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MOLECULAR STRUCTURES AND HYPOCHROMISM OF TWO PURINOPHANES[1)]

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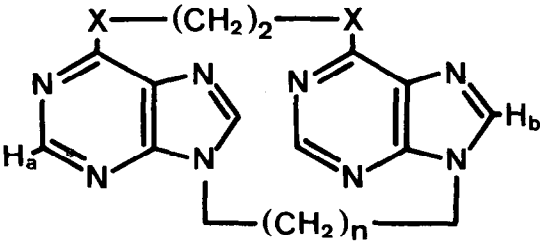
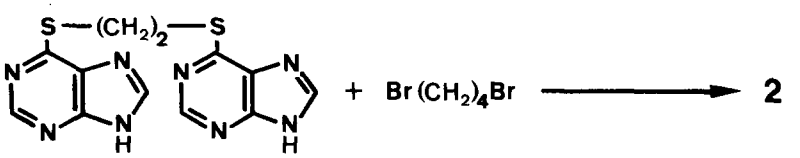
Abstract The structures of purinophane 1 and its higher homolog 2 were determined by X-ray crystallographic analysis. Hypochromism of 1 and 2 in various media is reported.

Previously, we reported the first synthesis of layered compounds containing two purine rings, 1 and 3,[2)] as a model for the stacking interaction of nucleic acid bases in DNA. However, their structures could not be unequivocally determined because only one of two possible isomers (eclipsed and crossed stacking forms) was obtained in each case. For the sake of satisfactory assignment of the isomeric structures by NMR analysis, we planned to synthesize a higher homolog 2, whose two isomers were expected to form since the two purine rings would be stacked with longer inter-ring distance to reduce steric repulsion.



1: X=S, n=3
2: X=S, n=4
3: X=NH, n=3

The synthesis of 2 was performed in a manner similar to that of 1. Thus, a mixture of 4[3)] and 1,4-dibromobutane in dimethyl sulfoxide was added to a stirred suspension of potassium carbonate in the same solvent at room temperature. Careful separation of the reaction mixture by column chromatography on silica gel gave, contrary to our expectation, only an isomer [2:[4)] colorless prisms



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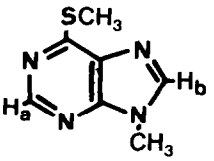
from ethanol, dec. > 275°C; Mass m/e 384 (M^+)]. Chemical shifts of aromatic protons (Ha and Hb) of **1**, **2**, and reference compound **5** are shown in Table 1.

Table 1. Observed Chemical Shifts (δ, ppm in $CDCl_3$) of Aromatic Protons of **1**, **2**, and **5**.

	1	2	5
Ha	8.60	8.56	8.74
(Δδ*)	(-0.14)	(-0.18)	—
Hb	7.52	7.54	7.93
(Δδ*)	(-0.41)	(-0.39)	—

* differences from those of 5.



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Owing to the different extent of upfield shifts (Δδ) between Ha and Hb as compared with those of 5, that is, ca. 0.15 ppm for Ha and ca. 0.40 ppm for Hb, the structures of 1 and 2 were tentatively assigned to crossed forms. To confirm this and to get further information about stacking of the two chromophores, we carried out X-ray crystallographic analysis of **1** and **2**.

The crystal data are summarized in Table 2. Independent reflections (2394 for 1 and 2561 for 2) were collected on a Rigaku Denki full automatic four-circle diffractometer with Ni-filtered Cu-Kα radiation. The structures were

Table 2. Crystal Data of 1 and 2.

		1	2
Crystal System		monoclinic	monoclinic
Space Group		$P2_1/n$	$P2_1/n$
Cell Dimension	a	10.561(1) Å	10.870(2) Å
	b	16.674(3)	17.058(2)
	c	9.136(1)	9.289(1)
	β	90.29(1)°	94.15(1)°
	V	1608.8(4) $Å^3$	1717.9(4) $Å^3$
Z		4	4

solved by a program MULTAN-78[5] and have been refined by block-diagonal least-squares method to R-factors 0.048 and 0.052 for 1 and 2, respectively. The resulting two molecular structures were confirmed to be crossed forms as shown in Fig. 1. The bond lengths and angles as well as the planarity of the purine rings are not significantly different from those of 6-methylthiopurine.[6] The characteristic points of both structures are i) very similar crossed form and ii) almost parallel stacking of the two purine rings (dihedral angle: 5.5° for 1 and 6.6° for 2 in Fig. 2), in spite of the differences in the corresponding non-bonded distances as seen in Table 3.

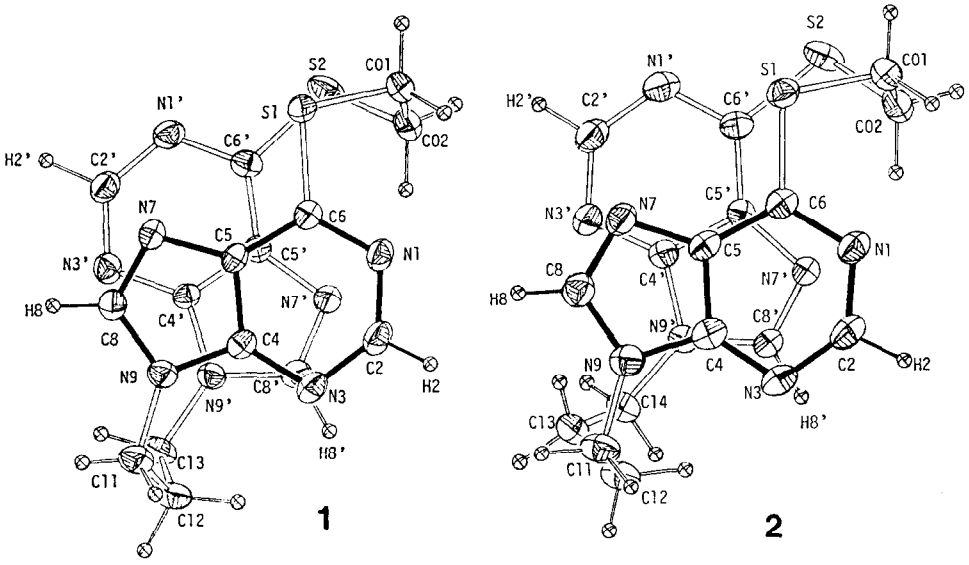


Fig. 1. View of 1 and 2 on the least-squares plane defined with a purine ring.

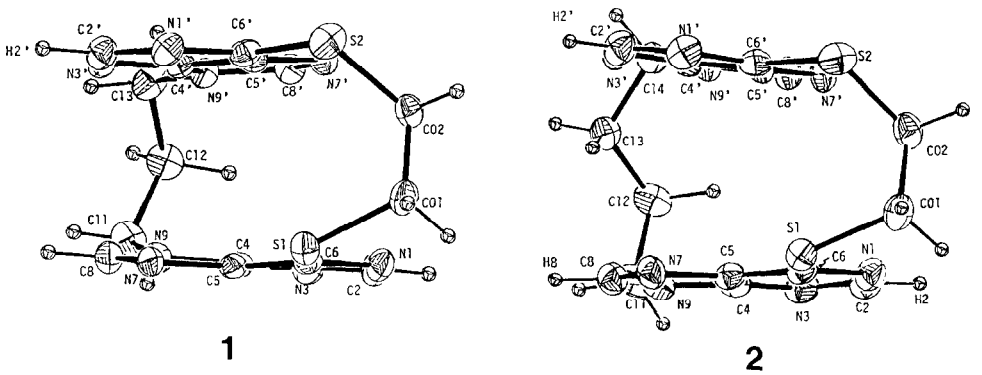


Fig. 2. Side view of two purinophanes, 1 and 2.

Table 3. Non-bonded Distances (Å) between Two Rings less than 3.5 Å for 1 and the Corresponding Distances for 2.

	1	2		1	2
N1-N7'	3.494	3.523	N9-N9'	3.084	3.785
N3-C8'	3.245	3.645	C4-C4'	3.460	3.916
C5-C4'	3.397	3.700	C4-C8'	3.304	3.703
C5-C5'	3.377	3.539	C4-N9'	3.174	3.734
N7-N3'	3.338	3.764	C6-C5'	3.424	3.549
N7-C4'	3.349	3.706	C8-N3'	3.222	3.882
N9-C4'	3.399	4.014	C8-C4'	3.323	3.874

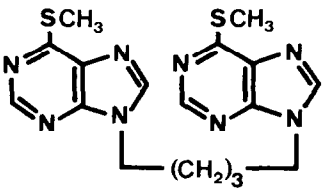
Remarkable hypochromism (H%) of the longest wavelength band was observed for **1** and **2** and it was calculated by using the equation (1), where f is

$$H(\%) = [1-f(dimer)/2f(5)]x100 \qquad (1)$$

oscillator strength, $f=4.32x10^{-9}\int\varepsilon/\lambda^2 d\lambda$. The values of the two purinophanes in four different kinds of media are listed together with those of singly bridged compound 6[2] in Table 4. The hypochromism values of 1 and 2 are quite large in

Table 4. Hypochromism (%) of 1, 2, and 6.

	H_2O	0.1N HCl	0.1N NaOH	EtOH
1	26.3	25.5	31.6	32.4
2	26.6	25.1	25.9	24.1
6	12.2	10.6	12.3	-0.6



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all media compared with those of 6 and are comparable to those of polyadenylic acid in water (32%).[7] A marked difference between the singly and the doubly bridged compounds is that the former shows non-stacked conformation in ethanol,[8] whereas the latter shows significant hypochromisms regardless the kind of medium. These facts clearly imply that the present compounds 1 and 2 have a frozen conformation of stacked purine rings in all media and consequently, they are quite suitable for a quantitative treatment of hypochromism. We are now proceeding along this line.

References and Notes

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