Bond Length and Reactivity: 1-Aryl Ethers and Esters. 1. Three 3,5-Dinitrobenzoate Esters of 1-Arylethanols: 1-(4-Methoxyphenyl)ethyl, 1-Phenylethyl and 1-(3-Fluorophenyl)ethyl 3,5-Dinitrobenzoates

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Abstract. $C_{16}H_{14}N_2O_7$ (2a), $M_r = 346 \cdot 30$, orthorhombic, *Pbca*, $a = 11 \cdot 177$ (2), $b = 15 \cdot 987$ (2), $c = 18 \cdot 577$ (3) Å, $U = 3319 \cdot 5$ Å^3, $Z = 8$, $D_x = 1 \cdot 39$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, $\mu = 0 \cdot 1$ mm^{-1}, $F(000) = 1440$, $T = 293$ K, $R = 0 \cdot 061$ for 1528 reflections. $C_{15}H_{12}N_2O_6$ (2b), $M_r = 316 \cdot 27$, orthorhombic, $P2_12_12_1$, $a = 6 \cdot 185$ (1), $b = 11 \cdot 029$ (2), $c = 21 \cdot 703$ (3) Å, $U = 1480 \cdot 4$ Å^3, $Z = 4$, $D_x = 1 \cdot 42$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, $\mu = 0 \cdot 11$ mm^{-1}, $F(000) = 656$, $T = 293$ K, $R = 0 \cdot 046$ for 2766 reflections. $C_{15}H_{11}FN_2O_6$ (2c), $M_r = 334 \cdot 27$, monoclinic, $P2_1/c$, $a = 15 \cdot 228$ (3), $b = 7 \cdot 356$ (1), $c = 14 \cdot 334$ (3) Å, $\beta = 108 \cdot 76$ (2)°, $U = 1521 \cdot 3$ Å^3, $Z = 4$, $D_x = 1 \cdot 46$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, $\mu = 0 \cdot 12$ mm^{-1}, $F(000) = 688$, $T = 293$ K, $R = 0 \cdot 077$ for 1813 reflections. The 3,5-dinitrobenzoate group is similar in the three compounds with the substituents rotated out of the ring plane by ~10°. The C—O bond at the benzylic centre is shorter in (2c) than in (2b), but not significantly lengthened in (2a) [1·481 (3), 1·459 (4), 1·479 (5) Å for (2b), (2c), (2a) respectively]. The fluoro substituent of (2c) is disordered over both *m* positions.

Introduction. We have shown that the linear correlation (Jones & Kirby, 1979) between the length of a C—O bond in a given system R—OX and the rate at which it is broken in solution is rather general (Allen & Kirby, 1984; Jones & Kirby, 1984). The more electron-withdrawing the group X, the longer the bond and the more rapidly it is broken ionically. We have suggested that the common factor relating all these properties is the contribution of the valence tautomeric form R^+ $^-$OX to the structure of the ground state: the more electron-withdrawing X is, the more stable XO$^-$ will be and thus the larger this contribution will be.

This analysis clearly predicts that the length of the C—O bond should depend equally on the stability of the cation R^+. We have found evidence to support this

prediction in three series of acetal structures (Jones & Kirby, 1986), and now wish to explore its generality. We have prepared a series of derivatives (1) of 1-phenylethanol, compounds that are known to undergo C—OX cleavage in solution (the S_N1 reaction) if the leaving group is good enough, at a rate depending strongly on the substitution in the benzene ring. The structure enables us to vary electron donation or withdrawal in both cation and leaving group by varying X and Y. We report here the effect on the C—O bond length of varying the aromatic substituent in three 3,5-dinitrobenzoate esters (2a)–(2c).

(1)
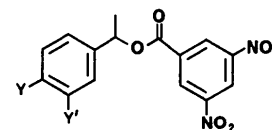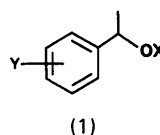
(2a) $Y = \text{OCH}_3, Y' = \text{H}$
(2b) $Y = Y' = \text{H}$
(2c) $Y = \text{H}, Y' = \text{F}$

Experimental. The esters were prepared from the alcohols and 3,5-dinitrobenzoyl chloride by routine methods, and had m.p. 359–361 K (2a), 373–374 K (2b) and 355–356 K (2c). Crystals were grown by the liquid diffusion technique, using methylene chloride/petrol (2b), (2c) or diethyl ether/pentane (2a).

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. Cell constants refined from $\pm 2\theta$ values in range 20–23°. Structure solution by routine direct methods. Refinement on F, all non-H atoms isotropic, H included using a riding model [C—H 0·96 Å, H—C—H 109·5°, $U(\text{H}) = 1 \cdot 2 \, U_{eq}(\text{C})$], weighting scheme $w^{-1} = \sigma^2(F) + gF^2$. Program system and atomic scattering factors from *SHELXTL* (Sheldrick, 1978).

Disorder of the F atom over both m positions in (2c) was allowed for with partial site occupation factors.*

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* 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 43005 (61 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)	Pale yellow plate 0·65×0·4×0·1	Colourless, irregular 0·55×0·4×0·3	Colourless prism 0·4×0·4×0·2
$2\theta_{max}(°)$	50	55	50
Region of reciprocal space	$+h+k+l$ and some $-h-k-l$ equivalents	$+h+k+l$, $-h-k-l$	$\pm h-k+l$ and some $+k$ equivalents
Index ranges after merging ($|h| \le$ etc.)	13, 18, 22	8, 14, 28	17, 8, 16
Total reflections	4128	3915	4938
Unique reflections	2912	3392	2669
R_{int}	0·017	0·018	0·023
Observed reflections $[>4\sigma(F)]$	1528	2768	1813
Reflections for cell-constant refinement	56	56	42
R	0·061	0·046	0·077
wR	0·053	0·047	0·058
g	0·0003	0·0003	0·00025
Refined parameters	232	211	230
S	1·59	1·56	1·63
Max. Δ/σ	0·35	0·01	0·08
Max. $\Delta\rho$ features (e Å^{-3})	+0·2, −0·25	±0·25	+0·25, −0·28

Table 2. *Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å$^2 \times 10^3$) for (2a)*

	x	y	z	U^*
C(1)	2589 (4)	4353 (2)	5615 (2)	55 (1)
O(1)	1924 (2)	3976 (1)	6108 (1)	60 (1)
O(2)	2468 (2)	5058 (1)	5397 (1)	69 (1)
C(3)	951 (4)	4466 (2)	6445 (2)	65 (2)
C(4)	1452 (5)	4795 (3)	7147 (2)	92 (2)
C(11)	3552 (3)	3784 (2)	5341 (2)	52 (1)
C(12)	3785 (4)	3013 (2)	5666 (2)	53 (1)
C(13)	4672 (3)	2516 (2)	5384 (2)	53 (1)
C(14)	5352 (3)	2737 (2)	4803 (2)	56 (1)
C(15)	5110 (3)	3503 (2)	4498 (2)	53 (1)
C(16)	4223 (3)	4032 (2)	4751 (2)	54 (1)
N(3)	4899 (3)	1693 (1)	5730 (1)	64 (1)
O(31)	5565 (3)	1210 (1)	5421 (1)	84 (1)
O(32)	4398 (2)	1551 (1)	6300 (1)	75 (1)
N(5)	5817 (3)	3760 (2)	3864 (2)	68 (1)
O(51)	6692 (3)	3346 (2)	3709 (2)	90 (1)
O(52)	5480 (2)	4381 (2)	3535 (1)	89 (1)
C(21)	−91 (4)	3885 (2)	6509 (2)	53 (1)
C(22)	−92 (4)	3205 (2)	6980 (2)	65 (1)
C(23)	−1023 (4)	2655 (2)	7009 (2)	66 (1)
C(24)	−2007 (4)	2763 (2)	6569 (2)	64 (1)
C(25)	−2041 (3)	3452 (2)	6103 (2)	67 (1)
C(26)	−1097 (4)	3996 (2)	6085 (2)	65 (2)
O(24)	−2978 (3)	2245 (2)	6538 (2)	88 (1)
C(27)	−2876 (4)	1465 (3)	6912 (2)	92 (2)

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

Discussion. Final atomic coordinates and derived parameters are presented in Tables 2–7, and thermal-ellipsoid plots of (2a)–(2c), showing the common atom-numbering scheme, appear as Figs. 1–3.

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

C(1)–O(1)	1·325 (5)	C(1)–O(2)	1·205 (5)
C(1)–C(11)	1·498 (6)	C(3)–O(1)	1·479 (5)
C(3)–C(4)	1·513 (6)	C(11)–C(12)	1·397 (5)
C(11)–C(16)	1·387 (6)	C(12)–C(13)	1·374 (6)
C(13)–C(14)	1·366 (6)	C(13)–N(3)	1·486 (5)
C(14)–C(15)	1·376 (5)	C(15)–C(16)	1·385 (6)
C(15)–N(5)	1·477 (5)	N(3)–O(31)	1·216 (5)
N(3)–O(32)	1·220 (5)	N(5)–O(51)	1·216 (5)
N(5)–O(52)	1·224 (5)	C(21)–C(3)	1·494 (6)
C(21)–C(22)	1·395 (6)	C(21)–C(26)	1·384 (7)
C(22)–C(23)	1·364 (7)	C(23)–C(24)	1·381 (7)
C(24)–C(25)	1·401 (6)	C(24)–O(24)	1·367 (6)
C(25)–C(26)	1·369 (6)	C(27)–O(24)	1·432 (6)

O(1)–C(1)–O(2)	126·5 (5)	O(1)–C(1)–C(11)	111·1 (4)
O(2)–C(1)–C(11)	122·3 (4)	C(1)–O(1)–C(3)	117·6 (4)
O(1)–C(3)–C(4)	106·1 (4)	O(1)–C(3)–C(21)	106·1 (4)
C(4)–C(3)–C(21)	115·8 (4)	C(1)–C(11)–C(12)	121·6 (4)
C(1)–C(11)–C(16)	118·9 (4)	C(12)–C(11)–C(16)	119·5 (4)
C(11)–C(12)–C(13)	118·7 (4)	C(12)–C(13)–C(14)	123·6 (4)
C(12)–C(13)–N(3)	118·1 (4)	C(14)–C(13)–N(3)	118·3 (4)
C(13)–C(14)–C(15)	116·5 (4)	C(14)–C(15)–C(16)	123·0 (4)
C(14)–C(15)–N(5)	118·1 (4)	C(16)–C(15)–N(5)	118·9 (4)
C(11)–C(16)–C(15)	118·7 (4)	C(13)–N(3)–O(31)	117·6 (4)
C(13)–N(3)–O(32)	117·5 (4)	O(31)–N(3)–O(32)	124·9 (4)
C(15)–N(5)–O(51)	117·8 (4)	C(15)–N(5)–O(52)	117·3 (4)
O(51)–N(5)–O(52)	124·8 (4)	C(3)–C(21)–C(22)	122·3 (4)
C(3)–C(21)–C(26)	120·5 (4)	C(22)–C(21)–C(26)	117·1 (4)
C(21)–C(22)–C(23)	121·9 (5)	C(22)–C(23)–C(24)	120·2 (4)
C(23)–C(24)–C(25)	119·1 (5)	C(23)–C(24)–O(24)	125·5 (4)
C(25)–C(24)–O(24)	115·4 (4)	C(24)–C(25)–C(26)	119·6 (5)
C(21)–C(26)–C(25)	122·1 (4)	C(24)–O(24)–C(27)	116·4 (4)

O(2)–C(1)–O(1)–C(3)	−1·7 (6)	C(11)–C(1)–O(1)–C(3)	178·4 (4)
O(1)–C(1)–C(11)–C(12)	−9·1 (6)	O(1)–C(1)–C(11)–C(16)	170·9 (4)
O(2)–C(1)–C(11)–C(12)	171·1 (5)	O(2)–C(1)–C(11)–C(16)	−9·0 (6)
C(1)–O(1)–C(3)–C(4)	−96·8 (5)	C(1)–O(1)–C(3)–C(21)	139·4 (4)
O(1)–C(3)–C(21)–C(22)	68·6 (5)	O(1)–C(3)–C(21)–C(26)	−110·0 (5)
C(4)–C(3)–C(21)–C(22)	−48·8 (6)	C(4)–C(3)–C(21)–C(26)	132·6 (5)
C(11)–C(12)–C(13)–N(3)	−179·3 (4)	C(12)–C(13)–N(3)–O(31)	179·9 (4)
C(12)–C(13)–N(3)–O(31)	170·1 (4)	C(12)–C(13)–N(3)–O(32)	−9·5 (6)
C(14)–C(13)–N(3)–O(31)	−9·7 (6)	C(14)–C(13)–N(3)–O(32)	170·7 (4)
C(13)–C(14)–C(15)–C(16)	−0·6 (6)	C(13)–C(14)–C(15)–N(5)	−179·3 (4)
C(14)–C(15)–C(16)–C(11)	0·5 (6)	N(5)–C(15)–C(16)–C(11)	179·2 (4)
C(14)–C(15)–N(5)–O(51)	−11·0 (6)	C(14)–C(15)–N(5)–O(52)	169·5 (4)
C(16)–C(15)–N(5)–O(51)	170·2 (4)	C(16)–C(15)–N(5)–O(52)	−9·2 (6)
C(22)–C(23)–C(24)–O(24)	178·5 (5)	C(23)–C(24)–O(24)–C(27)	−10·1 (7)
O(24)–C(24)–C(25)–C(26)	−178·7 (4)	C(24)–C(25)–C(26)–C(21)	0·7 (7)
C(25)–C(24)–O(24)–C(27)	169·5 (4)		

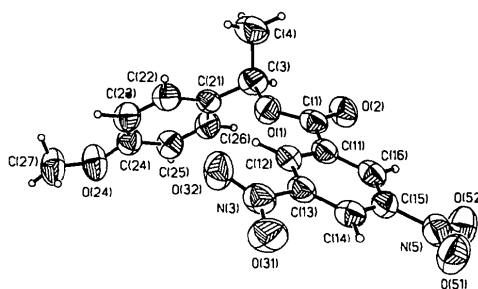Sign convention as defined by Klyne & Prelog (1960).

Fig. 1. Thermal-ellipsoid plot of (2a), showing the atom-numbering scheme.

Table 4. *Atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\text{Å}^2 \times 10^3)$ *for* (2b)

	x	y	z	U*
C(1)	1843 (3)	5561 (2)	3766 (1)	44 (1)
O(1)	3340 (2)	5114 (1)	4133 (1)	48 (1)
O(2)	615 (3)	6378 (2)	3892 (1)	71 (1)
C(3)	3507 (4)	5655 (2)	4756 (1)	54 (1)
C(4)	5350 (5)	6547 (3)	4751 (1)	91 (1)
C(11)	1791 (3)	4927 (2)	3155 (1)	39 (1)
C(12)	3365 (3)	4093 (2)	2982 (1)	38 (1)
C(13)	3140 (3)	3523 (2)	2418 (1)	37 (1)
C(14)	1432 (3)	3727 (2)	2023 (1)	41 (1)
C(15)	−44 (3)	4589 (2)	2208 (1)	41 (1)
C(16)	89 (3)	5184 (2)	2764 (1)	44 (1)
N(3)	4807 (3)	2642 (1)	2230 (1)	44 (1)
O(31)	6496 (2)	2617 (1)	2521 (1)	56 (1)
O(32)	4408 (3)	1986 (1)	1789 (1)	65 (1)
N(5)	−1910 (3)	4846 (2)	1804 (1)	53 (1)
O(51)	−3141 (3)	5651 (2)	1958 (1)	83 (1)
O(52)	−2128 (3)	4241 (2)	1340 (1)	69 (1)
C(21)	3763 (3)	4620 (2)	5201 (1)	43 (1)
C(22)	2194 (4)	4433 (2)	5643 (1)	52 (1)
C(23)	2396 (4)	3511 (2)	6069 (1)	69 (1)
C(24)	4141 (5)	2764 (2)	6054 (1)	74 (1)
C(25)	5722 (4)	2929 (2)	5619 (1)	74 (1)
C(26)	5536 (4)	3857 (2)	5190 (1)	60 (1)

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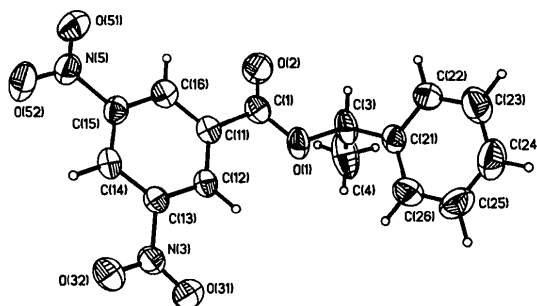

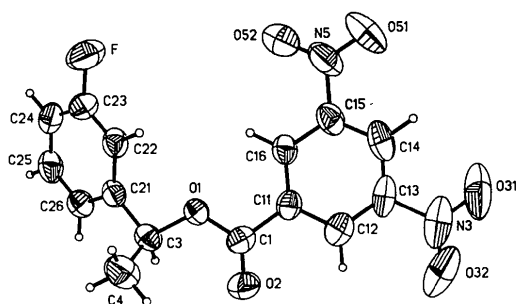Fig. 2. Thermal-ellipsoid plot of (2b), showing the atom-numbering scheme.

Fig. 3. Thermal-ellipsoid plot of (2c), showing the atom-numbering scheme. Only one position of the disordered F atom is shown.

The structures have many common features: the 3,5-dinitrobenzoate system is closely similar in all three compounds: all three substituents are rotated out of the benzene plane by an average of almost 10°, but the dimensions of the ester group are normal (Schweizer & Dunitz, 1982). Differences are mostly minor, occurring around the benzylic centre, C(3). The C(3)—O bond, 1·481 (3) Å in (2b), is shorter, as expected, in (2c), 1·459 (4) Å, but not significantly lengthened in the *p*-methoxy compound [1·479 (5) Å in (2a)]. C(3)—C(4) and C(3)—C(11) do not vary significantly with substitution, but there are possible trends discernible in some angles and torsion angles. So far the data are too few to attribute significance to these changes, so we defer detailed discussion of structure–reactivity correlations.

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

C(1)—O(1)	1·318 (3)	C(1)—O(2)	1·210 (4)
C(1)—C(11)	1·498 (3)	C(3)—O(1)	1·481 (3)
C(3)—C(4)	1·506 (5)	C(11)—C(12)	1·391 (3)
C(11)—C(16)	1·382 (4)	C(12)—C(13)	1·382 (3)
C(13)—C(14)	1·380 (3)	C(13)—N(3)	1·474 (3)
C(14)—C(15)	1·378 (4)	C(15)—C(16)	1·376 (3)
C(15)—N(5)	1·477 (3)	N(3)—O(31)	1·221 (3)
N(3)—O(32)	1·224 (3)	N(5)—O(51)	1·217 (4)
N(5)—O(52)	1·216 (3)	C(21)—C(3)	1·505 (4)
C(21)—C(22)	1·379 (4)	C(21)—C(26)	1·382 (4)
C(22)—C(23)	1·380 (4)	C(23)—C(24)	1·358 (5)
C(24)—C(25)	1·371 (5)	C(25)—C(26)	1·387 (4)

O(1)—C(1)—O(2)	125·7 (3)	O(1)—C(1)—C(11)	112·1 (3)
O(2)—C(1)—C(11)	122·3 (3)	C(1)—O(1)—C(3)	116·8 (2)
O(1)—C(3)—C(4)	108·0 (3)	O(1)—C(3)—C(21)	106·7 (2)
C(4)—C(3)—C(21)	114·9 (3)	C(1)—C(11)—C(12)	122·2 (3)
C(1)—C(11)—C(16)	117·7 (3)	C(12)—C(11)—C(16)	120·1 (3)
C(11)—C(12)—C(13)	118·1 (3)	C(12)—C(13)—C(14)	123·5 (3)
C(12)—C(13)—N(3)	118·4 (2)	C(14)—C(13)—N(3)	118·1 (2)
C(13)—C(14)—C(15)	116·0 (3)	C(14)—C(15)—C(16)	123·0 (3)
C(14)—C(15)—N(5)	118·5 (2)	C(16)—C(15)—N(5)	118·4 (3)
C(11)—C(16)—C(15)	119·1 (3)	C(13)—N(3)—O(31)	118·0 (2)
C(13)—N(3)—O(32)	117·7 (2)	O(31)—N(3)—O(32)	124·3 (3)
C(15)—N(5)—O(51)	117·7 (3)	C(15)—N(5)—O(52)	118·2 (3)
O(51)—N(5)—O(52)	124·0 (3)	C(3)—C(21)—C(22)	119·0 (3)
C(3)—C(21)—C(26)	122·3 (3)	C(22)—C(21)—C(26)	118·7 (3)
C(21)—C(22)—C(23)	120·8 (3)	C(22)—C(23)—C(24)	120·2 (3)
C(23)—C(24)—C(25)	120·2 (3)	C(24)—C(25)—C(26)	120·0 (3)
C(21)—C(26)—C(25)	120·2 (3)		

O(2)—C(1)—O(1)—C(3)	0·7 (4)	C(11)—C(1)—O(1)—C(3)	−178·7 (3)
O(1)—C(1)—C(11)—C(12)	−8·6 (3)	O(1)—C(1)—C(11)—C(16)	170·5 (3)
O(2)—C(1)—C(11)—C(12)	172·0 (3)	O(2)—C(1)—C(11)—C(16)	−8·9 (4)
C(1)—O(1)—C(3)—C(4)	−99·8 (3)	C(1)—O(1)—C(3)—C(21)	136·2 (3)
O(1)—C(3)—C(21)—C(22)	−117·4 (3)	O(1)—C(3)—C(21)—C(26)	63·6 (3)
C(4)—C(3)—C(21)—C(22)	122·9 (3)	C(4)—C(3)—C(21)—C(26)	−56·1 (4)
C(11)—C(12)—C(13)—N(3)	179·7 (2)	N(3)—C(13)—C(14)—C(15)	−177·7 (3)
C(12)—C(13)—N(3)—O(31)	−13·1 (3)	C(12)—C(13)—N(3)—O(32)	167·1 (3)
C(14)—C(13)—N(3)—O(31)	167·2 (3)	C(14)—C(13)—N(3)—O(32)	−12·6 (3)
C(13)—C(14)—C(15)—C(16)	−2·8 (4)	C(13)—C(14)—C(15)—N(5)	−179·9 (3)
C(14)—C(15)—C(16)—C(11)	0·9 (4)	N(5)—C(15)—C(16)—C(11)	178·1 (3)
C(14)—C(15)—N(5)—O(51)	−176·4 (3)	C(14)—C(15)—N(5)—O(52)	3·8 (4)
C(16)—C(15)—N(5)—O(51)	6·3 (4)	C(16)—C(15)—N(5)—O(52)	−173·5 (3)
C(3)—C(21)—C(22)—C(23)	−178·5 (3)	C(26)—C(21)—C(22)—C(23)	0·5 (4)
C(3)—C(21)—C(26)—C(25)	178·7 (3)	C(22)—C(21)—C(26)—C(25)	−0·3 (4)
C(21)—C(22)—C(23)—C(24)	−0·7 (4)	C(22)—C(23)—C(24)—C(25)	0·6 (5)
C(23)—C(24)—C(25)—C(26)	−0·3 (5)	C(24)—C(25)—C(26)—C(21)	0·2 (4)

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

There are no unusually short intermolecular contacts. Shortest contacts between non-H atoms are: $(2a)$ $O(24)\cdots N(3)(-1 + x,\ y,\ z)$ 2·94 (1); $(2b)$ $O(51)\cdots N(3)(-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z)$ 3·00 (1); $(2c)$ $O(51)\cdots O(31)-(1-x, 1-y, 2-z)$ 3·04 (1) Å.

Table 6. *Atomic coordinates* $(\times 10^4)$ *and equivalent isotropic temperature factors* $(Å^2 \times 10^3)$ *for* $(2c)$

	x	y	z	U^*
C(1)	1698 (2)	5167 (4)	6608 (2)	53 (1)
O(1)	1965 (1)	5773 (3)	5868 (1)	53 (1)
O(2)	909 (1)	4960 (4)	6577 (1)	77 (1)
C(3)	1259 (2)	6014 (4)	4909 (2)	53 (1)
C(4)	787 (2)	7834 (5)	4864 (3)	76 (2)
C(11)	2514 (2)	4715 (4)	7492 (2)	48 (1)
C(12)	2357 (2)	4215 (4)	8356 (2)	58 (1)
C(13)	3108 (2)	3683 (4)	9150 (2)	62 (2)
C(14)	3999 (2)	3635 (4)	9119 (2)	69 (1)
C(15)	4125 (2)	4176 (4)	8257 (2)	59 (1)
C(16)	3407 (2)	4719 (4)	7445 (2)	51 (1)
N(3)	2942 (2)	3150 (4)	10070 (2)	95 (2)
O(31)	3615 (2)	2588 (5)	10749 (2)	131 (2)
O(32)	2166 (2)	3282 (4)	10121 (2)	117 (2)
N(5)	5075 (2)	4176 (4)	8201 (2)	85 (2)
O(51)	5690 (2)	3522 (4)	8883 (2)	116 (1)
O(52)	5189 (2)	4883 (6)	7487 (2)	132 (2)
C(21)	1753 (2)	5820 (4)	4155 (2)	47 (1)
C(22)	2684 (2)	6269 (4)	4370 (2)	52 (1)
C(23)	3095 (2)	6080 (4)	3657 (2)	60 (1)
C(24)	2637 (2)	5503 (4)	2723 (2)	62 (1)
C(25)	1717 (2)	5068 (5)	2517 (2)	66 (2)
C(26)	1273 (2)	5224 (5)	3215 (2)	59 (1)
F	4015 (2)	6534 (4)	3907 (2)	92 (2)†
F'	1179 (4)	4446 (11)	1659 (4)	102 (3)†

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

† Site occupation factors: F 0·687 (3), F' 0·313 (3).

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

C(1)–O(1)	1·330 (5)	C(1)–O(2)	1·197 (5)
C(1)–C(11)	1·500 (5)	C(3)–O(1)	1·459 (4)
C(3)–C(4)	1·511 (6)	C(11)–C(12)	1·386 (6)
C(11)–C(16)	1·382 (5)	C(12)–C(13)	1·385 (5)
C(13)–C(14)	1·373 (6)	C(13)–N(3)	1·474 (6)
C(14)–C(15)	1·370 (6)	C(15)–C(16)	1·374 (5)
C(15)–N(5)	1·476 (6)	N(3)–O(31)	1·236 (5)
N(3)–O(32)	1·210 (6)	N(5)–O(51)	1·214 (5)
N(5)–O(52)	1·209 (6)	C(21)–C(3)	1·509 (6)

Table 7 *(cont.)*

C(21)–C(22)	1·390 (5)	C(21)–C(26)	1·383 (5)
C(22)–C(23)	1·368 (6)	C(23)–C(24)	1·363 (5)
C(23)–F	1·370 (5)	C(24)–C(25)	1·373 (6)
C(25)–C(26)	1·381 (6)	C(25)–F'	1·322 (7)
O(1)–C(1)–O(2)	125·0 (3)	O(1)–C(1)–C(11)	111·4 (4)
O(2)–C(1)–C(11)	123·6 (4)	C(1)–O(1)–C(3)	118·1 (3)
O(1)–C(3)–C(4)	110·1 (3)	O(1)–C(3)–C(21)	106·2 (3)
C(4)–C(3)–C(21)	113·1 (4)	C(1)–C(11)–C(12)	118·7 (4)
C(1)–C(11)–C(16)	121·3 (4)	C(12)–C(11)–C(16)	119·9 (3)
C(11)–C(12)–C(13)	118·4 (4)	C(12)–C(13)–C(14)	123·0 (4)
C(12)–C(13)–N(3)	118·5 (4)	C(14)–C(13)–N(3)	118·5 (4)
C(13)–C(14)–C(15)	116·6 (4)	C(14)–C(15)–C(16)	123·0 (4)
C(14)–C(15)–N(5)	118·2 (4)	C(16)–C(15)–N(5)	118·7 (4)
C(11)–C(16)–C(15)	119·0 (4)	C(13)–N(3)–O(31)	117·2 (4)
C(13)–N(3)–O(32)	119·0 (4)	O(31)–N(3)–O(32)	123·8 (4)
C(15)–N(5)–O(51)	118·1 (4)	C(15)–N(5)–O(52)	117·1 (4)
O(51)–N(5)–O(52)	124·7 (4)	C(3)–C(21)–C(22)	121·7 (3)
C(3)–C(21)–C(26)	120·0 (4)	C(22)–C(21)–C(26)	118·2 (4)
C(21)–C(22)–C(23)	119·3 (4)	C(22)–C(23)–C(24)	123·6 (4)
C(22)–C(23)–F	117·1 (4)	C(24)–C(23)–F	119·4 (5)
C(23)–C(24)–C(25)	116·7 (5)	C(24)–C(25)–C(26)	121·9 (4)
C(24)–C(25)–F'	124·4 (6)	C(26)–C(25)–F'	113·7 (5)
C(21)–C(26)–C(25)	120·3 (4)		
O(2)–C(1)–O(1)–C(3)	−7·4 (6)	C(11)–C(1)–O(1)–C(3)	171·0 (3)
O(1)–C(1)–C(11)–C(12)	174·4 (4)	O(1)–C(1)–C(11)–C(16)	−8·2 (5)
O(2)–C(1)–C(11)–C(12)	−7·1 (6)	O(2)–C(1)–C(11)–C(16)	170·2 (4)
C(1)–O(1)–C(3)–C(4)	83·5 (4)	C(1)–O(1)–C(3)–C(21)	−153·7 (4)
O(1)–C(3)–C(21)–C(22)	−28·7 (5)	O(1)–C(3)–C(21)–C(26)	152·9 (4)
C(4)–C(3)–C(21)–C(22)	92·2 (4)	C(4)–C(3)–C(21)–C(26)	−86·2 (4)
C(11)–C(12)–C(13)–N(3)	−180·0 (4)	N(3)–C(13)–C(14)–C(15)	−178·7 (4)
C(12)–C(13)–N(3)–O(31)	176·2 (4)	C(12)–C(13)–N(3)–O(32)	−3·8 (5)
C(14)–C(13)–N(3)–O(31)	−3·9 (5)	C(14)–C(13)–N(3)–O(32)	176·0 (4)
C(13)–C(14)–C(15)–C(16)	−1·1 (6)	C(13)–C(14)–C(15)–N(5)	178·9 (4)
C(14)–C(15)–C(16)–C(11)	−0·3 (6)	N(5)–C(15)–C(16)–C(11)	179·8 (4)
C(14)–C(15)–N(5)–O(51)	7·4 (6)	C(14)–C(15)–N(5)–O(52)	−170·4 (4)
C(16)–C(15)–N(5)–O(51)	−172·6 (4)	C(16)–C(15)–N(5)–O(52)	9·6 (6)
C(3)–C(21)–C(22)–C(23)	−179·5 (4)	C(26)–C(21)–C(22)–C(23)	−1·1 (5)
C(3)–C(21)–C(26)–C(25)	179·1 (4)	C(22)–C(21)–C(26)–C(25)	0·6 (6)
C(21)–C(22)–C(23)–C(24)	1·4 (6)	C(21)–C(22)–C(23)–F	−179·7 (4)
C(22)–C(23)–C(24)–C(25)	−1·2 (6)	F–C(23)–C(24)–C(25)	180·0 (4)
C(23)–C(24)–C(25)–C(26)	0·7 (6)	C(23)–C(24)–C(25)–F'	−178·3 (6)
C(24)–C(25)–C(26)–C(21)	−0·5 (6)	F'–C(25)–C(26)–C(21)	178·6 (6)

References

ALLEN, F. H. & KIRBY, A. J. (1984). *J. Am. Chem. Soc.* **106**, 6197–6200.

JONES, P. G. & KIRBY, A. J. (1979). *J. Chem. Soc. Chem. Commun.* pp. 288–289.

JONES, P. G. & KIRBY, A. J. (1984). *J. Am. Chem. Soc.* **106**, 6207–6212.

JONES, P. G. & KIRBY, A. J. (1986). *J. Chem. Soc. Chem. Commun.* pp. 444–445.

KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.

SCHWEIZER, W. B. & DUNITZ, J. D. (1982). *Helv. Chim. Acta*, **65**, 1547–1554.

SHELDRICK, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen.