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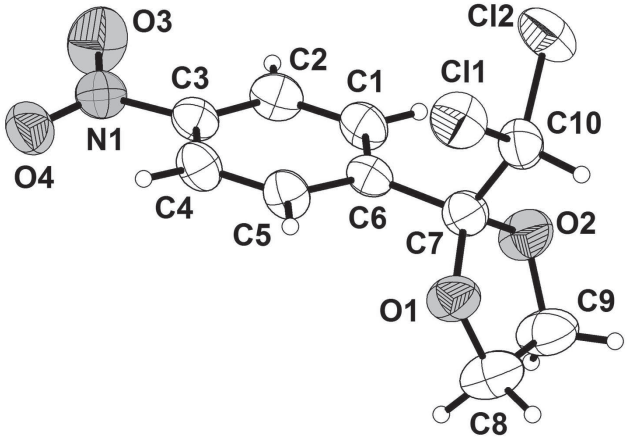
Crystal structure of 2-dichloromethyl-2-*p*-nitrophenyl-1,3-dioxolane, $C_{10}H_9Cl_2NO_4$



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Abstract

$C_{10}H_9Cl_2NO_4$, orthorhombic, *Pbca*, $a = 11.151(2)$ Å, $b = 7.0923(14)$ Å, $c = 29.243(6)$ Å, $V = 2312.7(8)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0459$, $wR_{ref}(F^2) = 0.1223$, $T = 293$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of *p*-nitrobenzaldehyde (0.1 mol), glycol (0.15 mol), $CuSO_4$ (1.5 g) and cyclohexane (40 mL) was exposed to microwave radiation (600 W) for 20 min with refluxing and removing water. The reaction mixture was cooled and washed with water until the organic phase was colourless. The organic layer was extracted with EtOAc and dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced

Table 1: Data collection and handling.

Crystal:	Colourless blocks
Size:	0.22 × 0.12 × 0.09 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	5.6 cm^{-1}
Diffractometer, scan mode:	Rigaku RAXIS-RAPID, ω-scans
$2\theta_{max}$, completeness:	55°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	20774, 2641, 0.053
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1765
$N(param)_{refined}$:	154
Programs:	SHELX [7], CrystalClear [8]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.97875(19)	0.9758(3)	0.38665(7)	0.0432(5)
C2	1.0763(2)	1.0560(3)	0.40896(7)	0.0487(5)
H2	1.1532	1.0366	0.3976	0.058*
C3	1.0604(2)	1.1636(3)	0.44748(7)	0.0498(5)
H3	1.1258	1.2175	0.4623	0.060*
C4	0.9462(2)	1.1905(3)	0.46385(7)	0.0454(5)
C5	0.8466(2)	1.1170(3)	0.44197(8)	0.0519(6)
H5	0.7698	1.1396	0.4531	0.062*
C6	0.8642(2)	1.0092(4)	0.40324(8)	0.0499(5)
H6	0.7983	0.9583	0.3881	0.060*
C7	0.9980(2)	0.8459(4)	0.34583(8)	0.0494(6)
C8	1.0891(3)	0.5609(4)	0.35709(12)	0.0732(8)
H8A	1.1091	0.5294	0.3885	0.088*
H8B	1.1373	0.4835	0.3368	0.088*
C9	0.9622(3)	0.5297(4)	0.34866(13)	0.0836(10)
H9A	0.9513	0.4576	0.3208	0.100*
H9B	0.9268	0.4600	0.3738	0.100*
C10	0.9963(2)	0.9450(4)	0.29915(8)	0.0574(6)
H10	1.0068	0.8482	0.2756	0.069*
Cl1	1.11593(7)	1.10883(11)	0.29357(2)	0.0677(2)
Cl2	0.85863(7)	1.05993(13)	0.28860(3)	0.0794(3)
N1	0.93076(19)	1.2955(3)	0.50668(6)	0.0530(5)
O1	1.11029(15)	0.7530(2)	0.34872(6)	0.0585(5)
O2	0.90781(16)	0.7057(2)	0.34454(7)	0.0655(5)
O3	0.82968(18)	1.3431(3)	0.51767(7)	0.0826(6)
O4	1.01977(17)	1.3326(3)	0.52943(6)	0.0620(5)

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pressure gave the crude products. 50% NaOH aq. was dropped into mixture of 0.05 mol dioxolane, $CHCl_3$ (60 mL), anhydrous Na_2SO_4 (30 g), and triethyl benzyl ammonium chloride (TEBA) (2 g) at 0° with vigorous stirring for 24 h. Then 100 mL water and 100 mL Et_2O were added into the mixture. The aqueous layer was extracted with ether. The organic layers were combined and washed with water and dried over anhydrous $MgSO_4$. The ether was removed by distillation and the residue was subjected to silica gel chromatography eluting with ethyl acetate-petroleum ether mixture. The product was collected as white solid in yield 32.6%.

Experimental details

H atoms were then constrained to an ideal geometry, with C—H distances of 0.93–0.98 Å. The U_{iso} values were set to $1.2U_{eq}$(C).

Discussion

The 2-dichloromethyl-1,3-dioxolanes as an important class of heterocyclic compounds have received considerable attention with their biological and pharmacological activities [1]. 1,3-Dioxolanes were commonly used as fragrance, pharmaceuticals and protecting groups for ketones, aldehydes, and 1,2-diols [2], and they were also an important industrial high boiling solvent which could be used as a plasticizer, curing agent, pigment dispersing agent [3]. MG-191 (2-dichloromethyl-1,3-dioxolane) is a herbicide safener with high efficiency and good selectivity, to protect corn, sorghum, and rice from amides and thiocarbamate herbicides injury [4, 5]. As part of our work to find more efficient and green methods for the synthesis of novel herbicide safener with better biological activity [6], the title compound was synthesized by microwave-irradiated acetalization followed by dichlorocarbene insertion of dioxolanes.

In the 1,3-dioxolane moiety, the distance of C8—C9 (1.453(4)Å), C7—O1 (1.417(3) Å), C7—O2 (1.415(3) Å) are in the normal ranges for a dioxolane. The angles of the 1,3-dioxolane, ranging from 106.4(2)° to 108.5(2)°. The torsion angle of C(7)—O(1)—C(9)—C(8) and C(7)—O(2)—C(10)—C(9) are 13.052(305)° and 5.293(312)°, respectively. The nitrophenyl moiety is almost perpendicular to the plane of the dioxolane ring. No significant $\pi-\pi$ interactions were found in the crystal structure.

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