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X-RAY STRUCTURAL STUDY OF 2-AMINO-5,5-DIMETHOXY-3-CYANO-4-DICYANOMETHYLENE-4,5-DIHYDROPYRROLE AND ITS SODIUM SALT

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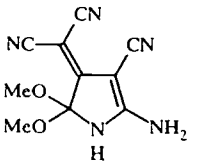
According to the XSA data, a conjugation system in which both endo- and exocyclic bonds are included is realized in the molecule of 2-amino-5,5-dimethoxy-3-cyano-4-dicyanomethylene-4,5-dihydropyrrole and the anion of its sodium salt due to the planar structure, and this is reflected in their unusual length. Due to the developed system of intermolecular hydrogen bonds, the molecules in the crystals are joined in infinite three-dimensional motifs.

The structure of some heterocyclic compounds containing one or more nitrogen atoms in the ring cannot be satisfactorily described with covalent or ionic formulas [1-3]. These are usually bipolar five- and six-membered mono- and bicyclic derivatives which have exocyclic N, O, and S atoms in the molecule. Such compounds are called mesoionic [4-6]. Their molecules have a conjugated system of bonds (both endo- and exocyclic) with fractional orders. The chemistry and structure of sydnones [7] and sydnone imines [8], whose derivatives exhibit biological activity and are used in synthesis of new heterocyclic compounds due to their high reactivity, have now been relatively completely investigated.

In continuing the studies of the structure of substituted hydrogenated five-membered heterocycles [9], an x-ray structural study of 2-amino-5,5-dimethoxy-3-cyano-4-dicyanomethylene-4,5-dihydropyrrole (I) and its sodium salt (II) was conducted.



I

The bond lengths and valence angles in two symmetrically independent molecules of compound I are reported in Tables 1 and 2; the overall form of molecule IA is shown in Fig. 1. The independent molecules in crystal I are similar in structure: all atoms of the ring and substituent, except for the methoxy groups at the $C_{(5)}$ atom, lie in one plane. The $O_{(52)}-C_{(5)}-O_{(51)}$ tetrahedral valence angle is decreased to 100.6(1)° in molecule A and to 101.2(2)° in molecule B. Deviations of the exocyclic $N_{(21)}$, $C_{(31)}$, and $C_{(41)}$ atoms from the midplane of the heterocycle, determined with an accuracy of ±0.012 Å in molecule A and ±0.015 Å in molecule B, are within the limits of 0.04-0.20 Å. The cyano and dicyano substituents in both molecules are located on different sides of the midplane of the ring; the $C_{(41)}-C_{(4)}-C_{(3)}-C_{(31)}$ torsion angle is −12.7° in molecule A and 8.2° in molecule B. The amino group is positioned on one side of the plane of the molecule with the dicyanomethylene substituent. The deviations of the $N_{(21)}$, $C_{(31)}$, and $C_{(41)}$ atoms are respectively −0.097, 0.198, and −0.103 Å in molecule A and −0.082, 0.113, and −0.043 Å in molecule B. The values of the $C_{(3)}-C_{(4)}-C_{(41)}-C_{(43)}$ torsion angles characterizing unfolding of the planar dicyanomethylene group relative to the plane of the heterocycle differ a little more: 175.4° in molecule A and 168.6° in molecule B. This unfolding is probably caused by steric repulsion between the $C_{(31)}$ and $C_{(42)}$ atoms as the distance between them inside the molecule is 3.121(2) Å in molecule A and 3.222(2) Å in molecule B.

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TABLE 1. Bond Lengths (d) in the Molecule of Compound I

Bond	d, Å	Bond	d, Å
Molecule A		Molecule B	
$O_{(51)}$—$C_{(5)}$	1,400(2)	$O_{(51')}$—$C_{(5')}$	1,392(3)
$O_{(51)}$—$C_{(51)}$	1,442(3)	$O_{(51')}$—$C_{(51')}$	1,436(3)
$O_{(52)}$—$C_{(5)}$	1,394(2)	$O_{(52')}$—$C_{(5')}$	1,391(2)
$O_{(52)}$—$C_{(52)}$	1,444(3)	$O_{(52')}$—$C_{(52')}$	1,442(3)
$N_{(1)}$—$C_{(2)}$	1,333(2)	$N_{(1')}$—$C_{(2')}$	1,331(2)
$N_{(1)}$—$C_{(5)}$	1,447(2)	$N_{(1')}$—$C_{(5')}$	1,446(2)
$N_{(21)}$—$C_{(2)}$	1,303(2)	$N_{(21')}$—$C_{(2')}$	1,304(2)
$N_{(31)}$—$C_{(31)}$	1,160(2)	$N_{(31')}$—$C_{(31')}$	1,155(2)
$N_{(42)}$—$C_{(42)}$	1,156(2)	$N_{(42')}$—$C_{(42')}$	1,156(2)
$N_{(43)}$—$C_{(43)}$	1,150(2)	$N_{(43')}$—$C_{(43')}$	1,152(2)
$C_{(2)}$—$C_{(3)}$	1,434(2)	$C_{(2')}$—$C_{(3')}$	1,430(2)
$C_{(3)}$—$C_{(4)}$	1,387(2)	$C_{(3')}$—$C_{(4')}$	1,400(2)
$C_{(3)}$—$C_{(31)}$	1,416(3)	$C_{(3')}$—$C_{(31')}$	1,412(3)
$C_{(4)}$—$C_{(41)}$	1,383(2)	$C_{(4')}$—$C_{(41')}$	1,376(2)
$C_{(4)}$—$C_{(5)}$	1,536(2)	$C_{(4')}$—$C_{(5')}$	1,537(3)
$C_{(41)}$—$C_{(42)}$	1,421(3)	$C_{(41')}$—$C_{(42')}$	1,429(3)
$C_{(41)}$—$C_{(43)}$	1,426(3)	$C_{(41')}$—$C_{(43')}$	1,430(3)

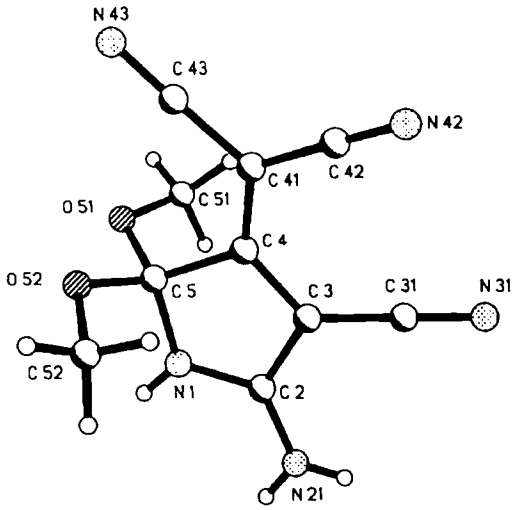

Fig. 1. General shape of independent molecule IA.

The lengths of the endocyclic $C_{(2)}-N_{(1)}$ (1.333(2) Å) and exocyclic $C_{(2)}-N_{(21)}$ bond (1.303(2) Å) are actually leveled and shortened in comparison to the mean statistical length of the $C_{sp2}-N_{sp2}$ bond (1.41 Å) [10], which indicates conjugation in the chain of $N_{(21)}-C_{(2)}-N_{(1)}$ atoms on which the positive charge of the molecule is delocalized. Another conjugation chain with a delocalized negative charge is realized between $C_{(31)}$, $C_{(3)}$, $C_{(4)}$, $C_{(41)}$, $C_{(43)}$, and $C_{(12)}$ atoms. In this chain, only the $C_{(3)}-C_{(4)}$ (1.387(3) Å) and $C_{(4)}-C_{(41)}$ bond lengths (1.383(2) Å) correspond to "pure" 1.5 bonds, and the others are slightly longer than 1.5, but much shorter than ordinary bonds (Table 1). The $C_{(2)}-C_{(3)}$ endocyclic bond is also shorter than ordinary bonds (1.430(2) Å in A and 1.434(2) Å in B), which either indicates partial preservation of conjugation at this bond in molecules A and B or can be caused by attraction of differently charged parts of the molecule. Another $C_{(4)}-C_{(5)}$ endocyclic bond (1.536(2) Å in A and 1.537(2) Å in B), not included in conjugation due to the $C_{(5)}$ atom in sp^3-hybridization, is on the contrary much longer than the standard $C_{sp2}-C_{sp3}$ bond length (1.501 Å) and can probably be the "weak link" in molecule I.

All of the features of the structure of molecule I noted above are preserved in its sodium salt (Fig. 2, Tables 3 and 4). However, in comparison to molecule I, anion II has a more planar structure. The midplane through 11 atoms of the molecule $N_{(1)}$, $C_{(2)}$, $C_{(3)}$, $C_{(4)}$, $C_{(5)}$, $N_{(21)}$, $C_{(31)}$, $N_{(31)}$, $C_{(41)}$, $C_{(43)}$, and $N_{(43)}$ is executed with an accuracy of ± 0.009 Å. This probably indicates stronger delocalization of electrons along the bonds in the charged molecule. This additional delocalization does not affect the other geometric parameters (bond lengths and valence angles).

TABLE 2. Valence Angles (ω) in the Molecule of Compound I

Angle	ω, deg	Angle	ω, deg
Molecule A		Molecule B	
C(5)—O(51)—C(51)	115,8(1)	C(5')—O(51')—C(51')	115,6(2)
C(5)—O(52)—C(52)	115,4(1)	C(5')—O(52')—C(52')	115,2(2)
C(2)—N(1)—C(5)	112,6(2)	C(2')—N(1')—C(5')	112,8(2)
N(21)—C(2)—N(1)	124,2(2)	N(21')—C(2')—N(1')	124,1(2)
N(21)—C(2)—C(3)	126,5(2)	N(21')—C(2')—C(3')	126,4(2)
N(1)—C(2)—C(3)	109,3(2)	N(1')—C(2')—C(3')	109,5(2)
C(4)—C(3)—C(31)	128,5(2)	C(4')—C(3')—C(31')	129,9(2)
C(4)—C(3)—C(2)	108,5(1)	C(4')—C(3')—C(2')	108,3(2)
C(31)—C(3)—C(2)	122,7(2)	C(31')—C(3')—C(2')	121,4(2)
C(41)—C(4)—C(3)	131,5(2)	C(41')—C(4')—C(3')	131,5(2)
C(41)—C(4)—C(5)	120,6(1)	C(41')—C(4')—C(5')	121,0(2)
C(3)—C(4)—C(5)	107,8(1)	C(3')—C(4')—C(5')	107,5(1)
O(52)—C(5)—O(51)	100,6(1)	O(52')—C(5')—O(51')	101,2(2)
O(52)—C(5)—N(1)	113,4(1)	O(52')—C(5')—N(1')	113,3(2)
O(51)—C(5)—N(1)	112,7(2)	O(51')—C(5')—N(1')	113,4(2)
O(52)—C(5)—C(4)	113,9(2)	O(52')—C(5')—C(4')	114,1(2)
O(51)—C(5)—C(4)	114,9(1)	O(51')—C(5')—C(4')	113,6(2)
N(1)—C(5)—C(4)	101,8(1)	N(1')—C(5')—C(4)'	101,8(2)
N(31)—C(31)—C(3)	177,3(2)	N(31')—C(31')—C(3')	174,5(2)
C(4)—C(41)—C(42)	122,2(1)	C(4')—C(41')—C(42')	123,3(2)
C(4)—C(41)—C(43)	121,2(2)	C(4')—C(41')—C(43')	121,5(1)
C(42)—C(41)—C(43)	116,4(2)	C(42')—C(41')—C(43')	115,1(1)
N(42)—C(42)—C(41)	176,2(2)	N(42')—C(42')—C(41')	178,0(2)
N(43)—C(43)—C(41)	179,1(2)	N(43')—C(43')—C(41')	176,9(2)

TABLE 3. Bond Lengths (d) in the Molecule of Compound II

Bond	d, Å	Bond	d, Å
O(51)—C(5)	1,414(2)	C(3)—C(4)	1,373(3)
O(51)—C(51)	1,428(2)	C(3)—C(31)	1,416(3)
O(52)—C(5)	1,415(2)	C(4)—C(41)	1,396(3)
O(52)—C(52)	1,428(3)	C(4)—C(5)	1,556(2)
N(1)—C(2)	1,311(2)	C(41)—C(42)	1,426(3)
N(1)—C(5)	1,429(2)	C(41)—C(43)	1,425(3)
N(21)—C(2)	1,329(2)	O(1s)—C(1s)	1,415(3)
N(31)—C(31)	1,148(3)	O(2s)—C(2s)	1,432(3)
N(42)—C(42)	1,151(3)	O(3s)—C(3s)	1,404(3)
N(43)—C(43)	1,150(3)	O(4s)—C(4s)	1,423(3)
C(2)—C(3)	1,476(3)		

TABLE 4. Valence Angles (ω) in the Molecule of Compound II

Angle	ω, deg	Angle	ω, deg
C(5)—O(51)—C(51)	114,8(1)	C(41)—C(4)—C(5)	121,9(2)
C(5)—O(52)—C(52)	114,8(2)	C(4)—C(41)—C(42)	122,9(2)
C(2)—N(1)—C(5)	107,8(2)	C(4)—C(41)—C(43)	121,8(2)
N(1)—C(2)—N(21)	123,9(2)	C(42)—C(41)—C(43)	115,3(2)
N(1)—C(2)—C(3)	113,2(2)	N(42)—C(42)—C(41)	178,0(2)
N(21)—C(2)—C(3)	122,8(2)	N(43)—C(43)—C(41)	176,7(2)
C(4)—C(3)—C(31)	129,8(2)	O(52)—C(5)—O(51)	99,8(1)
C(4)—C(3)—C(2)	106,9(2)	O(52)—C(5)—N(1)	112,9(2)
C(31)—C(3)—C(2)	123,3(2)	O(51)—C(5)—N(1)	113,2(1)
N(31)—C(31)—C(3)	176,7(2)	O(52)—C(5)—C(4)	111,3(1)
C(3)—C(4)—C(41)	132,8(2)	O(51)—C(5)—C(4)	113,0(2)
C(3)—C(4)—C(5)	105,3(2)	N(1)—C(5)—C(4)	106,7(1)

TABLE 5. Geometric Parameters of H Bonds Realized in the Crystal of Compound I

H bond	R (X...Y), Å	d (H...Y), Å	r (X-H), Å	∠XHY, deg
$N_{(1)}—H_{(1a)}...N_{(43')}$	2,967	2,20	0,81	158
$N_{(21)}—H_{(21a)}...O_{(51')}$	3,152	2,37	0,86	151
$N_{(21)}—H_{(21a)}...O_{(52')}$	3,126	2,35	0,86	150
$N_{(21)}—H_{(21b)}...N_{(42)}$	3,147	2,45	0,80	147
$N_{(1')}—H_{(1b)}...O_{(51)}$	3,152	2,56	0,72	140
$N_{(21')}—H_{(21d)}...N_{(31')}$	3,110	2,30	0,87	156
$N_{(21')}—H_{(21c)}...O_{(51)}$	3,064	2,34	0,85	143

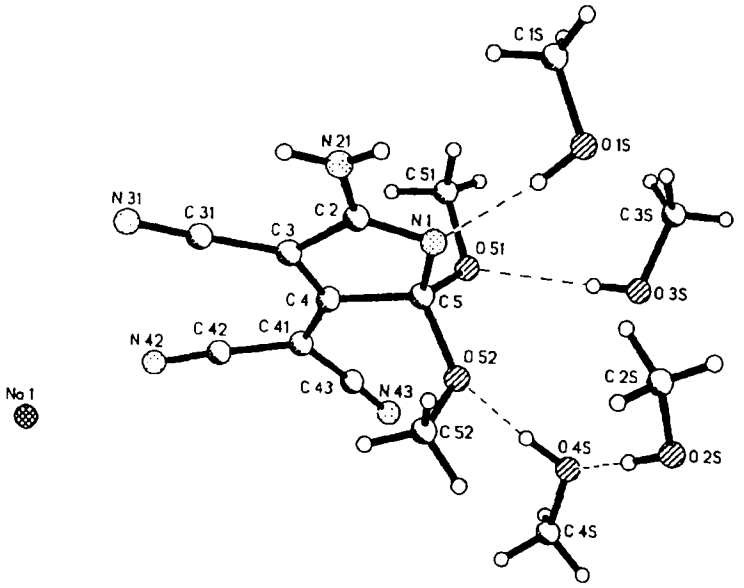

Fig. 2. Overall shape of the molecule of salt II.

In addition to the methoxy groups of the molecule objectively positioned outside of the plane of the molecule, due to sp^3-hybridization of the $C_{(5)}$ atom (the $O_{(51)}-C_{(5)}-O_{(52)}$ valence angle, as in the preceding case, is decreased in comparison to the tetrahedral angle and is 99.8(1)°), only the $C_{(42)}$ (0.078 Å) and $N_{(42)}$ atoms (0.166 Å) deviate from the plane of the molecule. This probably takes place due to the effect of the Na^+ counterion positioned in the crystal near these atoms.

A branched system of weak H bonds is realized in the crystals of both compounds studied. In the crystals of dihydropyrrole I, molecules A are joined in centrosymmetric dimers due to $N_{(21)}-H_{(21b)}...N_{(24)}$ $(-1-x, -y, 1-z)$ intermolecular H bonds. Molecules B are also joined into centrosymmetric dimers, but due to $N_{(21')}-H_{(21d)}...N_{(31')}$ bonds $(1-x, 1-y, 2-z)$ between the amino group and cyano group at the $C_{(3)}$ atom. The centrosymmetric dimers are joined in a layer by $N_{(21)}-H_{(21a)}...O_{(51')}$, $N_{(21)}-H_{(21a)}...O_{(52')}$, and $N_{(1)}-H_{(1a)}...N_{(43')}$ bonds (all three bonds between starting molecules A and B). The layers are subsequently "cross-linked" along axis y in a three-dimensional structural motif by $N_{(21')}-H_{(21c)}...O_{(51)}$ $(x, 1+y, z)$ and $N_{(1')}-H_{(1b)}...O_{(51)}$ bonds $(x, 1+y, z)$. The geometric parameters of these intermolecular H bonds are reported in Table 5.

In the crystal of salt II, there are four solvate molecules of methyl alcohol, which are also included in the overall system of intermolecular H bonds, per molecule. As for the molecules of compound I, the molecules of its salt II in the crystal form centrosymmetric dimers due to $N_{(21)}-H_{(21b)}...N_{(31)}$ H bonds $(-x, 3-y, -1-z)$ with the parameters $N_{(21)}....N_{(31)}$ of 3.030 Å, $H_{(21b)}...N_{(31)}$ of 2.80 Å, $N_{(21)}-H_{(21b)}$ of 0.86 Å, and $N_{(21)}-H_{(21b)}....N_{(31)}$ of 161 Å. Another amino group H atom participates in the H bond with one of the solvate molecules: $N_{(21)}-H_{(21a)}....O_{(1s)}$, forming a three-dimensional structural motif.

TABLE 6. Coordinates ($\times 10^4$, for H $\times 10^3$) and Isotropic (for nonhydrogen atoms — equivalent) Temperature Parameters ($\times 10^3$) of Atoms in the Molecule of Compound I

Atom	x	y	z	U_{iso}
1	2	3	4	5
		Molecule A		
O(51)	1120(2)	-3573(1)	6837(1)	26(1)
O(52)	-1686(2)	-3083(1)	7439(1)	28(1)
N(1)	-519(2)	-1160(1)	6960(1)	29(1)
N(21)	-1466(3)	1100(2)	6377(1)	28(1)
N(31)	-3154(2)	229(2)	4327(1)	29(1)
N(42)	-4735(3)	-3052(2)	4443(1)	35(1)
N(43)	-1188(3)	-5967(2)	6251(1)	47(1)
C(2)	-1324(3)	-241(2)	6363(1)	20(1)
C(3)	-2021(3)	-958(2)	5732(1)	17(1)
C(4)	-1727(3)	-2353(2)	5982(1)	18(1)
C(5)	-688(3)	-2560(2)	6816(1)	22(1)
C(31)	-2682(2)	-313(2)	4961(1)	20(1)
C(41)	-2280(3)	-3447(2)	5635(1)	20(1)
C(42)	-3588(3)	-3233(2)	4961(1)	22(1)
C(43)	-1677(3)	-4838(2)	5982(1)	27(1)
C(51)	2496(3)	-3428(2)	6203(1)	35(1)
C(52)	-3655(3)	-2248(2)	7597(1)	37(1)
H(3a)	-78(25)	-965(17)	7381(11)	18(5)
H(21a)	-960(31)	1456(20)	6764(13)	39(7)
H(21b)	-2055(26)	1623(19)	6030(11)	17(6)
H(51a)	3661(33)	-4154(21)	6292(11)	39(5)
H(51b)	1996(32)	-3549(20)	5652(15)	57(6)
H(51c)	2714(33)	-2466(25)	6209(12)	59(6)
H(52a)	-3738(32)	-1335(25)	7852(13)	60(7)
H(52b)	-4470(33)	-2036(21)	7068(14)	60(6)
H(52c)	-4215(34)	-2785(22)	7969(14)	57(7)
		Molecule B		
O(51')	-1010(2)	2264(1)	8121(1)	26(1)
O(52')	1782(2)	1601(1)	7515(1)	25(1)
N(1')	896(2)	3902(2)	8031(1)	25(1)
N(21')	2173(3)	5568(2)	8632(1)	33(1)
N(31')	4521(3)	3590(2)	10445(1)	34(1)
N(42')	3276(2)	97(2)	10836(1)	35(1)
N(43')	1485(2)	-1314(2)	8561(1)	34(1)
C(2')	1838(3)	4334(2)	8628(1)	20(1)
C(3')	2416(3)	3242(2)	9244(1)	19(1)
C(4')	1861(2)	2067(2)	8986(1)	17(1)
C(5')	863(4)	2452(2)	8146(1)	20(1)
C(31')	3549(3)	3388(2)	9925(1)	21(1)
C(41')	2052(3)	764(2)	9352(1)	19(1)
C(42')	2751(3)	407(2)	10170(1)	23(1)
C(43')	1692(3)	-367(2)	8909(1)	24(1)
C(51')	-2408(4)	3098(3)	8675(2)	43(1)
C(52')	3797(4)	1583(2)	7367(1)	33(1)
H(1b)	544(24)	4325(17)	7665(11)	5(5)
H(21c)	1753(28)	6170(21)	8248(12)	37(6)
H(21d)	2894(30)	5755(17)	9016(12)	28(6)
H(51d)	-1968(39)	2918(25)	9265(18)	87(9)
H(51e)	-2613(34)	4110(27)	8540(13)	66(7)
H(51f)	-3650(43)	2750(24)	8684(14)	73(9)
H(52d)	3943(30)	2545(23)	7212(11)	49(6)
H(52e)	4247(25)	969(17)	6908(11)	30(5)

TABLE 7. Coordinates ($\times 10^4$, $\times 10^3$ for H atoms) and Isotropic (for nonhydrogen atoms — equivalent) Temperature Parameters ($\times 10^3$) of Atoms in the Molecule of Compound II

Atom	x	y	z	U_{iso}
$Na_{(1)}$	-6247(1)	14155(1)	-702(1)	24(1)
$O_{(51)}$	658(2)	7970(1)	-2713(1)	20(1)
$O_{(52)}$	1565(2)	8862(1)	-1640(1)	21(1)
$N_{(1)}$	2167(2)	9997(2)	-3553(1)	19(1)
$N_{(21)}$	2365(2)	12334(2)	-4805(1)	20(1)
$N_{(31)}$	-1502(2)	14456(2)	-3946(2)	33(1)
$N_{(42)}$	-4141(2)	12364(2)	-1464(2)	33(1)
$N_{(43)}$	-2124(2)	7780(2)	-327(1)	29(1)
$C_{(2)}$	1589(2)	11387(2)	-3961(1)	16(1)
$C_{(3)}$	-23(2)	11809(2)	-3389(1)	18(1)
$C_{(31)}$	-874(2)	13260(2)	-3675(2)	21(1)
$C_{(4)}$	-442(2)	10571(2)	-2565(1)	16(1)
$C_{(41)}$	-1791(2)	10316(2)	-1750(2)	19(1)
$C_{(42)}$	-3091(2)	11456(2)	-1610(2)	22(1)
$C_{(43)}$	-1939(2)	8895(2)	-977(2)	20(1)
$C_{(5)}$	1017(2)	9350(2)	-2640(1)	18(1)
$C_{(51)}$	-11(3)	807(2)	-3636(2)	26(1)
$C_{(52)}$	2077(3)	10008(3)	-1320(2)	31(1)
$O_{(1s)}$	4362(2)	8277(2)	-4735(1)	30(1)
$O_{(2s)}$	5061(2)	6417(2)	-931(1)	31(1)
$O_{(3s)}$	2893(2)	5272(2)	-2336(1)	35(1)
$O_{(4s)}$	1854(2)	6145(2)	-49(1)	32(1)
$C_{(1s)}$	3956(3)	8718(3)	-5785(2)	38(1)
$C_{(2s)}$	5567(4)	7292(3)	-2026(2)	44(1)
$C_{(3s)}$	3258(5)	4733(4)	-3292(3)	64(1)
$C_{(4s)}$	937(4)	5828(3)	1039(2)	40(1)
$H_{(21a)}$	331(3)	1210(3)	-503(2)	32(7)
$H_{(21b)}$	197(3)	1326(3)	-502(2)	20(5)
$H_{(51a)}$	-16(3)	709(3)	-362(2)	30(6)
$H_{(51b)}$	69(4)	846(3)	-431(3)	54(8)
$H_{(51c)}$	-104(3)	870(3)	-359(2)	44(7)
$H_{(52a)}$	253(3)	948(3)	-66(2)	40(7)
$H_{(52b)}$	127(4)	1078(3)	-115(2)	55(8)
$H_{(52c)}$	283(3)	1049(3)	-190(2)	38(7)
$H_{(1so)}$	374(4)	880(3)	-430(2)	54(8)
$H_{(2so)}$	418(4)	669(3)	-71(3)	52(10)
$H_{(3so)}$	239(4)	607(4)	-245(2)	51(9)
$H_{(4so)}$	134(4)	684(4)	-48(3)	63(9)
$H_{(1sa)}$	335(5)	968(5)	-588(3)	103(14)
$H_{(2sb)}$	343(5)	806(5)	-590(3)	99(14)
H(1sc)	482(5)	874(4)	-634(3)	84(11)
$H_{(2sa)}$	483(4)	748(4)	-254(3)	84(11)
$H_{(2sb)}$	646(5)	683(4)	-232(3)	89(13)
$H_{(2sc)}$	560(4)	839(5)	-200(3)	91(12)
$H_{(3sa)}$	377(5)	375(5)	-316(4)	107(14)
$H_{(3sb)}$	379(5)	551(5)	-395(4)	114(15)
$H_{(3sc)}$	247(6)	463(6)	-361(4)	131(19)
$H_{(4sa)}$	18(6)	526(6)	109(4)	130(18)
$H_{(4sb)}$	57(4)	675(4)	127(3)	83(11)
$H_{(4sc)}$	150(5)	533(4)	157(3)	88(12)

EXPERIMENTAL

X-Ray Structural Study of Compounds I and II. The crystals of compound I are triclinic, at −120°C a = 7.095(5), b = 9.886(4), c = 16.290(6) Å, α = 88.19(3)°, β = 89.27(4)°, γ = 74.43(4)°, V = 1100.0(9) Å^3, d_{calc} = 1.396 g/cm^3, Z = 4, space group P-1. $C_{10}H_9N_5O_2$.

The crystals of compound II are triclinic, at −120°C a = 8.857(2), b = 9.321(3), c = 12.911(3) Å, α = 73.79(2), β = 75.98(2), γ = 79.14(2)°, V = 984.7(5) Å^3, d_{calc} = 1.286 g/cm^3, Z = 2, space group P-1. $C_{10}H_8N_5O_2Na$.

The unit cell parameters and intensities 2921 and 3381 of independent reflections (for compounds I and II respectively) were measured on a Siemens P3/PC four-ring automatic diffractometer (λMoKα, graphite monochromator, $\theta/2\theta$ scanning to θ_{max} = 27° and 25°, respectively). The structures were deciphered by a direct method which detects all nonhydrogen atoms and refined with the full-matrix method of least squares in the anisotropic approximation for nonhydrogen atoms. The hydrogen atoms were identified by Fourier synthesis and were refined isotropically. The final values of the divergence factors R_1 = 0.025 for 1672 independent reflections with $I > 2\sigma(I)$, WR_2 = 0.089 for 1757 independent reflections for I and R_1 = 0.040 for 2715 independent reflections with $I > 2\sigma(I)$, WR_2 = 0.102 for 2978 independent reflections for II. All of the calculations were conducted with the SHELXTL PLUS program [11] (PC version). The coordinates and isotropic equivalent heat parameters of nonhydrogen atoms (isotropic for H) are reported in Tables 6 and 7, respectively.

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