

Bond Length and Reactivity: 1-Arylethyl Ethers and Esters. 3.* Structures of Three Trityl Ethers of 1-Arylethanol: 1-Phenylethyl, 1-(4-Chlorophenyl)ethyl and 1-(4-Nitrophenyl)ethyl Triphenylmethyl Ethers

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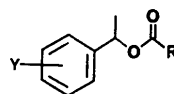
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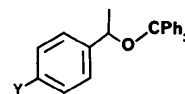
Abstract. $C_{27}H_{24}O$ (2a), $M_r = 364.49$, monoclinic, $C2$, $a = 18.701$ (3), $b = 8.429$ (2), $c = 14.313$ (3) Å, $\beta = 114.56$ (2)°, $U = 2052.0$ Å³, $Z = 4$, $D_x = 1.18$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.07$ mm⁻¹, $F(000) = 776$, $T = 293$ K, $R = 0.049$ for 2975 reflections. $C_{27}H_{23}ClO$ (2b), $M_r = 398.93$, isostructural with (2a), $C2$, $a = 19.217$ (6), $b = 8.443$ (2), $c = 14.350$ (5) Å, $\beta = 115.09$ (3)°, $U = 2108.6$ Å³, $Z = 4$, $D_x = 1.26$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.19$ mm⁻¹, $F(000) = 840$, $T = 293$ K, $R = 0.037$ for 3192 reflections. $C_{27}H_{23}NO_3$ (2c), $M_r = 409.49$, triclinic, $P\bar{1}$, $a = 8.601$ (2), $b = 9.829$ (3), $c = 13.731$ (4) Å, $\alpha = 72.83$ (3), $\beta = 79.76$ (3), $\gamma = 75.64$ (3)°, $U = 1067.5$ Å³, $Z = 2$, $D_x = 1.27$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.08$ mm⁻¹, $F(000) = 432$, $T = 293$ K, $R = 0.043$ for 3049 reflections. The trityl group is twisted about the C–O bond by 30–40° away from the staggered position with respect to the closest substituent on C (aromatic ring or methyl group). The O–C–Me bond angle in (2c) is appreciably larger than in (2a) and (2b) [111.8 (2), 106.3 (2), 106.5 (2)° respectively].

Introduction. As part of our broader search for correlations between the length of a bond in the crystal and the rate at which it is broken in solution (Jones & Kirby, 1984) we have reported crystal structures for a series of four 1-arylethyl esters (1) where R is either 3,5-dinitrophenyl or chloromethyl (Jones, Edwards & Kirby, 1986a,b). Because the parent acids RCO_2H have almost identical pK_a 's, the leaving-group capability of the anions RCO_2^- should be equal, so the observed changes in the length of the C–OCOR bond depend on the varying substituent Y in the aromatic group; we find that the introduction of electron-withdrawing substituents Y leads to a significant shortening of the C–OCOR bond, which can be correlated with Ham-

mett's substituent constant σ_y , giving a slope (ρ' value) of -0.03 . We report a similar investigation for three trityl ethers, (2), which have a significantly less electro-negative ether oxygen at the benzylic centre, and are thus expected (Allen & Kirby, 1984) to have significantly shorter C–O bonds.



(1)



(2a) $Y = H$
(2b) $Y = Cl$
(2c) $Y = NO_2$

Experimental. The ethers were prepared from the 1-arylethanol and triphenylmethyl chloride in methylene chloride, using triethylamine and a catalytic quantity of 4-dimethylaminopyridine. Crystals of (2a) were grown by the diffusion of petrol into a solution in diisopropyl ether and decomposed above 393 K. Crystals of (2b), which decomposed slowly above 428 K, were grown by the diffusion of petrol into a solution in diisopropyl ether. Crystals of (2c), m.p. 446–447 K (dec.), were grown by the diffusion of pentane into a solution in methylene chloride.

Details of data collection and refinement are given in Table 1. The following features were common: Stoe-Siemens four-circle diffractometer; monochromated Mo $K\alpha$ radiation; profile-fitting mode (Clegg, 1981). 3 check reflections, no significant intensity variation. Cell constants refined from $\pm 2\theta$ values of reflections in the range 20–23°. Structure solution: (2a) and (2c) automated direct methods, (2b) isostructural with (2a). Refinement on F , all non-H atoms anisotropic, H atoms included with riding model [C–H 0.96 Å, H–C–H 109.5°, $U(H) = 1.2 U_{eq}(C)$]. Weighting scheme $w^{-1} = \sigma^2(F) + gF^2$. The absolute structure (Jones, 1984) of (2b) was determined with Rogers' (1981) η refinement;

* Part 2: Jones, Edwards & Kirby (1986b).

that of (2a) was not determined. Program system *SHELXS84* (Sheldrick, 1984) [solution of (2a)], otherwise *SHELXTL* (Sheldrick, 1978). Atomic scattering factors as incorporated in computer programs.*

* 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 43007 (74 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Details of data collection and refinement for (2a)–(2c)

	(2a)	(2b)	(2c)
Crystal form and size (mm)	Yellow prism 0.45 × 0.4 × 0.25	Colourless octahedron 0.55 × 0.5 × 0.4	Colourless tablet 0.6 × 0.4 × 0.25
2θ _{max} (°)	55	50	50
Region of reciprocal space	±h+k+l and some Friedel opposites	+h±k±l and some -h equivalents	-h±k±l
Index ranges after merging (h ≤ etc.)	22, 10, 18	20, 10, 17	10, 11, 16
Total reflections	3876	5254	3753
Unique reflections	3735	3693	3753
R _{int}	0.014	0.016	—
Observed reflections (>4σ(F))	2975	3192	3049
Reflections for cell-constant refinement	44	40	36
R	0.049	0.037	0.044
wR	0.046	0.038	0.050
g	0.00025	0.0002	0.00025
Refined parameters	255	264	283
S	1.48	1.45	1.89
Max. Δ/σ	0.05	0.02	0.09
Max. Δρ features (e Å ⁻³)	+0.17, -0.24	+0.21, -0.32	+0.14, -0.19
Absolute structure parameter η (Rogers, 1981)	—	1.01 (12)	—

Table 2. Atom coordinates (×10⁴) and equivalent isotropic temperature factors (Å² × 10³) for (2a)

	x	y	z	U*
O(1)	3291 (1)	6000	2857 (1)	43 (1)
C(2)	3066 (1)	4605 (2)	3264 (1)	37 (1)
C(3)	3194 (1)	5925 (2)	1803 (1)	45 (1)
C(4)	3866 (1)	6866 (3)	1748 (2)	69 (1)
C(11)	3618 (1)	3203 (2)	3351 (1)	39 (1)
C(12)	3392 (1)	1651 (2)	3403 (2)	49 (1)
C(13)	3917 (1)	415 (3)	3577 (2)	61 (1)
C(14)	4675 (1)	719 (3)	3702 (2)	65 (1)
C(15)	4918 (1)	2252 (3)	3677 (2)	61 (1)
C(16)	4387 (1)	3492 (3)	3501 (2)	49 (1)
C(21)	3238 (1)	5033 (2)	4382 (1)	38 (1)
C(22)	3760 (1)	6233 (2)	4903 (1)	47 (1)
C(23)	3949 (1)	6519 (3)	5932 (2)	59 (1)
C(24)	3626 (1)	5619 (3)	6456 (2)	59 (1)
C(25)	3106 (1)	4420 (3)	5951 (2)	59 (1)
C(26)	2917 (1)	4122 (2)	4925 (2)	49 (1)
C(31)	2193 (1)	4274 (2)	2621 (1)	39 (1)
C(32)	1931 (1)	3252 (2)	1783 (1)	45 (1)
C(33)	1136 (1)	3101 (3)	1161 (2)	57 (1)
C(34)	590 (1)	3964 (3)	1359 (2)	62 (1)
C(35)	836 (1)	4986 (3)	2175 (2)	61 (1)
C(36)	1629 (1)	5141 (3)	2803 (2)	49 (1)
C(41)	2414 (1)	6590 (2)	1054 (1)	47 (1)
C(42)	2028 (1)	7786 (3)	1322 (2)	63 (1)
C(43)	1329 (2)	8403 (4)	590 (2)	83 (1)
C(44)	1018 (2)	7850 (4)	-405 (2)	85 (1)
C(45)	1401 (2)	6691 (4)	-678 (2)	79 (1)
C(46)	2092 (1)	6061 (3)	47 (2)	61 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Bond lengths (Å), bond angles and torsion angles (°) for (2a)

C(2)—O(1)	1.451 (3)	C(2)—C(21)	1.538 (4)
C(2)—C(31)	1.529 (3)	C(3)—O(1)	1.444 (4)
C(3)—C(4)	1.516 (5)	C(3)—C(41)	1.514 (4)
C(11)—C(2)	1.540 (4)	C(11)—C(12)	1.386 (4)
C(11)—C(16)	1.386 (4)	C(12)—C(13)	1.382 (4)
C(13)—C(14)	1.377 (5)	C(14)—C(15)	1.375 (4)
C(15)—C(16)	1.390 (4)	C(21)—C(22)	1.388 (3)
C(21)—C(26)	1.393 (4)	C(22)—C(23)	1.385 (4)
C(23)—C(24)	1.371 (5)	C(24)—C(25)	1.379 (4)
C(25)—C(26)	1.383 (4)	C(31)—C(32)	1.390 (4)
C(31)—C(36)	1.393 (4)	C(32)—C(33)	1.385 (4)
C(33)—C(34)	1.377 (5)	C(34)—C(35)	1.367 (5)
C(35)—C(36)	1.384 (4)	C(41)—C(42)	1.383 (5)
C(41)—C(46)	1.385 (4)	C(42)—C(43)	1.392 (4)
C(43)—C(44)	1.376 (5)	C(44)—C(45)	1.363 (6)
C(45)—C(46)	1.384 (4)		
C(2)—O(1)—C(3)	116.9 (2)	O(1)—C(2)—C(11)	110.9 (3)
O(1)—C(2)—C(21)	104.9 (2)	C(11)—C(2)—C(21)	104.6 (2)
O(1)—C(2)—C(31)	108.8 (2)	C(11)—C(2)—C(31)	114.9 (2)
C(21)—C(2)—C(31)	112.3 (3)	O(1)—C(3)—C(4)	106.5 (3)
O(1)—C(3)—C(41)	113.0 (3)	C(4)—C(3)—C(41)	110.1 (3)
C(2)—C(11)—C(12)	121.3 (3)	C(2)—C(11)—C(16)	119.8 (3)
C(12)—C(11)—C(16)	118.5 (3)	C(11)—C(12)—C(13)	120.8 (3)
C(12)—C(13)—C(14)	120.0 (3)	C(13)—C(14)—C(15)	120.3 (3)
C(14)—C(15)—C(16)	119.5 (3)	C(11)—C(16)—C(15)	120.9 (3)
C(2)—C(21)—C(22)	121.8 (3)	C(2)—C(21)—C(26)	119.9 (3)
C(22)—C(21)—C(26)	118.2 (3)	C(21)—C(22)—C(23)	120.6 (3)
C(22)—C(23)—C(24)	120.7 (3)	C(23)—C(24)—C(25)	119.5 (3)
C(24)—C(25)—C(26)	120.2 (4)	C(21)—C(26)—C(25)	120.8 (3)
C(2)—C(31)—C(32)	122.5 (3)	C(2)—C(31)—C(36)	119.5 (3)
C(32)—C(31)—C(36)	117.7 (3)	C(31)—C(32)—C(33)	120.7 (3)
C(33)—C(33)—C(34)	120.6 (3)	C(33)—C(34)—C(35)	119.5 (3)
C(34)—C(35)—C(36)	120.3 (3)	C(31)—C(36)—C(35)	121.2 (3)
C(3)—C(41)—C(42)	122.3 (3)	C(3)—C(41)—C(46)	119.5 (3)
C(42)—C(41)—C(46)	118.2 (3)	C(41)—C(42)—C(43)	119.9 (3)
C(42)—C(43)—C(44)	120.8 (4)	C(43)—C(44)—C(45)	119.5 (3)
C(44)—C(45)—C(46)	119.9 (3)	C(41)—C(46)—C(45)	121.6 (4)
C(3)—O(1)—C(2)—C(11)	67.3 (3)	C(3)—O(1)—C(2)—C(21)	179.7 (2)
C(3)—O(1)—C(2)—C(31)	-60.0 (3)	C(2)—O(1)—C(3)—C(4)	-145.3 (3)
C(2)—O(1)—C(3)—C(41)	93.7 (3)	O(1)—C(2)—C(11)—C(12)	-159.3 (3)
O(1)—C(2)—C(11)—C(16)	28.3 (3)	O(1)—C(2)—C(21)—C(22)	-20.8 (3)
O(1)—C(2)—C(21)—C(26)	164.4 (3)	O(1)—C(2)—C(31)—C(32)	92.8 (3)
O(1)—C(2)—C(31)—C(36)	-80.2 (3)	O(1)—C(3)—C(41)—C(42)	29.8 (4)
O(1)—C(3)—C(41)—C(46)	-154.1 (3)		

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

Table 4. Atom coordinates (×10⁴) and equivalent isotropic temperature factors (Å² × 10³) for (2b)

	x	y	z	U*
O(1)	3319 (1)	6000	2914 (1)	42 (1)
C(2)	3094 (1)	4592 (2)	3304 (1)	37 (1)
C(3)	3234 (1)	5972 (3)	1866 (1)	44 (1)
C(4)	3876 (1)	6990 (3)	1841 (2)	60 (1)
C(11)	3624 (1)	3196 (2)	3377 (1)	38 (1)
C(12)	3410 (1)	1648 (2)	3429 (1)	49 (1)
C(13)	3915 (1)	413 (3)	3587 (2)	61 (1)
C(14)	4652 (1)	700 (3)	3707 (2)	64 (1)
C(15)	4885 (1)	2235 (3)	3681 (2)	60 (1)
C(16)	4380 (1)	3469 (3)	3523 (1)	48 (1)
C(21)	3257 (1)	5000 (2)	4421 (1)	38 (1)
C(22)	3747 (1)	6215 (2)	4940 (1)	48 (1)
C(23)	3920 (1)	6514 (3)	5968 (2)	59 (1)
C(24)	3611 (1)	5592 (3)	6482 (2)	60 (1)
C(25)	3127 (1)	4376 (3)	5977 (2)	58 (1)
C(26)	2953 (1)	4079 (3)	4957 (1)	51 (1)
C(31)	2238 (1)	4270 (2)	2639 (1)	38 (1)
C(32)	1984 (1)	3277 (2)	1788 (1)	47 (1)
C(33)	1204 (1)	3108 (3)	1165 (2)	60 (1)
C(34)	670 (1)	3912 (3)	1373 (2)	64 (1)
C(35)	912 (1)	4922 (3)	2202 (2)	62 (1)
C(36)	1682 (1)	5098 (2)	2832 (1)	48 (1)
C(41)	2468 (1)	6621 (2)	1116 (1)	42 (1)
C(42)	2121 (1)	7848 (2)	1386 (1)	51 (1)
C(43)	1438 (1)	8506 (3)	681 (2)	56 (1)
C(44)	1110 (1)	7921 (3)	-303 (2)	54 (1)
C(45)	1444 (1)	6724 (3)	-609 (2)	61 (1)
C(46)	2125 (1)	6072 (3)	111 (1)	56 (1)
Cl(1)	245 (1)	8733 (1)	-1186 (1)	82 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Discussion. Final atom positions and derived parameters are presented in Tables 2–7, with plots of the molecules (2a)–(2c), showing the common atom-numbering system, appearing as Figs. 1–3. The conformations of compounds (2a)–(2c) are controlled primarily by non-bonded interactions. About O(1)–

Table 5. Bond lengths (Å), bond angles and torsion angles (°) for (2b)

C(2)–O(1)	1.456 (3)	C(2)–C(21)	1.537 (4)
C(2)–C(31)	1.536 (3)	C(3)–O(1)	1.442 (3)
C(3)–C(4)	1.518 (4)	C(3)–C(41)	1.510 (3)
C(11)–C(2)	1.533 (4)	C(11)–C(12)	1.383 (4)
C(11)–C(16)	1.396 (4)	C(12)–C(13)	1.376 (4)
C(13)–C(14)	1.375 (5)	C(14)–C(15)	1.376 (5)
C(15)–C(16)	1.375 (4)	C(21)–C(22)	1.378 (4)
C(21)–C(26)	1.385 (4)	C(22)–C(23)	1.391 (4)
C(23)–C(24)	1.369 (5)	C(24)–C(25)	1.367 (4)
C(25)–C(26)	1.380 (4)	C(31)–C(32)	1.388 (4)
C(31)–C(36)	1.399 (4)	C(32)–C(33)	1.390 (4)
C(33)–C(34)	1.364 (5)	C(34)–C(35)	1.374 (4)
C(35)–C(36)	1.376 (4)	C(41)–C(42)	1.373 (4)
C(41)–C(46)	1.388 (4)	C(42)–C(43)	1.389 (4)
C(43)–C(44)	1.372 (4)	C(44)–C(45)	1.366 (5)
C(44)–C(1)	1.746 (3)	C(45)–C(46)	1.391 (4)
C(2)–O(1)–C(3)	117.8 (2)	O(1)–C(2)–C(11)	110.9 (3)
O(1)–C(2)–C(21)	104.8 (2)	C(11)–C(2)–C(21)	105.4 (2)
O(1)–C(2)–C(31)	108.7 (2)	C(11)–C(2)–C(31)	114.4 (2)
C(21)–C(2)–C(31)	112.3 (3)	O(1)–C(3)–C(4)	106.3 (2)
O(1)–C(3)–C(41)	112.5 (3)	C(4)–C(3)–C(41)	109.5 (3)
C(2)–C(1)–C(12)	121.7 (3)	C(2)–C(11)–C(16)	120.2 (3)
C(12)–C(11)–C(16)	117.6 (3)	C(11)–C(12)–C(13)	121.3 (3)
C(12)–C(13)–C(14)	120.3 (3)	C(13)–C(14)–C(15)	119.4 (3)
C(14)–C(15)–C(16)	120.3 (3)	C(11)–C(16)–C(15)	121.0 (3)
C(2)–C(21)–C(22)	121.4 (3)	C(2)–C(21)–C(26)	120.4 (3)
C(22)–C(21)–C(26)	118.1 (3)	C(21)–C(22)–C(23)	120.6 (3)
C(22)–C(23)–C(24)	120.3 (3)	C(23)–C(24)–C(25)	119.6 (3)
C(24)–C(25)–C(26)	120.2 (3)	C(21)–C(26)–C(25)	121.2 (3)
C(2)–C(31)–C(32)	122.5 (3)	C(2)–C(31)–C(36)	119.6 (3)
C(32)–C(31)–C(36)	117.6 (3)	C(31)–C(32)–C(33)	120.5 (3)
C(32)–C(33)–C(34)	120.9 (3)	C(33)–C(34)–C(35)	119.2 (3)
C(34)–C(35)–C(36)	120.7 (3)	C(31)–C(36)–C(35)	120.9 (3)
C(3)–C(41)–C(42)	121.1 (3)	C(3)–C(41)–C(46)	120.6 (3)
C(42)–C(41)–C(46)	118.1 (3)	C(41)–C(42)–C(43)	121.2 (3)
C(42)–C(43)–C(44)	119.1 (3)	C(43)–C(44)–C(45)	121.6 (3)
C(43)–C(44)–C(1)	119.1 (3)	C(45)–C(44)–C(1)	119.3 (3)
C(44)–C(45)–C(46)	118.4 (3)	C(41)–C(46)–C(45)	121.5 (3)
C(3)–O(1)–C(2)–C(11)	66.5 (3)	C(3)–O(1)–C(2)–C(21)	179.8 (2)
C(3)–O(1)–C(2)–C(31)	–60.0 (3)	C(2)–O(1)–C(3)–C(4)	–147.8 (3)
C(2)–O(1)–C(3)–C(41)	92.3 (3)	O(1)–C(2)–C(11)–C(12)	–160.7 (3)
O(1)–C(2)–C(11)–C(16)	27.5 (3)	O(1)–C(2)–C(21)–C(22)	–19.1 (3)
O(1)–C(2)–C(21)–C(26)	165.3 (3)	O(1)–C(2)–C(31)–C(32)	92.4 (3)
O(1)–C(2)–C(31)–C(36)	–82.0 (3)	O(1)–C(3)–C(41)–C(42)	34.9 (4)
O(1)–C(3)–C(41)–C(46)	–150.1 (3)		

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

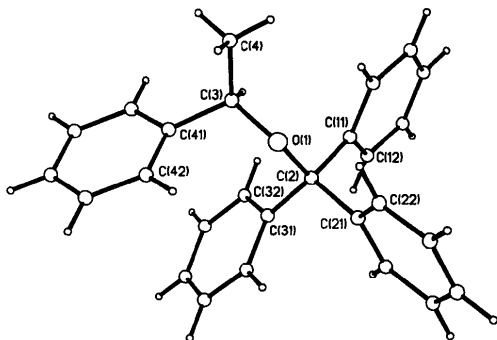


Fig. 1. The molecule of (2a) in the crystal, showing the atom-numbering scheme.

Table 6. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{Å}^2 \times 10^3$) for (2c)

	x	y	z	U^*
O(1)	2867 (1)	1582 (1)	6503 (1)	35 (1)
C(2)	3719 (2)	734 (1)	7384 (1)	32 (1)
C(3)	2757 (2)	3124 (1)	6172 (1)	36 (1)
C(4)	1156 (2)	3949 (2)	6592 (1)	53 (1)
C(11)	5548 (2)	645 (1)	7121 (1)	33 (1)
C(12)	6236 (2)	1097 (2)	6118 (1)	40 (1)
C(13)	7894 (2)	954 (2)	5889 (1)	49 (1)
C(14)	8898 (2)	348 (2)	6654 (1)	55 (1)
C(15)	8235 (2)	–150 (2)	7648 (1)	55 (1)
C(16)	6582 (2)	–6 (2)	7883 (1)	45 (1)
C(21)	3438 (2)	–808 (1)	7556 (1)	33 (1)
C(22)	3269 (2)	–1283 (2)	6736 (1)	40 (1)
C(23)	3021 (2)	–2668 (2)	6882 (1)	51 (1)
C(24)	2953 (2)	–3609 (2)	7847 (1)	54 (1)
C(25)	3162 (2)	–3170 (2)	8665 (1)	53 (1)
C(26)	3408 (2)	–1780 (2)	8523 (1)	45 (1)
C(31)	2962 (2)	1360 (1)	8302 (1)	36 (1)
C(32)	3724 (2)	2134 (2)	8699 (1)	42 (1)
C(33)	2929 (2)	2783 (2)	9469 (1)	54 (1)
C(34)	1351 (2)	2687 (2)	9845 (1)	60 (1)
C(35)	580 (2)	1919 (2)	9460 (1)	56 (1)
C(36)	1386 (2)	1252 (2)	8702 (1)	48 (1)
C(41)	2879 (2)	3583 (1)	5011 (1)	35 (1)
C(42)	3205 (2)	4939 (2)	4481 (1)	40 (1)
C(43)	3212 (2)	5444 (2)	3429 (1)	42 (1)
C(44)	2880 (2)	4562 (2)	2910 (1)	39 (1)
C(45)	2560 (2)	3214 (2)	3401 (1)	46 (1)
C(46)	2558 (2)	2726 (2)	4456 (1)	44 (1)
N(4)	2849 (2)	5107 (2)	1791 (1)	53 (1)
O(41)	3248 (2)	6261 (2)	1355 (1)	77 (1)
O(42)	2410 (2)	4386 (2)	1353 (1)	88 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

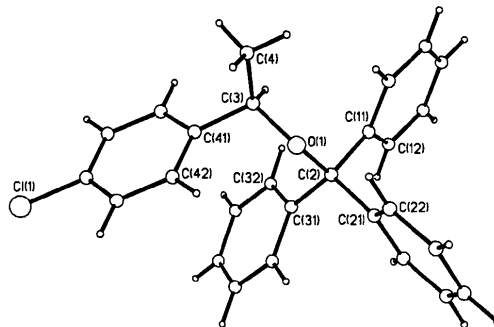


Fig. 2. The molecule of (2b) in the crystal, showing the atom-numbering scheme.

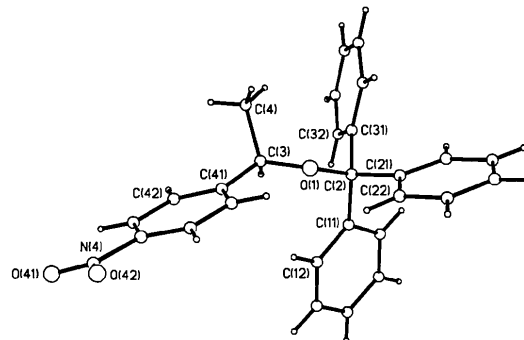


Fig. 3. The molecule of (2c) in the crystal, showing the atom-numbering scheme.

C(3) the large triphenylmethyl group is twisted 30–40° further away than the staggered position from the closest substituent on C(3) [the aromatic ring of (2a) and (2b), the methyl group of (2c)], to within 20–30° of eclipsing the benzylic H atom. Across C(3)–C(41) the C–methyl group bond is close to perpendicular to the plane of the aromatic ring.

Table 7. Bond lengths (Å), bond angles and torsion angles (°) for (2c)

C(2)–O(1)	1.453 (3)	C(2)–C(21)	1.537 (3)
C(2)–C(31)	1.536 (3)	C(3)–O(1)	1.433 (3)
C(3)–C(4)	1.525 (3)	C(3)–C(41)	1.515 (3)
C(11)–C(2)	1.537 (3)	C(11)–C(12)	1.386 (3)
C(11)–C(16)	1.396 (3)	C(12)–C(13)	1.386 (3)
C(13)–C(14)	1.379 (4)	C(14)–C(15)	1.377 (3)
C(15)–C(16)	1.382 (3)	C(21)–C(22)	1.382 (4)
C(21)–C(26)	1.388 (3)	C(22)–C(23)	1.381 (3)
C(23)–C(24)	1.375 (3)	C(24)–C(25)	1.370 (4)
C(25)–C(26)	1.386 (4)	C(31)–C(32)	1.388 (4)
C(31)–C(36)	1.387 (3)	C(32)–C(33)	1.385 (3)
C(33)–C(34)	1.379 (4)	C(34)–C(35)	1.378 (4)
C(35)–C(36)	1.383 (4)	C(41)–C(42)	1.387 (3)
C(41)–C(46)	1.391 (4)	C(42)–C(43)	1.381 (3)
C(43)–C(44)	1.379 (4)	C(44)–C(45)	1.369 (3)
C(44)–N(4)	1.473 (3)	C(45)–C(46)	1.385 (3)
N(4)–O(41)	1.218 (3)	N(4)–O(42)	1.213 (4)
C(2)–O(1)–C(3)	119.1 (2)	O(1)–C(2)–C(11)	110.9 (2)
O(1)–C(2)–C(21)	103.6 (2)	C(11)–C(2)–C(21)	106.8 (2)
O(1)–C(2)–C(31)	108.7 (2)	C(11)–C(2)–C(31)	114.6 (2)
C(21)–C(2)–C(31)	111.6 (2)	O(1)–C(3)–C(4)	111.8 (2)
O(1)–C(3)–C(41)	108.0 (2)	C(4)–C(3)–C(41)	108.6 (2)
C(2)–C(11)–C(12)	121.5 (2)	C(2)–C(11)–C(16)	120.4 (2)
C(11)–C(12)–C(13)	117.9 (2)	C(11)–C(12)–C(13)	120.8 (2)
C(12)–C(13)–C(14)	120.6 (2)	C(13)–C(14)–C(15)	119.1 (3)
C(14)–C(15)–C(16)	120.6 (3)	C(11)–C(16)–C(15)	120.9 (2)
C(2)–C(21)–C(22)	120.3 (2)	C(2)–C(21)–C(26)	121.6 (3)
C(22)–C(21)–C(26)	118.1 (2)	C(21)–C(22)–C(23)	120.8 (2)
C(22)–C(23)–C(24)	120.6 (3)	C(23)–C(24)–C(25)	119.4 (3)
C(24)–C(25)–C(26)	120.2 (2)	C(21)–C(26)–C(25)	120.9 (3)
C(2)–C(31)–C(32)	123.4 (2)	C(2)–C(31)–C(36)	118.4 (3)
C(32)–C(31)–C(36)	118.0 (3)	C(31)–C(32)–C(33)	120.9 (3)
C(32)–C(33)–C(34)	120.3 (3)	C(33)–C(34)–C(35)	119.5 (3)
C(34)–C(35)–C(36)	120.0 (3)	C(31)–C(36)–C(35)	121.3 (3)
C(3)–C(41)–C(42)	119.6 (3)	C(3)–C(41)–C(46)	121.8 (2)
C(42)–C(41)–C(46)	118.3 (2)	C(41)–C(42)–C(43)	121.6 (3)
C(42)–C(43)–C(44)	118.1 (2)	C(43)–C(44)–C(45)	122.3 (2)
C(43)–C(44)–N(4)	118.4 (2)	C(45)–C(44)–N(4)	119.3 (3)
C(44)–C(45)–C(46)	118.8 (3)	C(41)–C(46)–C(45)	120.9 (2)
C(44)–N(4)–O(41)	118.6 (3)	C(44)–N(4)–O(42)	118.1 (2)
O(41)–N(4)–O(42)	123.3 (2)		
C(3)–O(1)–C(2)–C(11)	–70.9 (3)	C(3)–O(1)–C(2)–C(21)	174.8 (2)
C(3)–O(1)–C(2)–C(31)	56.0 (3)	C(2)–O(1)–C(3)–C(4)	–97.3 (3)
C(2)–O(1)–C(3)–C(41)	143.4 (2)	O(1)–C(2)–C(11)–C(12)	–11.0 (3)
O(1)–C(2)–C(11)–C(16)	174.2 (2)	O(1)–C(2)–C(21)–C(22)	31.2 (3)
O(1)–C(2)–C(21)–C(26)	–151.3 (2)	O(1)–C(2)–C(31)–C(32)	–108.4 (2)
O(1)–C(2)–C(31)–C(36)	66.1 (3)	O(1)–C(3)–C(41)–C(42)	–164.2 (2)
O(1)–C(3)–C(41)–C(46)	20.6 (3)	C(43)–C(44)–N(4)–O(41)	5.9 (3)
C(43)–C(44)–N(4)–O(42)	–173.3 (3)	C(45)–C(44)–N(4)–O(41)	–174.8 (2)
C(45)–C(44)–N(4)–O(42)	5.9 (3)		

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

The only significant changes in the geometry at the benzylic centre with changing substituent occur for the 4-nitro compound (2c), for which the angle O(1)–C(3)–C(4) increases to 111.8 (2)°, compared with 106.5 (3), 106.3 (2)° in (2a), (2b), while angle O(1)–C(3)–C(41) changes by a similar amount in the opposite direction. This probably reflects the change in conformation referred to above. The C(3)–O(1) bond is marginally shorter for (2c), at 1.433 (3) Å compared with 1.444 (4) and 1.442 (3) Å. The C–O bond lengths themselves do not appear to be increased by steric effects deriving from the triphenylmethyl group, since C(2)–O(1), at 1.453 (3) Å for these three compounds is the length expected for a tertiary alkyl ether [1.450 (2) Å; Allen & Kirby (1984)].

The shortest non-bonded distances between non-H atoms are: (2a) C(14)···C(14)(1 – x, y, 1 – z) 3.40 (1); (2b) same contact 3.37 (1); (2c) O(42)···C(33)(x, y, –1 + z) 3.32 (1) Å.

These structures will be discussed in more detail, in the light of results from other similar systems, in a later paper (Edwards, Jones & Kirby, 1986).

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