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# 3,4,4aα,10aα-Tetrahydro-7,9-dinitro-2H,5H-[1]benzopyrano[2,3-b]pyran

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Abstract. $C_{12}H_{12}N_2O_6$, $M_r = 280.24$, monoclinic, $P2_1/c$, $a = 12.777$ (4), $b = 7.954$ (3), $c = 12.448$ (5) Å, $\beta = 101.21$ (4)°, $U = 1241$ Å^3, $Z = 4$, $D_x = 1.500$ Mg m^{-3}, μ(Mo $K\alpha$) = 0.08 mm^{-1}. The structure was refined to $R = 0.054$ for 1449 unique reflexions. The C–O lengths of the acetal group differ by 0.089 Å. One nitro group is at 43° to the plane of the benzene ring.

Introduction. We have shown (Jones, Kennard, Kirby & Martin, 1979, and references therein) that the differences observed between the two C–O lengths of alkyl aryl acetals (1) depend on the conformation about the acetal centre. In compounds which have a lone-pair orbital on the alkyl O atom antiperiplanar to the C–OAr bond, this bond is lengthened, and the C–OR bond shortened, compared with symmetrical acetals. This difference increases with increasing electronegativity of the OAr group, up to 0.06 Å for the 4-nitrophenyl compound (2, $X = $ H) (Jones *et al.*, 1979).

RO–CH₂OAr

(1)

(2)
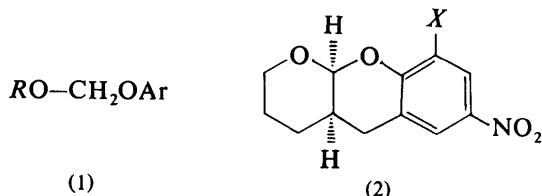
Because the leaving group remains attached to the molecule, the spontaneous hydrolysis of (2, $X = $ H) is

much slower than for comparable acetals with exocyclic leaving groups (Kirby & Martin, 1978), and it has been possible to prepare the corresponding dinitro

Table 1. *Atom coordinates* ($\times 10^4$)

Overall isotropic temperature factor for H atoms: 0.076 (3) Å^2.

	x	y	z
O(1)	5992 (2)	3309 (2)	2715 (1)
C(2)	5046 (3)	2447 (4)	2865 (2)
C(3)	4812 (3)	2737 (5)	3993 (3)
C(4)	5779 (3)	2232 (4)	4857 (2)
C(4A)	6761 (2)	3164 (3)	4662 (2)
C(5)	7789 (3)	2651 (3)	5435 (2)
C(5A)	8175 (2)	964 (3)	5123 (2)
C(6)	8858 (2)	−17 (3)	5874 (2)
C(7)	9202 (2)	−1556 (3)	5565 (2)
C(8)	8874 (2)	−2208 (3)	4529 (2)
C(9)	8199 (2)	−1224 (3)	3791 (2)
C(9A)	7841 (2)	359 (3)	4057 (2)
O(10)	7158 (2)	1199 (2)	3275 (1)
C(10A)	6892 (2)	2946 (3)	3486 (2)
N(1)	9943 (2)	−2535 (3)	6370 (2)
O(11)	10169 (2)	−2004 (3)	7309 (2)
O(12)	10302 (2)	−3837 (3)	6077 (2)
N(2)	7856 (2)	−1914 (3)	2679 (2)
O(21)	7614 (2)	−3405 (2)	2610 (2)
O(22)	7846 (2)	−999 (3)	1898 (2)
H(1)	4379	2896	2263
H(2)	5150	1116	2751
H(3)	4638	4051	4088
H(4)	4132	1988	4093
H(5)	5909	895	4809
H(6)	5634	2544	5660
H(7)	6626	4470	4830
H(8)	7643	2584	6260
H(9)	8395	3583	5397
H(10)	9121	426	6703
H(11)	9133	−3430	4308
H(12)	7517	3823	3405

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compound (2, X = NO$_2$). The crystal and molecular structure of this compound is the subject of this paper.

Colourless equidimensional crystals were obtained from dichloromethane/petroleum spirit. Intensities were measured on a Syntex $P2_1$ diffractometer with mono-chromated Mo $K\alpha$ radiation and a crystal 0·4 × 0·3 × 0·3 mm. 2664 reflexions were collected in the range 3° < 2θ < 55°; after application of Lp corrections, averaging equivalent reflexions gave 1449 unique re-flexions with $F > 4\sigma(F)$.

The structure was solved by multisolution Σ_2 sign expansion with 435 $E > 1\cdot2$. Least-squares refinement proceeded to $R = 0\cdot13$ (isotropic), 0·08 (anisotropic). At this stage a difference map revealed positions of 11 H atoms. In the final stages of refinement C—H distances were fixed at 1·08 Å and H—C—H angles at 109·5°. An overall isotropic temperature factor was employed for H atoms. The final R was 0·054, with a

corresponding $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o|$ of 0·045. The weighting scheme was $w = 1/[\sigma^2(F) + gF^2]$, where g refined to 0·0001. A final difference map had no peaks >0·25 e Å^{-3}.

Final atomic coordinates are given in Table 1, with bond lengths, angles and torsion angles in Tables 2 and 3.* A diagram of the structure is given in Fig. 1.

Discussion. Increasing the electronegativity of the leaving group O(10) has led to the expected increase in the difference between the acetal C—O lengths of (2, X = NO$_2$), compared with the mononitro compound (2, X = H). At almost 0·09 Å this difference is the largest yet observed for an acetal [C(10a)—O(10) = 1·466 (4); C(10a)—O(1) = 1·377 (4) Å]. This is despite the fact that the electronic effect of the second nitro group [O(21),N(2),O(22)] cannot be fully developed, since it is rotated by 43° out of the plane of the benzene ring. Such rotations are commonly observed in derivatives of 2-nitrophenol (Simon, Rogers, Saenger & Gougoutas,

Table 2. Bond lengths (Å) and angles (°)

C(2)—O(1)	1·433 (5)	C(2)—C(3)	1·509 (7)
C(3)—C(4)	1·526 (6)	C(4)—C(4A)	1·517 (7)
C(4A)—C(5)	1·525 (6)	C(4A)—C(10A)	1·516 (6)
C(5)—C(5A)	1·507 (6)	C(5A)—C(6)	1·388 (4)
C(5A)—C(9A)	1·398 (4)	C(6)—C(7)	1·381 (5)
C(7)—C(8)	1·377 (4)	C(7)—N(1)	1·462 (4)
C(8)—C(9)	1·375 (4)	C(9)—C(9A)	1·401 (5)
C(9)—N(2)	1·475 (4)	C(9A)—O(10)	1·351 (4)
C(10A)—O(1)	1·377 (4)	C(10A)—O(10)	1·466 (4)
N(1)—O(11)	1·223 (4)	N(1)—O(12)	1·218 (4)
N(2)—O(21)	1·224 (4)	N(2)—O(22)	1·212 (4)

|			
C(2)—O(1)—C(10A)	114·9 (3)	O(1)—C(2)—C(3)	111·9 (3)
C(2)—C(3)—C(4)	109·7 (4)	C(3)—C(4)—C(4A)	109·9 (4)
C(4)—C(4A)—C(5)	114·0 (3)	C(4)—C(4A)—C(10A)	110·4 (3)
C(5)—C(4A)—C(10A)	109·6 (4)	C(4A)—C(5)—C(5A)	111·1 (3)
C(5)—C(5A)—C(6)	121·4 (3)	C(5)—C(5A)—C(9A)	119·8 (3)
C(6)—C(5A)—C(9A)	118·8 (3)	C(5A)—C(6)—C(7)	120·2 (3)
C(6)—C(7)—C(8)	122·6 (3)	C(6)—C(7)—N(1)	118·7 (3)
C(8)—C(7)—N(1)	118·7 (3)	C(7)—C(8)—C(9)	116·7 (3)
C(8)—C(9)—C(9A)	123·0 (3)	C(8)—C(9)—N(2)	116·7 (3)
C(9A)—C(9)—N(2)	120·3 (3)	C(5A)—C(9A)—C(9)	118·7 (3)
C(5A)—C(9A)—O(10)	123·3 (3)	C(9)—C(9A)—O(10)	117·9 (3)
C(9A)—O(10)—C(10A)	118·6 (3)	O(1)—C(10A)—C(4A)	114·5 (4)
O(1)—C(10A)—O(10)	105·4 (3)	C(4A)—C(10A)—O(10)	110·8 (3)
C(7)—N(1)—O(11)	118·2 (3)	C(7)—N(1)—O(12)	118·6 (3)
O(11)—N(1)—O(12)	123·2 (3)	C(9)—N(2)—O(21)	116·8 (3)
C(9)—N(2)—O(22)	119·0 (3)	O(21)—N(2)—O(22)	124·2 (3)
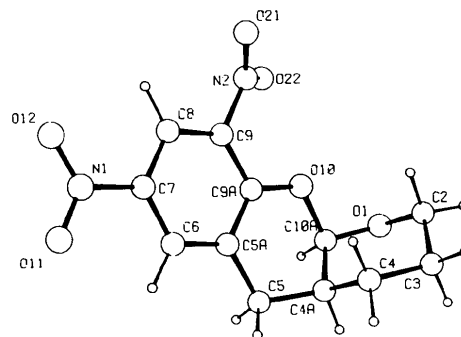
Fig. 1. The molecule of the title compound, showing the atom numbering. H atoms are numbered in ascending order according to the number of the C atom to which they are attached.

Table 3. Selected torsion angles (°)

The sign convention is that defined by Klyne & Prelog (1960).

C(10A)—O(1)—C(2)—C(3)	55·0 (4)	C(4A)—C(5)—C(5A)—C(6)	−158·2 (4)	C(7)—C(8)—C(9)—N(2)	179·4 (3)
C(2)—O(1)—C(10A)—C(4A)	−52·8 (4)	C(4A)—C(5)—C(5A)—C(9A)	21·7 (5)	C(8)—C(9)—C(9A)—O(10)	−178·4 (4)
C(2)—O(1)—C(10A)—O(10)	69·2 (4)	C(5)—C(5A)—C(6)—C(7)	−179·8 (4)	N(2)—C(9)—C(9A)—C(5A)	179·4 (3)
O(1)—C(2)—C(3)—C(4)	−55·4 (5)	C(5)—C(5A)—C(9A)—C(9)	−179·1 (4)	N(2)—C(9)—C(9A)—O(10)	1·6 (5)
C(2)—C(3)—C(4)—C(4A)	55·0 (5)	C(5)—C(5A)—C(9A)—O(10)	−1·5 (5)	C(8)—C(9)—N(2)—O(21)	42·3 (5)
C(3)—C(4)—C(4A)—C(5)	−175·8 (4)	C(6)—C(5A)—C(9A)—C(9)	0·8 (5)	C(8)—C(9)—N(2)—O(22)	−136·5 (4)
C(3)—C(4)—C(4A)—C(10A)	−52·0 (4)	C(5A)—C(6)—C(7)—N(1)	178·5 (4)	C(9A)—C(9)—N(2)—O(21)	−137·7 (4)
C(4)—C(4A)—C(5)—C(5A)	75·2 (4)	N(1)—C(7)—C(8)—C(9)	−178·4 (3)	C(9A)—C(9)—N(2)—O(22)	43·5 (5)
C(10A)—C(4A)—C(5)—C(5A)	−49·1 (4)	C(6)—C(7)—N(1)—O(11)	5·1 (5)	C(5A)—C(9A)—O(10)—C(10A)	10·7 (5)
C(4)—C(4A)—C(10A)—O(1)	51·1 (4)	C(6)—C(7)—N(1)—O(12)	−175·1 (4)	C(9)—C(9A)—O(10)—C(10A)	−171·7 (3)
C(4)—C(4A)—C(10A)—O(10)	−67·9 (4)	C(8)—C(7)—N(1)—O(11)	−174·7 (4)	C(9A)—O(10)—C(10A)—O(1)	−164·0 (3)
C(5)—C(4A)—C(10A)—O(1)	177·5 (3)	C(8)—C(7)—N(1)—O(12)	5·1 (5)	C(9A)—O(10)—C(10A)—C(4A)	−39·6 (4)
C(5)—C(4A)—C(10A)—O(10)	58·4 (4)				

1967; Gurtu, Chandler & Robertson, 1975; Cody, Shefter & Lehmann, 1976), and are presumably to avoid the short contact with the *ortho* O atom [O(10) in this structure].

Changes in the C—O lengths in the direction observed here also occur in acetal cleavage reactions, one bond becoming a double bond and the other being broken (Kirby & Martin, 1978). Compounds with more electronegative leaving groups may thus be considered to start (*i.e.* have ground states) farther along the reaction coordinate; we have recently demonstrated a simple relationship between bond length and reactivity in these compounds (Jones & Kirby, 1979).

D. S. Motherwell; all other crystallographic programs used were written by Professor G. M. Sheldrick.

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2,2,3,3,4,6,7-Heptachloro-1,1,5-triethoxyindan

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Abstract. $C_{15}H_{15}Cl_7O_3$, $M_r = 491.46$, $F(000) = 1984$, orthorhombic, $P2_12_12_1$, $a = 11.677 (2)$, $b = 16.381 (8)$, $c = 10.579 (2)$ Å, $V = 2023.6$ Å^3, $Z = 4$, $D_c = 1.61$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å. The structure was solved with *MULTAN* and refined by the block-diagonal least-squares method. The final R value is 0.040 for 2204 observed reflections. The five-membered ring is puckered with an 'envelope form'; moreover, bond distances are slightly influenced by the steric interaction between O and Cl substituents.

Introduction. Colourless prismatic crystals of this compound were kindly supplied by Professors Ballester and Riera (Ballester, Riera, Castañer & Juliá, 1978; Ballester & Olivella, 1974).

The structure was determined to locate the positions of the ethoxy groups in the molecule and to obtain molecular structural information as an aid to the elucidation of structure–toxicity relationships in this group of insecticides.

A crystal of 0.2 × 0.2 × 0.4 mm was used to obtain crystal data and intensity measurements on a Nonius CAD-4 diffractometer. The unit cell was determined by centring 25 independent reflections and refining the

Table 1. *Non-hydrogen atomic coordinates* ($\times 10^5$) *with standard deviations in parentheses*

	x	y	z
C(1)	38678 (31)	59130 (21)	78942 (43)
C(2)	31430 (31)	43820 (22)	76920 (42)
C(3)	39563 (33)	36927 (21)	81824 (45)
C(4)	52724 (32)	37793 (23)	101663 (47)
C(5)	58088 (32)	42757 (27)	110544 (46)
C(6)	57061 (36)	51249 (28)	109308 (46)
C(7)	50924 (33)	54731 (22)	99429 (45)
C(8)	45403 (30)	49681 (22)	90813 (43)
C(9)	46123 (29)	41169 (22)	92258 (42)
O(10)	45304 (25)	52388 (16)	68071 (30)
C(11)	54782 (40)	57914 (28)	68110 (56)
C(12)	59902 (43)	57483 (31)	54999 (54)
O(13)	32392 (24)	58894 (16)	81442 (32)
C(14)	25605 (46)	62279 (30)	71318 (60)
C(15)	22278 (50)	70660 (31)	75512 (73)
Cl(16)	19202 (8)	44441 (6)	86292 (13)
Cl(17)	26667 (9)	42044 (6)	61458 (11)
Cl(18)	49528 (10)	33761 (6)	70026 (13)
Cl(19)	31753 (10)	28210 (5)	86533 (14)
Cl(20)	55058 (11)	27403 (6)	102765 (15)
O(21)	64898 (27)	39563 (23)	119679 (35)
C(22)	58963 (45)	37262 (41)	131103 (61)
C(23)	67786 (66)	34528 (45)	140415 (65)
Cl(24)	64038 (13)	57249 (8)	120188 (14)
Cl(25)	50531 (10)	65211 (5)	98219 (13)