2,2-DIMETHYL-5-(5-R-2-FURFURYLIDENE)-1,3-DIOXANE-4,6-DIONES.

2.* CRYSTAL AND MOLECULAR STRUCTURE OF 2,2-DIMETHYL-5-(5-METHYL-2-FURFURYLIDENE)-1,3-DIOXANE-4,6-DIONE

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2,2-Dimethyl-5-(5-methyl-2-furfurylidene)-1,3-dioxane-4,6-dione crystals were subjected to an x-ray diffraction study. The unit cell of the crystal contains two symmetrically independent A and B molecules that exist in the x-cis conformation, which is stabilized by conjugation between the heteroring and, possibly, an intramolecular hydrogen bond.

The question of the three-dimensional structure of 1,3-dioxane-4,6-dione (Meldrum's acid) has long been the subject of debate, and it was demonstrated only recently by x-ray diffraction analysis [2, 3] that dioxanedione (and its 5-alkyl and 5-phenyl derivatives) exist in a boat conformation, while the substituent in the 5 position of the heteroring is equatorially oriented.

The question of the geometry of the dioxanedione ring in 5-ylidene derivatives, which have an sp^2-hybridized $C_{(5)}$ atom, remains open. On the basis of the UV, IR, and PMR spectra of ylidene derivatives of dioxanedione it has been assumed [4-7] that the $O_{(1)}$, $O_{(3)}$, $C_{(4)}$, $C_{(5)}$, and $C_{(6)}$ atoms of the dioxane ring and the oxygen atoms of the carbonyl groups are located in the same plane, while the alkylidene link is situated in a mutually perpendicular plane of "mirror symmetry" of the 1,3-dioxane ring.

TABLE 1. Coordinates of the Atoms ($\cdot 10^4$ for the O and C atoms; $\cdot 10^3$ for the H atoms)*

Atom	Molecule A			Molecule B		
	x	y	z	x	y	z
$O_{(1)}$	10012(4)	4521(3)	8643(3)	3990(4)	−165(3)	7596(2)
$O_{(2)}$	9011(5)	6105(3)	7730(3)	5019(3)	562(2)	8780(2)
$O_{(3)}$	8424(6)	5594(3)	6423(3)	5501(4)	2672(3)	8873(2)
$O_{(4)}$	10244(3)	2398(2)	8342(2)	3736(5)	1161(3)	6384(2)
$O_{(5)}$	8101(3)	995(2)	6165(2)	3739(4)	5568(3)	6723(2)
$C_{(1)}$	8788(6)	5194(4)	7128(3)	4954(6)	1872(5)	8474(4)
$C_{(2)}$	9067(7)	3785(5)	7380(4)	4341(6)	2176(5)	7677(3)
$C_{(3)}$	9769(4)	3473(3)	8138(2)	3965(6)	1078(5)	7164(4)
$C_{(4)}$	8997(7)	5677(5)	8714(4)	3917(7)	−352(5)	8636(4)
$C_{(5)}$	7328(8)	5353(6)	9459(5)	2244(6)	−91(5)	9385(4)
$C_{(6)}$	9831(9)	6787(6)	9021(5)	4557(7)	−1714(5)	8736(4)
$C_{(7)}$	8680(4)	2887(3)	6834(3)	4216(5)	3502(4)	7422(3)
$C_{(8)}$	8763(7)	1481(5)	6822(4)	3683(6)	4180(5)	6694(4)
$C_{(9)}$	9330(4)	427(3)	7259(3)	3083(6)	3914(4)	5974(3)
$C_{(10)}$	8985(5)	−730(3)	6866(3)	2742(5)	5135(4)	5559(3)
$C_{(11)}$	8253(6)	−352(5)	6221(4)	3157(6)	6120(5)	6015(4)
$C_{(12)}$	7596(7)	−1085(5)	5578(4)	3113(7)	7593(4)	5902(4)
$H_{(7)}$	823(4)	324(3)	633(3)	455(4)	415(4)	784(3)
$H_{(9)}$	992(5)	56(4)	778(3)	294(4)	305(4)	581(3)
$H_{(10)}$	932(5)	−166(4)	703(3)	231(5)	524(4)	507(3)

*The coordinates of the hydrogen atoms of the methyl groups are not presented and can be obtained from the authors.

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*See [1] for Communication 1.

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TABLE 2. Bond and Torsion Angles (deg)

Bond angle	Molecule		Bond angle	Molecule		Torsion angle	Molecule	
	A	B		A	B		A	B
$C_{(6)}-C_{(4)}-C_{(5)}$	114,8(5)	115,1(4)	$C_{(7)}-C_{(2)}-C_{(3)}$	125,5(4)	124,6(5)	$O_{(3)}-C_{(1)}-C_{(2)}-C_{(7)}$	8,5	7,0
$C_{(6)}-C_{(4)}-O_{(1)}$	105,2(5)	106,4(3)	$C_{(2)}-C_{(7)}-C_{(8)}$	133,9(5)	132,7(5)	$O_{(4)}-C_{(3)}-C_{(2)}-C_{(7)}$	6,7	11,8
$C_{(6)}-C_{(4)}-O_{(2)}$	105,1(4)	106,3(5)	$H_{(7)}-C_{(7)}-C_{(8)}$	110(2)	112(2)	$C_{(3)}-C_{(2)}-C_{(7)}-C_{(8)}$	1,9	2,8
$O_{(1)}-C_{(4)}-O_{(2)}$	110,1(4)	108,6(3)	$C_{(7)}-C_{(8)}-C_{(9)}$	139,0(6)	139,8(4)	$C_{(1)}-C_{(2)}-C_{(7)}-C_{(8)}$	179,4	179,9
$C_{(4)}-O_{(1)}-C_{(3)}$	117,3(4)	120,8(4)	$C_{(8)}-C_{(9)}-H_{(9)}$	122(2)	124(3)	$C_{(2)}-C_{(7)}-C_{(8)}-C_{(9)}$	−5,7	0,8
$C_{(4)}-O_{(2)}-C_{(1)}$	119,0(3)	118,2(4)	$C_{(8)}-C_{(9)}-C_{(10)}$	106,4(4)	107,7(4)			
$O_{(2)}-C_{(1)}-C_{(2)}$	116,7(5)	117,5(5)	$C_{(9)}-C_{(10)}-H_{(10)}$	124(3)	126(3)			
$O_{(1)}-C_{(3)}-C_{(2)}$	116,8(3)	116,0(5)	$C_{(10)}-C_{(11)}-C_{(12)}$	133,8(4)	134,0(6)			
$C_{(1)}-C_{(2)}-C_{(3)}$	119,0(5)	119,1(4)	$C_{(10)}-C_{(11)}-O_{(5)}$	110,6(5)	108,8(4)			
$C_{(2)}-C_{(1)}-O_{(3)}$	125,5(5)	125,9(5)	$C_{(9)}-C_{(8)}-O_{(5)}$	108,6(4)	107,8(4)			
$C_{(2)}-C_{(3)}-O_{(4)}$	127,0(4)	126,7(4)	$C_{(8)}-O_{(5)}-C_{(11)}$	106,7(4)	107,5(4)			
$C_{(7)}-C_{(2)}-C_{(1)}$	115,4(5)	116,2(5)						

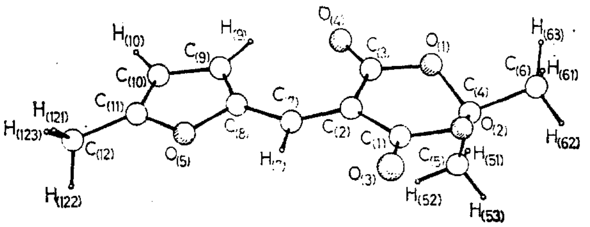

Fig. 1. Structure of the 2,2-dimethyl-5-(5-methyl-2-furfurylidene)-1,3-dioxane-4,6-dione molecule.

TABLE 3. Bond Lengths, d (Å)

Bond	Molecule		Bond	Molecule	
	A	B		A	B
$C_{(1)}—C_{(2)}$	1,476(6)	1,436(8)	$C_{(7)}—C_{(8)}$	1,415(6)	1,415(7)
$C_{(2)}—C_{(3)}$	1,443(8)	1,469(8)	$C_{(8)}—C_{(9)}$	1,371(7)	1,356(8)
$C_{(1)}—O_{(3)}$	1,200(7)	1,219(7)	$C_{(9)}—C_{(10)}$	1,409(5)	1,401(6)
$C_{(3)}—O_{(4)}$	1,208(4)	1,189(7)	$C_{(10)}—C_{(11)}$	1,336(8)	1,347(7)
$C_{(1)}—O_{(2)}$	1,355(6)	1,367(5)	$C_{(11)}—C_{(12)}$	1,488(9)	1,481(7)
$C_{(3)}—O_{(1)}$	1,374(5)	1,360(5)	$O_{(5)}—C_{(8)}$	1,389(7)	1,401(5)
$C_{(4)}—O_{(1)}$	1,441(6)	1,445(7)	$O_{(5)}—C_{(11)}$	1,358(5)	1,369(7)
$C_{(4)}—O_{(2)}$	1,424(7)	1,443(7)	$C_{(7)}—H_{(7)}$	0,98(4)	1,03(4)
$C_{(4)}—C_{(5)}$	1,506(8)	1,508(7)	$C_{(9)}—H_{(9)}$	1,07(5)	0,94(4)
$C_{(4)}—C_{(6)}$	1,529(9)	1,489(7)	$C_{(10)}—H_{(10)}$	1,02(4)	0,91(5)
$C_{(2)}—C_{(7)}$	1,352(7)	1,372(6)			

We have shown [1, 6, 7] that effective conjugation between the heterorings exists in furfurylidenedioxanedione molecules through the exocyclic C═C bond, with respect to which the furan ring exists in an s-cis conformation.

2,2-Dimethyl-5-(5-methyl-2-furfurylidene)-1,3-dioxane-4,6-dione was selected as a model compound of the furfurylidenedioxanedione series for the x-ray diffraction study.

According to the results of x-ray diffraction analysis, the unit cell of the crystal contains two symmetrically independent A and B molecules that have the same s-cis conformation of the mutual orientation of the furan ring and the exocyclic double bond (Fig. 1). The coordinates of the atoms, the bond lengths, and the bond angles are presented in Tables 1-3.

The dioxanedione ring is nonplanar and has a "crown" conformation: the base of the "crown" is the I plane [the $O_{(1)}$, $O_{(2)}$, and $C_{(2)}$ atoms], while the "teeth of the crown" consist of the II [the $O_{(1)}$, $O_{(2)}$, and $C_{(4)}$ atoms], III [the $C_{(2)}$, $C_{(3)}$, $O_{(1)}$, and $O_{(4)}$ atoms; the average deviation from the plane is 0.011 Å for the A molecule and 0.013 Å for the B molecule], and IV [the $C_{(1)}$, $C_{(2)}$, $O_{(2)}$, and $O_{(3)}$ atoms; the average deviations from the plane are 0.006 and 0.011 Å for the A and B molecules, respectively] planes. The angles between the planes are as follows: I and II form an angle of 44.7° in the A molecule (42.6° in the B molecule), I and III form an angle of 3.1° in the A molecule (10.6° in the B molecule), and I and IV form an angle of 8.1° in the A molecule (2.8° in the B molecule).

The furan ring is planar (plane V) within the limits of 0.003 Å. The $C_{(7)}$ and $C_{(12)}$ atoms lie in the plane of the furan ring, and the maximum deviation does not exceed 0.046 Å.

The angles between plane V and planes I, III, and IV in the A molecule are, respectively, 5.3°, 6.7°, and 12.6° (4.0°, 12.8°, and 6.1° in the B molecule).

Significant deviation of the bond lengths of the standard values is observed in the furfurylidene fragment of the molecules. Thus, the length of the $C_{(2)}$—$C_{(7)}$ bond appreciably exceeds the length of the standard C═C bond in the C═C—C═O fragments (1.36 Å [8]). Formally, the $C_{(7)}$—$C_{(8)}$ single bond is shortened (it has the same length as the exocyclic C—C bond in the furan-2-carboxylic acid molecule, i.e., 1.414 Å [9]). The lengths of the $O_{(5)}$—$C_{(8)}$ and $O_{(5)}$—$C_{(11)}$ bonds in the furan ring differ: the $O_{(5)}$—$C_{(11)}$ bond is shorter as a result of a shift of the unshared pair of electrons of the oxygen atom toward the $C_{(11)}$ atom. Thus, the flow of electrons in the conjugation system of the molecule is directed from the $C_{(11)}$ atom through the $C_{(10)}$, $C_{(9)}$, and $C_{(8)}$ atoms toward the $O_{(3)}$ and $O_{(4)}$ atoms.

In [1, 7] we explained the significant weak-field shift (to 8.3-8.8 ppm) of the signal of the proton in the 3 position of the furan ring of furfurylidenedioxanediones by means of the anisotropic effect of the adjacent carbonyl group. The results of x-ray diffraction analysis make it possible to assume the possibility of the formation of an intramolecular hydrogen bond that brings about closure of the $H_{(9)}-C_{(9)}-C_{(8)}-C_{(7)}-C_{(2)}-C_{(3)}-O_{(4)}$ fragment to a seven-membered ring, thereby fixing the s-cis conformation. The intramolecular $C_{(9)}-H_{(9)}\ldots O_{(4)}$ bond in the A molecule has the following geometrical parameters: the length of the $H_{(9)}\ldots O_{(4)}$ bond is 2.124(8) Å, the $C_{(9)}\ldots O_{(4)}$ distance is 2.886(5) Å, and the $C_{(9)}-H_{(9)}\ldots O_{(4)}$ and $H_{(9)}\ldots O_{(4)}-C_{(3)}$ angle are, respectively, 126.2(2)° and 125(2)° [in the B molecule these parameters are 2.222(4) Å and 2.882(7) Å and 126.4(2)° and 122.1(2)°]. The steric strain in the "exo" $H_{(9)}-C_{(9)}-C_{(8)}-C_{(7)}-C_{(2)}-C_{(3)}-O_{(4)}$ ring is manifested primarily in distortion of the bond angles of the sp^2-hybridized $C_{(7)}$ atom that links the heterorings together (Table 3). The $C_{(2)}$, $C_{(7)}$, $C_{(8)}$, and $C_{(9)}$ atoms are situated in the same plane (plane VI) within the limits of 0.013 Å (the A molecule) and 0.002 Å (the B molecule). In the A molecule the $C_{(3)}$, $O_{(4)}$, and $H_{(9)}$ atoms deviate from plane VI by, respectively, 0.039, 0.064, and 0.073 Å, as compared with 0.069, 0.324, and 0.030 Å in the B molecule.

In conclusion, let us note the following: a strictly determined orientation of the isopropylidene $C_{(6)}-C_{(4)}-C_{(5)}$ link, which is fixed by the effect of the crystal field, is observed in the crystal of the investigated compound. As noted in [1, 7], rapid oscillation of this fragment relative to plane I occurs in solution; as a result, the signal of the methyl groups of the isopropylidene link has the form of a singlet in the PMR spectra of furfurylidenedioxanediones even at −80°C. In solutions the groupings of atoms that lie in planes III and IV evidently also oscillate with a rather high frequency relative to plane I, since only one set of absorption bands that characterizes a certain average geometry of the molecule is observed in the IR and PMR spectra of the solutions.

EXPERIMENTAL

The transparent $C_{12}H_{12}O_5$ crystals are triclinic with the following cell parameters: $a = 8.959(5)$ Å, $b = 10.058(4)$ Å, $c = 14.105(6)$ Å, $\alpha = 86.41(3)°$, $\beta = 68.34(3)°$, $\gamma = 88.38(3)°$, $V = 1178.8(9)$ Å^3, structural class $P\bar{1}$, Z = 4(1.1). The experimental data were obtained with a PT Syntex automatic diffractometer (Mo K_α emission, β filter, θ/2θ scanning up to 20 θ_{max} = 48°). A total of 1591 reflections with $I \geq 3\sigma(I)$ was obtained. The structure was decoded by the direct method by means of a complex of SHELXTL programs [10] with a NOVA-3 computer and was refined within the anisotropic (isotropic for the hydrogen atoms) approximation up to divergence factors R = 0.04 and R_W = 0.043.*

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*The anisotropic temperature factors of the nonhydrogen atoms can be obtained from the authors.