Molecular Structures of Adducts of Benzoyl Isothiocyanate and Hydrazones Determined by the X-Ray Diffraction Method

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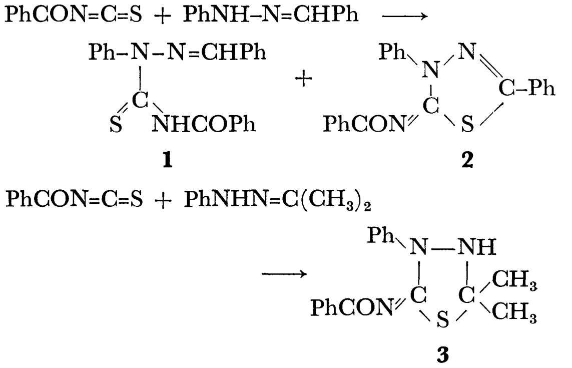
X-Ray diffraction analysis was used to establish the molecular structures of some adducts of benzoyl isothiocyanate with hydrazones: benzaldehyde 4-benzoyl-2-phenylthiosemicarbazone (**1**), 2-benzoylimino-3,5-diphenyl-2,3-dihydro-1,3,4-thiadiazole (**2**), and 5-benzoylimino-2,2-dimethyl-4-phenyl-1,3,4-thiadiazolidine (**3**). In adducts **2** and **3**, a strong intramolecular interaction between sulfur and carbonyl oxygen atoms has been found. The S···O distance is 2.56 Å for **2** and 2.76 Å for **3**, and the oxygen atom lies approximately in the plane defined by the sulfur atom and the two carbon atoms bonded to the sulfur atom. The absence of a characteristic absorption due to a carbonyl group in the IR spectra of **2** and **3** reflects the intramolecular interaction. The crystal of **1** is triclinic, space group P$\bar{1}$, with $a=12.041$, $b=8.414$, $c=11.298$ Å, $\alpha=116.13$, $\beta=103.39$, $\gamma=103.27°$; that of **2** is monoclinic, space group P2_1/c, with $a=20.842$, $b=3.977$, $c=21.120$ Å, $\beta=103.55°$; and that of **3** is monoclinic, space group P2_1, with $a=12.559$, $b=6.910$, $c=10.283$ Å, $\beta=115.46°$. The structure has been refined by the block-diagonal least-squares method to $R=0.089$ with 2508 reflections for **1**, to $R=0.088$ with 1872 reflections for **2**, and to $R=0.098$ with 1031 reflections for **3**.

Previously Yamamoto *et al.* reported the reaction of benzoyl isothiocyanate with hydrazones and discussed the reaction mechanism; the reaction of benzoyl isothiocyanate with the derivatives of hydrazone yielded seven-membered ring compounds whose structures were assigned on the basis of their spectroscopic results.[1] In view of the novelty of their structures we have reexamined the molecular structures of the products by the X-ray diffraction method. We now report investigations leading to a revised structure **3**, together with establishment of the structures **1** and **2**.



Experimental

The space group and preliminary unit cell constants for each crystal were determined by oscillation and Weissenberg photographs. The accurate cell constants for each crystal were determined by the least-squares method using at least 39 reflections measured on a four-circle diffractometer. The density of each crystal was obtained by the flotation method.

Crystal Data. (a) Product (**1**), $C_{21}H_{17}N_3OS$: $M=359.4$, triclinic, P$\bar{1}$, $a=12.041$, $b=8.414$, $c=11.298$ Å, $\alpha=116.13$, $\beta=103.39$, $\gamma=103.27°$, $V=924.9$ Å^3, $Z=2$, $D_m=1.30$ g·cm^{-3}, $D_x=1.29$ g·cm^{-3}. (b) Product (**2**), $C_{21}H_{15}N_3OS$: $M=357.4$, monoclinic, P2_1/c, $a=20.842$, $b=3.977$, $c=21.120$ Å, $\beta=103.55°$, $V=1701.9$ Å^3, $Z=4$, $D_m=1.40$ g·cm^{-3}, $D_x=1.39$ g·cm^{-3}. (c) Product (**3**), $C_{17}H_{17}N_3OS$: $M=311.4$, monoclinic, P2_1, $a=12.559$, $b=6.910$, $c=10.283$ Å, $\beta=115.46°$, $V=805.7$ Å^3, $Z=2$, $D_m=1.28$ g·cm^{-3}, $D_x=1.28$ g·cm^{-3}.

Intensity Measurements of 1 and 3. The intensities were measured on a Rigaku tape-controlled four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation. The approximate crystal size used for these intensity measurements was $0.1\times0.1\times0.4$ mm for **1** and $0.3\times0.06\times0.1$ mm for **3**. The θ-2θ scan technique was employed with a scan speed of 4°/min for 2θ. The backgrounds were counted for 6 s at both sides of the scan range. The intensities of 2677 independent reflections were measured in the range $0<\sin\theta/\lambda<0.56$ for **1**, and those of 1031 independent reflections in the range $0<\sin\theta/\lambda<0.53$ for **3**.

Intensity Measurement of 2. The intensities of reflections with $\sin\theta/\lambda$ less than 0.53 were measured from a crystal with dimensions of $0.5\times0.1\times0.05$ mm with Ni-filtered Cu $K\alpha$ radiation. The stationary-crystal stationary-counter technique was applied using a Toshiba four-circle diffractometer. A background for each reflection was taken from a curve which was determined by a plot of the backgrounds measured at several values of 2θ against their 2θ values. A total of 2132 reflections were measured, of which 1872 were recorded as non-zero intensity.

The intensities were corrected for the Lorentz and polarization factors, but were not corrected for absorption.

Structure Determination of 1. The structure was solved by an application of the direct method.[2] An E map based on the phases of 207 reflections revealed the positions of all non-hydrogen atoms. The structure was refined by the block-diagonal least-squares method,[3] initially with isotropic temperature factors and subsequently with anisotropic ones. The atomic species were assigned by inspection of temperature factors as well as interatomic distances and angles. All hydrogen atoms were revealed on a difference Fourier synthesis. Final refinement, by including these hydrogen atoms with isotropic temperature factors, reduced the R value to 0.089 for 2508 non-zero reflections. In the final refinement, the following weighting scheme was adopted: $w=0.0$ for $F_o=0$, $w=1.0$ for $0\leq F_o<10$, and $w=[1.0+0.15(F_o-10)]^{-1}$ for $10<F_o$. The final atomic coordinates are given in Table 1.

Structure Determination of 2. The structure was solved by the heavy atom method, and refined by the block-diagonal least-squares method in the same way as for **1**. Including the hydrogen atoms revealed on a difference Fourier synthesis,

Table 1. Final atomic coordinates of **1** with estimated standard deviations in parentheses

	x	y	z
S(1)	−0.0227(1)	−0.3150(2)	−0.0918(1)
C(2)	0.3805(4)	0.1129(7)	0.3058(5)
N(3)	0.2680(3)	0.0038(6)	0.2621(4)
N(4)	0.1941(3)	−0.0879(6)	0.1184(4)
C(5)	0.0734(4)	−0.1952(7)	0.0758(5)
N(6)	0.0451(3)	−0.1945(6)	0.1873(4)
C(7)	−0.0655(4)	−0.2836(7)	0.1911(5)
O(8)	−0.1644(3)	−0.3588(5)	0.0926(4)
C(9)	−0.0514(5)	−0.2747(7)	0.3284(5)
C(10)	0.0574(5)	−0.2598(8)	0.4157(6)
C(11)	0.0644(6)	−0.2543(10)	0.5439(7)
C(12)	−0.0356(7)	−0.2590(9)	0.5820(7)
C(13)	−0.1451(7)	−0.2757(9)	0.4945(7)
C(14)	−0.1513(5)	−0.2837(8)	0.3678(6)
C(15)	0.2469(4)	−0.0788(7)	0.0179(5)
C(16)	0.2511(5)	0.0661(7)	−0.0098(6)
C(17)	0.3102(5)	0.0792(8)	−0.0988(6)
C(18)	0.3597(5)	−0.0530(9)	−0.1607(6)
C(19)	0.3538(5)	−0.1982(8)	−0.1331(6)
C(20)	0.2962(5)	−0.2129(7)	−0.0437(6)
C(21)	0.4628(4)	0.2117(7)	0.4559(5)
C(22)	0.5795(5)	0.3424(8)	0.4994(6)
C(23)	0.6618(5)	0.4371(9)	0.6391(6)
C(24)	0.6305(6)	0.4005(8)	0.7366(6)
C(25)	0.5133(6)	0.2729(9)	0.6948(6)
C(26)	0.4307(5)	0.1746(8)	0.5542(6)
H(C2)	0.414(6)	0.166(9)	0.254(7)
H(N6)	0.106(6)	−0.129(9)	0.268(7)
H(C10)	0.141(6)	−0.250(9)	0.390(6)
H(C11)	0.159(7)	−0.229(10)	0.611(8)
H(C12)	−0.024(7)	−0.234(10)	0.680(8)
H(C13)	−0.210(7)	−0.275(11)	0.533(8)
H(C14)	−0.228(7)	−0.318(10)	0.296(7)
H(C16)	0.225(5)	0.171(8)	0.047(6)
H(C17)	0.296(6)	0.171(9)	−0.135(7)
H(C18)	0.404(6)	−0.027(10)	−0.225(7)
H(C19)	0.394(5)	−0.298(8)	−0.180(6)
H(C20)	0.289(6)	−0.329(9)	−0.028(7)
H(C22)	0.605(5)	0.385(8)	0.427(6)
H(C23)	0.755(6)	0.532(9)	0.664(7)
H(C24)	0.702(6)	0.480(9)	0.843(7)
H(C25)	0.482(6)	0.235(9)	0.760(7)
H(C26)	0.339(6)	0.068(9)	0.518(7)

Table 2. Final atomic coordinates of **2** with estimated standard deviations in parentheses

	x	y	z
S(1)	0.1462(1)	0.0855(4)	0.2217(1)
C(2)	0.1017(2)	−0.0802(14)	0.1481(2)
N(3)	0.1369(2)	−0.2005(12)	0.1097(2)
N(4)	0.2033(2)	−0.1599(12)	0.1384(2)
C(5)	0.2191(2)	−0.0143(14)	0.1978(2)
N(6)	0.2799(2)	0.0471(12)	0.2299(2)
C(7)	0.2870(3)	0.2083(16)	0.2890(2)
O(8)	0.2413(2)	0.2832(13)	0.3141(2)
C(9)	0.3571(3)	0.2902(15)	0.3210(2)
C(10)	0.4086(3)	0.2089(16)	0.2926(3)
C(11)	0.4727(3)	0.2828(18)	0.3252(3)
C(12)	0.4856(3)	0.4326(19)	0.3858(3)
C(13)	0.4344(3)	0.5173(18)	0.4137(3)
C(14)	0.3694(3)	0.4447(16)	0.3815(3)
C(15)	0.2480(2)	−0.2676(14)	0.0998(2)
C(16)	0.2266(3)	−0.2612(16)	0.0331(3)
C(17)	0.2676(3)	−0.3732(18)	−0.0055(3)
C(18)	0.3302(3)	−0.4843(18)	0.0226(3)
C(19)	0.3510(3)	−0.4937(18)	0.0899(3)
C(20)	0.3107(3)	−0.3857(16)	0.1299(3)
C(21)	0.0294(2)	−0.0945(14)	0.1312(2)
C(22)	−0.0064(3)	0.0244(16)	0.1743(3)
C(23)	−0.0746(3)	−0.0026(16)	0.1586(3)
C(24)	−0.1069(3)	−0.1427(17)	0.1009(3)
C(25)	−0.0719(3)	−0.2606(16)	0.0571(3)
C(26)	−0.0035(3)	−0.2395(15)	0.0724(3)
H(C10)	0.399(3)	0.111(20)	0.248(3)
H(C11)	0.512(3)	0.200(16)	0.300(3)
H(C12)	0.536(3)	0.466(17)	0.413(3)
H(C13)	0.443(3)	0.638(19)	0.460(3)
H(C14)	0.330(3)	0.514(17)	0.403(3)
H(C16)	0.179(3)	−0.167(16)	0.010(3)
H(C17)	0.250(3)	−0.367(17)	−0.057(3)
H(C18)	0.360(3)	−0.571(17)	−0.009(3)
H(C19)	0.399(3)	−0.571(16)	0.114(3)
H(C20)	0.325(3)	−0.358(16)	0.182(3)
H(C22)	0.016(3)	0.143(15)	0.216(3)
H(C23)	−0.100(3)	0.101(15)	0.190(3)
H(C24)	−0.155(3)	−0.168(16)	0.093(3)
H(C25)	−0.099(3)	−0.381(20)	0.013(3)
H(C26)	0.022(3)	−0.289(16)	0.038(3)

final refinement was carried out using the following weighting scheme: $w=0.0$ for $F_o=0$, $w=1.0$ for $0<F_o\leq 24$, and $w=[1.0+0.67(F_o-24)]^{-1}$ for $24<F_o$. The final R value was 0.088 for 1872 non-zero reflections. The final atomic coordinates are given in Table 2.

*Structure Determination of **3**.* The structure was solved by the direct method[2] followed by successive Fourier synthesis, and refined in the same way as for **1**. The final refinement, including the contribution of the hydrogen atoms and anomalous scattering of sulfur atom, reduced R to 0.098 for 1031 reflections ($R=0.088$ for non-zero reflections). The weighting scheme adopted in the final refinement was: $w=0.2$, for $F_o=0$, $w=1.0$ for $0<F_o\leq 24$, and $w=[1.0+0.43(F_o-24)]^{-1}$ for $24<F_o$. The final atomic coordinates are given in Table 3.

The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[4] The temperature factors and the list of observed and calculated structure factors for each compound are kept as Document No. 7924 at the Chemical Society of Japan.

TABLE 3. FINAL ATOMIC COORDINATES OF **3** WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	x	y	z
S (1)	0.4879(2)	0.0000(7)	0.5865(3)
C (2)	0.5000(9)	0.0443(19)	0.7734(9)
N (3)	0.4556(7)	0.2379(15)	0.7660(8)
N (4)	0.3601(7)	0.2645(17)	0.6260(9)
C (5)	0.3662(9)	0.1551(17)	0.5199(11)
N (6)	0.2831(7)	0.1743(16)	0.3844(8)
C (7)	0.3038(9)	0.0809(18)	0.2800(11)
O (8)	0.4002(6)	0.0286(18)	0.2907(8)
C (9)	0.1953(9)	0.0673(17)	0.1391(9)
C (10)	0.0843(10)	0.0791(25)	0.1353(11)
C (11)	−0.0144(13)	0.0611(32)	0.0022(17)
C (12)	0.0003(13)	0.0300(32)	−0.1212(13)
C (13)	0.1106(14)	0.0188(27)	−0.1153(13)
C (14)	0.2132(11)	0.0340(23)	0.0167(11)
C (15)	0.2720(9)	0.4015(19)	0.6114(10)
C (16)	0.2201(10)	0.3900(24)	0.7097(12)
C (17)	0.1311(10)	0.5195(34)	0.6896(14)
C (18)	0.0991(12)	0.6609(27)	0.5886(14)
C (19)	0.1528(13)	0.6727(28)	0.4975(13)
C (20)	0.2380(10)	0.5471(23)	0.5070(12)
C (21)	0.6335(10)	0.0428(26)	0.8798(12)
C (22)	0.4280(11)	−0.1060(21)	0.8062(12)
H (N3)	0.508(12)	0.330(24)	0.760(15)
H (C10)	0.077(11)	0.116(23)	0.230(14)
H (C11)	−0.100(10)	0.073(21)	−0.006(13)
H (C12)	−0.071(12)	0.006(29)	−0.220(15)
H (C13)	0.128(11)	0.006(27)	−0.207(14)
H (C14)	0.286(12)	−0.042(24)	0.030(15)
H (C16)	0.243(11)	0.279(25)	0.781(14)
H (C17)	0.093(12)	0.490(29)	0.766(16)
H (C18)	0.039(10)	0.763(21)	0.584(12)
H (C19)	0.132(12)	0.779(26)	0.422(15)
H (C20)	0.281(10)	0.533(23)	0.430(12)
H (C21a)	0.649(10)	−0.093(22)	0.906(13)
H (C21b)	0.626(9)	0.114(19)	0.941(12)
H (C21c)	0.674(11)	0.052(23)	0.829(14)
H (C22a)	0.455(12)	−0.258(24)	0.799(15)
H (C22b)	0.338(9)	−0.073(18)	0.731(11)
H (C22c)	0.440(9)	−0.087(18)	0.901(11)

TABLE 4. SELECTED BOND LENGTHS (l/Å) AND ANGLES (φ/°) FOR NON-HYDROGEN ATOMS

(a) Adduct **1**			
S (1)–C (5)	1.646(6)	C (2)–N (3)	1.281(8)
C (2)–C (21)	1.467(8)	N (3)–N (4)	1.391(7)
N (4)–C (5)	1.361(8)	N (4)–C (15)	1.445(7)
C (5)–N (6)	1.376(8)	N (6)–C (7)	1.390(8)
C (7)–O (8)	1.216(7)	C (7)–C (9)	1.487(8)
N (3)–C (2)–C (21)	120.9(5)	C (2)–N (3)–N (4)	118.6(5)
N (3)–N (4)–C (5)	117.5(5)	N (3)–N (4)–C (15)	120.5(5)
C (5)–N (4)–C (15)	121.8(5)	S (1)–C (5)–N (4)	122.2(4)
S (1)–C (5)–N (6)	125.7(5)	N (4)–C (5)–N (6)	112.0(5)
C (5)–N (6)–C (7)	130.9(5)	N (6)–C (7)–O (8)	123.3(5)
N (6)–C (7)–C (9)	113.5(5)	O (8)–C (7)–C (9)	123.2(5)
(b) Adduct **2**			
S (1)–C (2)	1.743(6)	S (1)–C (5)	1.757(6)
C (2)–N (3)	1.305(7)	C (2)–C (21)	1.467(8)
N (3)–N (4)	1.384(7)	N (4)–C (5)	1.351(7)
N (4)–C (15)	1.437(7)	C (5)–N (6)	1.312(7)
N (6)–C (7)	1.379(8)	C (7)–O (8)	1.230(8)
C (7)–C (9)	1.495(9)	S (1)···O (8)	2.558(6)
C (2)–S (1)–C (5)	88.4(3)	S (1)–C (2)–N (3)	115.8(4)
S (1)–C (2)–C (21)	122.2(4)	N (3)–C (2)–C (21)	122.0(5)
C (2)–N (3)–N (4)	109.6(5)	N (3)–N (4)–C (5)	117.2(5)
N (3)–N (4)–C (15)	115.5(4)	C (5)–N (4)–C (15)	127.2(5)
S (1)–C (5)–N (4)	109.0(4)	S (1)–C (5)–N (6)	127.1(4)
N (4)–C (5)–N (6)	123.8(5)	C (5)–N (6)–C (7)	116.2(5)
N (6)–C (7)–O (8)	125.0(6)	N (6)–C (7)–C (9)	113.4(5)
O (8)–C (7)–C (9)	121.6(6)	O (8)··· S (1)–C (2)	162.2(4)
O (8)··· S (1)–C (5)	73.8(4)		
(c) Adduct **3**			
S (1)–C (2)	1.89(1)	S (1)–C (5)	1.75(1)
C (2)–N (3)	1.44(2)	C (2)–C (21)	1.56(2)
C (2)–C (22)	1.51(2)	N (3)–N (4)	1.44(2)
N (4)–C (5)	1.36(2)	N (4)–C (15)	1.41(2)
C (5)–N (6)	1.34(2)	N (6)–C (7)	1.37(2)
C (7)–O (8)	1.22(2)	C (7)–C (9)	1.51(2)
S (1)···O (8)	2.76(1)		
C (2)–S (1)–C (5)	89(1)	S (1)–C (2)–N (3)	104(1)
S (1)–C (2)–C (21)	108(1)	S (1)–C (2)–C (22)	109(1)
N (3)–C (2)–C (21)	109(1)	N (3)–C (2)–C (22)	113(1)
C (21)–C (2)–C (22)	114(1)	C (2)–N (3)–N (4)	108(1)
N (3)–N (4)–C (5)	115(1)	N (3)–N (4)–C (15)	118(1)
C (5)–N (4)–C (15)	127(1)	S (1)–C (5)–N (4)	112(1)
S (1)–C (5)–N (6)	129(1)	N (4)–C (5)–N (6)	119(1)
C (5)–N (6)–C (7)	116(1)	N (6)–C (7)–O (8)	126(1)
N (6)–C (7)–C (9)	113(1)	O (8)–C (7)–C (9)	121(1)
O (8)··· S (1)–C (2)	158(1)	O (8)··· S (1)–C (5)	70(1)

Results and Discussion

The present X-ray analysis has determined the molecular structures of the adducts unambiguously, showing the benzoyl isothiocyanate adducts with benzaldehyde phenylhydrazone to be benzaldehyde 4-benzoyl-2-phenylthiosemicarbazone (**1**) and 2-benzoylimino-3,5-diphenyl-2,3-dihydro-1,3,4-thiadiazole (**2**), and that with acetone phenylhydrazone to be 5-benzoylimino-2,2-dimethyl-4-phenyl-1,3,4-thiadiazolidine (**3**). Thus the structural formula (16a) which was given in Ref. 1 should be revised to **3**. The molecular structures and the numbering scheme used in the present paper are shown in Fig. 1, and the crystal structure of **3** in Fig. 2. Selected bond lengths and angles are given in Table 4, and the equations of the least-squares planes, deviations of atoms from each plane, and selected torsion angles in Table 5. The molecules of **2** are stacked along the b axis, with interplanar distances of about 3.6 Å. Except for the intermolecular hydrogen bond in the crystal of **3**, there is neither an intermolecular hydrogen bond nor any abnormally short intermolecular contact in the crystals of **1** and **2**.

*Molecular Structure of **1**.* The S(1)–C(5) length of 1.646 Å is reasonable, compared with the thione bond lengths observed in various compounds, although these lengths differ from compound to compound.6) The distribution of the bond lengths among the C(2), N(3), N(4), C(5), and C(7) atoms and the fact that these

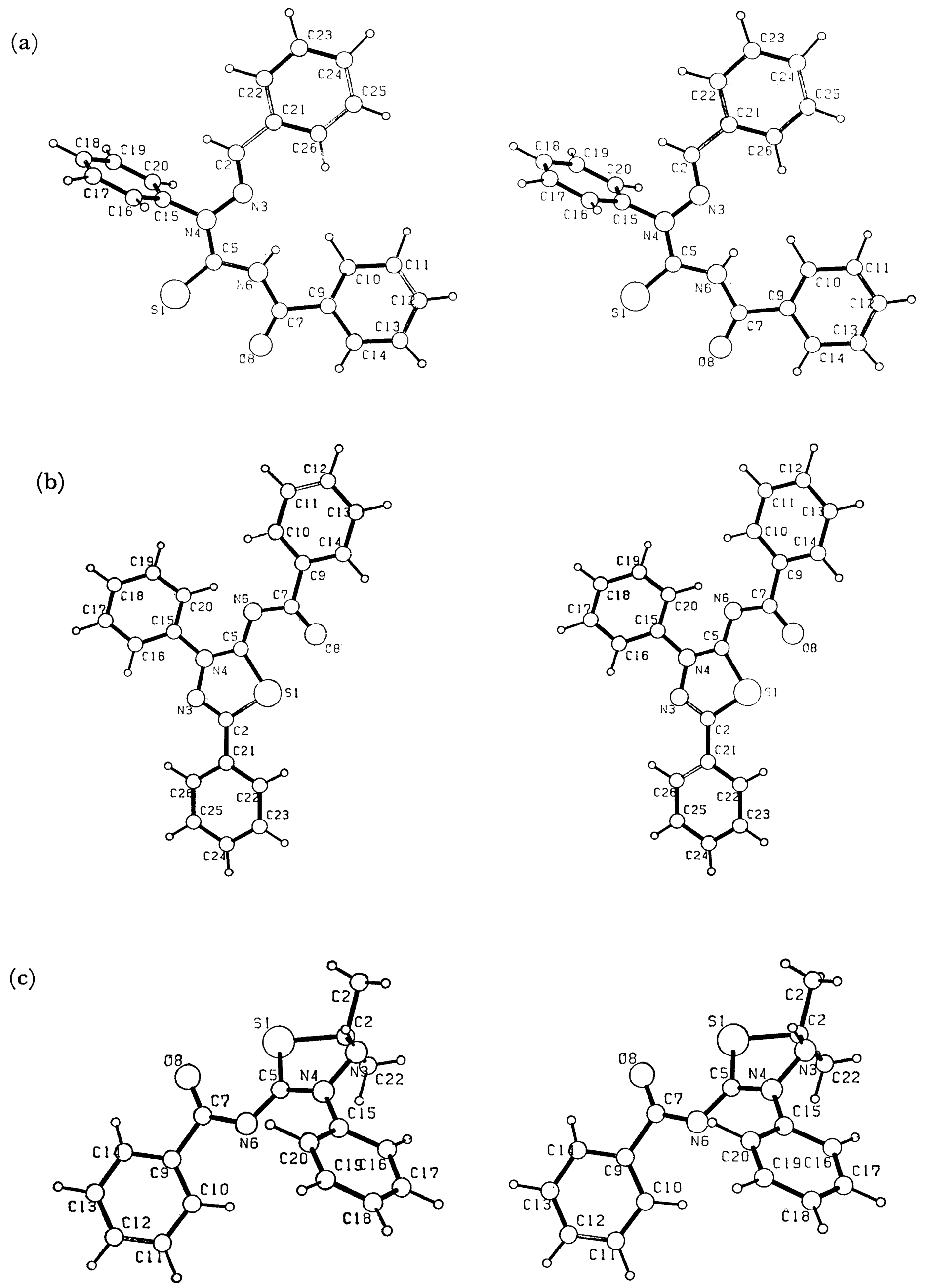


Fig. 1. Molecular structures and numbering schemes of (a) adduct **1**, (b) adduct **2**, and (c) adduct **3**.

atoms are nearly coplanar suggest appreciable delocalization of π electrons.

*Molecular Structures of **2** and **3** and S···O Interaction.* The benzoylimino group, the thiadiazoline ring, and the phenyl group of C(21)–C(26) in **2** are substantially coplanar. The geometry and the bond lengths of these groups indicate that a conjugated system exists among these groups. The five-membered ring of **3** has an envelope conformation with the C(2) atom deviating significantly from the plane through the S(1), N(3), N(4), and C(5) atoms; its conjugated system is disrupted by the C(2) and N(3) atoms, as expected from structural formula **3**.

The noteworthy feature of the molecular structures of **2** and **3** is the intramolecular S···O interaction; the distance between these atoms is 2.56 Å for **2** and 2.76 Å for **3**, which is significantly shorter than the sum of the van der Waals radii of the atoms. The oxygen atom of **3**, as well as that of **2**, lies approximately in the plane defined by S(1), C(2), and C(5) atoms. In the case of **3**, twists occur around the C(5)–N(6) double bond by 10° and the N(6)–C(7) bond by 21° such that the oxygen atom lies in the plane. Otherwise the deviation of the oxygen atom from the plane amounts to 0.7 Å, since the C(5)–N(6) bond deviates from the plane. The length of the intermolecular hydrogen bond between

Table 5. Least-squares planes, deviations of atoms from each plane, (d/Å) and selected torsion angles (φ/°)

(a) Adduct **1**

(I) Plane through the atoms of S(1), N(4), C(5), and N(6) $0.534X-0.829Y-0.164Z=2.148$

S(1)	−0.004	N(4)	−0.004
C(5)	0.011	N(6)	−0.004
N(3)[a]	−0.023	C(7)[a]	0.004
O(8)[a]	0.231	C(15)[a]	−0.090

(II) Plane through the atoms of N(6), C(7), O(8), and C(9) $0.490X-0.791Y-0.366Z=1.679$

N(6)	0.002	C(7)	−0.006
O(8)	0.002	C(9)	0.002
S(1)[a]	−0.543	C(5)[a]	−0.190

The atoms of each benzene ring are coplanar, with r.m.s. of deviations being about 0.01 Å. The dihedral angle between the plane (I) and the benzene ring of C(15)–C(20) is 89.2°and that between the plane (II) and the benzene ring of C(9)–C(14) is 26.3.°

(III) Torsion angles

C(21)–C(2)–N(3)–N(4)	−179.4
N(3)–N(4)–C(5)–N(6)	− 0.4
N(4)–C(5)–N(6)–C(7)	180.0
C(5)–N(6)–C(7)–O(8)	− 11.5
N(6)–C(7)–C(9)–C(10)	− 26.8

(b) Adduct **2**

(I) Plane through all non-hydrogen atoms except the atoms of C(15)–C(20)
$0.056X+0.893Y-0.446Z=-1.590$

S(1)	−0.028	C(2)	0.026
N(3)	0.002	N(4)	−0.047
C(5)	−0.072	N(6)	−0.087
C(7)	−0.063	O(8)	−0.087
C(9)	0.007	C(10)	0.045
C(11)	0.075	C(12)	0.050
C(13)	0.028	C(14)	−0.001
C(21)	0.051	C(22)	0.026
C(23)	−0.001	C(24)	0.008
C(25)	0.043	C(26)	0.053

The atoms of each of two six-membered and five-membered rings are coplanar, with the r.m.s. deviation being less than 0.01 Å. The dihedral angle between the above plane and the plane defined by the atoms of C(15)–C(20) is 31.3.°

(c) Adduct **3**

(I) Plane through the atoms of S(1), N(3), N(4), and C(5) $0.687X+0.702Y-0.188Z=1.415$

S(1)	0.01	N(3)	−0.01
N(4)	0.02	C(5)	−0.01
C(2)[a]	0.58	C(21)[a]	−0.06
C(22)[a]	2.09	N(6)[a]	−0.04
C(15)[a]	0.04		

The r.m.s. of the deviations of the atoms of benzene ring is about 0.01 Å.

(II) Torsion angles

C(5)–S(1)–C(2)–N(3)	−30.3
S(1)–C(2)–N(3)–N(4)	36.7
C(2)–N(3)–N(4)–C(5)	−27.9
N(3)–N(4)–C(5)–S(1)	3.0
S(1)–C(5)–N(6)–C(7)	−10.1
C(5)–N(6)–C(7)–O(8)	−21.1
N(6)–C(7)–C(9)–C(10)	−23.0
N(3)–N(4)–C(15)–C(16)	−50.5

[a] Not included in the least-squares calculations.

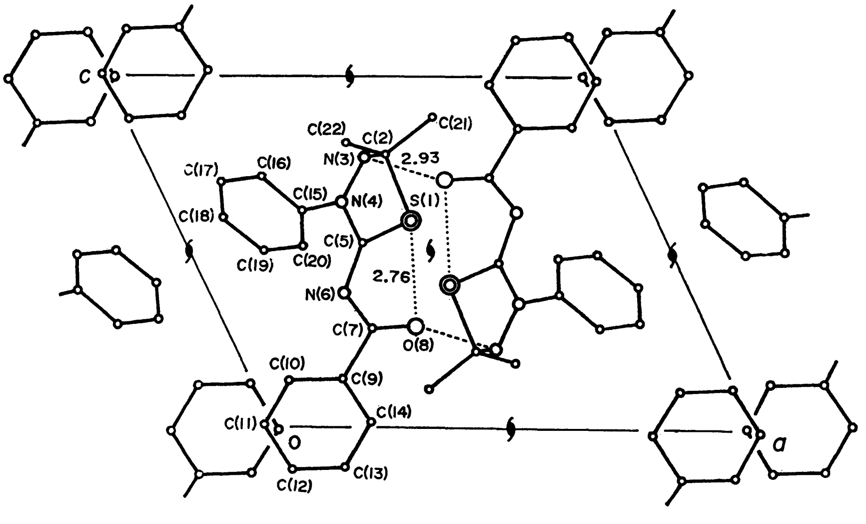


Fig. 2. Crystal structure of **3** viewed along the b axis. Broken lines indicate intermolecular hydrogen bond, and dotted lines S···O interaction (see text). Hydrogen atoms are omitted from the figure for the sake of clarity.

the N(3) and O(8) atoms is lengthened by the twists. A similar geometrical feature, where the oxygen atom lies in the plane defined by the sulfur atom and two adjacent atoms bonded to the sulfur atom, has been reported in other compounds.[7–11] The absence of a characteristic absorption due to C=O stretching in the IR spectra of **2** and **3** should be associated with the S···O interaction.[12]

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