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## SYNTHESIS AND STRUCTURE OF 1-(1-NAPHTHYL)DIHYDROURACIL DERIVATIVES

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The reaction of urea or thiocyanates in acidic media with N-(1-naphthyl)- $\alpha$ (and  $\beta$ )-methyl- $\beta$ -alanines was used to synthesize 5(and 6)-methyl-1-(1-naphthyl)dihydro-uracils and 5(and 6)-methyl-1-(1-naphthyl)-2-thioxodihydrouracils. The conformers of 6-methyl-1-(1-naphthyl)-2-thioxodihydrouracil were separated and subjected to x-ray diffraction analysis.

1-Aryldihydrouracil derivatives are of interest as stabilizers of the thermal-oxidative destruction of polymers [1].

The synthesis of 5(and 6)-methyl-1-(1-naphthyl)dihydrouracils I and II and 5(and 6)-methyl-1-(1-naphthyl)-2-thioxodihydrouracils III and IV was realized by heating N-(1-naphthyl)- $\alpha$ (or  $\beta$ )-methyl- $\beta$ -alanines with urea or thiocyanates in acidic media.

We have observed for the first time that 1-(1-naphthyl)-substituted dihydrouracils I-IV are produced in the form of mixtures of conformers. Doubled signals of  $-\text{CH}_2-\text{CH}-\text{CH}_3$ .

groups are observed in the PMR spectra of I-IV (Table 1) at 30°C. 6-Methyl-(1-naphthyl)-2-thioxodi-

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TABLE 1. PMR Spectra of I-IV

Com- ound	$R_f$	$\delta$ , ppm					$J$ , Hz				
		CH <sub>3</sub>	CH <sub>2</sub>		CH	aromatic H	NH	CH-CH <sub>3</sub> '	CH-CH <sub>2</sub>		
			CH <sub>3</sub>	H <sub>A</sub>	H <sub>B</sub>				AB	AX	BX
I	0,55	1,1	3,38	—3,78		2,67—3,12	7,2—7,92	10,18	7		
	0,58	1,14	3,38	—3,78		2,67—3,12	7,2—7,92	10,18	7		
II	0,47	0,96	2,51	2,92		3,92—4,19	7,21—7,92	10,3	6,5	16	7
	0,52	1,12	2,39	3,19		3,68—3,86	7,21—7,92	10,3	6,5	16	3,6
III	0,81	1,23	3,61	—3,87		2,7—3,23	7,1—7,92	8,61	6,7		6,6
IVa	0,68	0,9	2,65	3,05		3,38—4,07	7,27—7,99	11,36	6,5	16,6	7,3
IVb	0,75	1,14	2,47	3,34		3,95—4,24	7,27—7,99	11,36	6,5	16,4	3,3
											6,1

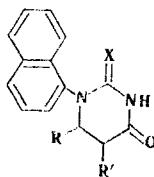
TABLE 2. Equations of the Planes\* and Deviations of the Atoms from the Planes

Con- former	Deviation of the atoms, Å								Plane equations	
	N1	C2	N3	C4	S	O	C5	C6	C17	
$\alpha$ Form IVa	-0,003	0,052	0,175	-0,137	-0,011	-0,028	-0,67	0,026	1,467	$-0,6091x+0,132y-$ $-0,7820z+5,6721=0$
$\beta$ -Form of IVa	-0,019	0,083	0,165	-0,095	-0,014	-0,039	-0,371	0,084	1,414	$-0,4297x+0,7828y-$ $-0,450z+2,3684=0$
IVb	0,022	-0,067	-0,194	0,075	0,012	0,056	0,539	-0,104	-1,536	$-0,5863x-0,2976y-$ $-0,7535z+5,9379=0$

\*The planes were drawn through the N1, C2, N3, C4, S, and O atoms.

TABLE 3. Torsion Angles ( $\phi$ )

Torsion angles	$\phi$ , deg		
	$\alpha$ form of IVa	$\beta$ form of IVa	IVb
C6—N1—C2—N3	1,6	5,9	4,2
N1—C2—N3—C4	-20,3	13,4	16,6
C2—N3—C4—C5	-0,9	-6,1	-0,7
N3—C4—C5—C6	36,7	-19,6	-33,0
C4—C5—C6—N1	-50,3	34,4	48,8
C5—C6—N1—C2	32,7	-28,9	-36,6
H6—C6—C5—1H5	-37,2	-88,0	65,8
H6—C6—C5—2H5	73,9	27,6	-66,1
C4—C5—C6—C17	72,9	-92,6	-73,6
H6—C6—C17—1H17	177,5	-178,6	-171,4
H6—C6—C17—2H17	-65,5	-62,8	-34,8
H6—C6—C17—3H17	50,5	61,9	77,5
O—C4—C5—1H5	102,0	34,3	-91,2
O—C4—C5—2H5	-18,5	-79,7	31,7
O—C4—N3—H3	-2,2	-1,1	4,4
H3—N3—C2—S	-15,5	16,8	7,1
C2—N1—C7—C8	-105,5	102,1	-76,9



I — IV

I, II X=O; III, IV X=S; I, III R=H, R'=CH<sub>3</sub>; II, IV R=CH<sub>3</sub>, R'=H

hydouracil (IV) was separated into individual conformers IVa ( $R_f$  0,68) and IVb ( $R_f$  0,75) by column chromatography and crystallization. The IR and mass spectra of these conformers were identical. The interconversion of conformers IVa, b was investigated by PMR spectroscopy. Solutions of the conformers in (CD<sub>3</sub>)<sub>2</sub>SO were heated at 190°C, and their spectra were recorded at 20° intervals. The change in the signals of the methyl group in the spectra of conformers IVa, b as a function of the temperature is shown in Fig. 1. In addition to signals

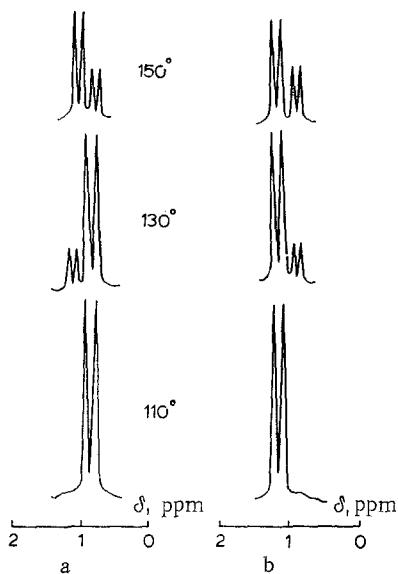


Fig. 1. Change in the signals of the methyl group in the PMR spectra of 6-methyl-1-(1-naphthyl)-2-thioxodihydrouracil as a function of the temperature: a) conformer IVa; b) conformer IVb.

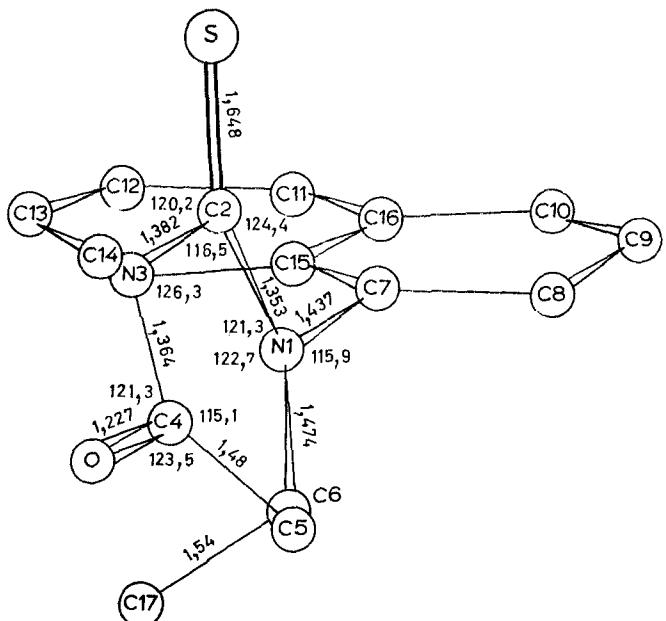


Fig. 2. Geometry of the  $\alpha$  form of IVa.

of the principal substance, signals of a second conformer appear in the spectra at 130°C, and a mixture of these conformers in a ratio of 9:11 is formed at 150°C. The ratio of the conformers remains unchanged when the temperature is increased above 150°C and when the mixture is cooled.

In order to determine the molecular structures of conformers IVa, b we subjected them to x-ray diffraction analysis. It should be noted that crystals of conformer IVa exist in two forms, which were arbitrarily designated as the  $\alpha$  and  $\beta$  forms; the  $\alpha$  form predominates. The geometries of the molecules and the bond lengths and bond angles of the conformers of IV are shown in Figs. 2-4. The naphthalene skeleton of the conformers is planar within the limits of the experimental error. The alternation of the bond lengths that is characteris-

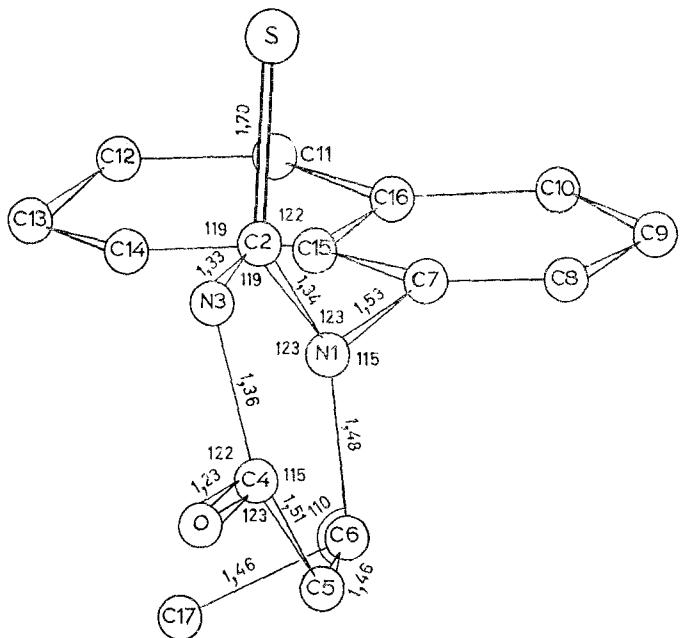


Fig. 3. Geometry of the  $\beta$  form of IVA.

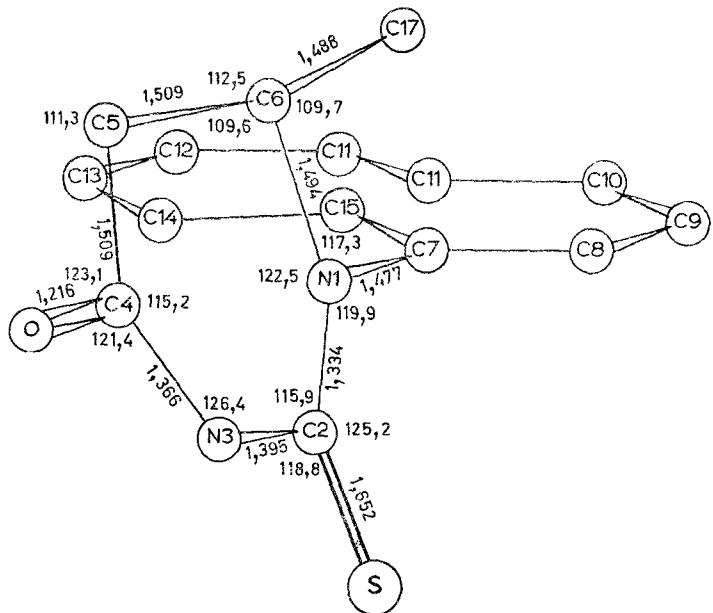


Fig. 4. Geometry of the IVb molecule.

tic for naphthalenes [2] is observed for it. The conformation of the 6-methyl-2-thioxodihydrouracil rings is close to an envelope configuration in which the C5 atoms deviate from the plane of the ring (Table 2). This sort of conformation is observed in the 6-methyl-dihydrouracil molecule [3]. The methyl group occupies a pseudoaxial position. In the examined molecules the dihydrouracil ring is almost perpendicular to the naphthalene skeleton, and the dihedral angles between the planes of these fragments of the  $\alpha$  and  $\beta$  forms of IVa are  $75.9^\circ$  and  $69.1^\circ$ , respectively, as compared with  $79.8^\circ$  for IVb. The torsion angles are presented in Table 3.

The intermolecular contacts have the normal values [4]. In a crystal of the  $\alpha$  form of IVa the molecules form infinite chains along the b axis through N3-H3 $\cdots$ O hydrogen bonds ( $1/2 - x, 1/2 + y, 1/2 - z$ ) with  $N3 \cdots O = 3.01 \text{ \AA}$ ,  $H3 \cdots O = 1.96 \text{ \AA}$ , and angle  $N3-H3 \cdots O = 169.8^\circ$ . In the  $\beta$  form of IVa the molecules form centrosymmetrical dimers through N3-H3 $\cdots$ S hydrogen bonds ( $-x, 1 - y, 1 - z$ ); the N3 $\cdots$ S and H3 $\cdots$ S distances are 3.40 and 2.46  $\text{\AA}$ , and angle  $N3-H3 \cdots S$  is  $148.9^\circ$ . The IVb crystal is constructed from centrosymmetrical dimers,

TABLE 4. Coordinates of the Nonhydrogen Atoms (in cell fractions  $\cdot 10^4$ )

Atom	$\alpha$ Form of IVa			$\beta$ Form of IVa			IVb		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
S	1700(1)	5110(3)	4102(1)	885(7)	4464(5)	4395(1)	3252(1)	3119,4 (7)	3843,7 (8)
O	2567(2)	943(7)	2556(3)	-4816(17)	3713(10)	5169(3)	-336(4)	6023(2)	4267(2)
N1	1475(2)	1594(8)	4036(3)	-1829(19)	3117(13)	4114(4)	3450(4)	4832(2)	2919(2)
C2	1735(3)	3046(9)	3782(4)	-1264(21)	3869(13)	4408(5)	2821(4)	4307(2)	3597(2)
N3	2045(2)	2710(9)	3214(3)	-2378(20)	4038(11)	4736(4)	1666(4)	4812(2)	4103(2)
C4	2281(3)	1093(11)	3059(4)	-3892(24)	3478(15)	4853(5)	782(5)	5689(3)	3827(3)
C5	2197(4)	-411(11)	3568(7)	-4417(25)	2539(20)	4551(6)	1138(6)	6137(3)	2883(4)
C6	1530(3)	-237(11)	3747(5)	-3702(26)	2605(19)	4117(6)	3061(6)	5915(3)	2756(4)
C7	1129(3)	1754(9)	4614(5)	-374(22)	2706(18)	5755(7)	4699(5)	4379(3)	2375(3)
C8	1446(5)	1190(11)	5376(6)	197(26)	1652(16)	3803(7)	6479(6)	4252(3)	2803(4)
C9	1136(5)	1215(12)	5968(6)	1307(26)	1230(17)	3456(6)	7694(7)	3821(3)	2261(4)
C10	489(5)	1876(12)	5760(6)	1546(23)	1878(17)	3106(6)	7074(6)	3532(3)	1312(4)
C11	-523(5)	3083(13)	4780(9)	846(27)	3661(19)	2694(5)	4509(7)	3337(3)	-143(3)
C12	-832(5)	3636(14)	4043(9)	39(28)	4684(18)	2703(6)	2711(7)	3425(3)	-553(4)
C13	-535(5)	3630(13)	3440(8)	-1026(24)	5131(16)	3010(5)	1489(7)	3845(3)	-31(3)
C14	116(4)	3010(11)	3633(7)	-1277(22)	4493(16)	3388(5)	2107(6)	4172(3)	911(3)
C15	962(3)	2401(9)	4399(5)	-481(16)	3422(16)	3413(5)	3976(5)	4092(2)	1381(3)
C16	149(4)	2436(10)	4995(6)	677(22)	2973(15)	3082(5)	5208(5)	3657(3)	844(3)
C17	930(4)	-686(13)	3015(7)	-4961(28)	3172(22)	3822(6)	4474(9)	6506(5)	3439(6)

and the dimer molecules are linked by two N3-H3 $\cdots$ O hydrogen bonds ( $-x$ ,  $1-y$ ,  $1-z$ ); the N3 $\cdots$ O and H3 $\cdots$ O distances are 2.87 and 2.10 Å, and angle N3-H3 $\cdots$ O is 168.8°.

#### EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra were obtained with a Bruker WH-90/DS spectrometer. The mass spectra were obtained with an LKB 2091 spectrometer with a system for the direct introduction of the substances into the ion source. The intensities of the reflections were measured with a Syntex-P2<sub>1</sub> diffractometer with the aid of Mo radiation, graphite monochromator, and  $\omega$  scan. Because of the low quality of the crystals, the number of measurements was doubled (except for the  $\beta$  form of IVa) through the inclusion of equivalent reflections. Absorption was disregarded. The structures were decoded by the direct method with the MULTAN-XTL program and were refined by the method of least squares within the full-matrix anisotropic-isotropic (for hydrogen atoms) approximation.

The principal crystallographic data for the  $\alpha$  form of IVa are as follows:  $a = 21.10$ ,  $b = 7.45$ ,  $c = 17.70$  Å,  $\beta = 108.3^\circ$ ,  $Z = 8$ , and space group C2/c. The principal data for the  $\beta$  form of IVa are as follows:  $a = 7.201$ ,  $b = 11.781$ ,  $c = 31.480$  Å,  $Z = 8$ , and space group Pbca. The principal data for conformer IVb are as follows:  $a = 7.448$ ,  $b = 13.468$ ,  $c = 13.803$  Å,  $\beta = 102.11^\circ$ ,  $Z = 4$ , and space group P2<sub>1</sub>/n. The coordinates of the atoms are presented in Table 4.

The hydrochlorides of the N-(1-naphthyl)- $\alpha$ (and  $\beta$ )-methyl- $\beta$ -alanines were obtained by the method in [5].

**5-Methyl-1-(1-naphthyl)-dihydrouracil (I).** A mixture of 26.5 g (0.1 mole) of N-(1-naphthyl)- $\alpha$ -methyl- $\beta$ -alanine hydrochloride, 12 g (0.2 mole) of urea, and 50 ml of acetic acid was heated at 110°C for 10 h, after which 20 ml of concentrated HCl was added, and the mixture was heated for another 5 h. Water (30 ml) was added, and the mixture was allowed to stand at 4°C for 24 h. The resulting crystals were removed by filtration, washed with water, and dried to give 20 g (79%) of I in the form of a mixture of conformers with mp 207-209°C (from ethanol). IR spectrum: 3230 (NH) and 1710 cm $^{-1}$  (C=O). Mass spectrum, m/z (%): 254 (61.8), 239 (14.5), 235 (23.6), 169 (40), 156 (29), 155 (100), 154 (70), 144 (30), 143 (30), 142 (30), 141 (32.7), 140 (23.6), 129 (7.2), 128 (21.8), 127 (45.4). Found: C 70.8; H 5.5; N 11.1%. C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>. Calculated: C 70.9; H 5.5; N 11.0%.

**6-Methyl-1-(1-naphthyl)dihydrouracil (II).** This compound was similarly obtained from 26.5 g (0.1 mole) of N-(1-naphthyl)- $\beta$ -methyl- $\beta$ -alanine hydrochloride and 12 g (0.2 mole) of urea in the form of a mixture of conformers [18 g (71%)] with mp 211-213°C (from dioxane).

IR spectrum: 3220 (NH) and 1720  $\text{cm}^{-1}$  (C=O). Mass spectrum, m/z (%): 254 (79.5), 239 (13.9), 225 (2.1), 197 (2), 196 (3), 183 (2), 182 (2), 169 (100), 168 (25), 167 (7.9), 166 (2.7), 155 (9.4), 154 (57.7), 153 (4.2), 144 (4.2), 143 (4.3), 142 (4), 141 (14.1), 140 (15.6), 139 (2.7), 129 (4), 128 (31.5), 127 (55.5). Found: C 71.1; H 5.6; N 10.9%.  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2$ . Calculated: C 70.9; H 5.5; N 11.0%.

5-Methyl-1-(1-naphthyl)-2-thioxodihydrouracil (III). This compound was obtained from 26.5 g (0.1 mole) of N-(1-naphthyl)- $\alpha$ -methyl- $\beta$ -alanine hydrochloride and 19 g (0.2 mole) of potassium thiocyanate by a procedure similar to that used to prepare I. Workup gave 17 g (63%) of a product with mp 172-174°C (from ethanol). IR spectrum: 3240 (NH) and 1720  $\text{cm}^{-1}$  (C=O). Found: C 66.3; H 5.3; N 10.3%.  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{OS}$ . Calculated: C 66.6; H 5.2; N 10.4%.

6-Methyl-1-(1-naphthyl)-2-thioxodihydrouracil (IV). This compound was obtained from 26.5 g (0.1 mole) of N-(1-naphthyl)- $\beta$ -methyl- $\beta$ -alanine hydrochloride and 19 g (0.2 mole) of potassium thiocyanate in the form of a mixture of conformers by a method similar to that used to prepare I. Workup gave 14 g (52%) of a product with mp 227-229°C (from acetic acid). IR spectrum: 3200 (NH) and 1720  $\text{cm}^{-1}$  (C=O). Mass spectrum, m/z (%): 270 (100), 255 (5.4), 237 (5.9), 227 (6.4), 212 (7.2), 201 (13.8), 185 (15.1), 174 (12.8), 169 (16.9), 168 (16.9), 161 (6.2), 160 (35.9), 159 (13.8), 164 (17.7), 153 (6.2), 143 (8.5), 141 (8.4), 140 (13.6), 128 (17.7), 127 (48.7). Found: C 66.8; H 5.3; N 10.3%.  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{OS}$ . Calculated: C 66.6; H 5.2; N 10.4%. Compound IV was passed through a column packed with L 40/100 silica gel by elution with hexane-chloroform-methyl ethyl ketone (2:2:1) to give conformer IVa, with mp 226-227°C (from methyl ethyl ketone) and  $R_f$  0.68, and conformer IVb with mp 230-230.5°C (from methyl ethyl ketone) and  $R_f$  0.75.

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