Les molécules ne sont liées que par un ensemble de faibles forces et il n'existe aucune distance inter-moléculaire inférieure à la somme des rayons de van der Waals.

L'analyse radiocristallographique a permis de définir la structure de cette molécule nouvelle issue de l'isomérisation de l'époxy-8,9β isopimarate. Nous montrons ainsi que le méthyle $CH_3$ (carbone 20) a subi deux migrations successives à partir de la molécule de départ. L'hydrocarbure diterpénique ainsi obtenu s'apparente de par la nature de son squelette, en ce qui concerne essentiellement les cycles $C$ et $D$, aux diterpènes possédant le squelette aphidicolane. Peu de composés possédant ce type de squelette ont été rencontrés à ce jour, alors qu'ils possèdent des propriétés physiologiques importantes (Hufford, Guerrera & Doorenbos, 1976; Bucknall, Moores, Simons & Hesp, 1973; Ikegani, Taguchi, Ohashi, Oguro, Nagana & Mano, 1978).

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# Structure of (±)-2-(2-Chloro-3,4-dimethoxyphenyl)-N-isopropyl-2-methoxyethylamine Hydrochloride, $C_{14}H_{23}ClNO_3{}^+.Cl^-$

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**Abstract.** $M_r = 324.2$, triclinic, $P\bar{1}$, $a = 7.537$ (4), $b = 9.174$ (5), $c = 12.625$ (6) Å, $\alpha = 103.81$ (2), $\beta = 76.24$ (2), $\gamma = 101.89$ (2)°, $V = 813.0$ (8) Å³, $Z = 2$, $D_m = 1.32$ (1), $D_x = 1.324$ Mg m⁻³, $\lambda(Mo\,K\alpha) = 0.71069$ Å, $\mu = 0.355$ mm⁻¹, $F(000) = 344.0$, $T = 298$ K. Final $R = 0.045$ for 1689 observed reflections. The substituted ethylamine side chain is extended and is orientated approximately perpendicular to the phenyl ring. The phenyl ring is planar with the methoxy group adjacent to the Cl atom orientated out of the plane and the other one approximately coplanar. Hydrogen bonds of the type $N-H\cdots Cl^-$ link pairs of inversion-related cations.

**Introduction.** The title compound is one of a series of structurally related β-adrenoceptor blocking drugs whose conformations we are studying by X-ray analysis, ¹H NMR and quantum mechanical methods.

**Experimental.** Wedge-shaped crystals grown from 2-propanol solution by slow cooling. Density determined by flotation in PhBr–PhCl mixture. Crystal

system from Weissenberg and precession photographs with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). Crystal dimensions $0.24 \times 0.20 \times 0.16$ mm, Philips PW 1100 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Cell constants by least-squares refinement of angular data for 25 reflections in range $15 < 2\theta < 26°$. Three standard reflections monitored after every 56 reflections; no significant intensity variation. 2275 reflections measured by $\omega$–$2\theta$ technique, scan speed $0.043°\theta\,s^{-1}$, scan width $1.3°\theta$, $\theta$ range 3–23° ($hkl$ limits ±8, ±10, 13); 2199 unique reflections ($R_{int} = 0.0852$) of which 510 reflections with $I_o < 2\sigma(I_o)$ omitted as unobserved $|\sigma(I_o)$ based on counting statistics|. Lorentz and polarization corrections applied, no absorption correction. Space group $P\bar{1}$ confirmed by Patterson analysis and intensity statistics. Structure solved by Patterson and Fourier methods and refined by full-matrix least squares, program *SHELX76* (Sheldrick, 1976); $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1/\sigma^2(F_o)$ which yielded a constant distribution of $\langle w\Delta^2\rangle$ with $(\sin\theta)/\lambda$ and $|F_o/F_o(max.)|^{1/2}$. All non-H atoms thermally anisotropic; all H atoms located in

difference syntheses but included in idealized positions in a riding model (C—H, N—H = 1·08 Å) with common $U_{iso}$ values for five groups of atoms [final values 0·043 (7)–0·11 (1) Å²]. $R = 0.045$, $wR = 0.040$ for 1689 observations and 201 parameters, all $\Delta/\sigma < 0.001$ in final cycle, residual density in final difference map $< 0.25$ e Å⁻³. Scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Table 1* lists final atomic parameters for non-H atoms. Selected bond lengths and torsion angles, and hydrogen-bond data are listed in Table 2.

Atomic coordinates refer to the (*R*)-enantiomeric cation which is illustrated in Fig. 1. Active dichloro-isoproterenol analogues have the *R* configuration, while the configuration of active propranolol analogues is *S* (Howe & Rao, 1968; Dukes & Smith, 1971).

The aromatic ring is planar (r.m.s. deviation for the six C atoms 0·002 Å) with the methoxy groups C(14)—O(4) approximately coplanar and C(13)—O(3) orientated out of the plane. The substituted ethylamine side chain is extended and its mean plane is nearly perpendicular to the aromatic ring (see torsion angles $\tau_2$ and $\tau_1$ respectively, Table 2). Torsion angle O(7)—C(7)—C(8)—N(9) indicates a *gauche* conformation, which is common for O—C—C—N groupings (Paxton & Hamor, 1977). The distance N(9)···O(7), 2·831 (3) Å, is within the range of analogous distances (2·65–3·04 Å) reported for structurally related adrenergics (Ammon, Balsamo, Macchia, Macchia, Howe & Keefe, 1975). Atom C(10) of the isopropyl group is approximately *gauche* to the chiral centre of the cation, the former group being somewhat folded back in the direction of the methoxy group attached to C(7).

The N atom is 5·16 Å from the calculated centre of the aromatic ring. This distance is in good agreement with values reported for related molecules containing the 2-phenylethylamine nucleus (Pattanayek, Dattagupta, Bhattacharyya & Saha, 1984). The C(7)—O(7) bond is orientated at 23·4 (3)° to the plane of the ring. Corresponding angles in Th 1165a† and salbutamol‡ are 48·3 and 45·2° respectively (Beale & Stephenson, 1972). Close contacts between ring *ortho*-substituents and atoms bonded to C(7) are observed in the present case, Cl(1)···H(7) 2·66, O(7)···H(6) 2·43 Å (H atoms in calculated positions).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths, bond angles, torsion angles and least-squares-planes' calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39891 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† (±)-5-[1-Hydroxy-2-{[2-(4-hydroxyphenyl)-1-methylethyl]-amino}ethyl]-1,3-benzenediol hydrobromide.

‡ (±)-5-[2-(*tert*-Butylamino)-1-hydroxyethyl]salicyl alcohol.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *for non-H atoms with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Cl(1) | 6147 (1) | 1769 (1) | 3800 (1) | 49 (1) |
| Cl(2) | 2726 (1) | −2022 (1) | 649 (1) | 48 (1) |
| C(1) | 2656 (5) | 2368 (4) | 4082 (3) | 31 (2) |
| C(2) | 4209 (5) | 2574 (4) | 4555 (3) | 31 (2) |
| C(3) | 4277 (5) | 3415 (4) | 5617 (3) | 32 (2) |
| O(3) | 5872 (3) | 3650 (3) | 6030 (2) | 42 (2) |
| C(4) | 2752 (5) | 4070 (4) | 6235 (3) | 34 (2) |
| O(4) | 2916 (3) | 4864 (3) | 7285 (2) | 46 (2) |
| C(5) | 1193 (5) | 3891 (4) | 5784 (3) | 37 (2) |
| C(6) | 1170 (5) | 3042 (4) | 4716 (3) | 35 (2) |
| C(7) | 2576 (5) | 1460 (4) | 2909 (3) | 33 (2) |
| O(7) | 719 (3) | 898 (3) | 2772 (2) | 38 (1) |
| C(8) | 3396 (5) | 2479 (4) | 2075 (3) | 39 (2) |
| N(9) | 3411 (4) | 1604 (3) | 903 (2) | 33 (2) |
| C(10) | 2125 (5) | 2008 (4) | 304 (3) | 42 (2) |
| C(11) | 2738 (6) | 3632 (4) | 123 (3) | 58 (3) |
| C(12) | 2142 (6) | 871 (5) | −795 (3) | 56 (3) |
| C(13) | 5815 (6) | 2716 (5) | 6791 (4) | 69 (3) |
| C(14) | 1321 (6) | 5430 (5) | 7986 (3) | 55 (3) |
| C(15) | −80 (6) | −401 (4) | 3270 (3) | 51 (3) |

Table 2. *Selected bond lengths* (Å), *torsion angles* (°) *and hydrogen-bond data with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| C(2)—Cl(1) | 1·742 (3) | C(8)—N(9) | 1·504 (4) |
| C(3)—O(3) | 1·379 (4) | N(9)—C(10) | 1·510 (4) |
| C(4)—O(4) | 1·372 (4) | C(13)—O(3) | 1·419 (4) |
| C(1)—C(7) | 1·525 (4) | C(14)—O(4) | 1·424 (4) |
| C(7)—O(7) | 1·425 (4) | C(15)—O(7) | 1·435 (4) |
| C(7)—C(8) | 1·512 (5) | | |

| | | | |
|---|---|---|---|
| C(2)—C(1)—C(7)—C(8) ($\tau_1$)* | −86·1 (4) | O(7)—C(7)—C(8)—N(9) | −61·6 (4) |
| C(1)—C(7)—C(8)—N(9) ($\tau_2$)* | 177·6 (3) | C(8)—N(9)—C(10)—C(11) | 65·6 (4) |
| C(2)—C(1)—C(7)—O(7) | 156·6 (3) | C(2)—C(3)—O(3)—C(13) | −102·3 (4) |
| C(1)—C(7)—O(7)—C(15) | −76·9 (4) | C(3)—C(4)—O(4)—C(14) | 174·1 (3) |
| C(7)—C(8)—N(9)—C(10) | 112·1 (3) | | |

| | | | |
|---|---|---|---|
| N(9)···Cl(2) | 3·209 (3) Å | N(9)—H(9B)···Cl(2) | 167° |
| H(9B)···Cl(2) | 2·15 | | |
| N(9)···Cl(2ⁱ) | 3·106 (3) | N(9)—H(9A)···Cl(2ⁱ) | 172 |
| H(9A)···Cl(2ⁱ) | 2·03 | | |

Symmetry code: (i) $1-x$, $-y$, $-z$.

* See Murray-Rust, Murray-Rust, Hartley, Hallett & Clifton (1984).
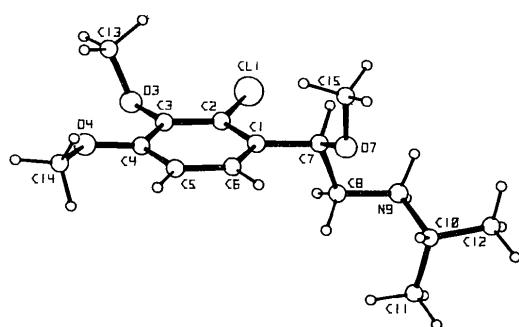


Fig. 1. Conformation of the (*R*)-enantiomeric cation showing atomic numbering (drawn with CRISTEP, De Wet, 1980).

$C_{14}H_{23}ClNO_3^+.Cl^-$
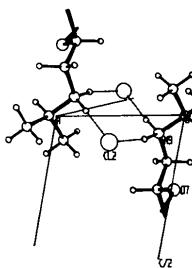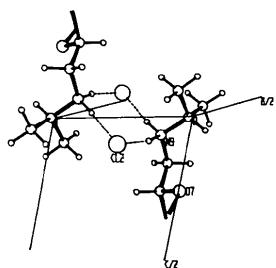


Fig. 2. Stereoview of the hydrogen-bonding geometry. Only the relevant portions of the side chains are shown; hydrogen bonds are indicated by dashed lines (drawn with *CRISTEP*, De Wet, 1980).

Fig. 2 shows the hydrogen-bonding arrangement in the crystal. The shortest $Cl^-\cdots Cl^-$ distance is that between ions related by the inversion centre at $\frac{1}{2},0,0$. These ions link centrosymmetrically related cations *via* $N-H\cdots Cl^-$ hydrogen bonds involving both amino H atoms (Table 2).

We thank Professors J. Offermeier and D. Venter, Department of Pharmacology, University of Potchefstroom for Christian Higher Education, for providing the drug, the CSIR, Pretoria, for intensity data collection and the P.E. Technikon for their support.

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# 2,2'-[o-Phenylenebis(methyleneoxy)]diacetophenone, C₂₄H₂₂O₄

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**Abstract.** $M_r = 374.4$, monoclinic, $P2_1$, $a = 10.842$ (2), $b = 5.131$ (1), $c = 17.390$ (3) Å, $\beta = 92.12$ (1)°, $V = 966.7$ (7) Å³, $Z = 2$, $D_x = 1.29$, $D_m = 1.25$ g cm⁻³, $\lambda(Mo\,K\alpha) = 0.71073$ Å, $\mu = 0.76$ cm⁻¹, $F(000) = 396.0$, $T = 297$ K, $R = 0.044$ for 1383 observations. Although the molecule could possess symmetry 2 or $m$, it is crystallographically asymmetric, with the two acetophenone rings forming dihedral angles of 98.5 (2) and 159.5 (3)° with the *o*-phenylene ring. This is in contrast with the structure in solution, where the two chemically equivalent halves are, on a time-averaged basis, conformationally equivalent.

**Introduction.** In the course of our studies utilizing 2,3-bis(2-substituted-phenyl)-2-butenes as models for intramolecular reactions (Tirado-Rives, Oliver, Fronczek & Gandour, 1984), the title compound's crystal

structure has been determined. This structure serves as a reference for predicting the stereochemistry of the low-valent titanium-induced reductive coupling of the carbonyl groups.

**Experimental.** Title compound prepared previously (Tirado-Rives *et al.*, 1984). Suitable crystals, needles, from hexane/ether. Crystal size $0.32 \times 0.20 \times 0.44$ mm. $D_m$ by flotation in aq. KBr. Space-group determination by systematic absences 0*k*0 with *k* odd and successful refinement in non-centrosymmetric space group. Cell dimensions determined from setting angles of 25 reflections having $12 < \theta < 13°$. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator. $\omega-2\theta$ scans designed to yield $I = 25\sigma(I)$. Scan rates ($\omega$) varied, 0.31–5.0° min⁻¹. Measured reflections (1597) having $0.025 \le \sin\theta/\lambda \le 0.550$ Å⁻¹, $1 < \theta < 23°$, $0 \le h \le 11$, $0 \le k \le 5$, $-19 \le l \le 19$, corrected for background, Lorentz, and polarization effects, equivalent data (0*kl* and 0*k̄l*)

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