Fig. 2. Vue stéréoscopique montrant l'empilement moléculaire.

−156,2°. Ces valeurs sont voisines de celles observées dans l'azido-2 désoxy-2 β-D-galactopyrannoside *tert*-butylique (Oddon *et al.*, 1983). Cette conformation autour de la liaison glycosidique fait apparaître une intéraction *gauche* entre la liaison C(1′)—C(3′) et la liaison O(1)—C(1) qui pourrait expliquer en résonance magnétique nucléaire du ^{13}C le blindage important du carbone anomère [δC(1) = 101,00 p.p.m.] dans ce composé comparé à celui du glycoside méthylique correspondant (103,5 p.p.m.).

Par rapport au dérivé *tert*-butylique déjà cité, on note une diminution de l'encombrement stérique attestée par une diminution sensible des longueurs de liaisons C(1)—O(1), O(1)—C(1′) et surtout de l'angle de la liaison glycosidique C(1)—O(1)—C(1′) qui est de 114,3° au lieu de 118,6° dans le dérivé *tert*-butylique (Oddon *et al.*, 1983).

La liaison C(6)—O(6) est *trans* par rapport à la liaison C(4)—C(5) et *gauche* par rapport à C(5)—O(5). Cette conformation '*trans–gauche*' [C(4)—C(5)—C(6)—O(6) = −171,1°] est analogue à celles observées dans le dérivé *tert*-butylique correspondant (Oddon *et al.*, 1983) et dans l'α-mélibiose (Kanters, Roelofsen, Doesburg & Koops, 1976).

Interactions intermoléculaires. Une vue stéréoscopique (Fig. 2) de l'empilement moléculaire permet de mettre en évidence l'orientation de la molécule. La cohésion du cristal est assurée par deux liaisons hydrogène intermoléculaires:

–liaison H entre H(O3) et O(4^{i}): le calcul donne O(3)—H(O3) = 0,84 (8), O(4^{i})···H(O3) = 2,03 (8), O(3)···O(4^{i}) = 2,873 (5) Å, avec O(3)—H(O3)—O(4^{i}) = 173 (4)° [(i) 1−*x*, 0,5−*y*, 1,5−*z*].

–liaison H entre H(O6) et O(3^{ii}): O(6)—H(O6) = 0,86 (8), H(O6)···O(3^{ii}) = 1,99 (8), O(6)···O(3^{ii}) = 2,837 (5) Å et O(6)—H(O6)—O(3^{ii}) = 167 (4)° [(ii) −1 + *x*, *y*, *z*].

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Acta Cryst. (1984). C**40**, 294–297

Structure of DL-Normetanephrine Hydrochloride [α-(Aminomethyl)vanillyl Alcohol Hydrochloride], $C_9H_{14}NO_3^+.Cl^-$

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Abstract. $M_r = 219\cdot7$, monoclinic, $P2_1/c$, $a = 5\cdot218$ (1), $b = 17\cdot081$ (4), $c = 12\cdot260$ (2) Å, $\beta = 91\cdot50$ (1)°, $V = 1092\cdot2$ Å^3, $Z = 4$, $D_m = 1\cdot340$, $D_x = 1\cdot336$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 3·295 mm^{-1}, $T = 298$ (2) K, $F(000) = 464$, $R = 0\cdot069$ for 1651 reflections. The ethylamine side chain is planar, fully extended and approximately perpendicular to the attached phenyl ring. The conformational features of the molecule are similar to those mostly observed for adrenergic drugs. The structure is stabilized by a three-dimensional network of H bonds of types N—H···Cl, O—H···Cl and N—H···O.

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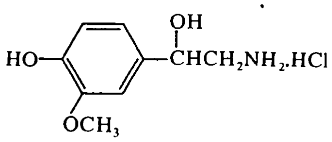
Introduction. It is well known that when the enzyme catechol *O*-methyl transferase transfers the methyl group of *S*-adenosylmethionine to the 3-hydroxyl group of epinephrine and norepinephrine, two metabolic products metanephrine and normetanephrine are formed *in vivo,* which constitute a major metabolic pathway of epinephrine and norepinephrine (McLean, 1960). The crystal structure of DL-metanephrine hydrochloride has already been reported (Pattanayek, Dattagupta & Saha, 1983) and that of DL-normetanephrine hydrochloride (I) is presented here.



(I)

Experimental. Single crystals (Sigma Chemical Co.) obtained by slow evaporation of aqueous solution at room temperature. Density determined by flotation method in a mixture of bromoform and benzene. Systematic absences *h*0*l*: *l* odd and 0*k*0: *k* odd indicated space group $P2_1/c$. Unit cell: least-squares refinement of seven selected Friedel pairs in the interval $0{\cdot}230 < \sin\theta/\lambda < 0{\cdot}460$ Å^{-1}. Crystal 0·28 × 0·18 × 0·18 mm. Enraf–Nonius CAD-4 diffractometer, $2\theta/\omega$ scan mode, graphite-monochromatized radiation. Lorentz and polarization corrections, no absorption correction. Three standard reflections monitored after every 50 data reflections: no significant change in intensity. 1836 reflections measured within the range $2° \le \theta \le 25°$; 184 considered unobserved by the criterion $F \le 2\sigma(F)$ where $\sigma(F)$ is the e.s.d. based on counting statistics. Structure solved by heavy-atom method and refined isotropically by full-matrix least-squares methods (*MAMIE*; *X-RAY ARC*, 1971) and anisotropically by block-diagonal least-squares methods (*BLOCK*; *X-RAY ARC*, 1971); $R = 0{\cdot}104$, $R_w = 0{\cdot}925$, $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1/\sigma^2(F)$. Scattering factors from *International Tables for X-ray Crystallography* (1974). H atoms located from difference Fourier map and stereochemical considerations, and assigned isotropic temperature factors of the heavier atoms to which they are attached; their inclusion with fixed parameters gave $R = 0{\cdot}070$ and $R_w = 0{\cdot}005$.* Reflection 1,10,0 affected by extinction and excluded in the final cycle. Refinement was stopped when the parameter shifts were less than

Table 1. *Positional parameters* (×10⁴) *with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\,(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	$B_{\rm eq}$(Å^2)
Cl	−1187 (2)	2975 (1)	5836 (1)	3·9
N	3878 (7)	2585 (2)	4389 (3)	3·2
O(1)	3849 (6)	−1810 (2)	2644 (3)	4·7
O(2)	6661 (6)	−871 (2)	1537 (3)	4·5
O(3)	226 (6)	1720 (2)	3301 (3)	4·8
C(1)	1450 (9)	77 (3)	3649 (4)	3·6
C(2)	1706 (9)	−725 (3)	3517 (4)	3·8
C(3)	3494 (8)	−1022 (2)	2821 (4)	3·3
C(4)	5015 (8)	−510 (2)	2230 (3)	3·1
C(5)	4766 (8)	290 (2)	2361 (3)	3·0
C(6)	2979 (8)	587 (2)	3073 (3)	2·9
C(7)	2793 (8)	1472 (2)	3204 (4)	3·2
C(8)	4220 (8)	1727 (2)	4246 (3)	3·0
C(9)	8273 (9)	−380 (3)	902 (4)	4·5

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

The sign convention for the torsion angles is as defined by Klyne & Prelog (1960).

C(1)–C(2)	1·386 (6)	C(5)–C(6)	1·390 (6)
C(1)–C(6)	1·387 (6)	C(6)–C(7)	1·524 (6)
C(2)–C(3)	1·377 (6)	C(7)–C(8)	1·525 (6)
C(3)–C(4)	1·397 (6)	C(7)–O(3)	1·413 (5)
C(3)–O(1)	1·375 (5)	C(8)–N	1·488 (5)
C(4)–C(5)	1·383 (6)	C(9)–O(2)	1·432 (6)
C(4)–O(2)	1·369 (5)		

Average C–H, N–H, O–H: 1·04, 1·05, 1·05 Å, respectively.

C(2)–C(1)–C(6)	120·3 (4)	C(4)–C(5)–C(6)	120·0 (4)
C(1)–C(2)–C(3)	120·3 (4)	C(1)–C(6)–C(5)	119·6 (4)
C(2)–C(3)–C(4)	119·6 (4)	C(1)–C(6)–C(7)	122·1 (4)
C(2)–C(3)–O(1)	123·6 (4)	C(5)–C(6)–C(7)	118·3 (4)
C(4)–C(3)–O(1)	116·7 (4)	C(6)–C(7)–C(8)	109·9 (3)
C(3)–C(4)–C(5)	120·1 (4)	C(6)–C(7)–O(3)	111·6 (3)
C(3)–C(4)–O(2)	114·5 (4)	C(8)–C(7)–O(3)	106·7 (3)
C(5)–C(4)–O(2)	125·4 (4)	C(7)–C(8)–N	108·8 (3)
		C(4)–O(2)–C(9)	117·5 (3)

Torsion angles (mean standard deviation 0·6°)

C(1)–C(6)–C(7)–C(8)	78·9	O(3)–C(7)–C(8)–N	−55·5
C(6)–C(7)–C(8)–N	−176·7	C(5)–C(4)–O(2)–C(9)	0·5
C(1)–C(6)–C(7)–O(3)	−39·3		

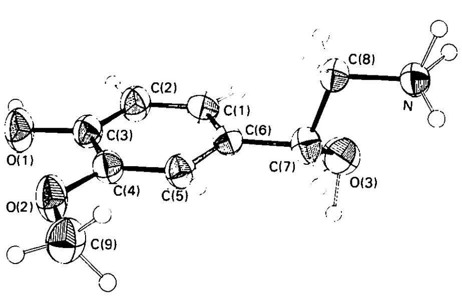


Fig. 1. *ORTEP* (Johnson, 1965) drawing of DL-normetanephrine hydrochloride with anisotropic thermal parameters at the 50% probability level. H atoms are shown as spheres of arbitrary radius.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, H-bond data, and least-squares-planes' details have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38919 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU England.

their standard deviations. Final $R = 0{\cdot}069$, $R_w = 0{\cdot}054$, $S = 1{\cdot}89$. Final difference Fourier map featureless.

Discussion. The atomic numbering scheme is shown in Fig. 1. The atomic parameters are listed in Table 1. The intramolecular bond distances, angles and torsion angles are listed in Table 2. The bond lengths and angles are in close agreement with the standard values and are comparable with those obtained by averaging 34 similar compounds (Hebert, 1979). Of the four exocyclic angles C(2)—C(3)—O(1), C(5)—C(4)—O(2), C(4)—C(3)—O(1) and C(3)—C(4)—O(2) the former two are greater than 120° and the latter are smaller, which indicates a tilt of the C—O bonds. However, such a tilt is common in catecholamines. Similarly the angles around C(7) deviate from tetrahedral values. These deviations are probably due to the influence of H bonding and are commonly observed in similar biogenic amines.

The phenyl group is planar within 0·012 Å and the exocyclic atoms O(1), O(2) and C(7) deviate slightly from the plane of the ring: 0·002 (3), 0·038 (3), –0·027 (4) Å respectively. The ethylamine side chain is also nearly planar, is maximally extended and is approximately perpendicular to the ring {dihedral angles τ_1[C(1)—C(6)—C(7)—C(8)] = 78·9° and τ_2[C(6)—C(7)—C(8)—N] = –176·7°}. Some relevant torsion angles are listed in Table 2. The distance of the amino N from the centre of the phenyl ring is 5·11 Å and the height of the N atom from the plane is 1·43 Å. The torsion angle O(3)—C(7)—C(8)—N (–55·5°) shows that the N atom is *gauche* to the hydroxyl group at the side chain, as is found in synephrine monohydrogenphosphate monohydrate (Dattagupta, Meyer & Mukhopadhyay, 1982) and *p*-hydroxyephedrine hydrochloride (Dattagupta, Pattanayek & Saha, 1981) and this again is a commonly observed conformation for O—C—C—N^+ groupings (Paxton & Hamor, 1977). In comparison, the side chain in metanephrine is folded ($\tau_1 = -112{\cdot}2$ and $\tau_2 = 53{\cdot}8°$). Thus it is noteworthy that the conformational features and skeleton of normetanephrine compare well with those of active adrenergic drugs. It should also be noted that this conformation of the adrenergic drug molecules seems to be a preferred one and is thought to be necessary for activity at the receptor site (Duax, 1978; Carlström, Bergin & Falkenberg, 1973). In view of the fact that normetanephrine does not have any direct drug action, it appears that conformational features are not the only criteria for biological activity which also depends on the functional group at the *m* and *p* positions of the phenyl ring. For example, the methoxy group at the *m* position of the benzene ring seems to have influenced the activity of normetanephrine.

The three-dimensional arrangement of the molecules in the crystal is shown in Fig. 2. The crystal structure is stabilized by a three-dimensional network of H bonds. All the H atoms available for H bonding participate in the H-bond formation of types N—H···Cl, N—H···O and O—H···Cl. It is observed that one amino H atom [H(N)*B*] is involved in two short contacts of 2·08 and 2·19 Å with two acceptor atoms [O(1)($-x+1, \frac{1}{2}+y, \frac{1}{2}-z$) and O(2)($-x+1, \frac{1}{2}+y, \frac{1}{2}-z$)] of a neighbouring molecule, forming a bifurcated or three-centred bond (Jeffrey & Małuszyńska, 1982). The other H-bond contacts are between N and Cl($x+1, y, z$) 3·159 (4) Å, N and Cl(x,y,z) 3·289 (4) Å, O(1) and Cl($-x, -y, -z+1$) 3·081 (3) Å, and O(3) and Cl($x, \frac{1}{2}-y, -\frac{1}{2}+z$) 3·136 (3) Å. The intramolecular distance between N and the hydroxyl O of the side chain is 2·732 (5) Å; this interaction does not represent an H bond as all of the amino and hydroxyl H atoms are engaged in intermolecular H bonds. Such an intramolecular contact, however, is found in the crystal structures of several other sympathomimetic amines (Andersen, 1976).

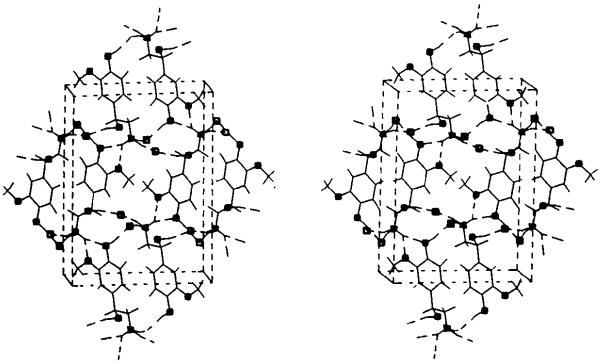

Fig. 2. Stereoview of the packing in the unit cell, viewed approximately down the *a* axis. Unit-cell edges are indicated by a solid line for *a*, long-dashed lines for *b*, and short-dashed lines for *c*. N atoms are designated by tetrahedral marks, O atoms by octahedral marks and the Cl atoms by cubic marks. H bonding is denoted by dashed lines between atoms. Drawings were made by program *PACK* (Swanson, Rosenfield & Meyer, 1982).

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Structure of Bis(acetamidinium) Carbonate Monohydrate, $2(C_2H_7N_2^+).CO_3^{2-}.H_2O$, at 108 K

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Abstract. $M_r = 196\cdot21$, orthorhombic, $Pn2_1a$, $a = 10\cdot482(5)$, $b = 8\cdot546\ (5)$, $c = 11\cdot123\ (5)$, $V = 996\cdot4\ (9)$ Å^3, $Z = 4$, $D_x = 1\cdot308\ (1)$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 1\cdot0$ cm^{-1}, $F(000) = 424$, $T = 108$ K, final $R = 0\cdot051$ for 1127 reflections. The title compound is shown to be the reaction product when acetamidine is exposed to air. The orientations of the methyl groups in the two symmetry-independent acetamidinium ions differ, most probably due to different intermolecular interactions. The different molecules in the structure are connected by hydrogen bonds, with the amino groups and the water molecule as hydrogen donors and the carbonate oxygens as acceptors.

Introduction. Pure crystalline acetamidine, which smells unpleasantly of mouse, can be prepared by a procedure recently described by Crossland & Grevil (1980). One of the problems with the pure compound is that it is not stable in air. When a crystalline specimen is exposed to air it reacts rapidly and gives a clear liquid. It was observed that this liquid gradually evaporates to give a colourless crystalline solid of yet unknown composition and without any obvious smell. In order to analyse the composition of this reaction product and to yield some information on the chemistry of acetamidine, a single-crystal structure determination has been carried out on the reaction product.

Experimental. Highly hygroscopic crystalline acetamidine exposed to air, liquid obtained evaporated after about 1 d at 293 K (40% relative humidity) to give colourless prisms of title compound; $0\cdot2 \times 0\cdot1 \times 0\cdot05$ mm, CAD-4 diffractometer with a cryogenic device (*cf.* van Bolhuis, 1971) operated at 108 K, graphite-monochromatized Mo $K\alpha$, lattice parameters from settings of 12 reflections with $7\cdot6 \geq \theta \geq 11\cdot2°$; absorption correction, transmission factors 0·93–0·97; 1665 reflections ($0,0,0 \leq h,k,l \leq 13,15,16$), $\theta < 30°$, 1524 unique, 1127 with $\sigma(I)/I < 0\cdot33$ used for refinements; symmetry-equivalent reflections gave $R_{\rm int} = 0\cdot035$; two standard reflections (140 and 311), no significant intensity decrease during data collection; direct methods and subsequent $\rho_{\rm diff}$ to locate all atoms, least-squares minimization of $\sum w(\Delta F)^2$, anisotropic nonhydrogens, isotropic hydrogens, nitrogen–hydrogen and carbon–hydrogen bond distances constrained (Sheldrick, 1976) to be equal within each molecule, $R = 0\cdot051$, $wR = 0\cdot067$, w proportional to $[\sigma^2(F_o) + 0\cdot001|F_o|^2]^{-1}$, $\Delta_{\max}/\sigma = 0\cdot2$ (nonhydrogen parameters), 170 parameters refined, max. and min. $\Delta\rho$ excursions 0·25 and $-0\cdot52$ e Å^{-3}, atomic scattering factors from *International Tables for X-ray Crystallography* (1974), programs *SHELX*76 (Sheldrick, 1976) and *XTAPL* (Norrestam, 1982).[*]

Discussion. An examination of the bond distances and angles for two of the symmetry-independent molecular entities found in the present structure at the stage when the nonhydrogens were located showed closer resemblances to the geometry observed for the protonated acetamidine ion (Cannon, White & Willis, 1976) rather than to that of acetamidine (Norrestam, Mertz & Crossland, 1983) itself. Furthermore, difference electron density maps gave probable hydrogen

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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 38942 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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