Korean J. Cryst., Vol. 5, No. 1, pp. 14~19, 1994.

트리풀르오로메칠트리페닐-1,2,4-트리오키소란의 결정 및 분자구조

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The Crystal and Molecular Structure of Trifluoromethyltriphenyl-1,2,4-Trioxolane

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요 약

트리풀르오로메칠트리페닐 1,2,4-트리오키소란($C_{21}H_{15}F_3O_3$)은 삼사정계인 공간군 $P\bar{1}$으로 a=10.477(1), b=11.056(1), c=9.917(3) Å, α=104.7(1), β=122.7(1), γ=63.9(1)°, Z=2, V=867.9(3) Å^3, Dc=1.43 g/cm^3, λ(Mo Kα)=0.71069 Å, μ =0.0116 cm^{-1}, F(000)=384, 그리고 I 〉 1.0 σ(I) 인 1713 개의 관측 된 회절점에 대한 R 값은 0.067 였다. 직접법에 의하여 구조를 풀었으며 전행열-최소자승법에 의하여 정밀화하였고 C-H결합길이는 0.96 Å 에 고정하였다.106.6°의 두 사이각을 갖는 페닐고리(2)와 고리(3)는 트리오키소란분자평면의 위쪽에 있으나 CF_3기와 페닐고리(1)은 아래쪽으로 있다. 트리오키소란 꼬리는 봉투모양의 구조를 갖고 있으며 그의 두 탄소원자(C(2)와 C(3))는 탄소원자의 내각에 거의 비슷한 각으로 치환기들과 연결되어 있다.분자들은 van der Waals 힘에 의하여 결합되었고 가장 가까운 거리는 O(2) 와 F(2)(-x, 1 + y, 1 - z)사이의 3.256 Å이다.

Abstract

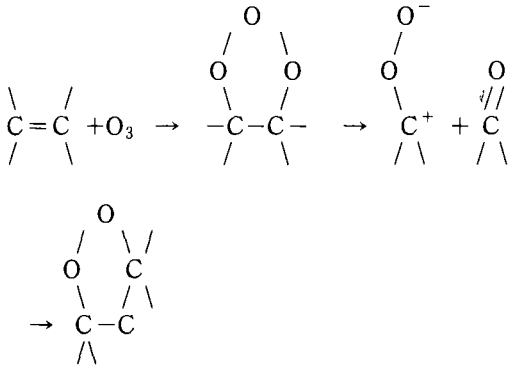
Trifluoromethyltriphenyl-1,2,4-trioxolane($C_{21}H_{15}F_3O_3$)is triclinic, space group $P\bar{1}$ with a=10.477(1), b=11.056(1), c=9.917(3)Å, α=104.7(1), β=122.7(1), γ=63.9(1), Z=2, V=867.9(3) Å^3, Dc=1.43g/cm^3, λ(Mo Kα)=0.71069 Å, μ=0.0166 cm^{-1}, F(000)=384, and R=0.067 for 1713 unique observed reflections with I 〉 1.0 σ(I). The structure was solved by direct methods and refined by full-matrix least-squares refinement with the fixed C-H bond lengths at 0.96 Å. Two phenyl rings((2) and (3)) that have the dihydral angle of 106.6°

are located on the molecular plane of trioxolane upward, while the CF_3 group and the phenyl ring(1) are downward. The trioxolane ring has an envelope conformation, connecting with its carbon atoms(C(2) and C(3)) to the substituents withnearly internal angles of a carbon atom.

Molecules are contacted by van der Waals force with the shortest distance of 3.256 Å between O(2) and F(2)(-x, 1 + y, 1 - z).

1. Introduction

The ozonides produced in the ozonolysis of alkenes in solvents were first explained by the mechanism proposed by Criegee[1,2] and revised to include stereochemical effects[3,4]



More recently, attention has forcused on the structural and mechanistic details of ozonides. Few experimentally-determined ozonide structures have been reported, with only those of simple ozonides known in detail by microwave spectroscopy[5,6]

Here we report the crystal structure of trifluoromethyltriphenyl-1, 2,4-trioxolane by using X-ray diffraction method, since the structure of ozonides are important in its own right but little information is available in the literature on the structure of ozonides, particularly those with substituents.

2. Experimental

Title compound was synthesized by published procedure[7] and single crystals were grown by slow evaporation in pentane solvent at room temperature. The crystals have the habits of a colorless irregular lump and the 0.54 x 0.48 x 0.73㎜ sizes of a crystal were used for data collection.

Accurate lattice parameters were obtained by least-squares refinement,setting for the 24 reflections in the ranges $7.7 < \theta < 12.8^{\circ}$ measured with graphite-monochromatized Mo-Kα radiation(λ= 0.71069) on the Enraf-Nonius CAD4 diffrasctometer at 297 K. Intensities were recorded by the w-2θscan technique (w-scan width = 0.8 + 0.34 tan θ°)with $2\theta_{max}=46.0^{\circ}$ for the ranges $-10 \le h \le 11$, $0 \le k \le 12$, $-10 \le l \le 10$. The three standard reflections monitored every 100 miniutes showed only 2.8 % variations of intensity during the course of data collection. Of 2410 measured reflections, the 1713 unique observed reflections with $I > 1.0\ \sigma(I)$ were used in structure determination. Corrections for Lorentz and polarization effects were applied to the intensity data, while no absorption or extinction correction was carried out.Structure was solved by direct methods and refined by full-matrix least-squares refinement, with all non-hydrogen atoms by anisotropic thermal parameters and hydrogen atoms fixed at 0.96 Å by isotropic ones. The final R and wR values with 244 least-squares parameters were 0.067 and 0.059, where $w^{-1} = \sigma^2(F) + 0.0004\ F^2$ and goodness of fit = 1.29. The $(\Delta/\sigma)_{max}$ of the final cycle was 0.001 and a difference Fourier map

showed the highest peak 0.27 eÅ^{-3} and the lowest hole -0.27 eÅ^{-3}.

All atomic scattering factors were from the International Tables for X-ray Crystallography (1974)[8] and calculations were performed using the SHELX-programs[9].

3. Results and Discussion

Fig. 1 depicts the plot of a molecular structure with the atomic numbering scheme and Table 1 gives crystal data. Table 2 lists the final atomic coordinates of the non-hydrogen atoms with the equivalent isotropic thermal parameters. Table 3 and 4 give bond lengths and bond angles, and for a Table 5 selected torsion angles. In a molecule there are three benzene rings, of which the ring(1) has the C-C bond lengths within the ranges from 1.349(10)-1.402(10) Å and the C-C-C bond angles from 117.8(6)-121.6(7)°, the ring(2) with bond lengths from 1.358(15)-1.393(10) Å and bond angles from 118.8(7)-!21.5(7)°, and the ring(3) with bond lengths 1.363(13)-1.399(11) Å and bond angles from 118.5(6)-121.1(8)°. Of these rings the maximum deviation from their own molecular planes was -0.012 Å for the C(13) of the benzene ring(1). The carbon atom C(1) of the CF_3 group has tetrahydral angles of 107.0(6), 107.4(6) and 107.(8)° with the C-F bond lenghts of 1.315(10), 1.335(7) and 1.336(12) Å, which are a little shorter than those of fluoroethyleneozonide(=1.375(5) Å)[11] and 1,1-difluoroethyleneozonide (=1.359(20) Å)[12] in microwave spectroscopy.

With respect to the five-membered ring of trioxolane, it has bond length of 1.463(7) Å for a O(1)-O(2) bond and of 1.418(7)-1.461(9) Å for the C-O bonds with the puckering carbon angles within the ranges from 100.7(5)-106.6(5)°, which resulted in the similar data already reported by Kuczkowsky et al.[3,10,11,12], in microwave spectroscopy.

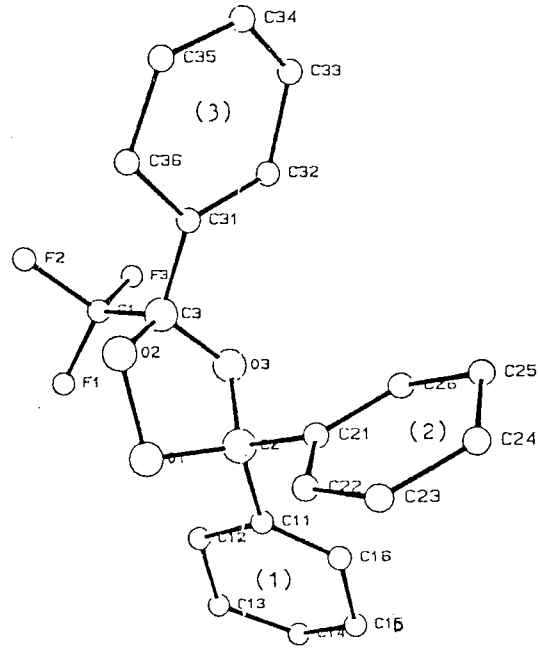


Fig1. A molecular conformation with the atomic labelling sheme oftrifluoromethyltriphenyl-1,2,4- trioxolane.

Table 1. Crystal data.

Formula	$C_{21}H_{15}F_3O_3$
Formula weight	372.3
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell demensions	a=10.477(1) Å α=104.7(1)°
	b=11.056(1) β=122.7(1)
	c=9.917(3) γ=63.9(1)
Volume	867.9(3) Å
Z	2
Density(cal.)	1.43 g/cm^3
Absorption coefficient	0.116 mm^{-1}
F(000)	384

Table 2. Fractional atomic coordinates($\times 10^4$) and equivalent isotropic temperature factors($Å^2 \times 10^3$) of non-H atoms.

atom	x	y	z	Ueq
F(1)	-3132(5)	-2269(5)	2716(6)	.078
F(2)	-2015(5)	-2851(5)	5118(6)	.070
F(3)	-2464(5)	-866(5)	4657(6)	.065
O(1)	-519(6)	-3828(5)	2140(6)	.045
O(2)	164(6)	-4007(5)	3842(6)	.043
O(3)	-383(5)	-1873(5)	3425(5)	.036
C(1)	-2006(10)	-2161(10)	4199(10)	.049
C(2)	-17(9)	-2798(7)	2227(9)	.039
C(3)	-276(8)	-2653(7)	4424(8)	.034
C(11)	-1128(9)	-2116(7)	623(8)	.036
C(12)	-2805(9)	-1865(8)	-200(9)	.053
C(13)	-3809(11)	-1209(9)	-1610(10)	.065
C(14)	-3246(11)	-743(9)	-2234(10)	.065
C(15)	-1599(11)	-972(9)	-1476(10)	.065
C(16)	-556(9)	-1657(8)	-37(9)	.053
C(21)	1776(9)	-3299(8)	2769(9)	.043
C(22)	2534(10)	-4561(8)	2308(10)	.056
C(23)	4154(11)	-5003(9)	2716(10)	.064
C(24)	5004(11)	-4181(11)	3604(11)	.073
C(25)	4288(10)	-2925(10)	4081(10)	.063
C(26)	2660(9)	-2490(8)	3682(9)	.052
C(31)	995(8)	-2630(8)	6168(9)	.035
C(32)	1517(9)	-1568(8)	6813(9)	.047
C(33)	2626(10)	-1556(9)	8453(10)	.060
C(34)	3214(10)	-2591(10)	9408(10)	.061
C(35)	2691(10)	-3639(9)	8750(10)	.059
C(36)	1563(9)	-3671(8)	7131(10)	.048

*$Ueq=[1/3(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma](U_{11}\sin^2\alpha+U_{22}\sin^2\beta+U_{33}\sin^2\gamma+2U_{12}\sin\alpha\sin\beta\cos\gamma+2U_{13}\sin\alpha\sin\gamma\cos\beta+2U_{23}\sin\beta\sin\gamma\cos\alpha)$.

Table 3. Bond distances(Å) with e.s.d.'s in parentheses.

F(1) - C(1) 1.315 (10)	F(2) - C(1) 1.335 (7)
F(3) - C(1) 1.336 (12)	O(1) - O(2) 1.463 (7)
O(1) - C(2) 1.418 (7)	O(2) - C(3) 1.423 (9)
O(3) - C(2) 1.461 (9)	O(3) - C(3) 1.402 (6)
C(1) - C(3) 1.544 (10)	C(2) - C(11) 1.512 (9)
C(2) - C(21) 1.505 (10)	C(3) - C(31) 1.511 (10)
C(11) -C(12) 1.402 (10)	C(11) -C(16) 1.381 (7)
C(12) -C(13) 1.356 (10)	C(13) -C(14) 1.349 (8)
C(14) -C(15) 1.384 (12)	C(15) -C(16) 1.392 (10)
C(21) -C(22) 1.370 (12)	C(21) -C(26) 1.375 (11)
C(22) -C(23) 1.382 (12)	C(23) -C(24) 1.362 (13)
C(24) -C(25) 1.358 (15)	C(25) -C(26) 1.393 (10)
C(31) -C(32) 1.376 (11)	C(31) -C(36) 1.389 (9)
C(32) -C(33) 1.399 (11)	C(33) -C(34) 1.372 (10)
C(34) -C(35) 1.363 (13)	C(35) -C(36) 1.391 (12)

Table 4. Bond angles(°) with e.s.d.'s in parentheses.

F(2) -C(1) -F(1) 107.4 (6)	F(3) -C(1) -F(1) 107.8 (7)
F(3) -C(1) -F(2) 107.0 (6)	O(3) -C(2) -O(1) 101.8 (5)
O(3) -C(3) -O(2) 106.3 (5)	C(1) -C(3) -O(2) 109.3 (5)
C(1) -C(3) -O(3) 106.7 (6)	C(2) -O(1) -O(2) 100.7 (5)
C(3) -O(2) -O(1) 102.4 (5)	C(3) -O(3) -C(2) 106.6 (5)
C(3) -C(1) -F(1) 114.1 (6)	C(3) -C(1) -F(2) 110.7 (7)
C(3) -C(1) -F(3) 109.6 (6)	C(11) -C(2) -O(1) 107.6 (6)
C(11) -C(2) -O(3) 109.1 (5)	C(12) -C(11) -C(2) 120.3 (6)
C(13) -C(12) -C(11) 120.2 (6)	C(14) -C(13) -C(12) 121.6 (7)
C(15) -C(14) -C(13) 120.5 (8)	C(15) -C(16) -C(11) 121.5 (6)
C(16) -C(11) -C(2) 121.7 (6)	C(16) -C(11) -C(12) 117.8 (6)
C(16) -C(15) -C(14) 118.3 (7)	C(21) -C(2) -O(1) 113.1 (6)
C(21) -C(2) -O(3) 110.6 (6)	C(21) -C(2) -C(11) 113.9 (6)
C(22) -C(21) -C(2) 119.9 (6)	C(23) -C(22) -C(21) 120.5 (7)
C(24) -C(23) -C(22) 119.5 (8)	C(25) -C(24) -C(23) 121.5 (7)
C(25) -C(26) -C(21) 120.5 (7)	C(26) -C(21) -C(2) 120.9 (7)
C(26) -C(21) -C(22) 119.2 (6)	C(26) -C(25) -C(24) 118.8 (7)
C(31) -C(3) -O(2) 107.7 (6)	C(31) -C(3) -O(3) 114.8 (5)
C(31) -C(3) -C(1) 111.9 (5)	C(32) -C(31) -C(3) 121.0 (7)
C(33) -C(32) -C(31) 118.8 (7)	C(34) -C(33) -C(32) 121.1 (8)
C(35) -C(34) -C(33) 119.4 (8)	C(35) -C(36) -C(31) 119.1 (7)
C(36) -C(31) -C(3) 118.5 (6)	C(36) -C(31) -C(32) 120.5 (7)
C(36) -C(35) -C(34) 121.1 (8)	

Table 5. Selected torsion angles(°) with e.s.d.'s in parentheses.

C(2) -O(1) -O(2) -C(3)	45.1(5)
O(2) -O(1) -C(2) -O(3)	-44.0(4)

O(1)	-O(2)	-C(3)	-O(3)	-28.0(4)
C(3)	-O(3)	-C(2)	-O(1)	27.6(5)
C(2)	-O(3)	-C(3)	-O(2)	.8 (5)
F(1)	-C(1)	-C(3)	-O(3)	59.0 (6)
F(2)	-C(1)	-C(3)	-O(3)	-179.8 (8)
F(3)	-C(1)	-C(3)	-O(3)	-61.9 (6)
F(1)	-C(1)	-C(3)	-O(2)	-55.5 (6)
F(2)	-C(1)	-C(3)	-O(2)	65.7 (6)
F(3)	-C(1)	-C(3)	-O(2)	-176.4 (8)
F(1)	-C(1)	-C(3)	-C(31)	-174.6 (9)
F(2)	-C(1)	-C(3)	-C(31)	-53.4 (6)
F(3)	-C(1)	-C(3)	-C(31)	64.4 (7)
O(2)	-O(1)	-C(2)	-C(11)	-158.6 (6)
O(2)	-O(1)	-C(2)	-C(21)	74.7 (6)
C(3)	-O(3)	-C(2)	-C(11)	141.2 (6)
C(3)	-O(3)	-C(2)	-C(21)	-92.8 (6)
O(1)	-O(2)	-C(3)	-C(1)	86.8 (6)
O(1)	-O(2)	-C(3)	-C(31)	-151.5 (6)
C(2)	-O(3)	-C(3)	-C(1)	-115.8 (6)
C(2)	-O(3)	-C(3)	-C(31)	119.6 (6)

Table 6. Least-squares planes with displacement(Å) from the best plane and dihedral angles. Equation is expressed in the form of Ax + By + Cz = D, where x, y, and z are in Å.

A. least-squares planes related to an envelope.

atom in plane	shifts	atoms out of plane	shifts	constants A	B	C	D
C(2)	-.0040			.785	-.158	.598	1.535
O(3)	.0023						
C(3)	-.0054						
O(2)	.0019						
		O(1)	-.6579				

atom in plane	shifts	atoms out of plane	shifts	constants A	B	C	D
C(2)	0.0000			-.718	.694	-.043	-.182
O(1)	0.0000						
O(2)	0.0000						
		O(3)	.9927				
		C(3)	.9856				

B. dihydral angles

group	benzene ring	angle(°)	benzene ring	benzene ring	angle(°)
trioxolane	1	99.2	1	2	97.0
	2	97.9	1	3	52.8
	3	144.1	2	3	06.6

It has been discussed that there were two main types of structural conformation of 1,2,4-trioxolane, one as an envelope conformation[10] with the puckering of the O-O atoms of the molecule proposed by Kuczkowski[10], the other as one with the C-C half chair conformation proposed by Bauld-Baily[3]The structure of trioxolane of the title compound has an envelope conformation. The O(1) atom, which is located on an apex of a triangular plane of C(2)-O(1)-O(2), is 0.658 Å upward from its molecular plane involved the C(2)-O(3)-C(3)-O(2) atoms, resulting in the angle of 134° between two planes. Two benzene rings (2) and (3), which are locating above the molecular plane of trioxolane, has the dihedral angle of 106.6°,and the rings (1) and (2) ,which are downward and upward out of the plane, has 97.0°. The unit cell packing diagram of molecules is given in Fig.2.

The molecules are contacted by van der Waals forcewith the shortest distance of 3.256(6)Å between O(2) and F(2)(- x, 1 + y, 1 - z).

Acknowledgement

Authors thank Mr. Jin-Ho Lee, Department of Physics, Chungnam National University for helping the calculation of data.

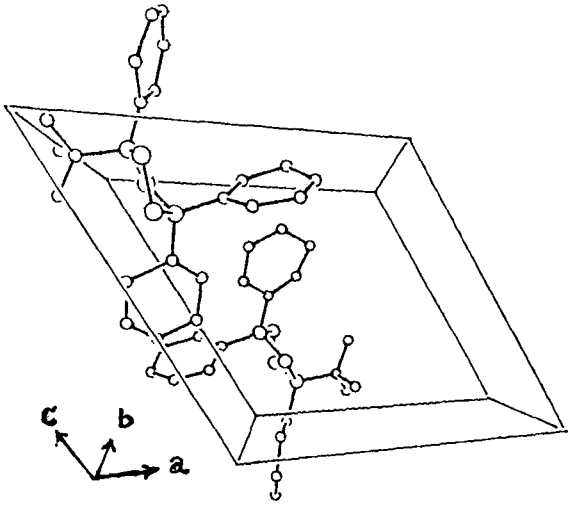


Fig.2. The unit cell packing diagram of molecules.

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The following supplemental data are available on request.

1. anisotropic thermal parameters of non-H atoms and Ueq of H-atom.
2. atomic coordinates of H-atom.
3. a table of Fo and Fc values.