

## Bond Length and Reactivity: 1-Arylethyl Ethers and Esters. 2.\* Structure of 1-(4-Nitrophenyl)ethyl Chloroacetate

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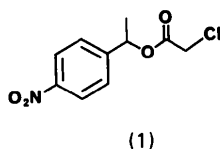
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**Abstract.**  $C_{10}H_{10}ClNO_4$ ,  $M_r = 243.65$ , monoclinic,  $P2_1/c$ ,  $a = 7.292$  (2),  $b = 15.039$  (4),  $c = 10.153$  (3) Å,  $\beta = 94.38$  (2)°,  $U = 1110.2$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.46$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.34$  mm<sup>-1</sup>,  $F(000) = 504$ ,  $T = 293$  K,  $R = 0.044$  for 1400 reflections. The benzylic C–O bond length in a series of esters of 1-arylethanol [here 1.452 (4) Å] shows a reasonable linear correlation with Hammett's substituent constant  $\sigma$ . The internal angle at the carbonyl group is smaller than usual [108.3 (3)°] probably because the C=O and C–Cl bonds are almost perfectly eclipsed.

**Introduction.** As part of a wider investigation of bond length and reactivity in a series of 1-phenylethanol derivatives, we have reported crystal structures of three 1-arylethyl 3,5-dinitrobenzoates (Jones, Edwards & Kirby, 1986). We were unable to grow suitable crystals of the 3,5-dinitrobenzoate of 1-(4-nitrophenyl)ethanol, limiting the range of electron-withdrawing substituent in the series. We therefore prepared the chloroacetate ester (1), since the  $pK_a$ 's of chloroacetic and 3,5-dinitrobenzoic acids are very similar, 2.86 and 2.82 (Barlin & Perrin, 1966), respectively, and report its crystal and molecular structure.



**Experimental.** Ester (1) was prepared by arylating the corresponding alcohol with chloroacetyl chloride, in the usual way. Pale yellow prisms, m.p. 346–347 K, were grown by diffusing pentane into a solution in diisopropyl ether.

Crystal size 0.35 × 0.3 × 0.3 mm. Stoe–Siemens four-circle diffractometer, monochromated Mo  $K\alpha$  radiation. 2205 profile-fitted reflections (Clegg, 1981),  $2\theta_{\text{max}} 50^\circ$ ,  $-h, +k, \pm l$ . Three check reflections, no significant intensity variation.  $R_{\text{int}} 0.020$  for 1948 unique reflections, 1400 of which with  $F > 4\sigma(F)$  used for all calculations (program system *SHELXTL*; Sheldrick, 1978). Index ranges after merging:  $|h| < 8$ ,  $k < 17$ ,  $|l| < 12$ . Cell constants refined from  $\pm 2\theta$  values of 40 reflections in the range 20–23°. Structure solution by routine direct methods. Refinement on  $F$  to  $R 0.044$ ,  $wR 0.047$ . All non-H atoms anisotropic; H atoms included with riding model [C–H 0.96 Å, H–C–H 109.5°,  $U(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ ]. 148 parameters, weighting scheme  $w^{-1} = \sigma^2(F) + 0.0002F^2$ ,  $S = 1.70$ . Max.  $\Delta/\sigma$  0.03; max. and min. features in final  $\Delta\rho$  map +0.15, –0.23 e Å<sup>-3</sup>. Atomic scattering factors from *SHELXTL*.†

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43006 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

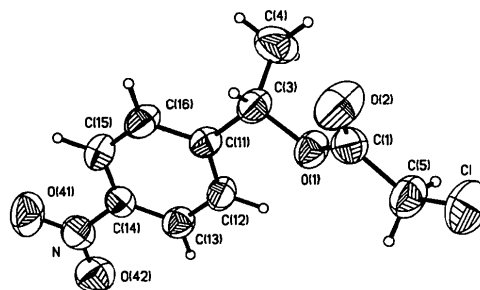


Fig. 1. Thermal-ellipsoid plot of (1), showing the atom-numbering scheme.

\* Part 1: Jones, Edwards & Kirby (1986).

**Discussion.** Final atomic coordinates and derived parameters are presented in Tables 1 and 2, and a thermal-ellipsoid plot of (1) is shown in Fig. 1. The dimensions of the ester group are similar to those of the 3,5-dinitrobenzoates described previously (Jones, Edwards & Kirby, 1986), although with both O(1)—C(1)—O(2) and O(2)—C(1)—C(5) angles above 125°, the internal angle O(1)—C(1)—C(5) at the

carbonyl centre [108.3 (3)°] is a little smaller than usual (Schweizer & Dunitz, 1982), probably because the C=O and C—Cl bonds are almost perfectly eclipsed [torsion angle O(2)—C(1)—C(5)—Cl 7.2 (5)°].

The C(3)—O bond length is 1.452 (4) Å, the shortest in the series of four esters (2) of 1-arylethanol we have measured, as expected if electron withdrawal in the aromatic ring reduces the contribution of the charge-separated valence tautomer ArCHMe<sup>+</sup>-O<sub>2</sub>CR to the ground-state structure. For the four (equivalent) esters the length of this bond shows a reasonable linear correlation with Hammett's substituent constant  $\sigma$  (correlation coefficient  $r$  0.931) with a slope, corresponding to a 'reaction constant'  $\rho$ , of -0.03. The magnitude of this figure depends of course on the units of bond length used, and it should not be compared with  $\rho$  values for reaction. It actually represents a sensitivity to substitution in the aromatic ring about twice that found for aryl tetrahydropyranyl acetals (Briggs, Glenn, Jones, Kirby & Ramaswamy, 1984).

Table 1. Atom coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

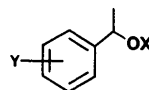
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sup>*</sup>
Cl	7932 (1)	398 (1)	437 (1)	82 (1)
C(1)	5206 (3)	1516 (2)	-475 (3)	53 (1)
O(1)	4092 (2)	2164 (1)	-146 (2)	55 (1)
O(2)	5329 (3)	1243 (1)	-1560 (2)	81 (1)
C(3)	2952 (3)	2585 (2)	-1204 (2)	53 (1)
C(4)	1138 (4)	2103 (2)	-1374 (4)	83 (1)
C(5)	6239 (4)	1182 (2)	758 (3)	66 (1)
C(11)	2736 (3)	3548 (2)	-847 (2)	45 (1)
C(12)	3083 (3)	3864 (2)	420 (2)	52 (1)
C(13)	2894 (3)	4755 (2)	715 (2)	51 (1)
C(14)	2352 (3)	5326 (2)	-296 (3)	47 (1)
C(15)	1987 (3)	5042 (2)	-1571 (3)	55 (1)
C(16)	2180 (3)	4151 (2)	-1838 (2)	56 (1)
N	2229 (3)	6279 (2)	5 (3)	62 (1)
O(41)	1725 (3)	6783 (1)	-894 (2)	91 (1)
O(42)	2655 (3)	6536 (1)	1125 (2)	80 (1)

\* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

Table 2. Bond lengths (Å), bond angles and torsion angles (°)

C(1)—O(1)	1.329 (4)	C(1)—O(2)	1.185 (5)
C(1)—C(5)	1.497 (5)	C(3)—O(1)	1.452 (4)
C(3)—C(4)	1.506 (5)	C(5)—Cl	1.755 (4)
C(11)—C(3)	1.504 (4)	C(11)—C(12)	1.377 (4)
C(11)—C(16)	1.392 (4)	C(12)—C(13)	1.382 (5)
C(13)—C(14)	1.373 (5)	C(14)—C(15)	1.370 (5)
C(14)—N	1.470 (4)	C(15)—C(16)	1.376 (5)
N—O(41)	1.222 (4)	N—O(42)	1.218 (5)
O(1)—C(1)—O(2)	125.3 (3)	O(1)—C(1)—C(5)	108.3 (3)
O(2)—C(1)—C(5)	126.3 (3)	C(1)—O(1)—C(3)	117.4 (3)
O(1)—C(3)—C(4)	108.8 (3)	O(1)—C(3)—C(11)	107.8 (3)
C(4)—C(3)—C(11)	112.6 (3)	Cl—C(5)—C(1)	112.7 (3)
C(3)—C(11)—C(12)	122.8 (3)	C(3)—C(11)—C(16)	118.9 (3)
C(12)—C(11)—C(16)	118.2 (3)	C(11)—C(12)—C(13)	121.5 (3)
C(12)—C(13)—C(14)	118.2 (3)	C(13)—C(14)—C(15)	122.3 (3)
C(13)—C(14)—N	118.2 (3)	C(15)—C(14)—N	119.4 (3)
C(14)—C(15)—C(16)	118.4 (3)	C(11)—C(16)—C(15)	121.3 (3)
C(14)—N—O(41)	118.0 (4)	C(14)—N—O(42)	119.2 (3)
O(41)—N—O(42)	122.9 (3)		
O(2)—C(1)—O(1)—C(3)	-1.1 (5)	C(5)—C(1)—O(1)—C(3)	180.0 (3)
O(1)—C(1)—C(5)—Cl	-173.9 (3)	O(2)—C(1)—C(5)—Cl	7.2 (5)
C(1)—O(1)—C(3)—C(4)	91.2 (4)	C(1)—O(1)—C(3)—C(11)	-146.4 (3)
O(1)—C(3)—C(11)—C(12)	-18.0 (4)	O(1)—C(3)—C(11)—C(16)	161.3 (3)
C(4)—C(3)—C(11)—C(12)	102.1 (4)	C(4)—C(3)—C(11)—C(16)	-78.6 (4)
C(12)—C(13)—C(14)—N	-177.3 (3)	C(13)—C(14)—N—O(41)	-179.1 (3)
C(13)—C(14)—N—O(42)	1.9 (4)	C(15)—C(14)—N—O(41)	3.1 (4)
C(15)—C(14)—N—O(42)	-175.9 (3)		

Sign convention as defined by Klyne & Prelog (1960).



(2)

This first set of data is therefore consistent with our expectations about the effect of substitution in the aromatic ring on the length of the C—OX bond in compounds (2). In the following paper we present data for a set of 1-arylethyl ethers, where the group OX is substantially less electron withdrawing (Jones, Sheldrick, Edwards & Kirby, 1986).

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