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POLYFURYL(ARYL)ALKANES AND THEIR DERIVATIVES.

13.* MOLECULAR STRUCTURE OF BIS(5-METHYL-2-FURYL)(4-METHOXYPHENYL)METHANE AND TRIS(5-METHYL-2-FURYL)METHANE

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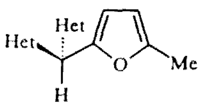
4-Methoxyphenylbis(5-methyl-2-furyl)methane (I) and tris(5-methyl-2-furyl)methane (II) were investigated by x-ray crystallographic analysis. It was established that the molecules of (I) have a propeller conformation with C_s symmetry, and the furan rings are turned with the oxygen atoms towards the methine hydrogen atom. The molecule of (II) has a different conformation with C_{2v} symmetry; one of the furan rings and the methine C–H bond lie ideally in one plane, and the other two furan rings are arranged symmetrically with the oxygen atoms in relation to this bond and incline toward eclipsing of the exocyclic C–C bond.

The molecules of triarylmethanes with a central sp^3-hybridized carbon atom are suitable models for the study of conformations determined by cooperative effects. The conformational structure of triphenylmethane has been studied well both in solutions and in the crystalline state. It was shown by means of the Kerr effect that the principal conformation in solution is the propeller conformation with C_3 symmetry [2, 3]. The chirality of such a conformer changes in four different ways, i.e., by simultaneous reorientation and by rotation of one, two, and all three rings [4]. Two independent asymmetric propeller conformations (with C_s symmetry) with angles of rotation of the benzene rings of 53, 34, and 30° for one of the conformers and 47, 38, and 21° for the other were found in the single crystal by x-ray crystallographic analysis [5].

To the authors' knowledge, information on the stereochemical structure of the heteroanalogs of triphenylmethane (di- and trifurylmethanes) has only been found in a single recent publication [6]. In this paper the conformational equilibrium in such compounds was investigated by means of the Kerr effect and the dipole moments, and it was suggested that four mutually transforming conformers with a preponderance of one of them exist in the solution.

It seemed of interest to determine what conformation the derivatives of difurylarylmethane and trifurylmethane acquire in the crystal in order to possess minimum energy in the force field of the neighbors surrounding it. For this purpose, an x-ray crystallographic analysis of bis(5-methyl-2-furyl)(4-methoxyphenyl)methane (I) and tris(5-methyl-2-furyl)methane (II) was undertaken. The results are given in Tables 1-6, and projections of stereochemical models of compounds (I) and (II) are shown in Fig. 1 and 2.

For convenience of discussion of the conformations of the molecules of compounds (I) and (II), as in [6], we will call the arrangement of the furan ring in the plane passing through the methine hydrogen atom, the central carbon atom, and the atom of the ring attached to it with the oxygen atom turned toward the methine hydrogen the ideal "*trans*" conformation. The real conformations of the methanes (I) and (II) can then be characterized easily by the angles of rotation of the plane of the aromatic ring from this ideal "*trans*" form.



The molecule of (I) in the crystal has a propeller conformation with C_s symmetry; all three rings are turned from the "ideal" plane to the same side but by different angles. The furan ring $C_{(8)}C_{(9)}C_{(10)}C_{(11)}O_{(2)}$ is deflected from the ideal "*trans*"

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*For Communication 12, see [1].

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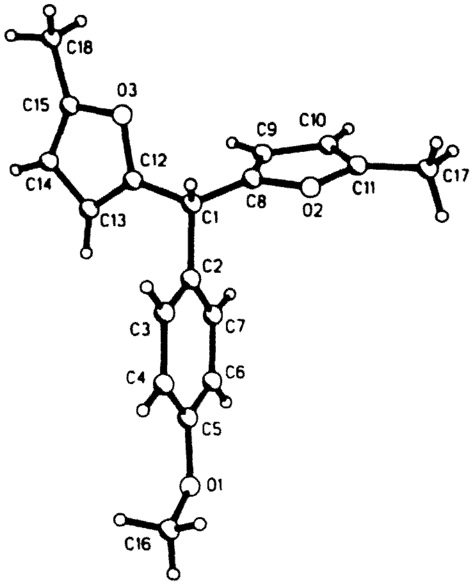

Fig. 1. Projection of the stereochemical model of the bis(5-methyl-2-furyl)(4-methoxyphenyl)methane molecule (I).

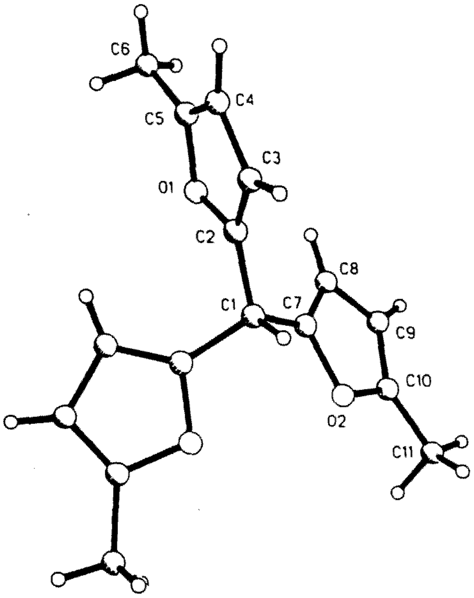

Fig. 2. Projection of the stereochemical model of the tris(5-methyl-2-furyl)methane molecule (II).

form by 71.6°, the furan ring $C_{(12)}C_{(13)}C_{(14)}C_{(15)}O_{(3)}$ by 51.0°, and the benzene ring by 22.6°. The bond angles at the central carbon atom are increased to 110-112° (Table 3), and the carbon–carbon bonds at the $C_{(1)}$ atom are elongated in comparison with the standard $C_{sp^3}-C_{sp^2}$ bonds (in the present case it is convenient to compare, for example, the lengths of the $C_{(1)}-C_{(8)}$ and $C_{(11)}-C_{(17)}$ bonds) as a result, clearly, of the bulky substituents, which the furan and benzene rings turned from the "ideal" plane represent.

The molecule of (II) in the crystal has a completely different conformation with C_{2v} symmetry; the furan ring $O_{(1)}C_{(2)}C_{(3)}C_{(4)}C_{(5)}$ lies in one plane (it is a plane with mirror symmetry) with exocyclic $C_{(1)}$ and $H_{(1)}$ atoms so that the $C_{(2)}-C_{(3)}$ double bond formally screens the $C_{(1)}-H_{(1)}$ single bond, i.e., the ideal "*cis*" form is realized. The other two furan rings are arranged symmetrically in relation to the plane of mirror symmetry, and their double bonds $C_{(7)}-C_{(8)}$ and $C_{(7a)}-C_{(8a)}$ are formally close to screening with the same exocyclic $C_{(1)}-C_{(2)}$ bond ($C_{(2)}-C_{(1)}-C_{(7)}-C_{(8)}$ torsion angle

TABLE 1. Coordinates of the Nonhydrogen Atoms (Å × 10^4) and the Temperature Factors (Å^2 × 10^3) of the Molecule of (I)

Atom	*x*	*y*	*z*	*U(eq)*
$O_{(1)}$	4273(1)	3999(2)	7449(1)	64(1)
$O_{(2)}$	1200(1)	1494(2)	9577(1)	56(1)
$O_{(3)}$	2403(1)	-2583(2)	9653(1)	57(1)
$C_{(1)}$	2515(2)	-25(2)	9457(2)	47(1)
$C_{(2)}$	3006(2)	1057(2)	8945(2)	45(1)
$C_{(3)}$	3972(2)	1550(3)	9570(2)	50(1)
$C_{(4)}$	4427(2)	2525(3)	9107(2)	53(1)
$C_{(5)}$	3910(2)	3019(2)	7994(2)	49(1)
$C_{(6)}$	2944(2)	2531(3)	7348(2)	55(1)
$C_{(7)}$	2501(2)	1568(3)	7820(2)	55(1)
$C_{(8)}$	1415(2)	273(2)	9125(2)	51(1)
$C_{(9)}$	558(2)	-357(3)	8441(3)	65(1)
$C_{(10)}$	-236(2)	508(4)	8461(3)	74(1)
$C_{(11)}$	163(2)	1611(3)	9137(2)	63(1)
$C_{(12)}$	2666(2)	-1491(2)	9107(2)	48(1)
$C_{(13)}$	2993)2)	-2027(3)	8338(2)	58(1)
$C_{(14)}$	2936(2)	-3537(3)	8399(3)	64(1)
$C_{(15)}$	2578(2)	-3829(2)	9192(2)	57(1)
$C_{(16)}$	5237(3)	4601(4)	8108(4)	81(1)
$C_{(17)}$	-235(3)	2854(4)	9535(4)	87(1)
$C_{(18)}$	2288(4)	-5155(3)	9626(5)	83(1)

TABLE 2. Bond Lengths in the Molecule of (I)

Bond	*l*, Å	Bond	*l*, Å	Bond	*l*, Å
$O_{(1)}—C_{(5)}$	1,372(3)	$C_{(1)}—C_{(2)}$	1,523(3)	$C_{(9)}—C_{(10)}$	1,417(4)
$O_{(1)}—C_{(16)}$	1,422(4)	$C_{(2)}—C_{(3)}$	1,378(3)	$C_{(10)}—C_{(11)}$	1,319(4)
$O_{(2)}—C_{(8)}$	1,371(3)	$C_{(2)}—C_{(7)}$	1,390(3)	$C_{(11)}—C_{(17)}$	1,478(4)
$O_{(2)}—C_{(11)}$	1,378(3)	$C_{(3)}—C_{(4)}$	1,387(3)	$C_{(12)}—C_{(13)}$	1,334(3)
$O_{(3)}—C_{(12)}$	1,372(3)	$C_{(4)}—C_{(5)}$	1,375(3)	$C_{(13)}—C_{(14)}$	1,428(3)
$O_{(3)}—C_{(15)}$	1,376(3)	$C_{(5)}—C_{(6)}$	1,381(3)	$C_{(14)}—C_{(15)}$	1,324(4)
$C_{(1)}—C_{(12)}$	1,491(3)	$C_{(6)}—C_{(7)}$	1,375(3)	$C_{(15)}—C_{(18)}$	1,488(4)
$C_{(1)}—C_{(8)}$	1,499(3)	$C_{(8)}—C_{(9)}$	1,331(3)		

TABLE 3. Bond Angles in the Molecule of Compound (I)

Angle	ω, deg	Angle	ω, deg
$C_{(5)}—O_{(1)}—C_{(16)}$	117,3(2)	$C_{(9)}—C_{(8)}—O_{(2)}$	109,5(2)
$C_{(8)}—O_{(2)}—C_{(11)}$	107,0(2)	$C_{(9)}—C_{(8)}—C_{(1)}$	134,8(2)
$C_{(12)}—O_{(3)}—C_{(15)}$	107,0(2)	$O_{(2)}—C_{(8)}—C_{(1)}$	115,6(2)
$C_{(12)}—C_{(1)}—C_{(8)}$	110,8(2)	$C_{(8)}—C_{(9)}—C_{(10)}$	106,4(3)
$C_{(12)}—C_{(1)}—C_{(2)}$	110,2(2)	$C_{(11)}—C_{(10)}—C_{(9)}$	108,4(3)
$C_{(8)}—C_{(1)}—C_{(2)}$	112,3(2)	$C_{(10)}—C_{(11)}—C_{(2)}$	108,7(2)
$C_{(3)}—C_{(2)}—C_{(7)}$	117,5(2)	$C_{(10)}—C_{(11)}—C_{(17)}$	135,4(3)
$C_{(3)}—C_{(2)}—C_{(1)}$	121,4(2)	$O_{(2)}—C_{(11)}—C_{(17)}$	115,9(3)
$C_{(7)}—C_{(2)}—C_{(1)}$	121,2(2)	$C_{(13)}—C_{(12)}—O_{(3)}$	109,2(2)
$C_{(2)}—C_{(3)}—C_{(4)}$	121,8(2)	$C_{(13)}—C_{(12)}—C_{(1)}$	134,5(2)
$C_{(5)}—C_{(4)}—C_{(3)}$	119,7(2)	$O_{(3)}—C_{(12)}—C_{(1)}$	116,3(2)
$O_{(1)}—C_{(5)}—C_{(4)}$	125,0(2)	$C_{(12)}—C_{(13)}—C_{(14)}$	107,0(2)
$O_{(1)}—C_{(5)}—C_{(6)}$	115,4(2)	$C_{(15)}—C_{(14)}—C_{(13)}$	107,2(3)
$C_{(4)}—C_{(5)}—C_{(6)}$	119,6(2)	$C_{(14)}—C_{(15)}—O_{(3)}$	109,5(2)
$C_{(7)}—C_{(6)}—C_{(5)}$	120,1(2)	$C_{(14)}—C_{(15)}—C_{(18)}$	134,6(3)
$C_{(6)}—C_{(7)}—C_{(2)}$	121,4(2)	$O_{(3)}—C_{(15)}—C_{(18)}$	115,7(3)

15.7°). This results in the appearance of a conformation with rotation of the other two furan rings by 47° from the ideal "*trans*" form to opposite sides and in the approach of the oxygen atoms $O_{(2)}$ and $O_{(2a)}$ to 3.055 Å (the sum of the van der

TABLE 4. Coordinates of the Nonhydrogen Atoms (Å × 10^4) and the Temperature Factors ($Å^2 \times 10^3$) of the Molecule of (II)

Atom	x	y	z	$U(eq)$
$O_{(1)}$	1093(2)	707(2)	7500	53(1)
$O_{(2)}$	-2715(2)	-1563(1)	6413(1)	50(1)
$C_{(1)}$	-466(4)	-999(2)	7500	44(1)
$C_{(2)}$	1179(4)	-394(2)	7500	45(1)
$C_{(3)}$	2811(4)	-699(3)	7500	55(1)
$C_{(4)}$	3826(5)	249(3)	7500	61(1)
$C_{(5)}$	2752(4)	1080(3)	7500	55(1)
$C_{(6)}$	2929(6)	2264(3)	7500	87(2)
$C_{(7)}$	-1475(2)	-807(1)	6611(1)	44(1)
$C_{(8)}$	-1431(3)	-86(2)	5910(2)	57(1)
$C_{(9)}$	-2673(3)	-397(2)	5226(2)	59(1)
$C_{(10)}$	-3421(3)	-1285(2)	5549(1)	51(1)
$C_{(11)}$	-4775(4)	-2006(3)	5185(2)	76(1)

TABLE 5. Bond Lengths in the Molecule of (II)

Bond	l, Å	Bond	l, Å	Bond	l, Å
$O_{(1)}$—$C_{(2)}$	1,373(3)	$C_{(5)}$—$C_{(6)}$	1,481(5)	$C_{(1)}$—$C_{(7)}$	1,497(2)
$O_{(2)}$—$C_{(7)}$	1,380(2)	$C_{(8)}$—$C_{(9)}$	1,421(3)	$C_{(2)}$—$C_{(3)}$	1,332(4)
$C_{(1)}$—$C_{(2)}$	1,491(4)	$C_{(10)}$—$C_{(11)}$	1,479(4)	$C_{(4)}$—$C_{(5)}$	1,333(5)
$C_{(1)}$—$C_{(7A)}$	1,497(2)	$O_{(1)}$—$C_{(5)}$	1,379(3)	$C_{(7)}$—$C_{(8)}$	1,334(3)
$C_{(3)}$—$C_{(4)}$	1,423(5)	$O_{(2)}$—$C_{(10)}$	1,379(2)	$C_{(9)}$—$C_{(10)}$	1,332(3)

TABLE 6. Bond Angles in the Molecule of Compound (II)

Angle	ω, deg	Angle	ω, deg
$C_{(2)}$—$O_{(1)}$—$C_{(5)}$	106,9(2)	$C_{(7)}$—$O_{(2)}$—$C_{(10)}$	106,7(1)
$C_{(2)}$—$C_{(1)}$—$C_{(7)}$	112,0(1)	$C_{(2)}$—$C_{(1)}$—$C_{(7A)}$	112,0(1)
$C_{(7)}$—$C_{(1)}$—$C_{(7A)}$	113,2(2)	$O_{(1)}$—$C_{(2)}$—$C_{(1)}$	117,5(2)
$O_{(1)}$—$C_{(2)}$—$C_{(3)}$	109,4(3)	$C_{(1)}$—$C_{(2)}$—$C_{(3)}$	133,1(3)
$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	107,4(3)	$C_{(3)}$—$C_{(4)}$—$C_{(5)}$	107,0(3)
$O_{(1)}$—$C_{(5)}$—$C_{(4)}$	109,4(3)	$O_{(1)}$—$C_{(5)}$—$C_{(6)}$	115,1(3)
$C_{(4)}$—$C_{(5)}$—$C_{(6)}$	135,5(3)	$O_{(2)}$—$C_{(7)}$—$C_{(1)}$	115,5(2)
$O_{(2)}$—$C_{(7)}$—$C_{(8)}$	109,2(2)	$C_{(1)}$—$C_{(7)}$—$C_{(8)}$	135,2(2)
$C_{(7)}$—$C_{(8)}$—$C_{(9)}$	107,4(2)	$C_{(8)}$—$C_{(9)}$—$C_{(10)}$	107,2(2)
$O_{(2)}$—$C_{(10)}$—$C_{(9)}$	109,4(2)	$O_{(2)}$—$C_{(10)}$—$C_{(11)}$	116,1(2)
$C_{(9)}$—$C_{(10)}$—$C_{(11)}$	134,5(2)		

Waals radii of two oxygen atoms is 3.10 Å) [7]. This intramolecular contact may lead to a small degree of twisting of the furan rings about the $C_{(1)}-C_{(7)}$ and $C_{(1)}-C_{(7a)}$ bonds from screening with the $C_{(1)}-C_{(2)}$ bond (Table 6). The bond angles at the central carbon atom in the molecule of (II) are also changed somewhat in comparison with the ideal values; the $C_{(2)}-C_{(1)}-C_{(7)}$ and $C_{(7)}-C_{(1)}-C_{(7a)}$ angles are increased to 112 and 113.3° respectively, and the $H_{(1)}-C_{(1)}-C_{(2)}$ and $H_{(1)}-C_{(1)}-C_{(7)}$ angles are reduced to 105.3 and 106.9° respectively.

As in the molecule of (I), the carbon–carbon bonds at the central atom $C_{(1)}$ are elongated compared with the exocyclic 5-C–CH_3 bonds, formed by atoms with the same hybridization (Table 5). In turn, the $C_{(1)}-C_{(7)}$ bond is a little longer than the $C_{(1)}-C_{(2)}$ bond, and this is probably due to the intramolecular contacts $O_{(2)}\cdots O_{(2a)}$ and $H_{(8)}(H_{(8a)})\cdots C_{(2)}$. (The hydrogen atom $H_{(8)}$ is at a distance of 2.266 Å from the plane of the furan ring $C_{(2)}C_{(3)}C_{(4)}C_{(5)}O_{(1)}$.)

The interatomic separations and the bond angles in the furan rings correspond to the standard values [8], but the $C_{(2)}C_{(3)}C_{(4)}C_{(5)}O_{(1)}$ and $C_{(7)}C_{(8)}C_{(9)}C_{(10)}O_{(2)}$ rings are not identical. The furan ring $C_{(2)}C_{(3)}C_{(4)}C_{(5)}O_{(1)}$ is ideally planar. (The average deviation of the atoms from the plane drawn through the atoms of this ring amounts to 0.0000 Å.) The exocyclic atoms

$C_{(1)}$, $H_{(1)}$, and $C_{(6)}$ are also arranged ideally in this plane. The furan ring $C_{(7)}C_{(8)}C_{(9)}C_{(10)}O_{(2)}$ is less planar. (The average deviation from the plane amounts to 0.0032 Å.)

The stacking of the molecules in the crystal is characterized by normal van der Waals contacts and does not reveal any specific intermolecular interactions.

It is interesting that the transition from triphenylmethane to the corresponding triphenylmethyl cation changes the nature of the mutual arrangement of the benzene rings little. For example, in the single crystal of tris(4-aminophenyl)methyl perchlorate the cation is an asymmetric propeller with the rings rotated by 29, 34, and 34° [9]. On the other hand, the transition from trifurylmethane (I) to the corresponding trifuryl perchlorate leads to the transformation of the organic fragment of the molecule to a symmetrical (C_3) propeller with the furan rings rotated by 10.4° in relation to the plane of the central atom [10].

EXPERIMENTAL

Compounds (I) and (II) were synthesized by the method in [11].

X-Ray Crystallographic Investigations. The colorless monoclinic crystals of compound (I) with the composition $C_{18}H_{18}O_3$ were grown from hexane; the unit cell parameters were $a = 14.454(4)$, $b = 9.412(2)$, $c = 12.568(3)$ Å, $\beta = 113.69(2)°$, $V = 1565.7(7)$ Å^3. Space group $P_{2(1)/c}$, $z = 4$. The unit cell parameters and the intensities of 1404 independent reflections with $I > 2\sigma(I)$ were obtained on a Nicolet P3 diffractometer without a monochromator (MoKα radiation, $\theta/2\theta$ scan). The structure was interpreted by the direct method by means of the SHELXTL Plus software (PC version) and was interpreted in anisotropic approximation (isotropic for the hydrogen atoms) to divergence factors $R = 0.0318$ and $R_W = 0.0794$.

The colorless prismatic crystals of compound (II) with composition $C_{16}H_{16}O_3$ were grown from hexane; unit cell parameters $a = 7.823(2)$, $b = 12.456(2)$, $c = 14.057(2)$ Å, $V = 1369.8(0.8)$ Å^3. Space group P_{nam}, $z = 4$. The unit cell parameters and the intensities of 581 independent reflections with $I > 3\sigma(I)$ were obtained on an Enraf-Nonius CAD4 diffractometer without a monochromator (MoKα radiation, $\theta/2\theta$ scan). The structure was interpreted by the direct method by means of the SHELXTL Plus software (PC version) and was refined in anisotropic approximation (isotropic for the hydrogen atoms) to divergence factors $R = 0.023$ and $R_W = 0.023$.

The atomic coordinates can be obtained from the authors.

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