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MOLECULAR AND CRYSTAL STRUCTURE OF 2-(2-*p*-TOLYLOXYETHOXY)ETHYLCHLOROACETATE

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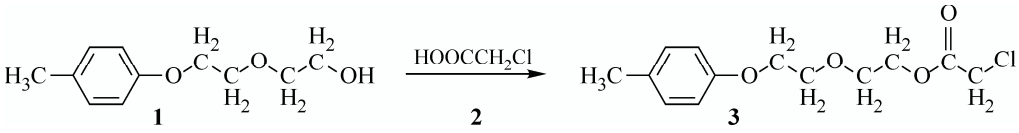
2-(2-*p*-Tolyloxyethoxy)ethylchloroacetate is synthesized and its single crystal X-ray diffraction analysis is performed.

Keywords: 2-(2-*p*-tolyloxyethoxy)ethylchloroacetate, crystal and molecular structure, X-ray diffraction analysis.

β-(Alkylaryloxy) ethylchloroacetates are the additives to lubricating oils [1a, b], plasticizers [1c], and feed stock for 2H-1,2-benzisothiazolin-3-one 1,1-dioxides that are used as intermediates for the synthesis of anti-inflammatory drugs [2]. Aryloxypoly(ethyleneoxy) chloroacetates [3] are the synthons for N-[alkylphenoxypoly(ethyleneoxy)carbonylmethyl] heterylonium chlorides that possess bactericidal, virusocidal, and fungicidal activity and the properties of corrosion inhibitors [4a], and N-[alkylphenoxypoly(ethyleneoxy) carbonylmethyl] ammonium and -morpholinium chlorides are regulating additives of viscoelastic properties of crude oil systems [4b] and inhibitors of asphalt-tar-paraffin sediments in crude oil [4c].

β-(Alkylaryloxy)ethylchloroacetates were obtained by the condensation of chloroacetic acids and β-oxyphenetole with chloric [1c, 5] or sulphuric acid [1b] as a catalyst. The acylation of 2-phenoxyethanol by monochloroacetic acid chloride yields 2-phenoxyethylchloroacetate [2]. Aryloxypoly(ethyleneoxy)chloroacetates [3] were synthesized by the interaction of aryloxypolyethylene glycols with chloroacetic acid in the presence of the H^+-form of KU-2-8 cation-exchange resin as the catalyst of heterogeneous catalysis.

β-[β-(Alkylphenoxy)ethoxy]ethyl ethers of chloroacetic acids have not been described so far. This work contains the approach to obtain 2-(2-*p*-tolyloxyethoxy)ethylchloroacetate (**3**) by the interaction of 2-(2-*p*-tolyloxyethoxy)ethanol (**1**) with monochloroacetic acid (**2**) in the presence of KU-2-8 cation-exchange resin as the catalyst.



1 **2** **3**

The geometry of the molecule of **3** in the crystal is shown in Fig. 1*a*; the geometrical parameters are standard. The packing of molecules in the crystal of compound **3** (Fig. 1*b*) represents the layers formed by C–H…O and H…π interactions (Table 1). Within each layer the molecules are arranged so that it is possible to determine the hydrophilic and hydrophobic

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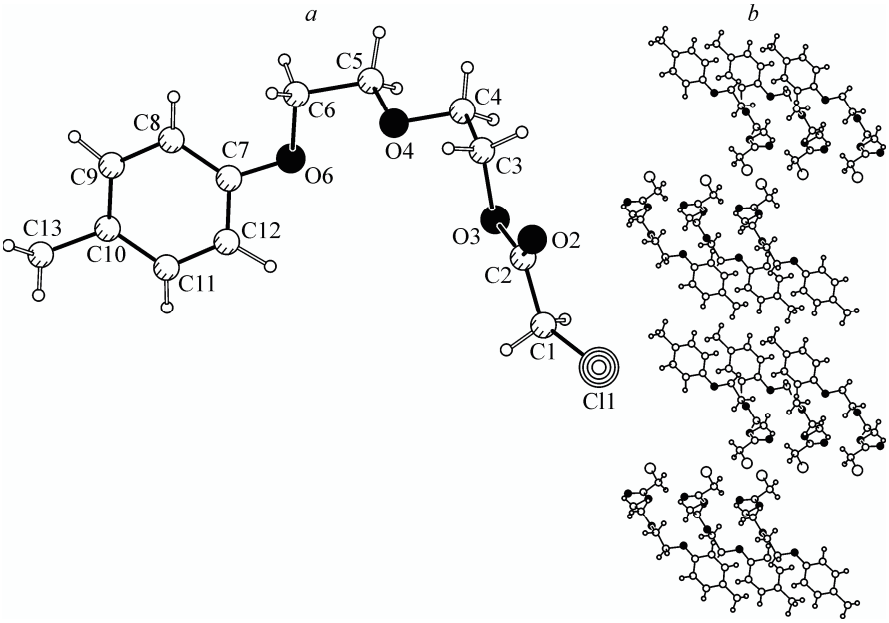

Fig 1. Compound 3: *a*) molecule geometry in the crystal, *b*) molecule packing in the crystal.

TABLE 1. C–H…O and *C–H…π Parameters of Interactions in the Crystal of Compound **3**

Bond	Symmetric transformation	Distance, Å		Angle, deg
		H…A	D…A	D–H…A
C^{1}–H^{12}…O^{2}	*x*, 3/2–*y*, –1/2+*z*	2.49(2)	3.2798(3)	145(2)
C^{3}–H^{31}…O^{6}	*x*, 1/2–*y*, 1/2+*z*	2.49(2)	3.4083(3)	162(2)
C^{3}–H^{32}…O^{3}	*x*, 1/2–*y*, 1/2+*z*	2.54(2)	3.3369(3)	139(2)
C^{12}–H^{134}…O^{4}	*x*, 1/2–*y*, –1/2+*z*	2.52(2)	3.249(3)	129(2)
*C^{6}–H^{61}…Cg(1)	*x*, 3/2–*y*, 1/2+*z*	H…Cg = 2.74(2)		C–H…Cg = 151(1)

regions in each layer. The layers are distributed within the crystal so that hydrophilic and hydrophobic regions are separated in the space. As expected based on the literature data, the benzene ring does not participate in NEP…π interactions. The aromatic system of the benzene ring is characterized by H…π contacts that belong to weak hydrogen bonds [6, 7], which are observed in the crystals of compound **3**. These interactions have been studied extensively by now and their significance for various chemical and biological systems has been shown. [8a-d]. However, H…π interactions are much weaker than C–H…O hydrogen bonds that seem to be the structure forming elements in the crystals of compound **3**.

Experimental. ^{1}H NMR spectra were recorded on a Bruker Avance-600 spectrometer (600 MHz), IR spectra were measured on a Bruker Vector-22 IR Fourier spectrometer.

2-(2-*p*-Tolyloxyethoxy)ethylchloroacetate 3. To 3.52 g 2-(2-*p*-tolyloxyethoxy)ethanol **1** in 7 ml absolute toluene we added 1.77 g of monochloroacetic acid **2** in 7 ml toluene and 0.175 g KU-2-8 in the H^{+} form (5% **1** alcohol mass) in 10 ml toluene. Azeotropic distillation was used to separate water; the catalyst was filtered; toluene was distilled, the residue was also distilled; and we obtained 2.85 g (58.3%) ethylchloroacetate **3**, b.p. 190-195°C (10 mm Hg), n_{D}^{20} 1.5125. Acetate **3** crystallized the next day, T_m 33-34°C. Found, %: C 57.04, H 6.11, Cl 13.27. $C_{13}H_{17}ClO_4$. Calculated, %: C 57.25, H 6.24, Cl 13.03. ^{1}H ($CDCl_3$) NMR spectrum, δ, ppm (*J*, Hz): 2.30 s (3H, C**H**$_3$); 3.82 t [2H, $^{3}J_{HH}$ 4.9, C**H**$_2$COC(O)]; 3.86 t (2H, $^{3}J_{HH}$ 4.9, ArOCC**H**$_2$); 4.08 s (2H, C**H**$_2$Cl); 4.12 t (2H, $^{3}J_{HH}$ 4.9, ArOC**H**$_2$); 4.38 t [2H, $^{3}J_{HH}$ 4.9, C**H**$_2$OC(O)]; 6.83 d (2H, $^{3}J_{HH}$ 8.6, ^{Ar}C**H**^{o}); 7.09 d (2H, $^{3}J_{HH}$ 8.6, ^{Ar}C**H**^{m}). IR spectrum, ν, cm^{-1}: 3031 (C^{Ar}–H, CH_2–Cl); 2876-2953, and 1455 (CH_3 и CH_2); 1759

(C=O); 1512 (benzene ring); 1245 and 1039-1068 (C^{Ar}–O–C^{Alk}); 1134-1179 (C^{Alk}–O–C^{Alk}); 820 (two adjacent hydrogen atoms of the benzene ring); 703 (C–Cl) [9].

Crystallographic data for 3: formula $C_{13}H_{17}ClO_4$, colorless prismatic crystals, formula weight 272.72 g mol^{-1}, monoclinic, a = 22.31(1) Å, b = 7.396(4) Å, c = 8.394(4) Å, β = 93.448(6)°, V = 1382.3(1) $Å^3$, T = 293 K, space group $P2_1/c$, Z = 4, μ(MoK_α) 2.8 cm^{-1}, $F(000)$ = 576, d_x = 1.31 g·cm^{-3}, 3017 reflections measured, 1788 unique. Final indices $R_1(F)$ = 0.040, w$R_2(F^2)$= 0.0835 using 1788 reflections with $I > 2\sigma(I)$. Goodness-of-fit on F^2 was 1.018, θ_{max} 27.00º, largest diff. peak and hole 0.243 e$Å^3$ and –0.244 e$Å^3$.

X-Ray diffraction data for the crystals of compound **3** were collected at 293 K on a Bruker AXS Smart Apex II CCD diffractometer in ω and φ-scan modes using graphite monochromated MoK_α (λ 0.71073 Å) radiation. The data were corrected for the absorption effect using the SADABS program [10]. The structures were solved by the direct method and refined by the full matrix least-squares method using the SHELXL [12] and WinGX [13] programs. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from the electron density difference synthesis and refined isotropically. Data collections: images were indexed, integrated, and scaled using the APEX2 [11] data reduction package. All figures were made using PLATON [14].

The crystallographic data (excluding structure factors) for structure **3** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 724494. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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