Table 3. C—H···O *contact distances* (≤ 3 Å), *bond valences* (s) *and their sums for the two atoms* O(1) *and* O(2) *of the β-diketone fragment*

	Symmetry operation	d	s	Σs
O(1)···H(15)	x, y, z	2.39 (3)	0.017	0.017
O(2)···H(9)	x, y, z	2.45 (3)	0.014	
O(2)···H(6)	$x, y+1, z$	2.61 (3)	0.009	
O(2)···H(9)	$1-x, 2-y, -z$	2.72 (3)	0.007	
O(2)···H(5)	$x, y+1, z$	2.84 (3)	0.005	0.035

$\Delta = \Sigma s[\mathrm{O}(2)] - \Sigma s[\mathrm{O}(1)] = 0.018$

a case where the intermolecular and intramolecular forces are able to modify the chemical constitution of the molecule.

The entire molecule is approximately planar. The dihedral angles between the β-diketone mean plane [O(1), C(1), C(2), C(3), O(2): $\Sigma(\Delta/\sigma)^2 = 16.6$] and the two phenyl rings [C(4)–C(9): $\Sigma(\Delta/\sigma)^2 = 12.0$ and C(10)–C(15): $\Sigma(\Delta/\sigma)^2 = 26.6$] are 15.1 (1) and 18.9 (1)° respectively. Although this is a situation favourable for a π-electronic delocalization on the whole molecule, C(1)—C(10) and C(3)—C(4) bond distances of 1.478 (4) and 1.475 (4) Å can be considered pure C(sp^2)—C(sp^2) single-bond distances indicating that the phenyl rings do not participate in the π delocalization of the β-diketone enol fragment. This seems to suggest that the planarity systematically observed in this class of compounds (Bertolasi *et al.*, 1991), could be attributed to a greater packing efficiency of planar objects and/or to the energetically favourable C—H···O interactions of the C—O and C=O atoms with the *o*-phenyl H atoms (Table 3).

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References

Bertolasi, V., Gilli, P., Ferretti, V. & Gilli, G. (1991). *J. Am. Chem. Soc.* **113**, 4917–4925.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.

Brown, I. D. & Shannon, R. D. (1973). *Acta Cryst.* **A29**, 266–282.

Emsley, J. (1984). *Struct. Bonding (Berlin)*, **57**, 147–191.

Etter, M. C., Jahn, D. A. & Urbańczyk-Lipkowska, Z. (1987). *Acta Cryst.* **C43**, 260–263.

Etter, M. C. & Vojta, G. M. (1989). *J. Mol. Graph.* **7**, 3–11.

Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi. Delft Univ. Press.

Gilli, G., Bellucci, F., Ferretti, V. & Bertolasi, V. (1989). *J. Am. Chem. Soc.* **111**, 1023–1028.

Gilli, G. & Bertolasi, V. (1990). *The Chemistry of Enols*, edited by Z. Rappoport, ch. 13, pp. 713–764. New York: John Wiley.

Hollander, F. J., Templeton, D. H. & Zalkin, A. (1973). *Acta Cryst.* **B29**, 1552–1553.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Jones, R. D. G. (1976). *Acta Cryst.* **B32**, 1807–1811.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declerq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Ogoshi, H. & Nakamoto, K. (1966). *J. Chem. Phys.* **45**, 3113–3120.

Tayyari, S. F., Zeegers-Huyskens, Th. & Wood, J. L. (1979). *Spectrochim. Acta*, **35**, 1265–1276.

Williams, D. E. (1966). *Acta Cryst.* **21**, 340–349.

Williams, D. E., Dumke, W. L. & Rundle, R. E. (1962). *Acta Cryst.* **15**, 627–635.

Acta Cryst. (1992). C**48**, 1801–1804

A Urea with Non-Planar Nitrogen-Bonding Geometry

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Abstract. (4R,5S)-1,5-Dimethyl-4-phenylimidazolidin-2-one, $C_{11}H_{14}N_2O$, $M_r = 190.2$, orthorhombic, $P2_12_12_1$, $a = 6.161$ (2), $b = 8.045$ (3), $c = 20.811$ (6) Å, $V = 1031.5$ Å^3, $Z = 4$, $D_x = 1.23$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 0.75$ cm^{-1}, $F(000) = 408$, $T = 293$ K, $R = 0.041$ for 839 observed reflections. The N-methyl atom of this urea derivative, a chiral auxiliary in asymmetric syn-

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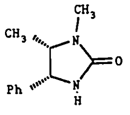
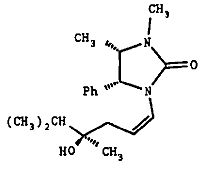
thesis, is partially pyramidalized [sum of angles at N = 349 (1)°] to minimize steric repulsions between adjacent ring substituents.

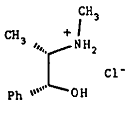
Introduction. We were interested in the imidazolidin-2-one (1), a cyclic derivative of urea, as a chiral auxiliary for reactions of crotyl anions. This auxiliary was first used successfully in highly enantioselective homo-aldol addition reactions (Roder, Helmchen, Peters, Peters & von Schnering, 1984) and subsequently by other groups (Cardillo, D'Amico, Orena & Sandri, 1988; Fehr & Galindo, 1988). The *cis* stereochemistry of the 4- and 5-substituents was assigned from the X-ray structure of the homo-aldol adduct (2) derived from (1) (Roder, Helmchen, Peters, Peters & von Schnering, 1984), though epimerization during the transformation at the ring atom bearing the phenyl group cannot be excluded. Substance (1) is prepared by fusing (–)-ephedrine hydrochloride (3) with urea at elevated temperature and was originally assigned the *trans* configuration assuming that a urea N atom displaced the hydroxy group with inversion of configuration. To remove doubts about the relative stereochemistry of (1) the X-ray crystal structure was undertaken.



(1)



(2)



(3)

Experimental. Compound (1) was prepared from (–)-ephedrine hydrochloride and urea as reported (Close, 1950): ^{1}H NMR (100 MHz, $CDCl_3$, δ) 0.75 (3H, *d*, $J = 7$ Hz, 5-CH_3), 2.76 (3H, *s*, N-CH_3), 3.92 (1H, *dq*, $J = 8.5$, 7 Hz, 5-*H*), 4.81 (1H, *d*, $J = 8.5$ Hz, 4-*H*), 5.45 (1H, *br.s*, N-*H*), 7.36 (5H, *m*, Ar-H_5), $[\alpha]_D^{24\,°\mathrm{C}}$ −47.9° ($c = 3$, methanol) [*cf.* −44.5° ($c = 3$, methanol) (Roder, Helmchen, Peters, Peters & von Schnering, 1984)]. Colourless blocks of (1) were grown from ethanol, m.p. 451–453 K, Enraf–Nonius CAD-4 diffractometer; Mo $K\alpha$ radiation, graphite monochromator; ω–2θ scans; crystal dimensions 0.3 × 0.2 × 0.2 mm, unit-cell dimensions by least-squares fit to setting angles of 25 automatically centred reflections with $8 < \theta < 12°$. Room-temperature measurement, no absorption correction, max. $(\sin\theta/\lambda)$ in intensity measurements 0.62 Å^{-1}, one standard reflection monitored (1% loss in intensity during data collection), 1229 reflections measured, 1207 unique, 839 counted as observed [$I > 2\sigma(I)$], index range h 0/7, k 0/9, l 0/25. $h00$ reflections absent for h = odd, $0k0$ absent for k = odd, $00l$ absent for l = odd. Structure solved in $P2_12_12_1$ (*SHELXS*86) and refined on F by full-matrix least-squares analyses including all non-H atoms using anisotropic displacement parameters (*SHELX*76). All H-atom positions were located from difference Fourier maps and included in the refinement with isotropic displacement parameters and a common displacement parameter for each set of methyl hydrogens. Absolute configuration assigned by assuming chiralty at 5-C unchanged in preparation from (3), 179 parameters refined, and with weights $w = (\sigma^2F + 0.0010F^2)^{-1}$ the model converged to $R = 0.041$, $wR = 0.043$, $S = 1.04$, Maximum Δ/σ in final cycle for non-H atoms: positional parameters, 0.2; displacement parameters, 0.2. Maximum and minimum residual electron density in final difference Fourier synthesis 0.15 and −0.18 e Å^{-3}. Computer programs: *SHELXS*86 (Sheldrick, 1986), *SHELX*76 (Sheldrick, 1976); molecular illustrations with *ORTEP*II (Johnson, 1976) and *PLUTON*90 (Spek, 1990). Atomic scattering factors for O, N, C from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965).

Discussion. The structure of (1) is shown in Fig. 1, fractional atomic coordinates and equivalent isotropic displacement parameters in Table 1,* and bond lengths and angles in Table 2. The *C*-phenyl and *C*-methyl substituents are oriented *cis* to one another. The most notable feature is the degree of pyramidality of the methylated ring N atom, N(1), despite being part of a urea. The sum of angles at N(1) is 349 (1)° and N(1) lies 0.27 (1) Å out of the plane defined by its three bonded neighbours. The ring system adopts an envelope-type conformation with four atoms nearly coplanar and one, C(2), lying

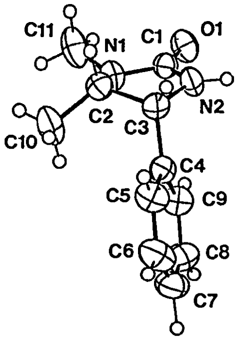


Fig. 1. View of (1) with atom labels and anisotropic displacement ellipsoids drawn at the 50% level.

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* Lists of H-atom coordinates and isotropic displacement parameters, anisotropic displacement parameters for non-H atoms, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55139 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0526]

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O(1)	0.0148 (4)	0.2873 (3)	0.9332 (1)	0.054 (2)
N(1)	−0.1698 (5)	0.1930 (4)	0.8444 (1)	0.043 (2)
N(2)	−0.3311 (6)	0.1826 (4)	0.9380 (2)	0.045 (2)
C(1)	−0.1477 (6)	0.2267 (4)	0.9084 (2)	0.039 (2)
C(2)	−0.3976 (6)	0.1644 (5)	0.8296 (2)	0.043 (2)
C(3)	−0.4897 (6)	0.1109 (4)	0.8949 (2)	0.038 (2)
C(4)	−0.5209 (6)	−0.0744 (4)	0.9043 (2)	0.040 (2)
C(5)	−0.7211 (7)	−0.1443 (6)	0.8912 (2)	0.053 (2)
C(6)	−0.7544 (8)	−0.3125 (6)	0.8985 (2)	0.064 (3)
C(7)	−0.5892 (9)	−0.4131 (6)	0.9185 (2)	0.066 (3)
C(8)	−0.3906 (9)	−0.3465 (6)	0.9312 (2)	0.063 (3)
C(9)	−0.3560 (7)	−0.1768 (5)	0.9247 (2)	0.052 (2)
C(10)	−0.4309 (9)	0.0464 (8)	0.7742 (2)	0.067 (3)
C(11)	−0.0319 (8)	0.2773 (8)	0.7987 (2)	0.069 (3)

Table 2. *Bond lengths* (Å) *and angles* (°) *for* (1) *with e.s.d.'s in parentheses*

O(1)—C(1)	1.227 (4)	C(3)—C(4)	1.516 (5)
N(1)—C(1)	1.367 (4)	C(4)—C(5)	1.383 (5)
N(1)—C(2)	1.455 (5)	C(4)—C(9)	1.375 (6)
N(1)—C(11)	1.445 (5)	C(5)—C(6)	1.377 (6)
N(2)—C(1)	1.334 (5)	C(6)—C(7)	1.365 (7)
N(2)—C(3)	1.446 (5)	C(7)—C(8)	1.362 (7)
C(2)—C(3)	1.536 (5)	C(8)—C(9)	1.389 (6)
C(2)—C(10)	1.506 (6)		

C(1)—N(1)—C(2)	109.5 (3)	N(2)—C(3)—C(4)	113.5 (3)
C(1)—N(1)—C(11)	119.4 (3)	C(2)—C(3)—C(4)	115.8 (3)
C(2)—N(1)—C(11)	120.1 (3)	C(3)—C(4)—C(5)	119.2 (4)
C(1)—N(2)—C(3)	113.1 (3)	C(3)—C(4)—C(9)	122.3 (4)
O(1)—C(1)—N(1)	124.7 (3)	C(5)—C(4)—C(9)	118.5 (4)
O(1)—C(1)—N(2)	127.1 (3)	C(4)—C(5)—C(6)	120.7 (5)
N(1)—C(1)—N(2)	108.2 (3)	C(5)—C(6)—C(7)	120.3 (5)
N(1)—C(2)—C(3)	102.3 (3)	C(6)—C(7)—C(8)	119.7 (4)
N(1)—C(2)—C(10)	113.2 (4)	C(7)—C(8)—C(9)	120.4 (5)
C(3)—C(2)—C(10)	116.8 (4)	C(4)—C(9)—C(8)	120.4 (4)
N(2)—C(3)—C(2)	100.8 (3)		

0.38 (1) Å out of the best plane through the other four [deviations from best plane: N(1), −0.005 (3); N(2), −0.008 (4); C(1), 0.007 (4); C(3), 0.004 (4) Å]. Both substituents are displaced from this plane in the opposite direction to C(2), with the methyl group in an equatorial orientation and the phenyl group in a pseudo-axial position such that its own best plane lies nearly perpendicular (85°) to the [N(1), N(2), C(1), C(3)] plane of the envelope. The steric hindrance between the phenyl and *C*-methyl group is reduced by a slight widening (1–2°) of angles between the C(2)—C(3) bond and the bonds to the substituents. The closest contacts between these groups are: C(4)···H(102) 2.67 (5) and C(5)···C(10) 3.39 (7) Å. The *N*-methyl group adopts a pseudoequatorial position to minimize steric interactions with the *C*-methyl group. The groups lie at van der Waals separation [shortest H···H distance between methyl groups: 2.39 (8) Å]. A pseudoaxial orientation would be disfavoured by steric interaction with the phenyl group.

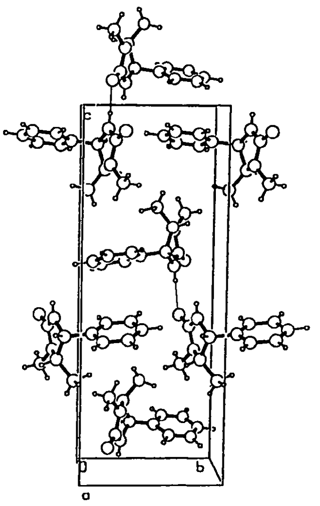

Fig. 2. Crystal packing of (1) viewed along the *a* axis.

The N atoms of ureas normally have planar bonding geometry. One exception is *N*-hydroxyurea in which a lone pair on the O atom induces pyramidality in the attached N atom (Thiessen, Levy & Flaig, 1978). In tetrasubstituted non-cyclic ureas steric hindrance prevents both N atoms from aligning a *p* orbital optimally with the carbonyl group; electron diffraction measurements suggest that tetramethylurea has pyramidal geometry at N (Fernholt, Samdal & Seip, 1981). In (1) the N atom is pyramidalized to minimize steric interactions with the neighbouring methyl group. Similar features exist in (2) but were not remarked on (Roder, Helmchen, Peters, Peters & von Schnering, 1984). The *cis* stereochemistry of (1) may arise by initial conversion of (3) under acidic conditions into an aziridine intermediate by intramolecular S_N2 attack by the N atom on the C-(OH) atom, followed by S_N2 ring opening at this latter atom by a urea N atom.

The crystal packing is shown in Fig. 2. Molecules are linked into infinite chains parallel to the *a* axis by H(N2)···O(1) hydrogen bonds [H···O 2.01 (3) Å, N—H···O angle 167 (2)°], with neighbours related by a 2_1 axis along *a*.

References

Cardillo, G., D'Amico, A., Orena, M. & Sandri, S. (1988). *J. Org. Chem.* **53**, 2354–2356.

Close, W. J. (1950). *J. Org. Chem.* **15**, 1131–1134.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

Fehr, C. & Galindo, J. (1988). *J. Am. Chem. Soc.* **110**, 6909–6911.

Fernholt, L., Samdal, S. & Seip, R. (1981). *J. Mol. Struct.* **72**, 217–231.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Roder, H., Helmchen, G., Peters, E.-M., Peters, K. & von Schnering, H.-G. (1984). *Angew. Chem. Int. Ed. Engl.* **23**, 898–899.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
SPEK, A. L. (1990). *PLUTON90*. Program for molecular illustrations. Univ. of Utrecht, The Netherlands.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
THIESSEN, N. E., LEVY, H. A. & FLAIG, B. D. (1978). *Acta Cryst.* B**34**, 2495–2502.

Acta Cryst. (1992). C**48**, 1804–1806

Structure du Chlorhydrate de (1*R*,2*S*) (3-Hydroxy-3-*m*-hydroxyphényl-2-propyl)-triméthylammonium Monohydrate

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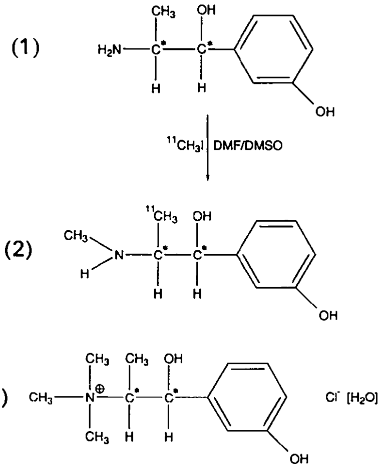
(*Reçu le* 21 *novembre* 1991, *accepté le* 3 *février* 1992)

Abstract. [3-Hydroxy-3-(3-hydroxyphenyl)-2-propyl]trimethylammonium chloride monohydrate, $C_{12}H_{20}NO_2^+.Cl^-.H_2O$, $M_r = 263.76$, m.p. = 513–514 K, orthorhombic, $P2_12_12_1$, $a = 9.821$ (1), $b = 10.222$ (3), $c = 13.871$ (1) Å, $V = 1392.5$ (4) Å^3, $Z = 4$, $D_x = 1.258$ g cm^{-3}, $\lambda(\text{Cu } K\bar{\alpha}) = 1.5418$ Å, $\mu = 23.06$ cm^{-1}, $F(000) = 568$, $T = 290$ (1) K, $R = 0.060$ for 1014 observed reflections. The (1*R*,2*S*) configuration is verified. The Cl^- ion participates in three O—H···Cl hydrogen bonds with distances in the range 3.049–3.119 (6) Å [the range of O—H···Cl angles is 140–180 (1)°]. The water molecule participates in an O···O hydrogen bond of length 2.680 (7) Å [OH···O(water) angle 172 (1)°].

Introduction. La norépinéphrine [1-(3,4-dihydroxyphényl)éthanolamine] est un neurotransmetteur endogène du système adrénergique. Son analogue, le métaraminol est un faux transmetteur synthétique qui s'accumule dans les terminaisons nerveuses et est relâché par excitation nerveuse, montrant seulement un léger effet post-synaptique. Le métaraminol (1), étant un monophénol, n'est pas un substrat de la catéchol-*O*-méthyl transférase; de plus le groupement α méthyle inhibe la monoamine oxydase. Cette stabilité métabolique lui confère un intérêt particulier pour le marquage par un émetteur de positon comme le Carbone 11 à des fins d'imagerie du système nerveux sympathique.

Il est important de remarquer que le métaraminol comporte deux carbones assymétriques. Seul un des isomères sera biologiquement actif: il s'agit du dérivé 1*R*,2*S*. Le radiopharmaceutique (2) s'obtient par monométhylation de l'amine libre au moyen de l'iodure de méthyle en milieu diméthylformamide–diméthylsulfoxyde, l'amine étant en large excès par rapport au réactif marqué (Van Dort, Gildersleeve & Wieland, 1990). Nous avons testé en macrochimie des conditions de réaction strictement identiques, mais en présence d'iodure de méthyle en excès, afin de vérifier s'il n'y avait pas d'altération de la stéréochimie. Nous avons obtenu et identifié l'ammonium quaternaire (3) dont la structure a été déterminée par radiocristallographie.



Partie expérimentale. Composé (3) cristallisé dans l'eau. Cristal incolore 0,49 × 0,46 × 0,42 mm. Paramètres de la maille déterminés à partir de 32 réflexions (18,1 ≤ θ ≤ 20°). Diffractomètre Siemens.