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THE CRYSTAL STRUCTURE OF AN UNUSUAL CHROMOPHORIC DIMERIC FURAN*

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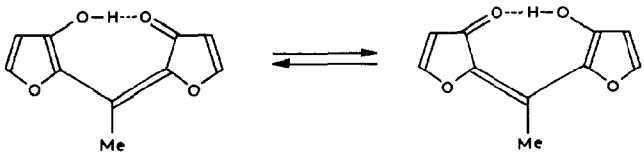
ABSTRACT

The red-orange crystals of (*E*)-2-[1-(3-hydroxy-2-furanyl)ethylidene]-(2*H*)-furan-3-one, $C_{10}H_8O_4$, crystallize in space group $P2_1/c$ with $Z = 8$, cell dimensions at 123 K [293 K], a = 16.222(4) [16.360(8)] Å, b = 7.089(2) [7.219(4)] Å, c = 16.631(5) [16.722(8)] Å, β = 115.20(3) [115.50(7)]°. There are two symmetry non-equivalent molecules in the unit cell, each of which has an unsymmetrical configuration with an unsymmetrical O–H···O=C intramolecular hydrogen bond. This is contrary to a previous report based on the solid-state i.r. spectrum. The two furan rings in each molecule are planar, but not coplanar. They are inclined at angles of 33.4° and 26.1° to each other, in opposite senses in the two molecules.



1a **1b**

INTRODUCTION

The molecules in the red-orange crystals of (*E*)-2-[1-(3-hydroxy-2-furanyl)ethylidene]-(2*H*)-furan-3-one, prepared by the acidic decomposition of isomaltol, were assigned[1] the symmetrical formula, **1a** ⇌ **1b**.

The evidence for this symmetrical, rather than a single unsymmetrical, configuration is a broad i.r. band for the solid compound in a KBr disk (3480–3395 cm^{-1}, centered at 3445 cm^{-1}). This is regarded as evidence for enolic-keto C=C–OH ⇌ O=C–CH tautomerism[2]. Since the two configurations **1a** and **1b** are symmetrical, this molecule could provide an interesting example of proton-tunnelling in the crystalline state[3]. One such example is naphthazarin C (**2**), the crystal structure of which has been studied in detail by neutron diffraction[4]. In the

*Dedicated to Professor Hans Paulsen.

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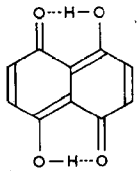
violet-colored naphthazarin C crystals, the protons are ordered at 30 K and disordered at 300 K, with an order–disorder transition at 110 K.

The crystal structure analysis at 293 and 123 K reported in this work was undertaken to discover whether this carbohydrate derivative exhibited a similar proton transfer in the solid-state, as suggested by the spectroscopic evidence.



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EXPERIMENTAL

Red-orange crystals were obtained by recrystallization from aqueous 60% ethanol of a sample kindly provided by Dr. J. C. Goodwin (Midwest Area Northern Regional Center of the Agricultural Research Service). The ν_{max}^{KBr} at 3480–3395 cm^{-1} was confirmed. The crystal data and details of the diffraction data collection at 123 K and 293 K and solution and refinement of the crystal structure are given in Table I. The structure was solved using MULTAN[5] with 250 E-values >1.97, to give the positions of the 28 non-hydrogen atoms in the two symmetry-independent molecules. All 16 hydrogen atoms were located subsequently by means of Fourier difference syntheses. The reflections (200), (021), ($\bar{2}$02), believed to be seriously affected by extinction, were excluded from the final refinement calculation. The atomic parameters were refined with anisotropic equivalent temperature factors for the carbon and oxygen atoms and with isotropic temperature factors for the hydrogen atoms. The positional parameters at the two temperatures are reported in Table II. The anisotropic temperature factors for the carbon and oxygen atoms at both temperatures have been deposited*. The atomic notation and thermal ellipsoids at 123 K are shown in Fig. 1.

DISCUSSION

The crystal structure analysis shows unequivocally that the configuration of the dimeric molecule is unsymmetrical with the hydroxyl hydrogen atom covalently bonded to the oxygen atom of one furan ring and hydrogen-bonded to the oxygen atom on the other, as shown in Fig. 1.

*Lists of structure factors, anisotropic thermal parameters, torsional angles, and hydrogen-bond distances and angles have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P. O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/387/*Carbohydr. Res.*, 174 (1988) 1–8.

TABLE I

CRYSTAL DATA AND X-RAY DIFFRACTION ANALYSIS DATA FOR (*E*)-2-[1-(3-HYDROXY-2-FURANYL)ETHYLIDENE]-(2*H*)-FURAN-3-ONE AT 123 K AND [293] K

Crystal data

$C_{10}H_8O_4$; mol. wt. 192.17; m.p. 124°; *P2/c*; $Z = 8$

Cell dimensions, $a = 16.222(4)$ [16.360(8)], $b = 7.089(2)$ [7.219(4)], $c = 16.631(5)$ [16.722(8)] Å

$\beta = 115.20(3)$ [115.50(7)]°

$D_x = [1.431]$; $D_m = [1.415]$ g.cc^{-1}

Experimental and refinement data

Crystal dimensions, 0.35 × 0.22 × 0.57 mm

Radiation MoK_α ($\lambda = 0.7107$ Å) Nb-filtered; $\mu_{Mo} = 0.72$ cm^{-1}

6258 intensities measured on a CAD-4 difractometer, by 96 point $\omega/2\theta$ scans[6], of which 5017 are unique; 1760 had $F_{obs} < 3\sigma(F_{obs})$.

No absorption or extinction corrections were applied.

Refinement on $R = \Sigma\omega(|F_o| - |kF_c|)^2$, where $\omega = \sigma^{-2}(F_o)$.

Number of observations, 3254; number of parameters, 317.

Final refinement values: $R = 0.064$; $R_w = 0.044$, $S = 1.309$

Final shifts, $< 0.01\sigma$.

TABLE II

ATOMIC POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS IN (*E*)-2-[1-(3-HYDROXY-2-FURANYL)ETHYLIDENE]-(2*H*)-FURAN-3-ONE[a]

Atoms	*Molecule A*				*Molecule B*			
	x/a	y/b	z/c	B_{eq} *or* B	x/a	y/b	z/c	B_{eq} *or* B
C-2	464(1)	1213(3)	7667(1)	133(7)	5457(1)	1147(3)	7986(1)	131(6)
	455(3)	1242(6)	7659(3)	333(20)	5463(3)	1136(6)	8024(3)	359(20)
C-3	1351(1)	803(3)	8284(1)	142(7)	4935(1)	1494(3)	8469(1)	138(7)
	1330(3)	847(6)	8266(3)	385(22)	4958(3)	1469(6)	8510(3)	386(22)
C-4	1908(1)	802(3)	7814(1)	192(8)	5542(1)	1372(3)	9389(1)	166(7)
	1884(3)	852(7)	7815(3)	517(24)	5569(3)	1371(7)	9413(3)	482(25)
C-5	1354(1)	1202(3)	6964(1)	215(8)	6365(1)	952(3)	9433(1)	175(7)
	1341(3)	1219(7)	6976(3)	565(28)	6372(3)	1008(7)	9452(3)	509(25)
C-6	−405(1)	1234(3)	7666(1)	121(6)	5336(1)	1265(3)	7104(1)	134(7)
	−398(3)	1254(6)	7666(3)	330(19)	5333(3)	1248(6)	7143(3)	360(21)
C-7	−1231(1)	946(3)	6783(1)	176(7)	6190(1)	1432(3)	6958(1)	190(8)
	−1215(3)	988(6)	6786(3)	472(22)	6166(3)	1362(7)	6983(3)	513(23)
C-2′	−553(1)	1485(3)	8417(1)	134(6)	4500(1)	1255(3)	6364(1)	142(7)
	−548(3)	1494(6)	8410(3)	355(21)	4493(3)	1252(6)	6408(3)	385(22)
C-3′	−28(1)	2207(3)	9298(1)	147(7)	3582(1)	821(3)	6190(1)	158(7)
	−27(3)	2186(6)	9285(3)	388(21)	3586(3)	842(6)	6240(3)	422(23)
C-4′	−656(1)	2414(3)	9691(1)	211(8)	3066(1)	945(3)	5246(1)	199(7)
	−653(3)	2372(8)	9671(3)	559(24)	3081(3)	965(7)	5310(3)	559(24)

TABLE II *(continued)*

Atoms	*Molecule A*				*Molecule B*			
	x/a	y/b	z/c	B_{eq} *or* B	x/a	y/b	z/c	B_{eq} *or* B
C-5′	−1465(1)	1832(4)	9084(1)	247(9)	3649(2)	1421(3)	4908(1)	224(9)
	−1445(3)	1787(8)	9073(3)	653(30)	3649(4)	1424(8)	4967(3)	623(26)
O-1	476(1)	1462(2)	6840(1)	175(5)	6354(1)	811(2)	8612(1)	169(5)
	461(2)	1485(4)	6834(2)	457(16)	6361(2)	840(4)	8642(4)	474(15)
O-3	1629(1)	371(2)	9134(1)	183(5)	4074(1)	1945(2)	8156(1)	197(5)
	1616(2)	429(4)	9111(2)	496(15)	4103(2)	1886(5)	8208(2)	547(16)
O-1′	−1452(1)	1255(2)	8309(1)	201(5)	4519(1)	1607(2)	5540(1)	199(5)
	−1440(2)	1235(5)	8300(2)	529(16)	4516(2)	1603(4)	5596(2)	538(16)
O-3′	820(1)	2634(2)	9654(1)	171(5)	3265(1)	326(2)	6748(1)	195(5)
	809(2)	2633(4)	9640(2)	439(14)	3273(2)	343(5)	6790(2)	556(16)
H-C-4	253(1)	56(3)	806(1)	21(4)	539(1)	155(3)	987(1)	16(4)
	250(2)	50(4)	806(1)	51(7)	541(1)	151(3)	990(1)	43(6)
H-C-5	146(1)	137(3)	646(1)	16(4)	694(1)	66(3)	993(1)	23(5)
	145(2)	140(3)	647(1)	48(6)	697(1)	72(4)	994(1)	45(7)
H-1–C-7	−108(2)	−7(4)	643(2)	38(6)	652(2)	256(4)	726(2)	38(5)
	−111(2)	−1(5)	641(2)	93(9)	653(2)	242(4)	726(2)	74(8)
H-2–C-7	−170(2)	54(4)	685(2)	43(6)	660(2)	43(4)	727(2)	36(6)
	−167(2)	29(4)	684(2)	56(7)	659(2)	34(4)	727(2)	77(8)
H-3–C-7	−127(2)	202(4)	644(2)	51(7)	603(2)	155(3)	633(2)	33(5)
	−128(2)	206(4)	647(2)	69(8)	602(2)	158(5)	635(2)	97(9)
H-C-4′	−52(1)	288(3)	1029(1)	33(5)	242(1)	75(3)	495(1)	23(4)
	−54(2)	286(4)	1026(2)	62(7)	244(2)	82(4)	500(1)	51(7)
H-C-5′	−208(1)	173(3)	908(1)	30(5)	354(1)	173(3)	430(1)	22(4)
	−205(2)	169(4)	907(2)	67(8)	355(2)	176(4)	434(2)	59(7)
H-O-3	130(2)	123(4)	934(2)	47(6)	368(2)	119(4)	749(2)	56(7)
	132(2)	121(3)	935(1)	46(6)	366(2)	121(4)	748(2)	76(8)

[a]Fractional coordinates $\times 10^4$ for non-hydrogen atoms, $\times 10^3$ for hydrogen atoms. First line, 123 K; second line, 293 K. E.s.d. values given in parentheses refer to the least significant digit. For non-hydrogen atoms, $B_{eq} = 4/3(\Sigma_{ij} B_{ij} \vec{a}_i \vec{a}_j)$, calculated in Å^2 ($\times 10^{-2}$) from the refined, anisotropic, thermal parameters; for hydrogen atoms, B (in Å$^2 \times 10^{-1}$).

Since there are no intermolecular hydrogen bonds in the crystal structure, the melting point is relatively low for a carbohydrate, and the thermal parameters for the room temperature analysis are large. Since the crystal structure is the same at both temperatures, we use the more precise low-temperature results for discussing the molecular structure.

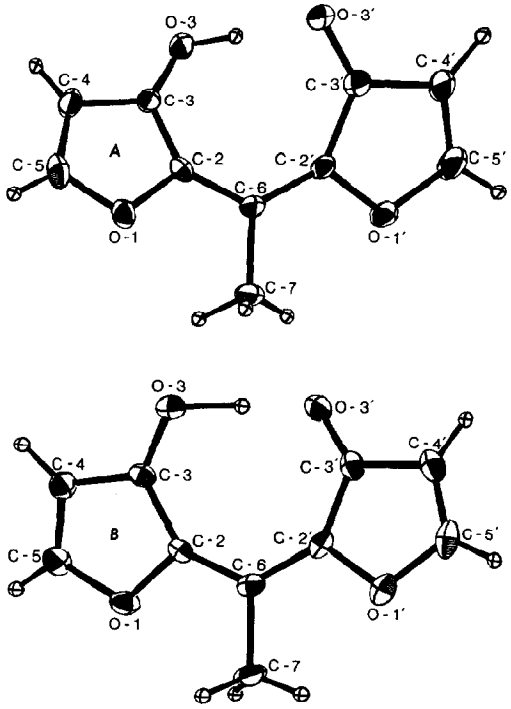

Fig. 1. Atomic notation and thermal ellipsoids at 50% probability for (*E*)-2-[1-(3-hydroxy-2-furanyl)-ethylidene]-(2*H*)-furan-3-one at 123 K.

The bond lengths and valence angles for the two symmetry independent molecules in the unit cell agree within the experimental errors, as shown in Fig. 2. However, the two molecules have conformations which are almost mirror-related. In each molecule, the two furan rings are planar (within ±0.005 Å), but they are not coplanar. The dihedral angles between the planes of the two furan rings are 33.4° in molecule A and 26.1° in molecule B, but opposite in sign. In terms of the relevant torsion angles, C-3–C-2–C-1–O-1 and C-2–C-1–C-2′–O-1′ are −163.1° and −173.1°, respectively, in molecule A and +168.6° and +172.9° in molecule B.

Although the formal C–C bonds are longer than the C=C bonds, the single valence bond representation, **1a**, is not a good description of the electronic structure because of the extensive π-bond resonance. In particular, the differences in bond lengths of 0.04 Å between O-1–C-5 and O-1–C-2 require contributions for the resonance forms **3** and **4**. Since molecule B is closer to planarity than molecule A, the O-3B---O-3B′ intramolecular separation is shorter than O-3A---O-3A′. Since this is an X-ray analysis, the hydrogen coordinates are those of the hydrogen electron-density maxima, which generally give shorter O–H and longer H···O bond-lengths than the inter-nuclear distances measured by neutron crystal-structure

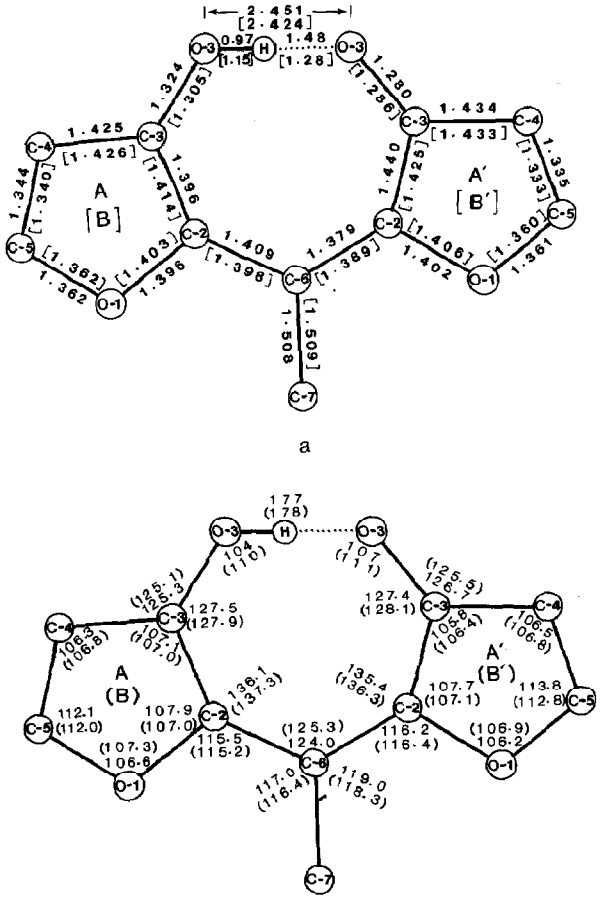

Fig. 2. (a) Bond distances (Å) and (b) valence angles (deg.) in (*E*)-2-[1-(3-hydroxy-2-furanyl)ethylidene]-(2*H*)-furan-3-one at 123 K, with values at 293 K in parentheses.

analysis. Comparison with some comparable intramolecular inter-nuclear O–H···O bond-lengths, given in Table III, suggests that this shortening effect applies to the hydrogen bond in molecule A, but not in molecule B. Although the formal standard deviations suggest that the hydrogen bonds are different in A and B, we believe that this difference is not significant. It is a reflection of the sensitivity of hydrogen positions to small errors in the electron density distribution.

There is no intermolecular hydrogen bonding. The molecules are arranged in stacks along the [010] direction as shown in Figs. 3 and 4. The separation between the mean planes of the molecules is 3.45 Å which is also the closest C---C intermolecular distance.

The π conjugation would favor a completely planar molecule. The deviation from coplanarity of the two furan rings is unlikely, in our view, to be a consequence

TABLE III

COMPARISON WITH SOME STRONG INTRAMOLECULAR COH···O=C HYDROGEN-BOND LENGTHS DETERMINED BY NEUTRON DIFFRACTION[a]

Crystal structure	*O–H (Å)*	*H···O (Å)*	*O---O (Å)*
This work (123 K) Molecule A	0.97(2)	1.48(2)	2.451(3)
Molecule B	1.15(2)	1.28(2)	2.424(3)
Pyridine 2,3-dicarboxylic acid[7]	1.163(5)	1.238(5)	2.398(3)
(at 100 K)	1.176(3)	1.227(3)	2.400(2)
Potassium hydrogen chloromaleate[8]	1.199(5)	1.206(5)	2.403(3)
1,3-Diphenyl-1,3-propanedione[9]	1.161(9)	1.360(9)	2.463(4)
6-Hydroxy-1-fulvenecarbaldehyde[10]	1.214(12)	1.343(12)	2.557(6)
1-Phenyl-1,3-butanedione[11]	1.238(11)	1.322(12)	2.489(5)
Naphthazarin C[4]	0.995(5)	1.577(4)	2.582(5)

[a]At room temperature unless otherwise noted.

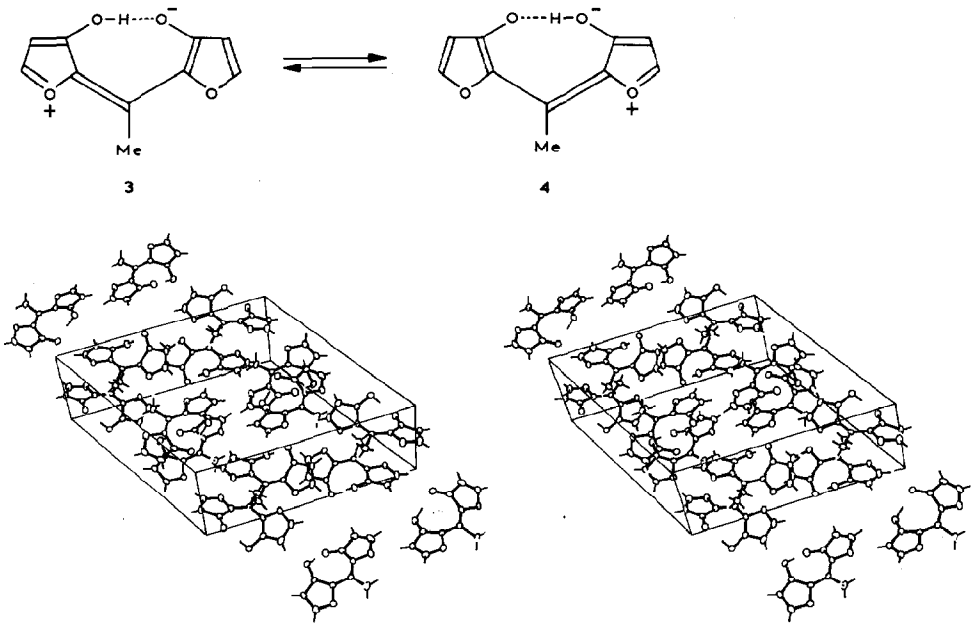

Fig. 3. Stereoview of the molecular packing in the crystal structure of (*E*)-2-[1-(3-hydroxy-2-furanyl)-ethylidene]-(2*H*)-furan-3-one at 123 K. The view is along the *b* axis, with the *c* axis to the left.

of a crystal field effect with this type of molecular packing. Rather, it suggests that the intramolecular hydrogen bonding is sterically compressed from its effective equilibrium distances. It is a compromise between this compression energy and the π-bond conjugation energy that gives rise to the non-planarity of the molecules. In solution, the molecules are expected to be in equilibrium between two non-planar mirror-related configurations similar to those observed in the crystals.

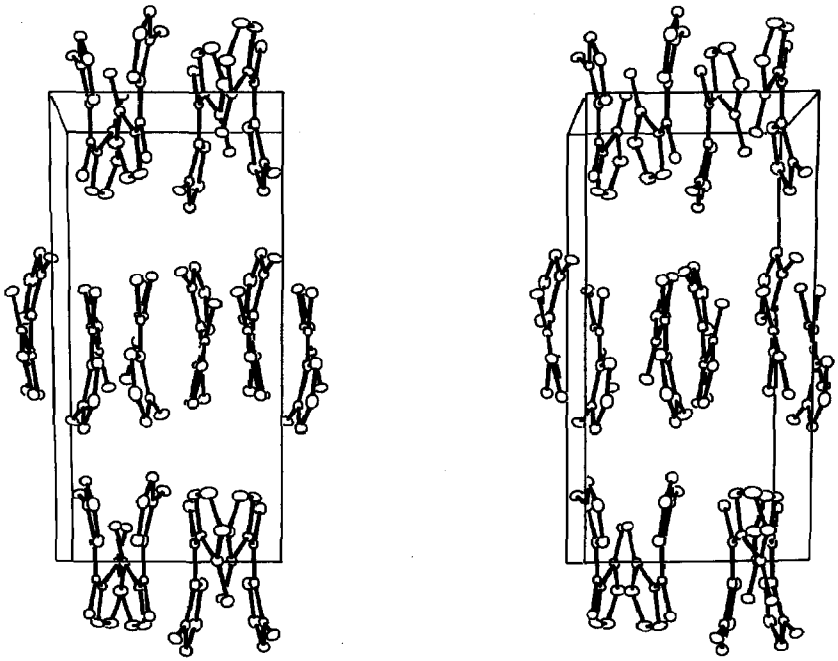

Fig. 4. Stereoview of the molecular packing in the crystal structure of (*E*)-2-[1-(3-hydroxy-2-furanyl)-ethylidene]-(2*H*)-furan-3-one at 123 K, viewed down the *c* axis, with the *a* axis vertical.

ACKNOWLEDGMENT

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