

phosphoric and 2-naphthalenesulfonic acids, and the comparison involves three good leaving groups with one (Ph_3CO^-) very poor one; but the bond length – $\text{p}K_a$ plot (Jones & Kirby, 1979, 1984) is not a very good straight line (correlation coefficient r 0.935). Nevertheless it is clear that (i) other things being equal, the bond to the better-leaving-group O atom is longer, and (ii) that electron withdrawal in the aromatic ring reduces the effect, as shown by the decrease in the length of the C(3)–O(1) bond from 1.481 to 1.452 Å when the 4-nitro group is introduced into the esters (Jones, Edwards & Kirby, 1986a,b).

The structures of all the compounds in this series will be discussed in more detail, in the context of the C–O cleavage reaction, in a forthcoming paper (Edwards, Jones & Kirby, 1986).

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Bond Length and Reactivity. Structure of a Grob Fragmentation Substrate, 4 α ,5 β ,8 $\alpha\beta$ -1-Methyldecahydroquinolin-5-yl 3,5-Dinitrobenzoate

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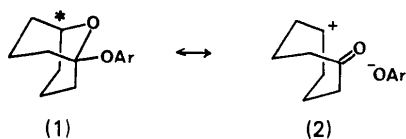
Abstract. $\text{C}_{17}\text{H}_{21}\text{N}_3\text{O}_6$, $M_r = 363.38$, orthorhombic, $Pbca$, $a = 6.338$ (2), $b = 25.355$ (8), $c = 21.774$ (6) Å, $U = 3499$ Å³, $Z = 8$, $D_x = 1.38$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.1$ mm⁻¹, $F(000) = 1536$, $T = 293$ K, $R = 0.089$ for 1758 reflections. The compound crystallizes in the chair,chair conformation with *O*-acyl and *N*-methyl substituents equatorial. The C–O-acyl bond [1.470 (5) Å] is relatively long because of the usual $\text{C}^+ - \text{O}^-$ contribution in this type of compound. There is no evidence for involvement of the σ electrons of the C(4 α)–C(8 α) bond in an exceptional $\sigma - \sigma_{\text{C}^* - \text{O}}$ interaction.

Introduction. As part of an extensive investigation of the relationship between the length of a bond in the crystal and the rate at which it is broken in ionic

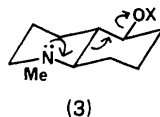
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reaction in solution (Jones & Kirby, 1984), we reported crystal structures for a set of equatorial tetrahydropyranyl acetals (aryloxytetrahydropyrans), such as (1) (Jones & Kirby, 1982; Briggs, Glenn, Jones, Kirby & Ramaswamy, 1984). These showed a remarkable trend in the pattern of bond lengths at the acetal centre: as the fragment ArO^- is made a better leaving group, by the addition of electron-withdrawing substituents, the usual (Briggs *et al.*, 1984) lengthening of the C–OAr bond and concomitant shortening of O–COAr is accompanied by a significant extension of the remote $\text{C}^* - \text{O}$ bond. We interpreted this as evidence for an incipient fragmentation reaction (1→2), valence tautomer (2) making an increasingly important contribution to the structure of the ground state as the anion ArO^- becomes more stable.



The effect has its origin in the σ - σ^* interaction between the antibonding orbital of the C-OAr bond and the bonding electrons of the (antiperiplanar) C*-O σ bond. A similar σ - σ^* interaction is involved in the classical Grob fragmentation reaction (Grob, 1969) of three-C systems, X-C-C-C-Y, such as that in the decahydroquinoline (3), X = *p*-toluenesulfonyl [shown by curved arrows in (3)]. It was therefore of interest to examine crystal structures of compounds (3), to look for changes in geometry, particularly bond length, in the N-C-C-C-OX system. We therefore prepared (3), X = 3,5-dinitrobenzoyl and report its crystal structure.



Experimental. The equatorial *trans* alcohol (3), X = H, was prepared, by a modification of the method of Grob & Kiefer (1965), as a mixture with the equatorial *cis* alcohol. These were readily separated only after conversion to the mixture of 3,5-dinitrobenzoate esters (by column chromatography on silica, eluent 10% methanol in chloroform). Crystals of (3), X = 3,5-dinitrobenzoyl, m.p. 408–418 K, dec., were grown by the liquid diffusion method using water–acetone; they formed as irregular yellow plates.

One crystal, 0.7 × 0.4 × 0.05 mm, used to collect two data sets (monochromated Mo K α radiation, $2\theta_{\max}$ 50°). Data set 1: Stoe–Siemens four-circle diffractometer, 4371 profile-fitted intensities (Clegg, 1981), cell constants refined from 2θ values of 31 reflections in the range 20–24°. Data set 2: Stoe two-circle diffractometer, layers *0kl*–*6kl*, 6403 reflections. After Lp corrections, merging equivalents (scale factors by least-squares analysis of common reflections, R_{int} 0.045, index ranges $h \leq 7$, $k \leq 30$, $l \leq 25$) gave 3225 unique reflections, 1758 of which with $F > 4\sigma(F)$ used for all calculations (program system *SHELXTL*; Sheldrick, 1978). Structure solution by routine direct methods; refinement on F to R 0.089 (weak diffractor), wR 0.051 [weighting scheme $w = \sigma^{-2}(F)$], non-H atoms anisotropic, H isotropic using riding model with C–H 0.96 Å, H–C–H 109.5°, $U(\text{H}) = 1.1U_{\text{iso}}(\text{C})$, 238 parameters, S 1.76; max. Δ/σ 0.003; max., min. heights in final $\Delta\rho$ map 0.3 e Å $^{-3}$. Atomic scattering factors from *SHELXTL*.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	U^*
N(1)	2246 (7)	1065 (1)	296 (1)	56 (1)
C(1)	1555 (11)	517 (2)	225 (2)	90 (3)
C(2)	481 (9)	1406 (2)	142 (2)	75 (2)
C(3)	1113 (10)	1982 (2)	158 (2)	83 (2)
C(4)	2015 (9)	2124 (2)	779 (2)	64 (2)
C(4a)	3752 (8)	1747 (1)	957 (2)	42 (1)
C(5)	4630 (8)	1872 (1)	1587 (2)	49 (2)
C(6)	6316 (9)	1497 (2)	1797 (2)	73 (2)
C(7)	5497 (10)	934 (2)	1765 (2)	75 (2)
C(8)	4746 (9)	804 (2)	1125 (2)	62 (2)
C(8a)	3011 (8)	1174 (1)	926 (2)	48 (2)
C(11)	5650 (8)	3312 (1)	1715 (2)	44 (2)
C(12)	4588 (8)	3764 (1)	1877 (2)	47 (2)
C(13)	5408 (8)	4249 (2)	1721 (2)	45 (2)
N(3)	4213 (7)	4729 (1)	1879 (2)	61 (2)
O(31)	4949 (7)	5149 (1)	1723 (2)	78 (2)
O(32)	2560 (7)	4680 (1)	2146 (1)	94 (2)
C(14)	7279 (8)	4295 (1)	1417 (2)	50 (2)
C(15)	8339 (7)	3841 (2)	1264 (2)	46 (2)
N(5)	10342 (7)	3878 (1)	927 (2)	61 (1)
O(51)	11034 (6)	4315 (1)	807 (2)	83 (1)
O(52)	11190 (6)	3471 (1)	774 (2)	83 (1)
C(16)	7572 (7)	3346 (1)	1410 (2)	44 (1)
C(17)	4629 (9)	2787 (2)	1863 (2)	51 (2)
O(1)	5561 (5)	2403 (1)	1560 (1)	53 (1)
O(2)	3122 (7)	2751 (1)	2187 (1)	77 (2)

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

Final atomic coordinates are given in Table 1 with derived parameters in Table 2; a diagram of the molecule is shown in Fig. 1.†

Discussion. Compound (3), X = 3,5-dinitrobenzoyl, crystallizes in the expected chair,chair conformation, with both *O*-acyl and *N*-methyl substituents equatorial. The C–O-acyl bond length is 1.470 (5) Å, not significantly longer than the value [1.460 (2) Å; Allen & Kirby (1984)] expected for such a bond to a secondary centre. There is no apparent lengthening of C(4a)–C(8a) or shortening of N–C(8a) or C(4a)–C(5). The C–O-acyl bond is relatively long because of the usual contribution from the C $^+$ –O-acyl form, apparent in particular from the internal angle C(4a)–C(5)–C(6) of 113.9 (5)°, and a modest flattening of the ring at C(5). But the σ electrons of the antiperiplanar C(8a)–C(4a) bond do not appear from the pattern of bond lengths in the N–C–C–C–O system to be engaged in exceptional σ - $\sigma_{\text{C-O}}^*$ interaction.

A likely explanation is that the electron pair on N, which acts as the ultimate donor orbital in the fragmentation of (3), is fixed axial by the equatorial *N*-methyl. Fragmentation (4) involves $n_{\text{N}}\sigma^*$ as well as

† 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 42998 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

C(1)—N(1)	1.466 (6)	C(2)—N(1)	1.453 (8)
C(2)—C(3)	1.516 (8)	C(3)—C(4)	1.512 (7)
C(4)—C(4a)	1.509 (7)	C(4a)—C(5)	1.513 (7)
C(4a)—C(8a)	1.528 (6)	C(5)—C(6)	1.502 (8)
C(5)—O(1)	1.470 (5)	C(6)—C(7)	1.520 (7)
C(7)—C(8)	1.511 (7)	C(8)—C(8a)	1.509 (7)
C(8a)—N(1)	1.481 (6)	C(11)—C(12)	1.377 (7)
C(11)—C(16)	1.390 (7)	C(11)—C(17)	1.514 (7)
C(12)—C(13)	1.376 (6)	C(13)—N(3)	1.475 (7)
C(13)—C(14)	1.364 (8)	N(3)—O(31)	1.211 (6)
N(3)—O(32)	1.204 (7)	C(14)—C(15)	1.374 (7)
C(15)—N(5)	1.469 (7)	C(15)—C(16)	1.383 (6)
N(5)—O(51)	1.220 (5)	N(5)—O(52)	1.210 (6)
C(17)—O(1)	1.318 (6)	C(17)—O(2)	1.191 (8)
C(1)—N(1)—C(2)	108.0 (5)	C(1)—N(1)—C(8a)	111.9 (4)
C(2)—N(1)—C(8a)	110.8 (4)	N(1)—C(2)—C(3)	111.4 (6)
C(2)—C(3)—C(4)	110.5 (5)	C(3)—C(4)—C(4a)	110.8 (5)
C(4)—C(4a)—C(5)	111.7 (4)	C(4)—C(4a)—C(8a)	111.5 (5)
C(5)—C(4a)—C(8a)	110.6 (4)	C(4a)—C(5)—C(6)	113.9 (4)
C(4a)—C(5)—O(1)	107.6 (4)	C(6)—C(5)—O(1)	107.8 (5)
C(5)—C(6)—C(7)	109.7 (5)	C(6)—C(7)—C(8)	110.8 (4)
C(7)—C(8)—C(8a)	111.0 (5)	N(1)—C(8a)—C(4a)	108.6 (4)
N(1)—C(8a)—C(8)	112.8 (4)	C(4a)—C(8a)—C(8)	110.8 (5)
C(12)—C(11)—C(16)	119.9 (5)	C(12)—C(11)—C(17)	117.9 (5)
C(16)—C(11)—C(17)	122.1 (5)	C(11)—C(12)—C(13)	119.7 (5)
C(12)—C(13)—N(3)	119.1 (5)	C(12)—C(13)—C(14)	121.7 (5)
N(3)—C(13)—C(14)	119.2 (4)	C(13)—N(3)—O(31)	117.6 (5)
C(13)—N(3)—O(32)	118.2 (4)	O(31)—N(3)—O(32)	124.2 (5)
C(13)—C(14)—C(15)	118.1 (5)	C(14)—C(15)—N(5)	119.3 (5)
C(14)—C(15)—C(16)	122.2 (5)	N(5)—C(15)—C(16)	118.5 (5)
C(15)—N(5)—O(51)	118.4 (4)	C(15)—N(5)—O(52)	117.8 (4)
O(51)—N(5)—O(52)	123.7 (5)	C(11)—C(16)—C(15)	118.3 (5)
C(11)—C(17)—O(1)	110.6 (5)	C(11)—C(17)—O(2)	122.5 (5)
O(1)—C(17)—O(2)	126.8 (5)	C(5)—O(1)—C(17)	118.5 (5)
C(1)—N(1)—C(2)—C(3)	-175.7 (5)	C(8a)—N(1)—C(2)—C(3)	61.4 (6)
C(1)—N(1)—C(8a)—C(4a)	178.6 (5)	C(1)—N(1)—C(8a)—C(8)	55.3 (6)
C(2)—N(1)—C(8a)—C(4a)	-60.8 (6)	C(2)—N(1)—C(8a)—C(8)	176.0 (5)
N(1)—C(2)—C(3)—C(4)	-56.3 (7)	C(2)—C(3)—C(4)—C(4a)	52.2 (7)
C(3)—C(4)—C(4a)—C(5)	-178.2 (5)	C(3)—C(4)—C(4a)—C(8a)	-53.9 (6)
C(4)—C(4a)—C(5)—C(6)	178.1 (5)	C(4)—C(4a)—C(5)—O(1)	-62.5 (6)
C(8a)—C(4a)—C(5)—C(6)	53.2 (6)	C(8a)—C(4a)—C(5)—O(1)	172.7 (4)
C(4)—C(4a)—C(8a)—N(1)	57.3 (6)	C(4)—C(4a)—C(8a)—C(8)	-178.3 (4)
C(5)—C(4a)—C(8a)—N(1)	-177.8 (5)	C(5)—C(4a)—C(8a)—C(8)	-53.4 (6)
C(4a)—C(5)—C(6)—C(7)	-54.5 (6)	O(1)—C(5)—C(6)—C(7)	-173.8 (4)
C(4a)—C(5)—O(1)—C(17)	111.0 (5)	C(6)—C(5)—O(1)—C(17)	-125.7 (5)
C(5)—C(6)—C(7)—C(8)	56.4 (7)	C(6)—C(7)—C(8)—C(8a)	-59.0 (7)
C(7)—C(8)—C(8a)—N(1)	179.2 (5)	C(7)—C(8)—C(8a)—C(4a)	57.2 (6)
C(17)—C(11)—C(12)—C(13)	-176.5 (5)	C(17)—C(11)—C(16)—C(15)	176.6 (5)
C(12)—C(11)—C(17)—O(1)	165.3 (5)	C(12)—C(11)—C(17)—O(2)	-11.0 (8)
C(16)—C(11)—C(17)—O(1)	-13.0 (7)	C(16)—C(11)—C(17)—O(2)	170.7 (5)
C(11)—C(12)—C(13)—N(3)	177.8 (5)	C(12)—C(13)—N(3)—O(31)	-178.3 (5)
C(12)—C(13)—N(3)—O(32)	0.6 (7)	C(14)—C(13)—N(3)—O(31)	0.8 (7)
C(14)—C(13)—N(3)—O(32)	179.7 (5)	N(3)—C(13)—C(14)—C(15)	-178.7 (5)
C(13)—C(14)—C(15)—N(5)	179.0 (5)	C(14)—C(15)—N(5)—O(51)	-1.9 (7)
C(14)—C(15)—N(5)—O(52)	-176.7 (5)	C(16)—C(15)—N(5)—O(51)	-178.8 (5)
C(16)—C(15)—N(5)—O(52)	2.6 (7)	N(5)—C(15)—C(16)—C(11)	-178.4 (5)
C(11)—C(17)—O(1)—C(5)	-172.8 (4)	O(2)—C(17)—O(1)—C(5)	3.3 (8)

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

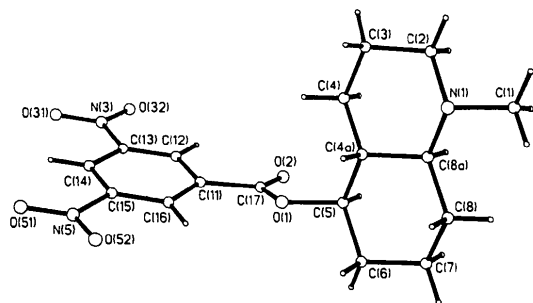
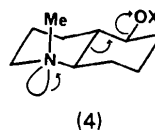
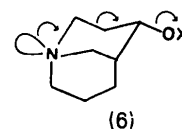
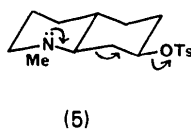


Fig. 1. The molecule of (3), X = 3,5-dinitrobenzoate, in the crystal, showing the atom-numbering scheme.

$\sigma\sigma^*$ overlap, and both require antiperiplanar geometry. In the ground-state conformation N can act only by σ -electron withdrawal, thus inhibiting fragmentation. In solution this stereoelectronic barrier (Kirby, 1983) is readily overcome by inversion at N, but electron demand from the electron-deficient centre at C(5) is clearly insufficient to drive this conformational change in the crystal.



This problem has been recognized by Grob (1969) and explains, for example, the failure of (5) to fragment, since the N lone pair is not antiperiplanar to the central C—C bond of the N—C—C—C—O system in either conformation of the N-methyl group. The related compound (6), X = *p*-toluenesulfonyl, on the other hand, which is fixed in a productive conformation, fragments cleanly (Grob, 1969). We have grown crystals of (6), X = 3,5-dinitrobenzoyl, but none so far suitable for X-ray analysis.



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