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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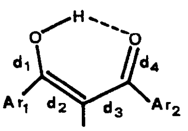
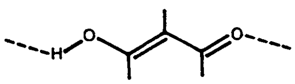
Abstract. 1-(4-Chlorophenyl)-3-hydroxy-3-phenyl-2-propen-1-one, $C_{15}H_{11}ClO_2$, $M_r = 258.7$, $C2/c$, $a = 24.324$ (4), $b = 6.537$ (2), $c = 15.598$ (2) Å, $\beta = 93.52$ (1)°, $V = 2475.5$ (9) Å^3, $Z = 8$, $D_x = 1.382$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.95$ cm^{-1}, $F(000) = 1072$, $T = 298$ 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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1,3-diaryl-1,3-propanedione enols, independent of the nature of the Ar_1 and Ar_2 substituents, have the structure (I) with a strong hydrogen bond characterized by π delocalization along the O=C—C=C—O heterodienic system, shortening of O···O distances to 2.432 Å and lengthening of O—H distances to 1.22 Å, though always with a slightly asymmetric localization of the proton (Bertolasi, Gilli, Ferretti & Gilli, 1991; Jones, 1976; Etter, Jahn & Urbańczyk-Lipkowska, 1987; Williams, 1966; Hollander, Templeton & Zalkin, 1973). The π delocalization on the fragment can be measured by the use of the antisymmetric vibrational coordinate $Q = (d_1 - d_4) + (d_3 - d_2)$ which is obviously zero when the delocalization is complete. Q has been found to be correlated with the strength of the hydrogen bond evaluated by both O···O distances and spectroscopic properties (Gilli *et al.*, 1989; Bertolasi *et al.*, 1991). Such interrelated effects have been interpreted by a mechanism called RAHB (resonance-assisted hydrogen bonding) (Gilli *et al.*, 1989) through which hydrogen-bond and π-system delocalization reinforce mutually with a gain in energy.

We report here the crystal structure of a new 1,3-diaryl-1,3-propanedione enol in order to obtain further insight into the relationship between structural parameters and the nature of the phenyl-ring substituents, and to ascertain the factors which contribute to the formation of the asymmetric hydrogen bond.

Experimental. Colourless needle-shaped crystals were obtained from ethanol, 0.08 × 0.21 × 0.40 mm, and used for data collection on a CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters were determined from 25 reflections ($6 \le \theta \le 13°$). 2304 unique reflections were measured ($0 \le h \le 31$, $0 \le k \le 8$, $-19 \le l \le 19$, $2 \le \theta \le 27°$) in $\omega/2\theta$ mode. Three standard reflections monitored every 2 h showed no significant change of intensity; 1192 reflections were observed [$I \ge 2\sigma(I_o)$]; Lp correction applied. Structure solution was carried out by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement (on F) with anisotropic parameters for non-H atoms and isotropic for H atoms (all found in ΔF synthesis) was performed. Final cycle: 212 parameters, maximum shift/e.s.d. = 0.06, $R = 0.043$, $wR = 0.045$, $S = 1.29$, $w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$, largest final ΔF peak = 0.18 e Å^{-3}. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed using the CAD-4 *SDP* system of programs (Frenz, 1978) and *PARST* (Nardelli, 1983).

The IR spectrum was recorded on a Bruker IFS88/FT-IR spectrometer from KBr pellets, and the ^1H NMR spectrum in a solution of $CDCl_3$ on a Bruker FT WP-80 spectrometer. The ν(OH) stretching frequency was identified according to Ogoshi & Nakamoto (1966) and Tayyari, Zeegers-Huyskens & Wood (1979) in the weak band at 2577 cm^{-1}; the enolic proton chemical shift, σ(OH), was found at 16.8 p.p.m.

Discussion. Atomic parameters are given in Table 1. Interatomic distances, interatomic angles and a selection of torsion angles are reported in Table 2.* An *ORTEP*II (Johnson, 1976) view of the molecule is shown in Fig. 1 and a stereoview of the crystal packing along **b** in Fig. 2.

The β-diketone enol fragment forms a strong intramolecular hydrogen bond as shown by the shortening of the O···O distance [O(1)···O(2) = 2.471 (4) Å] and by a corresponding lengthening of the O—H one [O(1)—H(1) = 1.09 (4) Å]; its strength is confirmed by the IR ν(O—H) stretching frequency of 2577 cm^{-1} and ^1H NMR chemical shift of the enolic proton, δ(OH) = 16.8 p.p.m. [by comparison the hydrogen bond in alcohols has d(O···O) ≃ 2.77 and d(O—H) ≤ 1.00 Å, ν(O—H) = 3400–3600 cm^{-1} and δ(OH) = 0.5–5 p.p.m.]. At the same time a remarkable π delocalization along the heterodienic system H(1)—O(1)—C(1)=C(2)—C(3)=O(2) is observed, which can be evaluated from the observed Q value of 0.030 Å to be some 90%. These data are in close agreement with those of other crystal structures of 1,3-diaryl-1,3-propanedione enols already reported, the neutron structural determination of dibenzoylmethane included (Jones, 1976).

The proton is found in asymmetrical position between the O atoms [O(2)···H(1) = 1.44 (4) Å, O(1)—H(1)···O(2) = 154 (2)°] in spite of the very short inter-O-atom distance. This is a characteristic feature of the hydrogen bond in this class of compound, the only known exception being the structure of bis(m-bromobenzoyl)methane (Williams, Dumke & Rundle, 1962) where the molecule is in a special position on a crystallographic mirror and the proton symmetry is ascribed to a statistical occupational disorder of the two asymmetric enol tautomers.

As far as the proton localization is concerned, structural analysis of a series of 1,3-diaryl-1,3-propanedione enols (Bertolasi *et al.*, 1991) shows

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* Lists of structure factors, anisotropic thermal parameters and fractional coordinates of H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55147 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0304]

Table 1. *Positional parameters* (× 10⁴, × 10³ *for the* H *atom*) *and isotropic/equivalent isotropic thermal parameters* (Å²)

Atom H(1) was refined with an isotropic B value. Non-H atoms were refined anisotropically; $B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B/B_{eq}
O(1)	4018 (1)	10267 (4)	−2129 (2)	6.66 (6)
O(2)	4880 (1)	9687 (3)	−1240 (2)	6.58 (6)
C(1)	3972 (1)	8298 (5)	−2218 (2)	4.15 (7)
C(2)	4366 (1)	7014 (4)	−1843 (2)	3.72 (6)
C(3)	4822 (1)	7755 (5)	−1358 (2)	3.91 (6)
C(4)	5263 (1)	6456 (4)	−960 (2)	3.61 (6)
C(5)	5328 (1)	4430 (5)	−1190 (2)	3.96 (7)
C(6)	5757 (1)	3269 (5)	−837 (2)	4.40 (7)
C(7)	6122 (1)	4140 (5)	−236 (2)	4.03 (7)
C(8)	6063 (1)	6137 (5)	13 (2)	4.72 (7)
C(9)	5638 (1)	7287 (5)	−347 (2)	4.30 (7)
C(10)	3481 (1)	7600 (5)	−2743 (2)	3.81 (6)
C(11)	3286 (1)	5606 (5)	−2713 (2)	4.61 (7)
C(12)	2819 (1)	5009 (5)	−3194 (2)	5.29 (8)
C(13)	2550 (1)	6393 (6)	−3729 (2)	6.23 (9)
C(14)	2739 (1)	8375 (6)	−3783 (2)	6.01 (9)
C(15)	3200 (1)	8976 (5)	−3287 (2)	5.07 (8)
Cl	6662.3 (3)	2677 (2)	210.3 (6)	6.04 (2)
H(1)	439 (2)	1043 (4)	−171 (2)	14 (1)

Table 2. *Interatomic distances* (Å), *interatomic angles* (°) *and selected torsion angles* (°)

O(1)—C(1)	1.299 (4)	C(7)—Cl	1.736 (3)
O(2)—C(3)	1.283 (4)	C(8)—C(9)	1.370 (4)
C(1)—C(2)	1.377 (4)	C(10)—C(11)	1.389 (4)
C(1)—C(10)	1.478 (4)	C(10)—C(15)	1.388 (4)
C(2)—C(3)	1.391 (4)	C(11)—C(12)	1.379 (4)
C(3)—C(4)	1.475 (4)	C(12)—C(13)	1.370 (4)
C(4)—C(5)	1.384 (4)	C(13)—C(14)	1.379 (5)
C(4)—C(9)	1.391 (4)	C(14)—C(15)	1.380 (4)
C(5)—C(6)	1.378 (4)	O(1)—H(1)	1.09 (4)
C(6)—C(7)	1.374 (4)	O(2)···H(1)	1.44 (4)
C(7)—C(8)	1.372 (5)		
O(1)—C(1)—C(2)	120.4 (3)	C(6)—C(7)—Cl	119.1 (2)
O(1)—C(1)—C(10)	115.2 (3)	C(8)—C(7)—Cl	120.0 (2)
C(2)—C(1)—C(10)	124.4 (3)	C(7)—C(8)—C(9)	119.7 (3)
C(1)—C(2)—C(3)	122.0 (3)	C(4)—C(9)—C(8)	120.9 (3)
O(2)—C(3)—C(2)	119.9 (3)	C(1)—C(10)—C(11)	122.5 (3)
O(2)—C(3)—C(4)	115.8 (3)	C(1)—C(10)—C(15)	119.3 (3)
C(2)—C(3)—C(4)	124.3 (2)	C(11)—C(10)—C(15)	118.2 (3)
C(3)—C(4)—C(5)	122.2 (3)	C(10)—C(11)—C(12)	121.3 (2)
C(3)—C(4)—C(9)	119.6 (3)	C(11)—C(12)—C(13)	119.4 (3)
C(5)—C(4)—C(9)	118.1 (2)	C(12)—C(13)—C(14)	120.6 (3)
C(4)—C(5)—C(6)	121.3 (3)	C(13)—C(14)—C(15)	119.7 (3)
C(5)—C(6)—C(7)	119.1 (3)	C(10)—C(15)—C(14)	120.7 (3)
C(6)—C(7)—C(8)	120.8 (3)	O(1)—H(1)···O(2)	154 (2)
O(1)—C(1)—C(2)—C(3)	0.2 (5)	O(2)—C(3)—C(2)—C(1)	1.0 (4)
O(1)—C(1)—C(10)—C(11)	−161.8 (3)	O(2)—C(3)—C(4)—C(5)	−164.5 (3)
O(1)—C(1)—C(10)—C(15)	18.0 (4)	O(2)—C(3)—C(4)—C(9)	13.8 (4)

that there are two distinct factors affecting the asymmetric position chosen by the H atom along the O(1)···O(2) coordinate. One factor is chemical and arises from the electronegativity difference between the Ar_1 and Ar_2 groups: the proton has been shown to prefer the side of the more electronegative substituent (Emsley, 1984; Bertolasi *et al.*, 1991); the other is connected with the different crystal environment around the two O atoms: the proton choses the O atom making less C—H···O contacts with other H atoms of the structure. The final situation has been found to be a subtle equilibrium between these two factors and it can be said that the proton settles on the O atom where the minimum partial negative charge has been induced by both the nature of 1,3-substituents and short contacts.

From the point of view of the substituents the enol proton should be bonded, in the present structure, to the carbonyl group carrying the *p*-chlorophenyl moiety. So the opposite situation found in the crystal should arise from the different crystal environments of the two O atoms, as actually shown by the data of Table 3 which reports the relevant inter- and intramolecular C—H···O contacts. A more quantitative evaluation of the relative importance of such C—H···O interactions can be obtained by computing their bond valences, s, which are calculated as $s = \exp[(R_o - R)/B]$, B and R_o being semiempirical parameters for the O···H interaction having values of 0.37 and 0.88 Å, and R being the actual O···H contact distance (Brown & Shannon, 1973; Brown & Altermatt, 1985). The results are reported in Table 3 together with the sums $\sum s[O(1)]$ and $\sum s[O(2)]$ which are the global contributions of the C—H···O interactions to the O(1) and O(2) atoms, respectively. The positive difference $\Delta = \sum s[O(2)] - \sum s[O(1)] = 0.018$ is indicative of a greater interaction of the protons of the environment with the O(2) atom and, therefore, of a greater negative charge induced on it by polarization which must be greater than the small positive charge induced by the *p*-chlorophenyl group. Accordingly, the proton is found to be bonded to the O(1) atom. It seems of interest to remark that this is

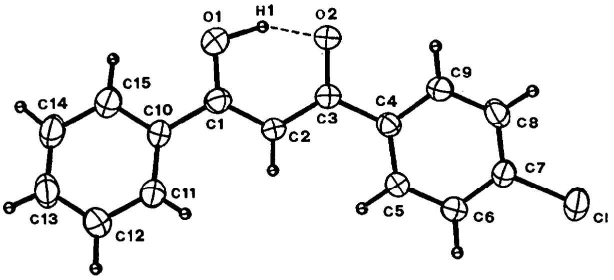

Fig. 1. *ORTEP*II (Johnson, 1976) view of the molecule showing the thermal ellipsoids at 30% probability.

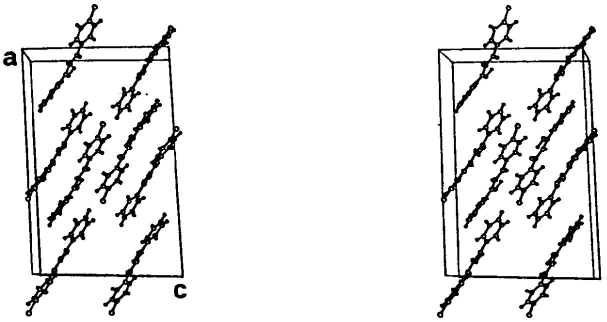

Fig. 2. Stereoview of the unit cell.

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*	Σ*s*
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

$\Delta = \sum s[O(2)] - \sum s[O(1)] = 0.018$

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): $\sum(\Delta/\sigma)^2 = 16.6$] and the two phenyl rings [C(4)–C(9): $\sum(\Delta/\sigma)^2 = 12.0$ and C(10)–C(15): $\sum(\Delta/\sigma)^2 = 26.6$] 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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A Urea with Non-Planar Nitrogen-Bonding Geometry

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Abstract. (4*R*,5*S*)-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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