)	0.6291(6)	6.7(3)	C(71)	0.6561(7)	0.2087(6)	0.2450(6)	7.4(4)
C(72)	0.2645(6)	0.1964(6)	0.8479(5)	5.4(3)	C(72)	0.8833(8)	0.2698(8)	0.3698(6)	8.0(5)
C(73)	0.1578(7)	0.2519(8)	0.6989(7)	6.9(4)	C(73)	0.8434(7)	0.4306(6)	0.3361(6)	7.0(4)
C(8)	0.5350(5)	0.4143(5)	0.9128(5)	4.2(3)	C(8)	0.6216(5)	0.2000(5)	−0.0053(5)	3.9(3)
H(2)	0.433(5)	0.149(5)	0.751(5)		H(2)	0.745(5)	0.079(5)	0.111(5)	
H(4)	0.427(5)	0.445(5)	0.805(5)		H(4)	0.768(5)	0.384(5)	0.098(5)	
H(51)	0.578(6)	0.536(5)	0.732(5)		H(51)	0.858(6)	0.392(5)	−0.036(5)	
H(52)	0.661(6)	0.499(5)	0.801(5)		H(52)	0.769(5)	0.251(5)	−0.111(5)	
H(62)	0.755(5)	0.330(5)	0.648(5)		H(62)	1.001(5)	0.095(5)	−0.076(5)	
H(63)	0.881(5)	0.250(5)	0.638(5)		H(63)	0.948(5)	−0.090(5)	−0.221(5)	
H(64)	0.815(5)	0.054(5)	0.648(5)		H(64)	0.747(5)	−0.273(5)	−0.280(5)	
H(65)	0.609(5)	−0.070(5)	0.644(5)		H(65)	0.603(5)	−0.263(5)	−0.205(5)	
H(66)	0.477(5)	0.006(5)	0.641(5)		H(66)	0.651(5)	−0.081(5)	−0.073(5)	
H(71a)	0.134(5)	0.045(5)	0.548(5)		H(71a)	0.644(5)	0.135(5)	0.222(5)	
H(71b)	0.080(5)	0.025(5)	0.645(5)		H(71b)	0.645(5)	0.215(5)	0.313(5)	
H(71c)	0.194(5)	0.018(5)	0.647(5)		H(71c)	0.606(5)	0.235(5)	0.194(5)	
H(72a)	0.310(5)	0.158(5)	0.860(5)		H(72a)	0.832(5)	0.185(5)	0.336(5)	
H(72b)	0.190(5)	0.137(5)	0.860(5)		H(72b)	0.863(6)	0.276(5)	0.445(5)	
H(72c)	0.314(5)	0.289(5)	0.915(5)		H(72c)	0.984(5)	0.325(5)	0.388(5)	
H(73a)	0.084(5)	0.210(5)	0.716(5)		H(73a)	0.780(5)	0.441(5)	0.284(5)	
H(73b)	0.206(5)	0.334(5)	0.742(5)		H(73b)	0.831(5)	0.443(5)	0.399(5)	
H(73c)	0.129(5)	0.248(5)	0.618(5)		H(73c)	0.938(5)	0.482(5)	0.363(5)	

considerable decrease in bond angle is observed at the bridged S atom [P–S(2)–C(3) of average 82.5°], which indicates the steric strain about the bicyclo skeleton. Table 3 gives bond angles of bridged S atom in several bicyclo compounds,[9–12] though the value of the P–S–C bridge angle has not been reported other than in the present study. As expected, the more the number of ring atoms increases, the larger the bridge C–S–C angle changes.

Figure 3, the Newman projection along the P–C(1) bond, shows that the torsion angles of S(1)–P–C(1)–C(61) are appreciably different for molecule A and molecule B. The conformational difference between molecules A and B is obviously illustrated in Fig. 4, which is the projection of phenyl group and its neighboring atoms onto the plane perpendicular to the C(1)=C(2) double bond. Although the S(1)···H(62) and H(2)···H(66) separations keep the van der Waals distances, their relative orientations are distinct from one another in the two molecules. In other words, molecule A and molecule B are rotational isomers to each other, because the C(1)–C(61) bond is kept from free rotation by the steric hindrance of ortho hydrogens, H(62) and H(66).

Planarity of the plane defined by atoms around the C(1)=C(2) double bond [C(1), C(2), C(3), C(61) and P] is not so good: the maximum deviation from the least-squares plane reaches to 0.09 Å of C(1) in molecule B.6) That is because of the strain of bicyclo skeleton and the overcrowding effect of bulky substituents, namely *t*-

Table 2. Bond angles of molecule A and molecule B with their estimated standard deviations in parentheses

Bond angle	ϕ/° Molecule A	Molecule B
P-S(2)-C(3)	82.3(2)	82.6(2)
S(1)-P-S(2)	121.3(1)	118.6(1)
S(1)-P-C(1)	123.4(2)	124.9(2)
S(1)-P-C(5)	118.2(3)	119.2(2)
S(2)-P-C(1)	94.7(2)	95.5(2)
S(2)-P-C(5)	93.0(3)	94.4(2)
C(1)-P-C(5)	99.7(3)	97.8(3)
P-C(1)-C(2)	106.5(4)	106.6(4)
P-C(1)-C(61)	127.0(5)	124.9(4)
C(2)-C(1)-C(61)	126.3(6)	127.2(5)
C(1)-C(2)-C(3)	118.2(5)	117.9(5)
C(2)-C(3)-C(4)	105.3(5)	105.1(5)
C(2)-C(3)-S(2)	105.6(4)	105.3(4)
C(2)-C(3)-C(7)	114.9(5)	116.1(5)
S(2)-C(3)-C(4)	103.7(4)	103.3(4)
S(2)-C(3)-C(7)	110.2(4)	109.5(4)
C(4)-C(3)-C(7)	116.1(5)	116.3(5)
C(3)-C(4)-C(5)	109.1(5)	110.5(5)
C(3)-C(4)-C(8)	113.0(5)	111.2(5)
C(5)-C(4)-C(8)	109.5(6)	108.5(5)
C(4)-C(8)-N	177.3(7)	176.9(7)
C(4)-C(5)-P	106.7(5)	105.5(4)
C(1)-C(61)-C(62)	121.9(6)	122.8(6)
C(1)-C(61)-C(66)	119.0(6)	119.4(5)
C(61)-C(62)-C(63)	119.5(7)	121.0(6)
C(62)-C(63)-C(64)	121.1(8)	120.8(7)
C(63)-C(64)-C(65)	119.8(8)	118.9(8)
C(64)-C(65)-C(66)	120.2(7)	121.1(7)
C(65)-C(66)-C(61)	120.4(6)	120.4(6)
C(66)-C(61)-C(62)	119.0(6)	117.8(6)
C(3)-C(7)-C(71)	107.7(6)	110.2(6)
C(3)-C(7)-C(72)	111.9(6)	108.5(6)
C(3)-C(7)-C(73)	111.6(6)	110.0(6)
C(71)-C(7)-C(72)	109.7(6)	111.2(7)
C(71)-C(7)-C(73)	108.1(7)	108.6(7)
C(72)-C(7)-C(73)	107.9(7)	108.4(7)

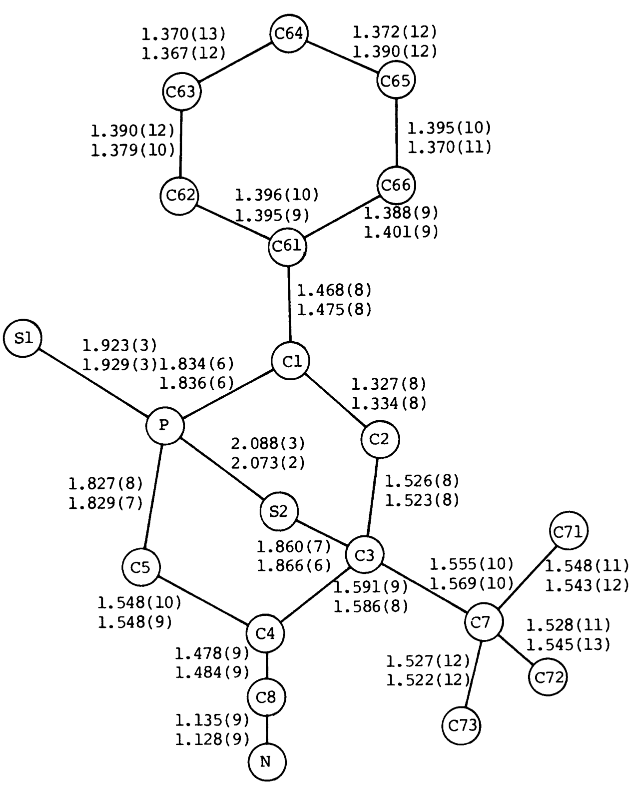


Fig. 1. Atom numbering and bond distances (Å) of molecule A (upper values) and molecule B (lower values). E.s.d.'s are in parentheses.

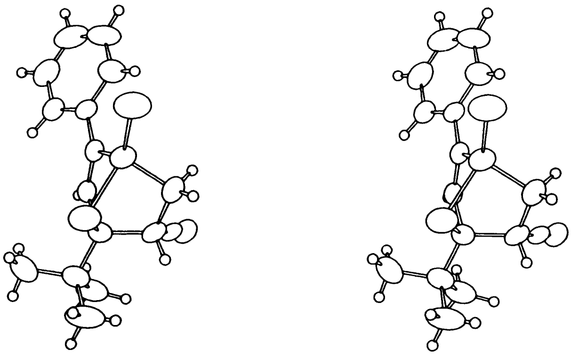


Fig. 2. Stereoscopic view of the molecule A. The thermal ellipsoids for non-H atoms are at the 50 % probability level, while H atoms are represented by spheres of arbitrary radius.

Table 3. Bond angle of bridged S atom in several bicyclo compounds

Bond	Angle ϕ/°	Skeleton of compound	Reference
P-S-C	82.5(2)a)	7-Thia-1-phosphabicyclo[2.2.1]hept-2-ene	This work
C-S-C	81.4(1)	7-Thiabicyclo[2.2.1]hept-5-en-2-one	9
C-S-C	81.2(1)	7-Thiabicyclo[2.2.1]hepta-2,5-diene	10
C-S-C	84.9	8-Thia-2-azabicyclo[3.2.1]oct-3-ene	11
C-S-C	94.6(6)	9-Thiabicyclo[3.3.1]nonane-2,6-dione	12

a) Average value of molecule A and molecule B.

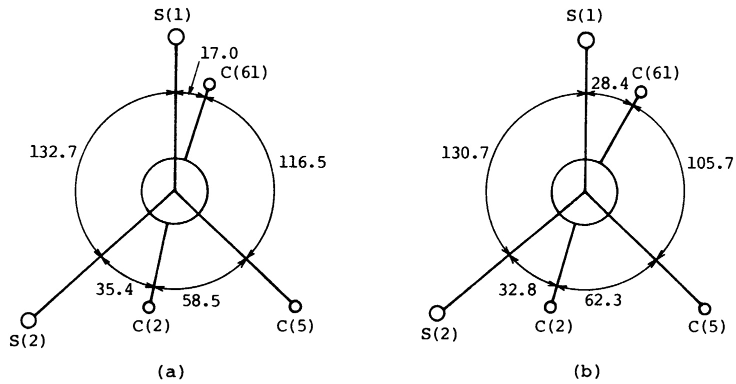


Fig. 3. Newman projections along the P–C(1) bond with torsion angles (°). (a) Molecule A, and (b) molecule B.

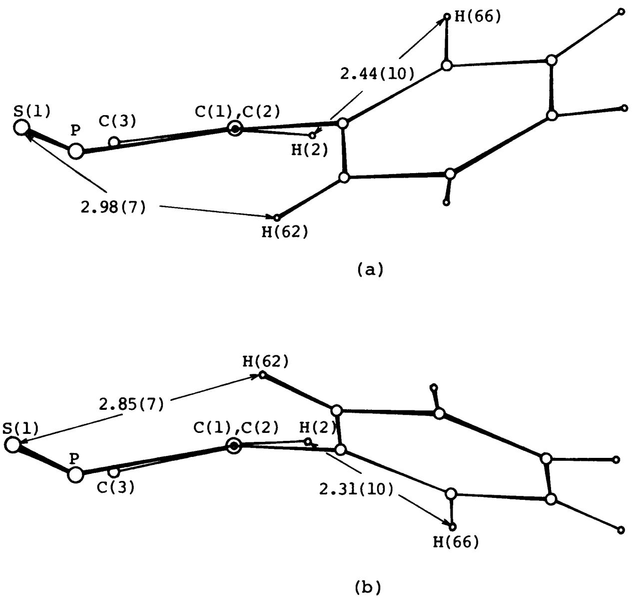


Fig. 4. Projections of several atoms along the C(1)=C(2) bond with several atomic distances (Å). (a) Molecule A, and (b) molecule B.

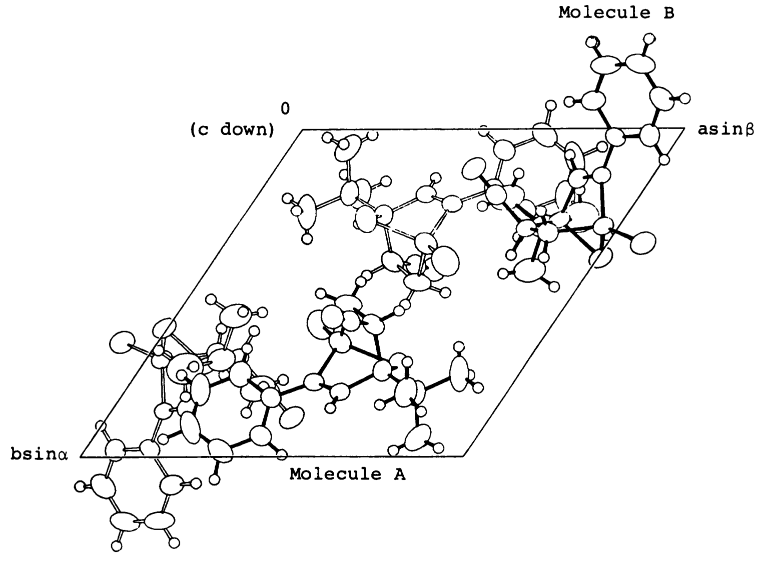


Fig. 5. The crystal structure projected along the *c* axis. The thermal ellipsoids for non-H atoms are at the 50% probability level, while H atoms are represented by spheres of arbitrary radius.

butyl and phenyl groups. Similar effects were observed in several substituted ethylenes, in which the ethylenic C=C double bonds were twisted owing to the steric interactions.13) The dihedral angles between the abovementioned plane and phenyl group, that composes a faily good plane, are 26.9° and −29.6° for molecule A and molecule B, respectively.6) Figure 5 shows the packing arrangement of the molecules in a unit cell.8) There is no particular interaction, for example hydrogen bonding between molecules, since all the intermolecular atomic distances are considered to be van der Waals contacts.

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