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The Crystal and Molecular Structures of Dithia[4.3](6,9)(6′,9′)-purinophane, Dithia[4.4](6,9)(6′,9′)purinophane, and Dithia[3.3](6,9)(9′,6′)purinophane

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Molecular structures of three purinophanes, dithia[4.3](6,9)(6′,9′)purinophane (**1**), dithia[4.4](6,9)(6′,9′)-purinophane (**2**), and dithia[3.3](6,9)(9′,6′)purinophane (**3**), have been determined by means of X-ray diffraction. **1**: monoclinic, space group $P2_1/n$, a=10.561(1), b=16.674(3), c=9.136(1) Å, β=90.29(1)°, V=1608.8(4) Å^3, D_c=1.529 g cm^{-3} for Z=4. **2**: monoclinic, space group $P2_1/n$, a=10.870(2), b=17.058(2), c=9,289(1) Å, β=94.15(1)°, V=1717.9(4) Å^3, D_c=1.487 g cm^{-3} for Z=4. **3**: monoclinic, space group $P2_1/n$, a=8.068(1), b=27.841(2), c=6.913(1) Å, β=111.0(1)°, V=1449.8(2) Å^3, D_c=1.631 g cm^{-3} for Z=4. All structures were solved by the direct method, and refined anisotropically by the least-squares procedure. Final R values are 0.045, 0.053, and 0.050 for **1**, **2**, and **3**, respectively. Molecular structures of **1** and **2** take very similar crossed form, whereas that of **3** reveals a different crossed form.

Previously, we reported syntheses and spectral properties of a few [*m.n*](6,9)purinophanes, in which two purine rings are intramolecularly stacked with each other, for studying relationship between such a base-to-base stacking structure and remarkable hypochromic effect (ca. 40%) in the electronic spectra of DNA.[1,2] In general, although two conformational isomers are theoretically expected for the stacking structures of all purinophanes, their structures can be presumed on the basis of chemical shifts of purine ring protons which would be shifted to higher field by magnetic anisotropy of faced another purine ring. The preferential formation of less overlapped conformer to decrease π-electron repulsive interaction was similarly proposed for all of the double-bridged purinophanes according to NMR assignment. For the confirmation of NMR determined structure and the structural relationship of hypochromism in electronic spectra, molecular structures of dithia[4.3](6,9)(6′,9′)-purinophane (**1**), dithia[4.4](6,9)(6′,9′)purinophane (**2**), and dithia[3.3](6,9)(9′,6′)purinophane (**3**) have been determined by means of X-ray diffraction.

Experimental

Crystal data: **1**, $C_{15}H_{14}N_8S_2$, M 370.45, monoclinic, space group $P2_1/n$, a=10.561(1), b=16.674(3), c=9.136(1) Å, β=90.29(1)°, V=1608.8(4) Å^3, D_c=1.529 g cm^{-3} for Z=4; **2**, $C_{16}H_{16}N_8S_2$, M 384.47, monoclinic, space group $P2_1/n$, a=10.870(2), b=17.058(2), c=9.289(1) Å, β=94.15(1)°, V=1717.9(4) Å^3, D_c=1.487 g cm^{-3} for Z=4; **3**, $C_{14}H_{12}N_8S_2$, M 356.43, monoclinic, space group $P2_1/n$, a=8.068(1), b=27.841(2), c=6.913(1) Å, β=111.0(1)°, V=1449.8(2) Å^3, D_c=1.631 g cm^{-3} for Z=4.

Colorless prismatic crystals with approximate dimensions of 0.25×0.20×0.20 (**1**), 0.25×0.20×0.10 (**2**), and 0.10×0.10×0.10 mm (**3**) were used. X-Ray experiments were carried out on a Rigaku automated, four-circle diffractometer combined with a rotating-anode X-ray generator at the Crystallographic Research Center, Institute for Protein Research, Osaka University. Nickel-filtered Cu $K\alpha$ radiation (λ=1.5418 Å) was used.

Intensity data of each crystal were collected by the θ-2θ scan technique at a 2θ scan rate of 8° min^{-1} and scan width $\Delta 2\theta$=(2.4+0.3 tan θ)°. Backgrounds were counted for 4 s at both ends of a scan. Three standard reflections were measured after every 60 reflections to monitor the stability and orientation of the crystal, which showed no significant decay throughout the data collection. Totals of 2130 reflections out of 2394 (**1**), 2478 out of 2561 (**2**), and 1842 out of 2150 (**3**) were observed ($|F_o|>3\sigma(F_o)$), where $\sigma(F_o)$ is the standard deviation obtained by the counting statistics of intensities. Usual Lorentz and polarization corrections were made but

Table 1. Final Atomic Parameters of Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses

1. Dithia[4.3](6,9)(6′,9′)purinophane

Atom	x	y	z	B_{eq}/Å^2
S(6)	0.60459(8)	0.06969(5)	0.09028(9)	3.3
S(6′)	0.8873(1)	0.03651(5)	0.2528(1)	4.3
N(1)	0.6908(3)	0.1116(2)	−0.1778(3)	3.5
C(2)	0.7272(4)	0.1680(2)	−0.2741(4)	3.9
N(3)	0.7245(3)	0.2475(2)	−0.2594(3)	3.7
C(4)	0.6761(3)	0.2691(2)	−0.1309(3)	2.9
C(5)	0.6268(3)	0.2176(2)	−0.0249(3)	2.7
C(6)	0.6427(3)	0.1364(2)	−0.0498(3)	2.8
N(7)	0.5850(3)	0.2603(2)	0.0962(3)	3.1
C(8)	0.6088(3)	0.3347(2)	0.0604(4)	3.4
N(9)	0.6653(3)	0.3450(2)	−0.0728(3)	3.2
N(1′)	0.8308(3)	0.1770(2)	0.3668(3)	3.5
C(2′)	0.8247(3)	0.2570(2)	0.3719(4)	3.6
N(3′)	0.8541(3)	0.3096(2)	0.2673(3)	3.2
C(4′)	0.8987(3)	0.2724(2)	0.1483(3)	2.5
C(5′)	0.9147(3)	0.1906(2)	0.1302(3)	2.6
C(6′)	0.8748(3)	0.1418(2)	0.2460(3)	3.1
N(7′)	0.9692(3)	0.1741(2)	−0.0048(3)	3.2
C(8′)	0.9817(3)	0.2455(2)	−0.0639(3)	3.2
N(9′)	0.9394(3)	0.3076(2)	0.0220(3)	3.0
C(61)	0.7057(4)	−0.0149(2)	0.0496(4)	3.5
C(62)	0.8459(4)	0.0027(2)	0.0692(4)	3.6
C(91)	0.7214(4)	0.4191(2)	−0.1296(4)	4.2
C(92)	0.8625(4)	0.4143(2)	−0.1471(4)	4.1
C(93)	0.9428(4)	0.3934(2)	−0.0129(4)	4.1

2. Dithia[4.4](6,9)(6′,9′)purinophane

Atom	x	y	z	B_{eq}/Å^2
S(6)	0.10416(6)	0.06026(4)	0.38499(6)	3.7
S(6′)	0.37646(7)	0.02478(4)	0.24613(7)	4.5
N(1)	0.1975(2)	0.09891(12)	0.6513(2)	4.0
C(2)	0.2307(3)	0.15251(16)	0.7551(3)	4.4
N(3)	0.2171(2)	0.23019(13)	0.7486(2)	4.2
C(4)	0.1638(3)	0.25336(14)	0.6230(3)	3.5
C(5)	0.1236(2)	0.20468(14)	0.5077(3)	3.4
C(6)	0.1443(2)	0.12509(13)	0.5272(3)	3.4
N(7)	0.0746(2)	0.24961(12)	0.3920(2)	3.8
C(8)	0.0854(3)	0.32123(15)	0.4383(3)	4.2
N(9)	0.1392(2)	0.32820(11)	0.5782(2)	3.9
N(1′)	0.3274(2)	0.16021(12)	0.1213(2)	4.2
C(2′)	0.3278(3)	0.23878(15)	0.1106(3)	4.3
N(3′)	0.3656(2)	0.29094(12)	0.2086(2)	3.9
C(4′)	0.4073(2)	0.25687(12)	0.3327(2)	3.0
C(5′)	0.4116(2)	0.17662(12)	0.3605(3)	3.1
C(6′)	0.3689(2)	0.12781(14)	0.2466(3)	3.5
N(7′)	0.4664(2)	0.16306(11)	0.4974(2)	3.7
C(8′)	0.4922(3)	0.23323(13)	0.5480(3)	3.6
N(9′)	0.4589(2)	0.29266(10)	0.4518(2)	3.2
C(61)	0.2021(3)	−0.02208(13)	0.4331(3)	4.2
C(62)	0.3384(3)	−0.00534(14)	0.4242(3)	4.3
C(91)	0.1812(3)	0.40024(15)	0.6514(3)	4.5
C(92)	0.3204(3)	0.40824(15)	0.6500(3)	4.3
C(93)	0.3641(3)	0.42078(13)	0.4992(3)	4.1
C(94)	0.4812(3)	0.37698(13)	0.4708(3)	3.8

3. Dithia[3.3](6,9)(9′,6′)purinophane

Atom	x	y	z	B_{eq}/Å^2
S(6)	0.97543(15)	0.29943(4)	0.41814(17)	3.1
S(6′)	1.48414(15)	0.41425(5)	0.00341(18)	3.4
N(1)	0.9746(5)	0.39583(12)	0.3992(6)	3.1
C(2)	1.0485(6)	0.43845(15)	0.3935(7)	3.2
N(3)	1.2136(5)	0.44830(12)	0.4105(6)	2.8
C(4)	1.3123(5)	0.40855(14)	0.4446(6)	2.5
C(5)	1.2569(6)	0.36172(14)	0.4657(6)	2.6
C(6)	1.0786(6)	0.35622(15)	0.4324(6)	2.7
N(7)	1.3946(5)	0.32964(13)	0.4970(6)	3.1
C(8)	1.5250(6)	0.35637(16)	0.4904(7)	3.0
N(9)	1.4854(4)	0.40430(12)	0.4585(5)	2.5
N(1′)	1.1491(5)	0.44506(12)	−0.0877(6)	3.2
C(2′)	0.9756(6)	0.43823(16)	−0.1157(7)	3.4
N(3′)	0.8941(5)	0.39737(13)	−0.1064(6)	3.3
C(4′)	1.0037(6)	0.35985(15)	−0.0691(7)	2.9
C(5′)	1.1812(6)	0.36096(15)	−0.0501(6)	2.9
C(6′)	1.2526(6)	0.40608(15)	−0.0514(6)	2.9
N(7′)	1.2559(6)	0.31542(13)	−0.0092(6)	3.8
C(8′)	1.1249(7)	0.28887(16)	−0.0046(7)	3.8
N(9′)	0.9678(5)	0.31310(13)	−0.0387(6)	3.3
C(61)	0.7819(6)	0.30835(15)	0.1813(8)	3.4
C(62)	0.8089(7)	0.29256(16)	−0.0140(8)	3.7
C(92)	1.5295(6)	0.46095(16)	0.2024(8)	3.5
C(91)	1.5981(6)	0.44120(15)	0.4217(7)	3.1

absorption correction was ignored [μ(Cu $K\alpha$)=30.9, 29.2, and 34.0 cm^{-1} for **1**, **2**, and **3**, respectively].

Structure Solution and Refinement

The structure of each crystal was established by the direct method (*MULTAN* 78),[3] and refined anisotropically by the block-diagonal least-squares procedure (*HBLS* V).[4] Hydrogen atoms could be located on the difference Fourier map, which were included in the refinement with isotropic temperature factors. Final R values were 0.045 (R_w=0.070) for **1** and 0.053 (R_w=0.079) for **2**, and 0.050 (R_w=0.064) for **3** for observed reflections. Weighting schemes used in the final cycles of the refinements were $\{\sigma^2(F_o)-0.0071\,|F_o|+0.0017\,|F_o|^2\}^{-1}$ for **1**, $\{\sigma^2(F_o)-0.2283\,|F_o|+0.0116\,|F_o|^2\}^{-1}$ for **2**, and $\{\sigma^2(F_o)-0.0281\,|F_o|+0.0001\,|F_o|^2\}^{-1}$ for **3** for observed reflections. Atomic parameters of non-hydrogen atoms are given in Table 1 with equivalent isotropic temperature factors.**[5] Atomic scattering factors were taken from those of International Tables for X-Ray Crystallography.[6] Calculations were done on ACOS 900 and ACOS 850 computers at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Results and Discussion

Molecular Structure. Throughout the three purinophanes the corresponding bond distances and bond angles in two purine rings are respectively equal within the range of error (Table 2). Each of these is not significantly different from the corresponding bond distances and bond angles in 6-(methylthio)-purine[8] and also from that in purine in the 2:1 complex of purine and urea.[9]

The characteristic feature of molecular structures of **1** and **2** is that these purinophanes take similar crossed form as to the overlapping of two purine rings (Fig. 1,a). However, because of the shorter -$(CH_2)_3$- bridge than -S-$(CH_2)_2$-S- the upper purine ring in **1** bent slightly convex upward (Fig. 1,b). Very close inter-purine ring nonbonded atomic distances are observed between atoms located near the -$(CH_2)_3$-bridge: the closest distance is 3.081(3) Å (between the N(9) and N(9′) atoms) and the others ranging from 3.172(4) Å (between the C(4) and N(9′) atoms) to 3.490(4) Å (between the N(1) and N(7′) atoms). Two purine rings in **2** are planar, and the tilting direction of the upper purine ring relative to the lower one differs from that in **1** because of the longer -$(CH_2)_4$- bridge. All the inter-purine nonbonded distances except N(1)···N(7′) [3.520(3) Å], N(3)···C(8)[3.489(3) Å], and C(5)···C(5′)-[3.538(3) Å] are longer than 3.6 Å.

Similar to the cyclophanes and heterophanes, the pyrimidine moiety of purine rings showed a tendency to be folded slightly at the N(1)···C(5) or N(1′)···C(5′) line while the imidazole moiety at the C(4)···C(8) or C(4′)···C(8′) line. The dihedral angle between the plane defined by the N(1), C(2), C(4), and C(5) atoms and that made by the N(1), C(5), and C(6) is only 4.8(3), which is the largest in **1**. In **2**, all the dihedral angles

** Tables of anisotropic temperature factors, atomic parameters of hydrogen atoms, and observed and calculated structure factors are kept at the Chemical Society of Japan, Document No. 8816.

Table 2. Selected Bond Distances and Bond Angles with Estimated Standard Deviations in Parentheses

	1	2	3		1	2	3
Bond distance (l/Å)							
N(1)-C(2)	1.345(4)	1.358(3)	1.335(6)	N(7')-C(8')	1.314(4)	1.309(3)	1.300(7)
N(1')-C(2')	1.336(4)	1.344(3)	1.356(6)	C(8)-N(9)	1.369(4)	1.392(3)	1.372(5)
N(1)-C(6)	1.342(4)	1.329(3)	1.354(6)	C(8')-N(9')	1.375(4)	1.382(3)	1.379(7)
N(1')-C(6')	1.336(4)	1.337(3)	1.337(6)	C(6)-S(6)	1.745(3)	1.753(2)	1.773(4)
C(2)-N(3)	1.333(4)	1.334(3)	1.323(6)	C(6')-S(6')	1.761(3)	1.760(2)	1.782(4)
C(2')-N(3')	1.335(4)	1.318(3)	1.327(6)	S(6)-C(61)	1.808(3)	1.799(3)	1.829(5)
N(3)-C(4)	1.332(4)	1.325(3)	1.334(5)	S(6')-C(62)	1.821(3)	1.809(3)	
N(3')-C(4')	1.339(4)	1.340(3)	1.332(6)	S(6')-C(92)			1.832(5)
C(4)-C(5)	1.398(4)	1.400(3)	1.403(6)	C(61)-C(62)	1.518(5)	1.517(4)	1.508(7)
C(4')-C(5')	1.385(4)	1.393(3)	1.391(6)	N(9)-C(91)	1.467(4)	1.462(3)	1.454(5)
C(4)-N(9)	1.376(4)	1.363(3)	1.370(5)	N(9')-C(93)	1.467(4)		
C(4')-N(9')	1.366(4)	1.349(3)	1.366(6)	N(9')-C(94)		1.467(3)	
C(5)-C(6)	1.382(4)	1.386(3)	1.382(6)	N(9')-C(62)			1.469(6)
C(5')-C(6')	1.401(4)	1.399(3)	1.383(6)	C(91)-C(92)	1.505(5)	1.520(4)	1.519(7)
C(5)-N(7)	1.390(4)	1.394(3)	1.381(6)	C(92)-C(93)	1.528(5)	1.526(4)	
C(5')-N(7')	1.391(4)	1.384(3)	1.389(6)	C(93)-C(94)		1.515(3)	
N(7)-C(8)	1.308(4)	1.298(3)	1.303(6)				
Bond angle (ϕ/°)							
C(2)-N(1)-C(6)	117.7(3)	117.8(3)	118.2(4)	C(5')-N(7')-C(8')	103.2(3)	104.1(2)	103.1(5)
C(2')-N(1')-C(6')	119.0(3)	118.3(3)	117.2(4)	N(7)-C(8)-N(9)	115.3(3)	114.3(3)	114.6(4)
N(1)-C(2)-N(3)	128.5(3)	127.8(3)	128.9(4)	N(7')-C(8')-N(9')	114.4(3)	113.5(2)	115.1(5)
N(1')-C(2')-N(3')	128.3(3)	128.7(3)	128.1(5)	C(4)-N(9)-C(8)	105.4(3)	105.4(2)	105.6(4)
C(2)-N(3)-C(4)	111.5(3)	112.1(3)	111.2(4)	C(4')-N(9')-C(8')	105.3(3)	105.8(2)	105.1(4)
C(2')-N(3')-C(4')	111.2(3)	111.8(3)	112.1(4)	C(4)-N(9)-C(91)	127.2(3)	126.7(2)	127.8(4)
N(3)-C(4)-C(5)	126.2(3)	126.1(3)	126.7(4)	C(4')-N(9')-C(93)	127.7(3)		
N(3')-C(4')-C(5')	126.7(3)	126.2(3)	126.1(5)	C(4')-N(9')-C(94)		126.7(2)	
C(5)-C(4)-N(9)	105.5(3)	106.2(2)	105.5(4)	C(4')-N(9')-C(62)			129.1(4)
C(5')-C(4')-N(9')	106.4(3)	106.6(2)	105.9(4)	C(8)-N(9)-C(91)	126.7(3)	127.1(2)	126.3(4)
N(3)-C(4)-N(9)	128.4(3)	127.7(3)	127.8(4)	C(8')-N(9')-C(93)	127.0(3)		
N(3')-C(4')-N(9')	126.9(3)	127.1(2)	127.9(4)	C(8')-N(9')-C(94)		127.4(2)	
C(4)-C(5)-C(6)	116.2(3)	116.3(2)	115.9(4)	C(8')-N(9')-C(62)			125.2(4)
C(4')-C(5')-C(6')	116.4(3)	116.1(2)	115.9(4)	C(6)-S(6)-C(61)	102.0(2)	101.2(2)	99.3(2)
C(4)-C(5)-N(7)	111.0(3)	110.1(2)	110.4(4)	C(6')-S(6')-C(62)	105.0(2)	105.5(2)	
C(4')-C(5')-N(7')	110.6(3)	110.0(2)	110.8(4)	C(6)-S(6')-C(92)			99.3(3)
C(6)-C(5)-N(7)	132.2(3)	133.5(3)	133.3(4)	S(6)-C(61)-C(62)	113.7(3)	113.7(3)	114.3(4)
C(6')-C(5')-N(7')	133.1(3)	133.8(2)	132.8(5)	S(6')-C(62)-C(61)	113.4(3)	113.1(2)	
N(1)-C(6)-C(5)	119.5(3)	119.9(2)	118.9(4)	N(9')-C(62)-C(61)			113.7(4)
N(1')-C(6')-C(5')	118.4(3)	119.0(3)	120.3(4)	S(6')-C(92)-C(91)			113.3(4)
N(1)-C(6)-S(6)	122.1(3)	120.7(2)	117.8(4)	N(9)-C(91)-C(92)	113.3(3)	110.4(2)	113.8(4)
N(1')-C(6')-S(6')	115.8(3)	115.1(2)	118.2(4)	N(9')-C(93)-C(92)	112.5(3)		
C(5)-C(6)-S(6)	118.4(2)	119.4(2)	123.2(4)	N(9')-C(94)-C(93)		112.5(3)	
C(5')-C(6')-S(6')	125.6(3)	125.7(2)	121.4(4)	C(91)-C(92)-C(93)	118.3(3)	113.4(3)	
C(5)-N(7)-C(8)	102.9(3)	104.0(2)	103.9(4)	C(92)-C(93)-C(94)		114.3(2)	

Table 3. Some Short Non-Bonded Distances between Two Purine Rings with Estimated Standard Deviations in Parentheses (l/Å)

	1	2		3
N(1)···N(7')	3.490(4)	3.520(3)	N(1)···N(3')	3.319(5)
N(3)···C(8')	3.243(4)	3.636(3)	C(2)···C(2')	3.354(7)
C(4)···C(4')	3.461(4)	3.913(3)	N(3)···N(1')	3.295(5)
C(4)···C(8')	3.306(4)	3.702(3)	C(4)···C(6')	3.288(6)
C(4)···N(9')	3.172(4)	3.743(3)	C(5)···C(5')	3.395(6)
C(5)···C(4')	3.398(4)	3.697(3)	C(6)···C(4')	3.300(6)
C(5)···C(5')	3.379(4)	3.538(3)	C(6)···N(9')	3.280(6)
C(6)···C(5')	3.424(4)	3.501(3)	N(7)···N(7')	3.293(6)
N(7)···N(3')	3.339(4)	3.766(3)	N(9)···C(6')	3.348(5)
N(7)···C(4')	3.351(4)	3.699(3)		
C(8)···N(3')	3.226(4)	3.878(3)		
C(8)···C(4')	3.327(4)	3.861(3)		
C(9)···C(4')	3.402(4)			
N(9)···N(9')	3.081(3)	3.796(3)		

Table 4. Torsional Angles in the Bridge Bonds (ϕ/°)

	1	2	3
C(6)-S(6)-C(61)-C(62)	292.9	292.7	268.2
S(6)-C(61)-C(62)-S(6')	302.5	303.9	
S(6)-C(61)-C(62)-N(9')			52.4
C(61)-C(62)-S(6')-C(6')	90.8	92.4	
N(9)-C(91)-C(92)-C(93)	33.7	66.7	
N(9)-C(91)-C(92)-S(6')			53.6
C(91)-C(92)-C(93)-N(9')	282.7		
C(91)-C(92)-C(93)-C(94)		219.8	
C(92)-C(93)-C(94)-N(9')			73.6
C(91)-C(92)-S(6')-C(6')			264.8

of this kind have small values which are not significant.

As the C(6) and C(6') atoms of purine rings are connected by the -S-$(CH_2)_2$-S- bridge in **1** and **2**, the C(6)-

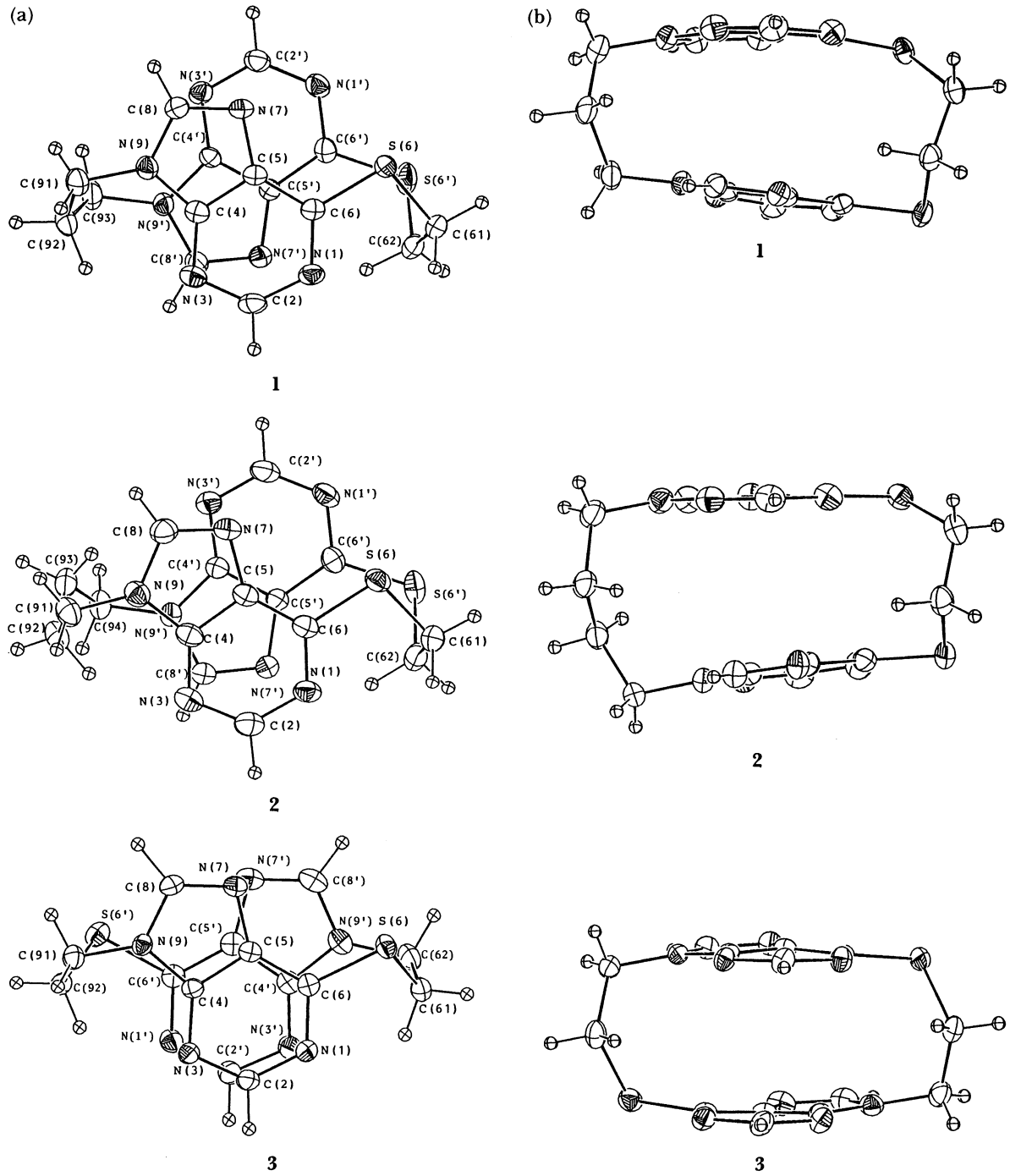

Fig. 1. Molecular structures[7] of three purinophanes, **1**, **2**, and **3**. Non-hydrogen atoms are expressed as thermal ellipsoids with 30% probability level, and hydrogen atoms as spheres with B=1.0 Å^2. a: projected onto the mean plane defined by the N(1), C(2), N(3), C(4), C(5), C(6), N(7), C(8), and N(9) atoms. b: projected along the line passing through the C(2) and C(5) atoms.

S(6) and C(6′)-S(6′) bonds are not parallel to the plane defined by the N(1), C(5), and C(6) atoms and that formed by the N(1′), C(5′), and C(6′) atoms, respectively, among which the largest angle is 4.8(3) in **2**. On the other hand, the N(9) and N(9′) atoms are connected by the -$(CH_2)_2$- (**1**) or -$(CH_2)_3$- (**2**) bridge. The angles between the N(9)-C(91) bond and the plane defined by the C(4), C(8), and N(9) atoms [7.4(3)(**1**) and 8.1(3)° (**2**)] are larger than the other two angles. The -S-$(CH_2)_2$-S- bridges in **1** and **2** have similar structures: corresponding bond distances, bond angles, and torsional angles are respectively equal within the range of error (Tables 2, 3, and 4).

The overlapping of two purine rings in **3** is another crossed form (Fig. 1, a). The molecule **3** has approximately two fold symmetry about the line passing

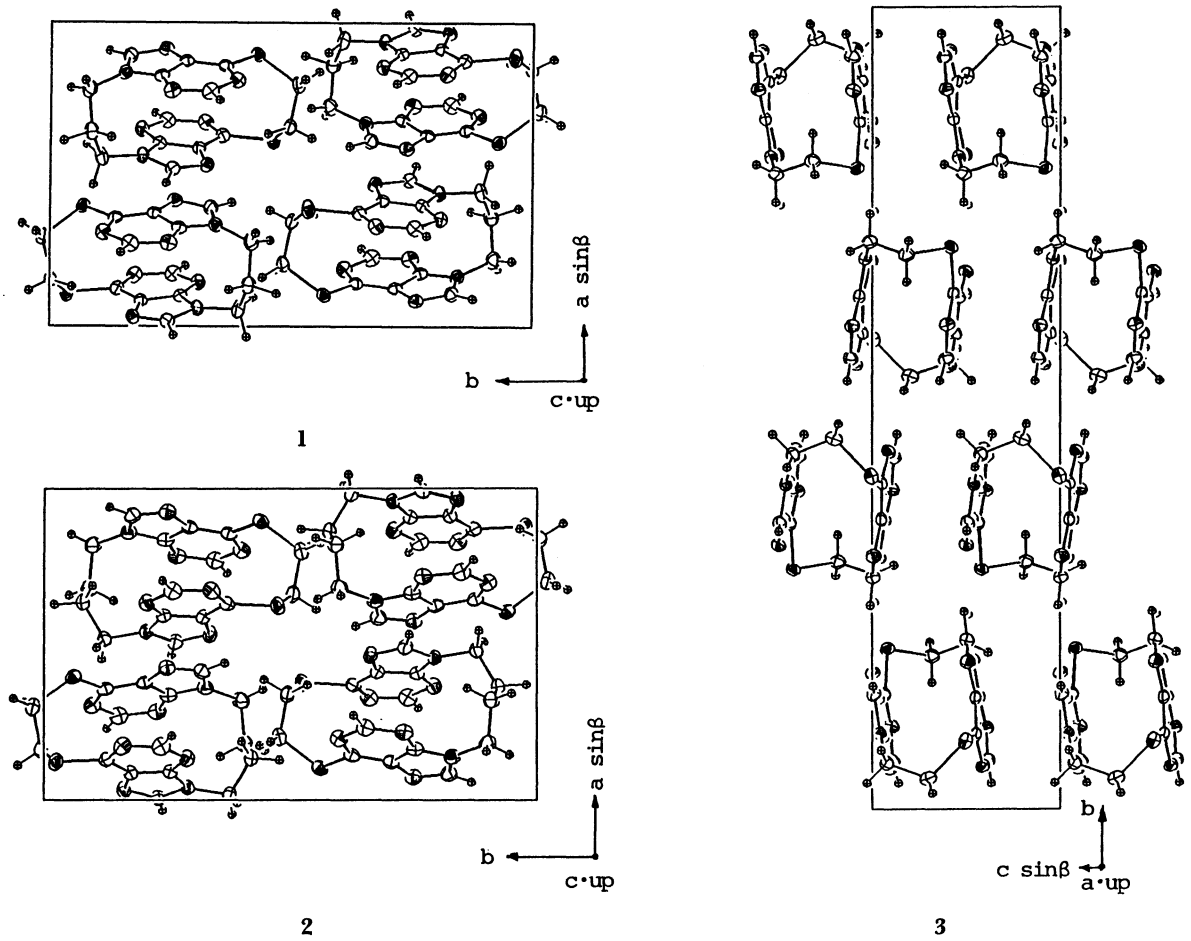

Fig. 2. Crystal structures[7] of three purinophanes, **1**, **2**, and **3**. Non-hydrogen atoms are drawn as thermal ellipsoids with 30% probability level, and hydrogen atoms as spheres with B=1.0 Å^2.

Table 5. Close Intermolecular Atomic Contacts (l/Å) less than 3.6 Å

In **1**			
C(2)···N(1′)[a]	3.467(4)	N(7)···C(2′)[d]	3.432(4)
N(3)···C(2′)[a]	3.540(4)	N(7)···N(1′)[d]	3.555(4)
N(3′)···C(61)[b]	3.431(4)	C(8)···N(1′)[d]	3.426(4)
S(6)···C(92)[c]	3.525(4)	N(9)···N(1′)[d]	3.592(4)
C(2)···N(9′)[d]	3.580(4)	N(9)···C(6′)[d]	3.486(4)
N(3)···C(4′)[d]	3.554(4)		
N(3)···C(5′)[d]	3.571(4)	Key	
C(4)···C(5′)[d]	3.573(4)	a) x, y, $-1+z$;	
C(5)···C(2′)[d]	3.348(4)	b) $1.5-x$, $0.5+y$, $0.5-z$;	
C(5)···N(3′)[d]	3.471(4)	c) $-0.5+x$, $0.5-y$, $0.5+z$;	
C(6)···N(3′)[d]	3.583(4)	d) $-0.5+x$, $0.5-y$, $-0.5+z$;	
In **2**			
N(1′)···C(2)[a]	3.490(3)	N(7)···C(2′)[d]	3.485(3)
C(2′)···N(3)[a]	3.492(3)	C(8)···N(1′)[d]	3.397(3)
C(8′)···N(7)[b]	3.269(3)	C(8)···C(2′)[d]	3.477(4)
C(61)···N(3′)[c]	3.508(3)	N(9)···N(1′)[d]	3.447(3)
C(2)···C(94)[d]	3.523(4)	N(3′)···C(61)[e]	3.508(3)
N(3)···C(4′)[d]	3.520(3)	Key	
N(3)···N(9′)[d]	3.516(3)	a) x, y, $-1+z$;	
C(4)···N(3′)[d]	3.476(3)	b) $0.5+x$, $0.5-y$, $0.5+z$;	
C(4)···C(4′)[d]	3.520(3)	c) $0.5-x$, $-0.5+y$, $0.5-z$;	
C(5)···C(2′)[d]	3.553(4)	d) $-0.5+x$, $0.5-y$, $0.5+z$;	
C(5)···N(3′)[d]	3.481(3)	e) $0.5-x$, $0.5+y$, $0.5-z$;	
In **3**			
N(1)···N(1′)[a]	3.586(5)		
N(1)···C(2′)[a]	3.553(6)		
C(2)···N(1′)[a]	3.386(6)	Key	
C(6)···C(5′)[a]	3.373(6)	a) x, y, $-1+z$;	
N(3)···C(91)[b]	3.443(6)	b) $-1+x$, y, z;	
N(1)···C(91)[c]	3.344(6)	c) $1+x$, y, z.	

through the midpoint of the C(2) and C(2′) atoms and that of the N(7) and N(7′), and two purine rings are approximately parallel to each other (Fig. 1, b). Close inter-purine nonbonded atomic distances observed are ranging from 3.289(6) Å (between the C(6) and N(9′) atoms) to 3.395(5) Å (between the C(5) and C(5′)).

Two purine rings in **3** are symmetrically connected by the -S(CH$_2$)$_2$- bridges. Only the dihedral angles concerned with the folding of the pyrimidine moiety have significant values. The angle made by the N(9)-C(91) (or N(9′)-C(93)) bond and the plane formed by the C(4), C(8), and N(9) (or C(4′), C(8′), and N(9′)) atoms [5.5(4)(or 6.7(5))°] is larger than the corresponding angle at the C(6)(or C(6′)) atom. In **3**, the

structures of two -S-$(CH_2)_2$- bridges are very similar to each other.

Based on the structures determined in this study, detailed discussions about the relationship between the stacked orientations of two purine rings and hypochromism values as well as the arguments of NMR determined structures are given in a separate paper.[10]

Crystal Structure. Crystal structures of **1**, **2**, and **3** are drawn in Fig. 2. Among the three, crystals of **1** and **2** show the similar mode of packings. Molecules are packed closely: the closest intermolecular atomic contacts are 3.348(4) Å [C(5)(x, y, z)···C(2′) ($-0.5+x$, $0.5-y$, $-0.5+z$)] and 3.397(3) Å [C(8′)(x, y, z)···N(7)($-0.5+x$, $0.5-y$, $0.5+z$)] in **1** and **2**, respectively (Table 5). In **3**, the shortest non-bonded distance between adjacent molecules is 3.344(6) Å [N(1)(x, y, z)···C(91)($1+x$, y, z)].

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