$1-z$); and $4(0.5-x, 0.5+y, 1-z)$. Short contacts are seen on phenyl groups between two positions. In each pair, the distance between the centres of gravity is 4.71 Å.

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Structures and Absolute Configurations of Enantiomers of Two Local Anaesthetics: (2*S*)-1-Methyl- and (2*R*)-1-Butyl-2′,6′-pipecoloxylidide Hydrochlorides

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Abstract. (2*S*)-2-(2,6-Dimethylphenylaminocarbonyl)-1-methylpiperidinium chloride (mepivacaine hydrochloride), $C_{15}H_{23}N_2O^+.Cl^-$, $M_r = 282.81$, orthorhombic, $P2_12_12_1$, $a = 9.777$ (1), $b = 10.628$ (1), $c = 15.316$ (1) Å, $V = 1591.4$ (3) Å^3, $Z = 4$, $D_x = 1.1804$ (1) Mg m^{-3}, λ(Cu $K\alpha$) = 1.54183 Å, $\mu = 2.09$ mm^{-1}, $F(000) = 608$, $T = 291$ K, $R = 0.037$ for 1340 observed reflections. (2*R*)-1-Butyl-2-(2,6-dimethylphenylaminocarbonyl)piperidinium chloride (bupivacaine hydrochloride), $C_{18}H_{29}N_2O^+.Cl^-$, $M_r = 324.89$, monoclinic, $P2_1$, $a = 9.702$ (1), $b = 10.922$ (1), $c = 9.952$ (1) Å, $\beta = 114.38$ (6)°, $V = 960.5$ (2) Å^3, $Z = 2$, $D_x = 1.1234$ (2) Mg m^{-3}, λ(Cu $K\alpha$) = 1.54183 Å, $\mu = 1.79$ mm^{-1}, $F(000) = 352$, $T = 291$ K, $R = 0.040$ for 1626 observed reflections. The absolute configurations were determined by Bijvoet ratio measurements of selected Friedel-pair reflections. Although the absolute configurations at C(2) are different, the two compounds have very similar molecular conformations. The amide plane is twisted through about 70° with respect to the benzene ring, and the amide group and the *N*-alkyl substituent of the chair-shaped piperidine ring are in *cis* position and are equatorially oriented in both compounds. Moreover, the protonated drug molecules in both cases are linked together by hydrogen bonds *via* the chloride anions so as to form parallel endless hydrogen-bonded chains in the crystals.

Introduction. Different 1-alkyl-2′,6′-pipecoloxylidides possess varying degrees of local anaesthetic activity. Mepivacaine with an *N*-methyl-substituted piperidine ring is a rather short-time anaesthetic agent, whereas the *N*-butyl-substituted derivative, bupivacaine, has

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prolonged action (Covino & Vassallo, 1976). The X-ray study was carried out to yield information about the conformational features of these compounds and about the effect of the size of the *N*-piperidine substituent on the molecular conformation.

Experimental. The compounds used in this study, prepared according to Af Ekenstam, Egnér & Pettersson (1957), were kindly supplied by Rune Sandberg (Astra Pain Control AB). Single crystals of the hydrochloride of L-(+)-mepivacaine, suitable for X-ray work, were grown from ethanol solution, and those of D-(−)-bupivacaine were taken from an acetone/water mixture. The collected net intensities were corrected for Lorentz, polarization and absorption effects. The absorption corrections were carried out with Sheldrick's (1976) numerical absorption correction program. Further experimental conditions for the intensity data collection and processing are given in Table 1. The structures were solved by direct methods, using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) for mepivacaine and *SHELXS* (Sheldrick, 1990) for bupivacaine, and then were refined by the full-matrix least-squares method (*SHELX*76; Sheldrick, 1976) based on F. The amide and amine H atoms were located from $\Delta\rho$ maps and were held riding on their parent atoms during the subsequent refinements, whereas the H atoms bonded to C were assumed to have geometrically predicted positions (C—H = 1.00 Å) which were recalculated after each refinement cycle. Details of the refinement calculations are shown in Table 1. In the final models the positions of the non-H atoms were refined together with their anisotropic displacement parameters, and isotropic vibration parameters were refined for the H-atom positions. 20 low-θ reflections for mepivacaine and eight for bupivacaine, which had considerably lower F_o than F_c most likely owing to extinction effects, were excluded from the final refinement calculations. The R and wR values reached are shown in Table 1. The wR_{tot} values were calculated for the final structural models using all unique non-zero reflections. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 71–102). The correction factors for anomalous dispersion for the non-H atoms were taken from Cromer & Liberman (1970). The illustrations were drawn by the program *PLUTO* (Motherwell & Clegg, 1978).

The absolute configurations were determined according to the method of Bijvoet (Bijvoet, Peerdeman & Van Bommel, 1951). The Bijvoet ratios $X_h = 2(I_h - I_{-h})/(I_h + I_{-h})$, calculated from the refined atomic positions, were compared with observed values based on carefully measured intensities of 14 and 15 selected Friedel-pair reflections for mepivacaine and bupivacaine, respectively. For each unique *hkl* the net intensities of four equivalent reflections in the space group $P2_12_12_1$ and two equivalent reflections in the monoclinic case were averaged for I_h and I_{-h}, respectively. This procedure led, without doubt, to the S absolute configuration for mepivacaine and the R configuration for bupivacaine. Moreover, in both cases the final refinement calculation was repeated assuming opposite absolute configuration for the chiral centre. The calculation for the mepivacaine model with R configuration yielded $R = 0.051$ and $wR = 0.068$, whereas the refinement of the S enantiomer of bupivacaine converged to $R = 0.045$ and $wR = 0.064$. These reliability indices are significantly higher than the respective values listed in Table 1, thus proving our previous assignment of absolute configurations. According to statistical tests of the crystallographic wR values (Hamilton, 1965; Rogers, 1981) the estimated probabilities, α, of making a wrong assignment [calculated according to Rogers (1981)] are in the present cases as low as approximately 10^{-98} for mepivacaine and approximately 10^{-61} for bupivacaine. Hence, Table 2 lists the refined atomic coordinates of the correct enantiomers.

Table 1. *Experimental conditions for the crystal structure determinations, with e.s.d.'s, where given, in parentheses*

	(*S*)-Mepivacaine	(*R*)-Bupivacaine
Crystal data		
Crystal shape	Needle	Irregular
Crystal colour	Colourless	Colourless
Crystal size (mm)	0.21 × 0.61 × 0.17	0.22 × 0.44 × 0.15
Diffractometer	Stoe/AED-2	Stoe/AED-2
Unit-cell determination		
No. of reflections	32	44
θ range (°)	16.6–28.7	18.5–30.0
Intensity data collection		
ω–2θ scan mode, $\Delta 2\theta$ (°)	1.4	1.4
Maximum $\sin\theta/\lambda$ (Å^{-1})	0.6075	0.6073
Range of h, k and l	0→11, 0→12, 0→18	−11→11, 0→13, 0→12
No. of standard reflections	6	5
Intensity instability (%)	< 2.5	< 6.5
No. of collected reflections	1646	1938
R_{int}	-	0.025
No. of unique non-zero reflections	1579	1789
No. of reflections used in the refinement	1340	1626
Criterion of significance	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Absorption correction		
Linear absorption coefficient (cm^{-1})	20.9	17.9
Transmission-factor range	0.48–0.73	0.58–0.80
Structure refinement		
Function minimized	$\sum w\Delta F^2$	$\sum w\Delta F^2$
No. of refined parameters	187	219
Final reliability indices		
R	0.037	0.040
wR	0.048	0.055
wR_{tot}	0.056	0.058
Weighting scheme, value of g in $w = [\sigma^2(F) + g\|F\|^2]^{-1}$	0.0007	0.0007
Final $(\Delta/\sigma)_{max}$	0.015	0.014
Final $\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.16/−0.19	0.14/−0.21

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for the non-*H *atoms, with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}
(*S*)-Mepivacaine				
Cl	−1.21551 (9)	−0.51661 (7)	−0.87094 (6)	0.0538 (3)
N(1)	−0.9024 (3)	−0.2590 (3)	−0.6978 (2)	0.041 (1)
C(1′)	−0.8378 (4)	−0.2575 (5)	−0.7860 (3)	0.062 (2)
C(2)	−1.0484 (3)	−0.3010 (3)	−0.7039 (2)	0.042 (1)
C(3)	−1.1103 (4)	−0.3180 (5)	−0.6140 (3)	0.064 (2)
C(4)	−1.0251 (5)	−0.4041 (4)	−0.5554 (3)	0.068 (2)
C(5)	−0.8825 (5)	−0.3495 (4)	−0.5486 (3)	0.058 (2)
C(6)	−0.8183 (4)	−0.3392 (4)	−0.6370 (3)	0.052 (1)
C(7)	−1.1282 (4)	−0.1985 (3)	−0.7510 (3)	0.044 (1)
O(7)	−1.1045 (3)	−0.0869 (2)	−0.7355 (2)	0.059 (1)
N(8)	−1.2280 (3)	−0.2396 (3)	−0.8031 (2)	0.046 (1)
C(9)	−1.3270 (4)	−0.1578 (3)	−0.8430 (3)	0.044 (1)
C(10)	−1.4244 (4)	−0.0996 (4)	−0.7907 (3)	0.053 (1)
C(11)	−1.5215 (4)	−0.0241 (4)	−0.8313 (3)	0.061 (2)
C(12)	−1.5212 (4)	−0.0092 (4)	−0.9212 (3)	0.066 (2)
C(13)	−1.4244 (4)	−0.0670 (4)	−0.9710 (3)	0.060 (2)
C(14)	−1.3240 (4)	−0.1432 (3)	−0.9335 (3)	0.048 (1)
C(15)	−1.2158 (5)	−0.2068 (4)	−0.9876 (3)	0.071 (2)
C(16)	−1.4274 (5)	−0.1172 (5)	−0.6934 (3)	0.073 (2)
(*R*)-Bupivacaine				
Cl	−0.2041 (1)	−0.5426	−0.7871 (1)	0.0604 (3)
N(1)	−0.6342 (3)	−0.8039 (3)	−1.0683 (3)	0.041 (1)
C(1′)	−0.6475 (5)	−0.8292 (4)	−0.9248 (4)	0.056 (2)
C(2′)	−0.6440 (11)	−0.7162 (6)	−0.8364 (7)	0.112 (4)
C(3′)	−0.6571 (8)	−0.7484 (7)	−0.6953 (6)	0.096 (3)
C(4′)	−0.5338 (12)	−0.8214 (13)	−0.5885 (8)	0.190 (7)
C(2)	−0.4817 (4)	−0.7539 (3)	−1.0455 (4)	0.041 (1)
C(3)	−0.4747 (5)	−0.7220 (5)	−1.1931 (4)	0.056 (2)
C(4)	−0.6090 (5)	−0.6442 (4)	−1.2933 (4)	0.058 (2)
C(5)	−0.7534 (5)	−0.7087 (4)	−1.3175 (5)	0.061 (2)
C(6)	−0.7650 (4)	−0.7282 (4)	−1.1713 (5)	0.053 (2)
C(7)	−0.3654 (4)	−0.8538 (3)	−0.9737 (4)	0.039 (1)
O(7)	−0.4002 (3)	−0.9615 (3)	−1.0029 (3)	0.055 (1)
N(8)	−0.2247 (3)	−0.8146 (3)	−0.8901 (3)	0.045 (1)
C(9)	−0.1005 (4)	−0.8990 (4)	−0.8330 (4)	0.047 (2)
C(10)	−0.0464 (4)	−0.9523 (4)	−0.9291 (5)	0.052 (2)
C(11)	0.0712 (4)	−1.0372 (5)	−0.8710 (5)	0.061 (2)
C(12)	0.1332 (5)	−1.0641 (4)	−0.7233 (6)	0.069 (2)
C(13)	0.0818 (4)	−1.0087 (4)	−0.6289 (5)	0.062 (2)
C(14)	−0.0376 (4)	−0.9244 (4)	−0.6822 (4)	0.053 (2)
C(15)	−0.0998 (5)	−0.8674 (5)	−0.5813 (5)	0.066 (2)
C(16)	−0.1107 (5)	−0.9206 (5)	−1.0905 (5)	0.064 (2)

Table 3. *Covalent bond distances* (Å) *between the non-*H *atoms, with e.s.d.'s of the observed bond lengths given in parentheses*

	Uncorrected	Corrected for riding motion*
(*S*)-Mepivacaine		
N(1)—C(1′)	1.491 (5)	1.5119
N(1)—C(2)	1.499 (4)	1.5007
N(1)—C(6)	1.506 (5)	1.5181
C(2)—C(3)	1.515 (5)	1.5358
C(2)—C(7)	1.522 (5)	1.5221
C(3)—C(4)	1.528 (6)	1.5326
C(4)—C(5)	1.514 (6)	1.5228
C(5)—C(6)	1.497 (6)	1.5094
C(7)—O(7)	1.231 (4)	1.2513
C(7)—N(8)	1.335 (5)	1.3386
N(8)—C(9)	1.438 (5)	1.4386
C(9)—C(10)	1.390 (5)	1.3995
C(9)—C(14)	1.394 (5)	1.3988
C(10)—C(11)	1.390 (6)	1.4010
C(10)—C(16)	1.503 (6)	1.5234
C(11)—C(12)	1.385 (6)	1.3875
C(12)—C(13)	1.361 (6)	1.3706
C(13)—C(14)	1.396 (6)	1.4079
C(14)—C(15)	1.504 (6)	1.5229
(*R*)-Bupivacaine		
N(1)—C(1′)	1.512 (6)	1.5275
N(1)—C(2)	1.503 (5)	1.5044
N(1)—C(6)	1.507 (4)	1.5194
C(1′)—C(2′)	1.508 (8)	1.5640
C(2′)—C(3′)	1.503 (11)	1.5211
C(3′)—C(4′)	1.465 (12)	1.5456
C(2)—C(3)	1.538 (6)	1.5522
C(2)—C(7)	1.520 (5)	1.5206
C(3)—C(4)	1.530 (6)	1.5318
C(4)—C(5)	1.496 (7)	1.4991
C(5)—C(6)	1.519 (7)	1.5275
C(7)—O(7)	1.225 (4)	1.2435
C(7)—N(8)	1.342 (4)	1.3489
N(8)—C(9)	1.435 (5)	1.4367
C(9)—C(10)	1.394 (6)	1.4011
C(9)—C(14)	1.394 (5)	1.4008
C(10)—C(11)	1.396 (6)	1.4052
C(10)—C(16)	1.504 (6)	1.5135
C(11)—C(12)	1.371 (7)	1.3773
C(12)—C(13)	1.373 (8)	1.3802
C(13)—C(14)	1.402 (6)	1.4124
C(14)—C(15)	1.504 (7)	1.5151

* Correction following Busing & Levy (1964).

Discussion. Final atomic coordinates and equivalent isotropic displacement parameters for the non-H atoms are listed in Table 2; the molecular structures with the correct absolute configuration and with the crystallographic labelling of the atoms are depicted in Fig. 1. Intramolecular bond distances between the non-H atoms, selected conformational features, torsion angles and hydrogen-bond dimensions are summarized in Tables 3–6.* Figs. 2 and 3 are stereoscopic packing illustrations of the crystal structures.

The corresponding bond distances [both uncorrected and corrected for riding motion according to Busing & Levy (1964)] (Table 3) and bond angles in the present two compounds are in agreement with each other, and they are also comparable with those previously published for two closely related derivatives, L-ropivacaine hydrochloride monohydrate and DL-bupivacaine hydrochloride hemiethanol solvate (Bruins Slot, Behm & Kerkkamp, 1990). No anomalous values were observed. Nevertheless, the differences of 0.04–0.08 Å between the observed and expected bond lengths (Kennard, 1968), and also between the uncorrected and corrected values for the C—C distances in the *N*-butyl chain of bupivacaine, are in all probability a result of the relatively high thermal mobility of the atoms involved (*cf.* Table 2). Despite the opposite absolute configurations, the molecular conformations of the present two derivatives resemble each other, and also those earlier published and mentioned above. The least-squares planes through the benzene ring and the amide group

* Lists of intramolecular bond angles involving the non-H atoms, fractional atomic coordinates of the H atoms, bond lengths and bond angles involving the amide and amine H atoms, equations of the least-squares planes and atomic deviations from the planes, Bijvoet ratios of selected Friedel-pair reflections, anisotropic displacement parameters of the non-H atoms, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55136 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA0013]

Table 4. *Selected conformational features, with e.s.d.'s in parentheses*

	(*S*)-Mepivacaine	(*R*)-Bupivacaine
Deviation from coplanarity of the six benzene ring atoms (Å)*	0.009 (4)	0.022 (5)
Dihedral angle (°) between the least-squares planes of the benzene ring and the amide group	68.2 (3)	72.1 (3)
Ring-puckering parameters of the piperidine ring†		
Q (Å)	0.562 (4)	0.559 (4)
φ (°)	26 (4)	−134 (3)
θ (°)	173.4 (4)	8.4 (4)
Ring conformation	'Near chair'	'Near chair'

* Least-squares planes and dihedral angles between the planes are calculated according to Nardelli, Musatti, Domiano & Andreetti (1965). [Further details of the calculations are given in the supplementary material (see deposition footnote).]

† Ring-puckering parameters are calculated according to Cremer & Pople (1975).

Table 5. *Comparison of selected torsion angles* (°), *with e.s.d.'s in parentheses, calculated for (S)-mepivacaine, (R)-bupivacaine, (S)-ropivacaine and racemic bupivacaine*

The right-hand rule is applied to the angles, according to Klyne & Prelog (1960). The e.s.d.'s are calculated according to Stanford & Waser (1972).

		(*S*)-Mepivacaine*	(*R*)-Bupivacaine*	(*S*)-Ropivacaine†	Racemic bupivacaine†
τ_1	N(8)—C(9)—C(10)—C(11)	−178.0 (4)	−177.9 (4)	−177.5 (3)	178.2 (3)
τ_2	N(8)—C(9)—C(14)—C(13)	177.6 (3)	178.9 (4)	177.6 (3)	−178.2 (3)
τ_3	C(7)—N(8)—C(9)—C(10)	−69.4 (5)	71.7 (5)	79.4 (5)	77.4 (4)
τ_4	C(7)—N(8)—C(9)—C(14)	112.5 (4)	−108.6 (4)	−103.1 (4)	−104.3 (4)
τ_5	O(7)—C(7)—N(8)—C(9)	−4.7 (5)	2.8 (6)	0.2 (6)	5.6 (6)
τ_6	C(2)—C(7)—N(8)—C(9)	170.6 (3)	−171.4 (3)	177.8 (3)	170.1 (3)
τ_7	N(1)—C(2)—C(7)—N(8)	144.4 (3)	−152.7 (3)	142.9 (3)	−143.0 (3)
τ_8	N(1)—C(2)—C(7)—O(7)	−40.0 (4)	32.8 (4)	−39.5 (5)	41.4 (4)
τ_9	C(3)—C(2)—C(7)—N(8)	−95.4 (4)	87.2 (4)	−97.3 (4)	98.1 (4)
τ_{10}	C(3)—C(2)—C(7)—O(7)	80.2 (4)	−87.3 (4)	80.3 (5)	−72.8 (4)
τ_{11}	C(1′)—N(1)—C(2)—C(7)	−68.6 (3)	66.1 (4)	−52.7 (4)	58.3 (4)
τ_{12}	C(4)—C(3)—C(2)—C(7)	−171.1 (3)	167.0 (3)	179.5 (3)	172.8 (3)
τ_{13}	C(6)—N(1)—C(2)—C(7)	168.3 (3)	−165.7 (3)	−178.5 (3)	173.2 (3)
τ_{14}	C(1′)—N(1)—C(6)—C(5)	−177.1 (3)	−177.4 (3)	170.9 (3)	−172.8 (3)
τ_{15}	C(1′)—N(1)—C(2)—C(3)	173.2 (3)	−176.6 (3)	−172.3 (3)	175.9 (3)
τ_{16}	N(1)—C(1′)—C(2′)—C(3′)		−179.8 (5)	−177.0 (4)	−179.9 (4)
τ_{17}	C(1′)—C(2′)—C(3′)—C(4′)		63.7 (9)		−167.0 (4)

* Present work.

† According to Bruins Slot, Behm & Kerkkamp (1990).

Table 6. *Bond distances* (Å) *and angles* (°) *in possible hydrogen bonds, with e.s.d.'s, where given, in parentheses*

The N-bonded H-atom positions were derived from $\Delta\rho$ maps and were not refined.

	Symmetry	N···Cl	N—H	H···Cl	N—H···Cl
(*S*)-Mepivacaine					
N(1)—H(1)···Cl	$-x-2, y+0.5, -z-1.5$	3.012 (3)	1.02	2.09	150
N(8)—H(8)···Cl	x, y, z	3.124 (3)	0.89	2.24	172
(*R*)-Bupivacaine					
N(1)—H(1)···Cl	$-x-1, y-0.5, -z-2$	3.076 (3)	0.94	2.21	152
N(8)—H(8)···Cl	x, y, z	3.123 (3)	1.06	2.09	165

are twisted with respect to each other through about 70° (Table 4). The chair-shaped piperidine ring has the amide group at C(2) and the *N*-alkyl substituent in *cis* position (*cf.* τ_{11} in Table 5) and they are equatorially oriented in all four compounds (*cf.* τ_{12}, τ_{13}, τ_{14} and τ_{15} in Table 5). The differences between corresponding torsion angles (disregarding the signs), and the different conformations of the *N*-butyl chain in the two bupivacaine derivatives (*cf.* τ_{17} in Table 5), are most likely a result of the variation in intermolecular interactions and packing forces.

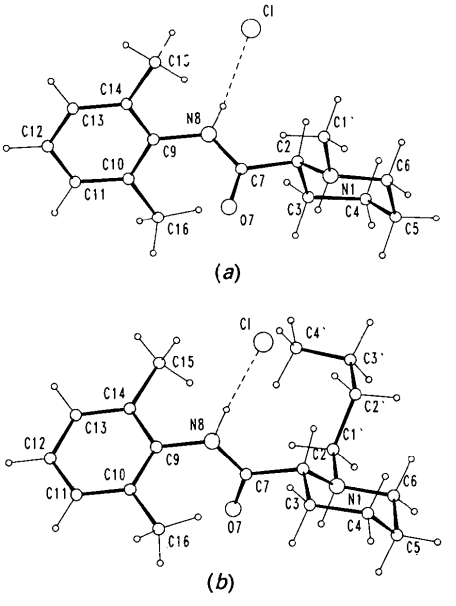

Fig. 1. Perspective views of the hydrochloride salts of (2*S*)-mepivacaine (*a*) and (2*R*)-bupivacaine (*b*), also showing the crystallographic labelling of the non-H atoms. Solid and dashed lines represent covalent and hydrogen bonds, respectively.

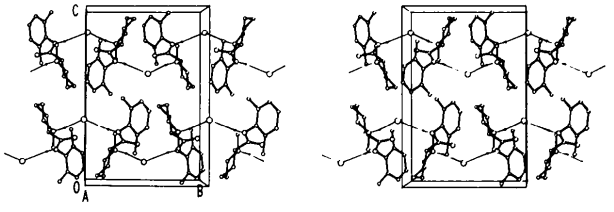

Fig. 2. Stereo packing diagram of (2*S*)-mepivacaine. The C-bonded H atoms are omitted for clarity.

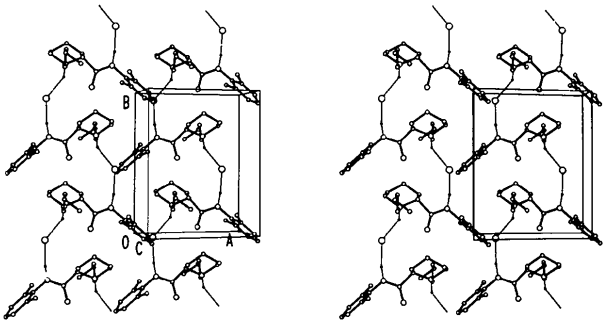

Fig. 3. Stereo packing illustration of (2*R*)-bupivacaine. The H atoms, except those involved in the hydrogen bonds, are omitted for clarity.

Although the hydrochlorides of (*S*)-mepivacaine and (*R*)-bupivacaine crystallize in different crystal systems, the organization or molecular packing in the present two crystals shows pronounced similarities. The Cl anion is hydrogen bonded to the amide and amine N atoms in both cases (Table 6). The N(1)···Cl···N(8) angle is 134.8 (1) in mepivacaine and 134.6 (1)° in bupivacaine. By virtue of the hydrogen bonds and the twofold rotational symmetry, endless helical chains are formed parallel to the crystallographic *b* axis in both compounds. The chains are held together by ordinary van der Waals forces.

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Structure of 3-(*p*-Chlorophenyl)-1-phenyl-1,3-propanedione Enol

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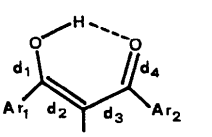
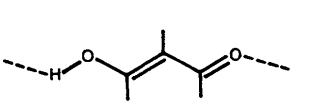
Abstract. 1-(4-Chlorophenyl)-3-hydroxy-3-phenyl-2-propen-1-one, $C_{15}H_{11}ClO_2$, $M_r = 258.7$, $C2/c$, $a = 24.324$ (4), $b = 6.537$ (2), $c = 15.598$ (2) Å, $\beta = 93.52$ (1)°, $V = 2475.5$ (9) Å^3, $Z = 8$, $D_x = 1.382$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 2.95$ cm^{-1}, $F(000) = 1072$, $T = 298$ K, final $R = 0.043$ for 1192 observed reflections. The compound displays a strong intramolecular asymmetric hydrogen bond [O···O = 2.471 (4), O—H = 1.09 Å, IR ν(OH) stretching frequency = 2577 cm^{-1}, ^{1}H NMR chemical shift of the enolic proton = 16.8 p.p.m.] which can be interpreted in terms of resonance-assisted hydrogen bonding. The proton localization, that is, the preference displayed by the proton for settling on an O atom of the β-diketone fragment rather than on the other O atom, is discussed and related to the different environments of the two O atoms in the crystal packing and, in particular, to the asymmetry of their C—H···O short contacts.

Introduction. β-Diketones in their enolic tautomeric forms have been extensively studied owing to their ability to form strong inter- or intramolecular hydrogen bonds (Emsley, 1984; Gilli, Bellucci, Ferretti & Bertolasi, 1989; Etter & Vojta, 1989; Gilli & Bertolasi, 1990). In general, these compounds are stabilized by an intramolecular hydrogen bond (I), while less frequently, and as a consequence of steric effects, infinite chains of intermolecular hydrogen-bonded molecules are found (II). Accordingly, all the



(I)



(II)

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