

Conformations of 2-Substituted 2,3-Dihydro-1,4-benzodioxines

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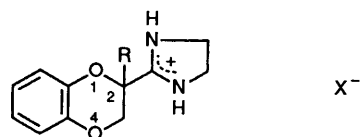
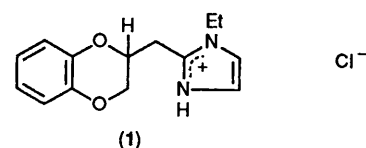
X-Ray crystallographic studies have shown that the imidazolium group in 2-(2-methoxy-2,3-dihydro-1,4-benzodioxin-2-yl)-4,5-dihydroimidazolium bromide (4), (+)-2-(2-methoxy-2,3-dihydro-1,4-benzodioxin-2-yl)-4,5-dihydroimidazolium hydrogen dibenzoyltartrate (5), and 2-(2,3-dihydro-1,4-benzopyran-2-yl)-4,5-dihydroimidazolium chloride (7) occupies the equatorial position on the dihydroxine ring of compounds (4) and (5) and the dihydropyran ring of compound (7). The imidazolium group in 2-(2,3-dihydro-1,4-benzodioxin-2-yl)-4,5-dihydroimidazolium chloride (2), (+)-2-(2,3-dihydro-1,4-benzodioxin-2-yl)-4,5-dihydroimidazolium hydrogen dibenzoyltartrate (3), and 2-(2-isopropyl-2,3-dihydro-1,4-benzodioxin-2-yl)-4,5-dihydroimidazolium chloride (6) occupies the axial position on the dihydrodioxine ring; the axial choice in compound (6) is attributed to the equatorial preference of the bulky isopropyl group, and the conformational anomaly in compounds (2) and (3) appears to be caused by an interaction between the axial imidazolium group and a lone-pair orbital on the oxygen atom O(4) of the dihydrodioxine ring.

Derivatives of 2,3-dihydro-1,4-dioxine incorporating imidazole or dihydroimidazole moieties have been identified as α_2 -adrenoreceptor antagonists.¹⁻⁵ 1-Ethyl-2-(2,3-dihydro-1,4-benzodioxin-2-ylmethyl)imidazolium chloride (1)⁶ and 2-(2,3-dihydro-1,4-benzodioxin-2-yl)-4,5-dihydroimidazolium chloride (2)⁷ have been examined by X-ray crystallography and the results reveal that the dihydrodioxine rings adopt distorted half-chair conformations with the substituent of C(2) equatorial, as expected, in compound (1) but axial in compound (2). It is unclear whether this conformational difference is a feature of isolated molecules or is to be attributed to crystal-packing forces, and we undertook X-ray studies of the related compounds (3)-(7) to investigate the conformational features of this series. Pharmacological evaluation of 2-(2-methoxy-2,3-dihydro-1,4-benzodioxin-2-yl)-4,5-dihydroimidazole indicated that the biological activity is confined to the (+)-enantiomer,^{4,5} and the X-ray analyses of compounds (4) and (5) served also to establish the absolute configuration of the (+)-enantiomer as *S*.

The molecular structures of compounds (3)-(7), derived from the X-ray studies, are shown in Fig. 1 and the torsion angles that define the dihydrodioxine conformations are listed in Table 1.

In compounds (4) and (5) the imidazolium group is equatorial and the methoxy group axial in regard to the dihydrodioxine ring; here the normal steric preference of the imidazolium group for the equatorial orientation is reinforced by the anomeric axial preference of the methoxy group.^{8,9} In compounds (3) and (6), on the other hand, the imidazolium group is in the axial orientation on the dihydrodioxine ring. The axial position of the imidazolium group in compound (6) can be attributed to the equatorial preference of the bulky isopropyl group but compounds (2) and (3) are clearly deviant.

It is unlikely that the conformational anomaly in compounds (2) and (3) arises from an interaction between the positively charged dihydroimidazolium group and the adjacent dihydrodioxine oxygen atom O(1), since protonation of the imidazole ring in *N*-glycosylimidazoles changes the preferred orientation from axial to equatorial.¹⁰ The trimethylammonium group at C(5) in 5-trimethylamino-1,3-dioxane has an axial preference¹¹ and this suggests that the axial orientation of the imidazolium group in compounds (2) and (3) involves an interaction between the imidazolium group and the dihydrodioxine oxygen atom O(4). Compound (7) has the



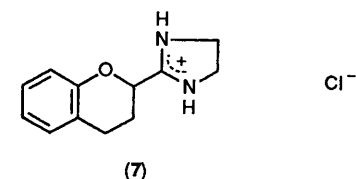
(2) R = H, X = Cl

(3) R = H, X = PhCO₂CHCO₂⁻
 |
 PhCO₂CHCO₂H

(4) R = OMe, X = Br

(5) R = OMe, X = PhCO₂CHCO₂⁻
 |
 PhCO₂CHCO₂H

(6) R = CHMe₂, X = Cl



oxygen atom O(4) replaced by a CH₂ group and here the imidazolium group is found to adopt the equatorial orientation. We conclude that a charge-dipole interaction between the imidazolium group and a lone-pair orbital at O(4) is responsible for the axial preference of the imidazolium group in compounds (2) and (3). The interaction is outweighed by the anomeric effect in compounds (4) and (5) but will also feature in compound (6).

The dihydrodioxine rings in compounds (3)-(6) and the

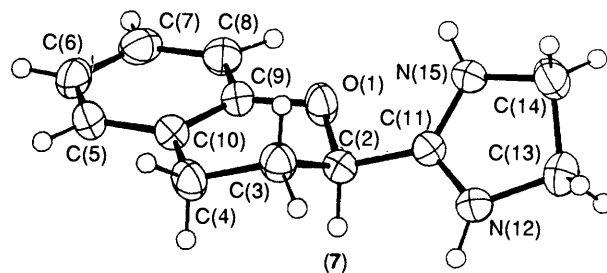
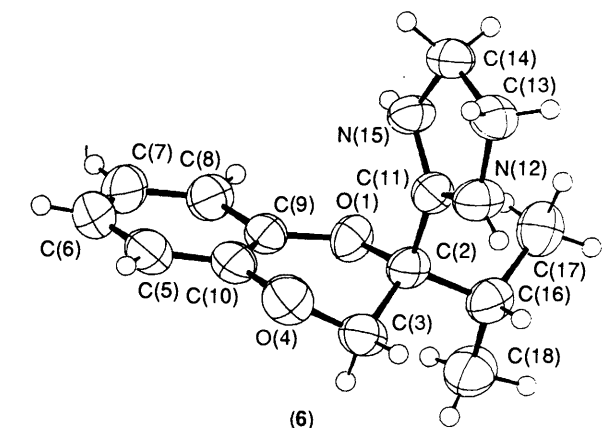
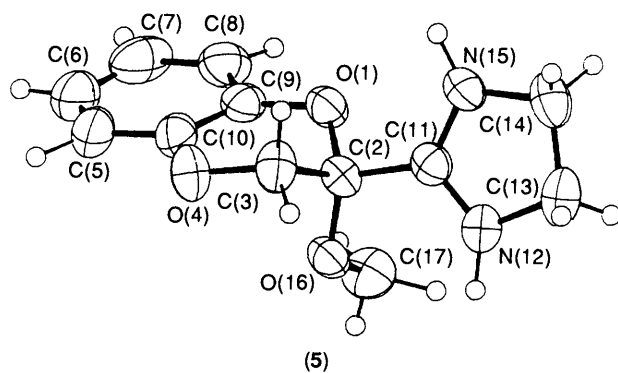
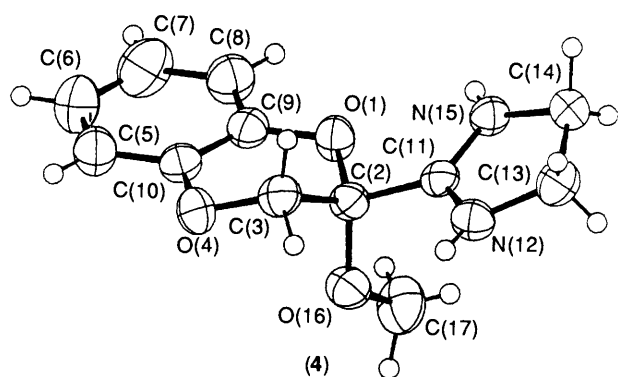
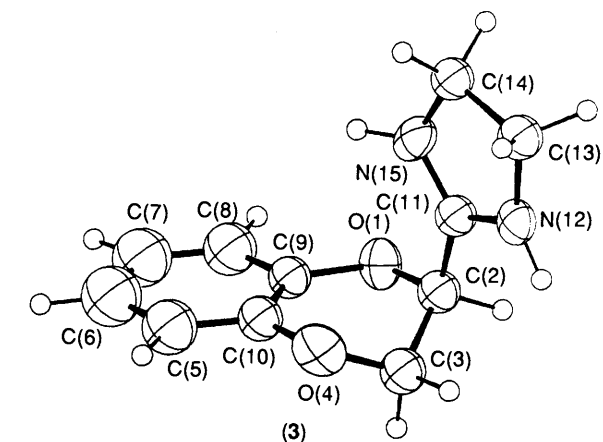


Figure 1. Atomic arrangements in the dihydrobenzodioxinylimidazolium cations of compounds (3)–(7). The thermal ellipsoids are drawn at the 50% probability level. The H-atoms are represented by spheres of radius 0.1 Å.

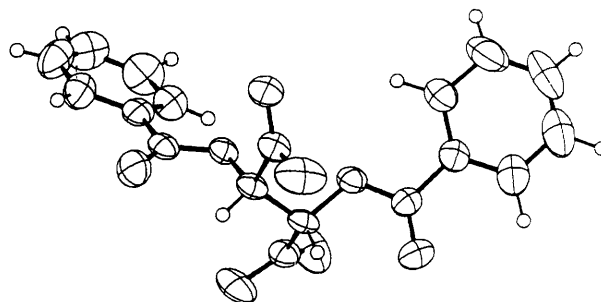


Figure 2. Atomic arrangement in the hydrogen (+)-dibenzoyltartrate anion of compound (5).

Table 1. Torsion angles/ $^{\circ}$ in compounds (2)–(7). Standard deviations are 0.2–0.9 $^{\circ}$.

	(2)	(3)	(4)	(5)	(6)	(7)
10–9–1–2	–5.3	–2.8	11.2	25.5	–5.6	17.6
9–1–2–3	34.2	32.6	–39.6	–53.9	35.6	–47.1
1–2–3–4	–59.1	–59.2	59.9	61.4	–61.0	60.7
2–3–4–10	52.7	54.6	–48.5	–38.4	54.1	–44.0
3–4–10–9	–24.7	–25.4	20.3	8.5	–23.6	17.1
4–10–9–1	–0.7	–2.0	–0.1	–0.7	–2.0	–2.4
9–1–2–11	–90.0	–91.3	–159.5	–171.1	–84.1	–169.0

dihydropyran ring in compound (7) have distorted half-chair conformations (Table 1). The O–C–C–O torsion angle, 59.1–61.4, mean 60.1 $^{\circ}$, does not vary much in the series. NMR investigations of 2,3-dihydro-1,4-dioxine^{12,13} and 2,3-dihydro-1,4-benzodioxine¹³ have established that these molecules have half-chair conformations with O–C–C–O torsion angles 60–61 $^{\circ}$. In compounds (4) and (5), the C(2)–O(1) distance is 1.420(5), 1.440(4) Å and the C(2)–O(16) distance is 1.400(6), 1.379(5) Å; the shorter axial C–O bond is a regular feature of pyranose acetals.^{14,15}

The imidazolium rings show small departure from planarity, with N–C–C–N torsion angles in the range 0.2–15.2 $^{\circ}$. The C(11)–N(12) and C(11)–N(15) bond lengths range over 1.287(6)–1.338(13) Å, with a mean of 1.307 Å. Similar results, 1.304–1.310(5), mean 1.308 Å, have been reported for 2-(1-naphthylmethyl)dihydroimidazolium chloride¹⁶ and 2-(4-*t*-butyl-2,6-dimethylbenzyl)dihydroimidazolium chloride.¹⁷ The virtual identity of the two C(11)–N distances indicates that the positive charge is delocalized over both N atoms.

Experimental

Crystal Data.—(+)-2,3-Dihydro-1,4-benzodioxin-2-yl)-4,5-dihydroimidazolium hydrogen dibenzoyltartrate (3),

Table 2. Fractional atomic co-ordinates for compound (3), with standard deviations in parentheses.

Atom	x	y	z
O(1)	0.995 3(10)	0.047 1(8)	0.100 2(2)
O(4)	0.626 7(10)	0.042 9(8)	0.103 5(2)
N(12)	0.856 8(12)	0.085 5(8)	0.184 1(2)
N(15)	0.892 3(12)	0.131 6(8)	0.165 4(2)
C(2)	0.935 9(16)	-0.062 2(10)	0.122 8(3)
C(3)	0.773 1(17)	-0.138 8(11)	0.108 5(3)
C(5)	0.545 1(19)	0.141 8(13)	0.064 7(3)
C(6)	0.598(2)	0.253(1)	0.044(0)
C(7)	0.778(2)	0.292(1)	0.042(0)
C(8)	0.902 7(18)	0.222 1(12)	0.060 2(3)
C(9)	0.855 5(15)	0.112 8(10)	0.081 3(3)
C(10)	0.674 3(16)	0.069 1(11)	0.083 5(3)
C(11)	0.896 4(15)	-0.002 0(11)	0.157 3(3)
C(13)	0.826 3(16)	0.000 3(11)	0.215 1(3)
C(14)	0.858 7(16)	0.150 7(11)	0.202 3(3)
O(1A)	1.238 6(10)	0.698 8(6)	0.166 8(2)
O(2A)	1.241 6(14)	0.666 5(8)	0.223 3(2)
O(3A)	0.913 6(10)	0.422 3(7)	0.153 4(2)
O(4A)	0.880 4(11)	0.636 9(7)	0.173 6(2)
O(5A)	1.189 9(9)	0.600 9(7)	0.100 5(2)
O(6A)	1.241 5(12)	0.430 4(7)	0.062 0(2)
O(7A)	1.558 5(11)	0.583 3(8)	0.104 9(2)
O(8A)	1.546 0(9)	0.434 3(8)	0.150 1(2)
C(1A)	1.184 1(14)	0.554 1(10)	0.161 0(2)
C(2A)	1.259 1(16)	0.743 2(10)	0.199 3(3)
C(3A)	1.308 2(15)	0.893 6(11)	0.201 2(3)
C(4A)	1.298 9(17)	0.957 5(12)	0.233 8(3)
C(5A)	1.331 4(18)	1.101 7(13)	0.236 8(3)
C(6A)	1.375 7(19)	1.178 3(12)	0.208 1(3)
C(7A)	1.390 9(18)	1.117 5(11)	0.176 5(3)
C(8A)	1.356 7(17)	0.972 1(11)	0.172 3(3)
C(9A)	1.259 2(17)	0.509 7(11)	0.126 9(3)
C(10A)	1.475 3(17)	0.513 5(12)	0.125 7(3)
C(11A)	1.201 7(15)	0.553 8(11)	0.068 2(2)
C(12A)	0.969 8(15)	0.537 4(10)	0.162 5(3)
C(13A)	1.164 0(16)	0.658 2(11)	0.041 7(3)
C(14A)	1.165 6(17)	0.799 5(11)	0.048 4(3)
C(15A)	1.136 3(18)	0.896 3(11)	0.022 4(3)
C(16A)	1.108 0(19)	0.848 8(12)	-0.010 8(3)
C(17A)	1.101 8(19)	0.709 5(12)	-0.017 4(3)
C(18A)	1.131 3(18)	0.611 5(12)	0.007 3(3)

Table 3. Fractional atomic co-ordinates for compound (4), with standard deviations in parentheses.

Atom	x	y	z
Br	0.217 23(7)	0.153 47(5)	0.784 07(2)
O(1)	0.810 5(5)	0.019 4(3)	0.640 8(1)
O(4)	0.988 7(5)	0.277 5(4)	0.585 6(2)
O(16)	0.632 8(5)	0.243 9(4)	0.628 4(2)
N(12)	0.712 2(8)	0.285 6(5)	0.761 1(2)
N(15)	0.729 8(8)	0.033 5(5)	0.758 1(2)
C(2)	0.779 3(7)	0.175 7(4)	0.659 5(2)
C(3)	0.944 3(7)	0.276 3(6)	0.648 1(2)
C(5)	1.086 9(9)	0.111 1(8)	0.506 0(3)
C(6)	1.095 4(11)	-0.032 6(10)	0.479 3(3)
C(7)	1.010 3(11)	-0.158 5(9)	0.506 8(3)
C(8)	0.917 7(9)	-0.139 5(7)	0.561 1(3)
C(9)	0.907 5(7)	0.005 7(5)	0.587 1(2)
C(10)	0.994 4(7)	0.131 0(6)	0.560 1(2)
C(11)	0.738 1(5)	0.164 0(5)	0.727 8(2)
C(13)	0.683 5(10)	0.243 1(7)	0.825 1(3)
C(14)	0.695 6(12)	0.064 7(6)	0.823 0(2)
C(17)	0.466 5(9)	0.156 8(11)	0.625 8(3)

Table 4. Fractional atomic co-ordinates for compound (5), with standard deviations in parentheses.

Atom	x	y	z
O(1)	-0.772 7(3)	0.0069	-0.204 2(2)
O(4)	-0.416 3(3)	0.040 9(2)	-0.222 8(2)
O(16)	-0.585 9(3)	-0.107 8(2)	-0.207 4(2)
O(100)	-0.957 7(5)	-0.368 3(2)	-0.608 9(3)
O(1A)	-0.330 8(3)	-0.457 3(2)	-0.318 5(2)
O(2A)	-0.302 3(5)	-0.547 9(2)	-0.441 5(2)
O(3A)	0.027 0(4)	-0.334 7(2)	-0.366 0(3)
O(4A)	0.041 7(4)	-0.444 9(2)	-0.264 0(3)
O(5A)	-0.260 6(3)	-0.262 7(2)	-0.251 6(2)
O(6A)	-0.264 4(4)	-0.158 3(2)	-0.312 1(2)
O(7A)	-0.629 1(3)	-0.300 0(2)	-0.324 9(2)
O(8A)	-0.616 8(4)	-0.345 6(3)	-0.485 1(2)
N(12)	-0.844 7(5)	-0.149 1(2)	-0.400 5(3)
N(15)	-0.982 2(4)	-0.031 0(2)	-0.413 2(2)
C(2)	-0.688 8(4)	-0.045 3(2)	-0.266 9(3)
C(3)	-0.557 8(5)	0.007 1(3)	-0.309 9(3)
C(5)	-0.343 2(7)	0.105 7(4)	-0.052 2(4)
C(6)	-0.389 7(8)	0.130 7(3)	0.038 2(4)
C(7)	-0.565 3(9)	0.118 0(3)	0.045 7(4)
C(8)	-0.692 3(7)	0.075 6(3)	-0.035 0(3)
C(9)	-0.645 9(5)	0.048 6(2)	-0.125 2(3)
C(10)	-0.470 4(5)	0.065 5(2)	-0.135 5(3)
C(11)	-0.843 6(5)	-0.076 0(2)	-0.360 5(3)
C(13)	-1.001 9(7)	-0.158 4(3)	-0.497 3(4)
C(14)	-1.102 7(6)	-0.177 8(3)	-0.501 7(4)
C(17)	-0.670 0(7)	-0.153 9(3)	-0.140 0(4)
C(100)	-0.941 4(8)	-0.338 2(4)	-0.705 9(4)
C(1A)	-0.253 6(4)	-0.396 3(2)	-0.373 1(3)
C(2A)	-0.352 7(4)	-0.530 9(2)	-0.362 8(3)
C(3A)	-0.444 1(5)	-0.589 3(2)	-0.307 1(3)
C(4A)	-0.516 3(6)	-0.564 4(3)	-0.224 9(3)
C(5A)	-0.598 4(8)	-0.622 0(4)	-0.173 5(4)
C(6A)	-0.603 1(7)	-0.702 9(4)	-0.205 2(5)
C(7A)	-0.536 3(7)	-0.726 4(3)	-0.286 2(5)
C(8A)	-0.454 3(6)	-0.670 4(3)	-0.338 3(4)
C(9A)	-0.337 3(4)	-0.314 4(2)	-0.360 3(3)
C(10A)	-0.548 0(4)	-0.319 8(2)	-0.392 9(3)
C(11A)	-0.228 4(4)	-0.238 3(2)	-0.238 5(3)
C(12A)	-0.042 0(5)	-0.396 0(2)	-0.325 1(3)
C(13A)	-0.138 5(4)	-0.184 7(3)	-0.123 3(3)
C(14A)	-0.136 5(5)	-0.103 7(3)	-0.093 0(4)
C(15A)	-0.053 1(6)	-0.183 1(3)	0.015 4(4)
C(16A)	0.030 9(6)	-0.139 1(4)	0.088 0(4)
C(17A)	0.035 3(7)	-0.218 2(4)	0.056 3(4)
C(18A)	-0.053 8(5)	-0.242 2(3)	-0.048 8(3)

$C_{11}H_{13}N_2O_2 \cdot C_{18}H_{13}O_8$, $M = 562.58$, orthorhombic, $a = 7.287(2)$, $b = 9.506(1)$, $c = 38.723(4)$ Å, $V = 2682$ Å³, $D_c = 1.39$ g cm⁻³, $Z = 4$, $F(000) = 1176$, $\mu(\text{Cu-K}\alpha) = 9.1$ cm⁻¹, space group $P2_12_12_1$.

2-(2-Methoxy-2,3-dihydro-1,4-benzodioxin-2-yl)-4,5-dihydroimidazolium bromide (4), $C_{12}BrH_{15}N_2O_3$, $M = 315.21$, orthorhombic, $a = 7.343(2)$, $b = 8.576(2)$, $c = 21.894(3)$ Å, $V = 1379$ Å³, $D_c = 1.52$ g cm⁻³, $Z = 4$, $F(000) = 640$, $\mu(\text{Mo-K}\alpha) = 31.6$ cm⁻¹, space group $P2_12_12_1$.

(+)-2-(2-Methoxy-2,3-dihydro-1,4-benzodioxin-2-yl)-4,5-dihydroimidazolium hydrogen dibenzoyltartrate methanol solvate (5), $C_{12}H_{15}N_2O_3 \cdot C_{18}H_{13}O_8 \cdot \text{MeOH}$, $M = 624.66$, monoclinic, $a = 7.547(2)$, $b = 16.385(2)$, $c = 12.863(2)$ Å, $\beta = 106.44(2)^\circ$, $V = 1526$ Å³, $D_c = 1.36$ g cm⁻³, $Z = 2$, $F(000) = 656$, $\mu(\text{Mo-K}\alpha) = 1.14$ cm⁻¹, space group $P2_1$.

2-(2-Isopropyl-2,3-dihydro-1,4-benzodioxin-2-yl)-4,5-dihydroimidazolium chloride (6), $C_{14}H_{15}ClN_2O_2$, $M = 282.80$, monoclinic, $a = 13.894(2)$, $b = 8.050(1)$, $c = 14.514(2)$ Å, $\beta = 115.63(2)^\circ$, $V = 1464$ Å³, $D_c = 1.28$ g cm⁻³, $Z = 4$, $F(000) = 600$, $\mu(\text{Cu-K}\alpha) = 23.1$ cm⁻¹, space group $P2_1/n$.

2-(2,3-Dihydro-1-benzopyran-2-yl)-4,5-dihydroimidazolium

Table 5. Fractional atomic co-ordinates for compound (6), with standard deviations in parentheses.

Atom	x	y	z
Cl(1)	-0.267 55(10)	-0.085 26(10)	-0.398 25(8)
O(1)	-0.194 50(17)	0.544 50(24)	-0.495 71(17)
O(4)	-0.358 8(2)	0.341 9(3)	-0.639 3(2)
N(12)	-0.345 7(3)	0.277 0(4)	-0.404 4(2)
N(15)	-0.335 9(2)	0.545 0(3)	-0.411 8(2)
C(2)	-0.218 6(3)	0.382 8(3)	-0.468 6(2)
C(3)	-0.262 5(3)	0.272 4(4)	-0.563 0(3)
C(5)	-0.414 3(4)	0.570 8(5)	-0.753 9(3)
C(6)	-0.400 7(4)	0.732 1(6)	-0.777 7(3)
C(7)	-0.318 6(4)	0.825 8(6)	-0.710 5(3)
C(8)	-0.248 8(3)	0.763 5(4)	-0.616 4(3)
C(9)	-0.263 0(3)	0.601 0(4)	-0.591 4(2)
C(10)	-0.344 6(3)	0.504 1(4)	-0.661 7(3)
C(11)	-0.300 8(3)	0.402 1(4)	-0.428 1(2)
C(13)	-0.420 2(3)	0.333 1(5)	-0.364 4(3)
C(14)	-0.407 7(3)	0.521 6(4)	-0.364 0(3)
C(16)	-0.114 0(3)	0.317 0(4)	-0.382 5(3)
C(17)	-0.080 7(3)	0.417 7(5)	-0.285 2(3)
C(18)	-0.023 2(4)	0.308 4(7)	-0.414 5(4)

Table 6. Fractional atomic co-ordinates for compound (7), with standard deviations in parentheses.

Atom	x	y	z
Cl	0.397 26(10)	0.329 43(8)	0.135 47(6)
O(1)	0.650 5(2)	0.010 2(2)	0.316 7(1)
N(1)	0.334 8(3)	-0.075 1(3)	0.081 5(2)
N(2)	0.281 8(3)	-0.359 1(3)	0.038 3(2)
C(2)	0.527 5(3)	-0.184 7(3)	0.267 1(2)
C(3)	0.423 6(3)	-0.279 1(3)	0.359 9(2)
C(4)	0.580 3(4)	-0.251 8(3)	0.500 3(2)
C(5)	0.877 7(4)	0.015 9(3)	0.682 4(2)
C(6)	1.032 3(4)	0.194 8(4)	0.724 2(2)
C(7)	1.058 6(4)	0.309 5(3)	0.630 1(3)
C(8)	0.929 1(4)	0.243 4(3)	0.494 2(2)
C(9)	0.775 0(3)	0.063 3(3)	0.453 2(2)
C(10)	0.746 5(3)	-0.054 7(3)	0.546 1(2)
C(11)	0.380 9(3)	-0.204 7(3)	0.127 7(2)
C(12)	0.173 9(4)	-0.147 5(4)	-0.053 8(2)
C(13)	0.166 2(4)	-0.333 1(4)	-0.093 0(2)

chloride (7), $C_{12}H_{15}ClN_2O$, $M = 238.74$, triclinic, $a = 8.100(1)$, $b = 8.132(1)$, $c = 10.674(1)$ Å, $\alpha = 90.34(1)$, $\beta = 110.70(1)$, $\gamma = 115.73(1)^\circ$, $V = 582$ Å³, $D_c = 1.36$ g cm⁻³, $Z = 2$, $F(000) = 252$, $\mu(\text{Cu-K}\alpha) = 27.4$ cm⁻¹, space group $P\bar{1}$.

Crystallographic Measurements.—Cell dimensions for each compound were derived from least-squares analyses of the setting angles of 25 reflections measured on an Enraf-Nonius CAD4 diffractometer. Subsequently, for compound (3), 2650 reflections were surveyed in the range $\theta < 70^\circ$ (Cu-K α) and 1334 independent intensities satisfied the criterion $I > 3\sigma(I)$. For compound (4), 1773 reflections were surveyed in the range $\theta < 28^\circ$ (Mo-K α) and 1364 independent intensities satisfied the criterion $I > 2.5\sigma(I)$. For compound (5), 3 115 reflections were surveyed in the range $\theta < 26^\circ$ (Mo-K α) and 2411 independent intensities satisfied the criterion $I > 2.5\sigma(I)$. For compound (6), 3111 reflections were surveyed in the range $\theta < 70^\circ$ (Cu-K α) and 2076 independent intensities satisfied the criterion $I >$

$3\sigma(I)$. For compound (7), 2567 reflections were surveyed in the range $\theta < 75^\circ$ (Cu-K α) and 1917 independent intensities satisfied the criterion $I > 3\sigma(I)$.

Structure Analysis.—The crystal structures were elucidated by the heavy-atom approach [compound (4)] and direct phasing [compounds (3), (5), (6) and (7)]. After preliminary least-squares adjustment, H-atoms were located in difference electron-density distributions. In subsequent least-squares calculations C-, N-, O-, Cl- and Br-atoms were generally assigned anisotropic thermal parameters and H-atoms isotropic parameters; in the calculations for compound (3), however, because of the paucity of intensity data isotropic thermal parameters were retained for all the C-atoms, and the H-atoms were kept in calculated positions with $U = 0.05$ Å². The weighting scheme used in all cases was $w = 1/\sigma^2(F_o)$. The absolute stereochemistry was established for compounds (4) and (5). Anomalous-dispersion corrections for the Br⁻ ion of compound (4) were included in the least-squares refinement which converged at $R = 0.030$, $R_w = 0.035$ for the absolute stereochemistry (S) shown in formula (4) and Fig. 1, and at $R = 0.052$, $R_w = 0.067$ for the mirror image. An alternative test for compound (4) was provided by adjustment of Rogers' η parameter;¹⁸ at convergence of the least-squares calculations, η was unambiguously positive, 0.997(31), with $R = 0.030$, $R_w = 0.035$, confirming the absolute stereochemistry shown in structure (4) (Fig. 1). For compound (5), the hydrogen (+)-dibenzoyltartrate anion was assigned the known absolute stereochemistry and this gave the dihydrodioxine cation the absolute stereochemistry shown in structure (5) in Fig. 1; the results are in full accord with these for compound (4). The various least-squares calculations converged at $R = 0.076$, $R_w = 0.087$ for compound (3), $R = 0.030$, $R_w = 0.035$ for compound (4), $R = 0.043$, $R_w = 0.050$ for compound (5), $R = 0.063$, $R_w = 0.087$ for compound (6), and $R = 0.051$, $R_w = 0.065$ for compound (7).

The direct phasing procedure was MITHRIL.¹⁹ Fourier, least-squares, geometry, and ORTEP calculations were performed with the GX system of programs.²⁰ Atomic co-ordinates are listed in Tables 2–6. The hydrogen (+)-dibenzoyltartrate anion of compound (5) is shown in Fig. 2.*

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* Supplementary data [see section 5.6.3 of Instructions for Authors (1990), January issue]. Tables of thermal parameters and molecular geometries have been deposited with the Cambridge Crystallographic Data Centre.

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