

STRUCTURE AND HYPOCHROMISM OF (6,9)(9',6')PURINOPHANES¹⁾

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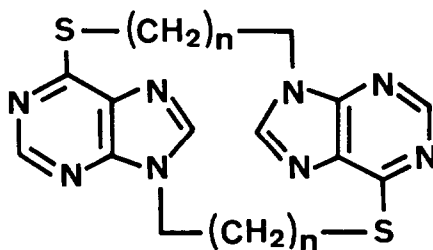
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Summary: The structure of the title compound 1a was determined to be a cross-stacking form with an interplanar distance of ca. 3.3 Å by X-ray analysis. On the basis of this structure, the hypochromicity of 1a was calculated by the ASMO SCF CI method.

As a conformationally frozen model to study the stacking interaction of nucleic acid bases in DNA, we have prepared a layered compounds, dithia(6,9)-(9',6')purinophanes 1 where the two purine rings are bound by two bridging chains.²⁾ On the basis of their ¹H-NMR spectra, we assumed the structure of 1 to be a crossed form of two possible isomers with different stacking mode. In order to confirm the NMR assignment and to determine its precise geometry required to calculate the hypochromicity, we carried out X-ray crystallographic analysis of 1a.³⁾

The resulting ORTEP drawings of 1a are shown in Figs. 1 and 2. The figures reveal the valid NMR assignment for the structure of 1a, that is, the crossed form. The bond lengths and angles as well as the planarity of the purine ring are not significantly different from those of 6-methylthiopurine.⁴⁾ The only difference is that the methylene carbon and sulfur atoms attached to the purine ring deviate from the plane of the ring (0.247 Å for CH₂ and 0.252 Å for S).



1 a: n=2

b: n=3

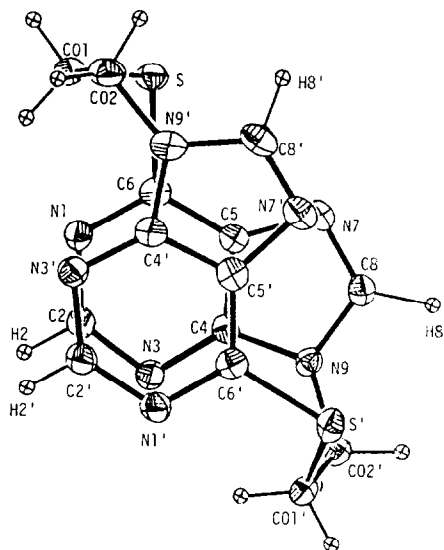


Fig. 1. View of 1a on the least-squares plane defined with a purine ring.

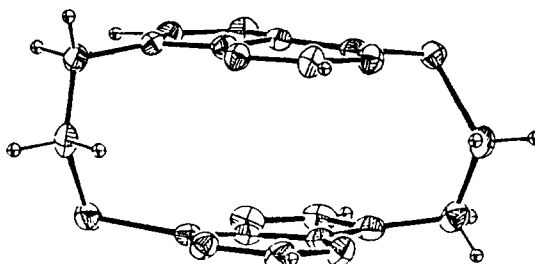


Fig. 2. Side view of 1a.

The two purine rings are stacked in parallel (dihedral angle: 2.3°). The non-bonded distances (Table 1) between the two rings are somewhat shorter than that of DNA (3.4 \AA). A noteworthy molecular packing should be pointed out here. Thus, as shown in Fig. 3. each purine ring is stacked not only intramolecularly, but also intermolecularly by interplanar distance of ca. 3.6 \AA and all the six-

Table 1. Non-bonded distances (\AA) between the two rings less than 3.4 \AA for 1a.

N1-N3'	3.320	C4-C6'	3.292	C6-N9'	3.281
C2-C2'	3.358	C5-C5'	3.395	N7-N7'	3.289
N3-N1'	3.290	C6-C4'	3.301	N9-C6'	3.349

membered rings of purine nuclei in each column are completely overlapped along the c axis.

Quite large hypochromicity ($H\%$) of 1a and 1b in four different media was observed as shown in Table 2. Especially, 1a shows the largest value in all the synthetic models with a pair of bases reported so far, reflecting the short interplanar distance learned by X-ray analysis. The hypochromicity of 1a in $0.1N \text{ HCl}$ and $0.1N \text{ NaOH}$ could not be determined because the nucleophilic substitution at 6-position of the purine ring by H_2O or OH^- occurred easily in these media at room temperature.⁵⁾

Such a remarkable hypochromism observed for 1a prompted us to calculate the theoretical hypochromicity. The calculation was performed by the ASMO SCF CI (Antisymmetrized Molecular Orbital Self-consistent Field Configuration Inter-

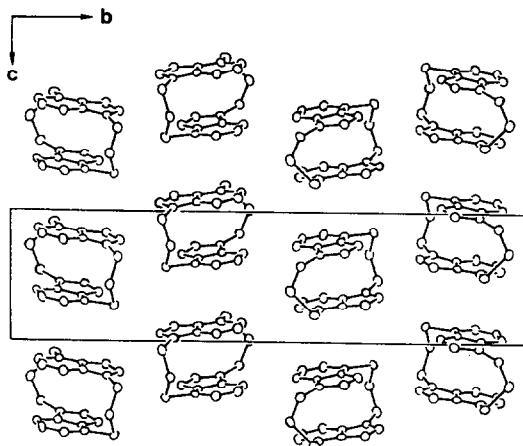


Fig. 3. Unit cell of 1a viewed down the a axis.

Table 2. Hypochromicity (%) of 1a,b.

	H ₂ O	0.1N HCl	0.1N NaOH	EtOH
1a	47.6	—	—	47.3
1b	23.0	28.6	29.5	22.4

action) method^{6,7)} on the basis of crystal data. The one center and the two center Coulomb repulsion integrals were evaluated using the Pariser-Parr approximation⁶⁾ and the Mataga-Nishimoto approximation,⁸⁾ respectively. The core resonance integral was represented by Wolfsberg-Helmholz's approximate equation.⁹⁾ As usual, the differential overlap integral and penetration integral were neglected. The configuration taken into CI calculation contains the ground state and 48 singly excited ones. The oscillator strength of the transition from the ground state to the excited state was calculated by using the equation (1),

$$f = 1.085 \times 10^{-5} \sigma_{ob} M_{ob}^2 \quad (1)$$

where σ_{ob} is the wave number of the transition and M_{ob} is the corresponding transition moment. The hypochromicity (H%) of the lowest energy transition is calculated by the following equation,

$$H = [1 - (f_{D1} + f_{D2}) / 2f_M] \times 100 \quad (2)$$

where f_M is the oscillator strength of the lowest energy transition of the monomer, and f_{D1} and f_{D2} are those of the dimer. The hypochromicity for 1a is calculated as 21.1%, which seems to be far smaller than the observed one. However, considering the largeness of the molecules, especially of the dimer, agreement between the calculated hypochromicity and the observed one is not unsatisfactory. Peculiarity of 1a in its large hypochromicity will be clari-

fied by comparative study with other purinophanes and it is now in progress.

References and Notes

- 1) Layered Compounds LXX. Part LXIX: reference 2).
- 2) F. Hama, Y. Sakata, and S. Misumi, *Nucleic Acid Res.*, Spec. Publ., 10, 73 (1981).
- 3) The crystal of 1a is monoclinic; space group $P2_1/n$; $a=8.068(1)$, $b=27.841(2)$, $c=6.913(1)$ Å, $\beta=111.0(1)^\circ$; $V=1449.8(2)$ Å³; $Z=4$. Intensity data were measured with Ni-filtered Cu-K α radiation ($2\theta_{\max}=120^\circ$) on a full automatic four-circle diffractometer. The crystal structure was solved by a program MULTAN-78¹⁰) and refined by block-diagonal least-squares method. Final R-factor is 0.059 for 2190 reflections. Tables of the atomic coordinates, bond distances, bond angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Center.
- 4) W. J. Cook and C. E. Buff, *J. Pharm. Sci.*, 64, 221 (1975).
- 5) Details will be reported elsewhere.
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(Received in Japan 12 April 1982)