Diskussion. Tabelle 1 enthält die Lageparameter der Atome (ohne H-Atome), Tabelle 2 Bindungsabstände und -winkel.* Die asymmetrische Einheit wird durch ein halbes Molekül der Titelverbindung gebildet (Fig. 1). Es handelt sich um das zentrosymmetrische *E*-Isomere. Der gesättigte Heterocyclus besitzt eine Sessel-Konformation ähnlich wie die entsprechende Verbindung mit annellierten Sechsringen (Engelhardt & Stromburg, 1987) und das *trans*-Isomere des Dithio-Analogen und im Gegensatz zu dessen *cis*-Isomeren, das eine Twist-Konformation des zentralen anorganischen Rings besitzt (Engelhardt & Stromburg, 1985). Wie den Interplanarwinkeln um die Bindungen (Tabelle 2) zu entnehmen ist, besitzen die Pyrazolidin-Ringe die für Fünfringe übliche stark abgeflachte, nur schwach gewellte Konformation mit einem C—N—N—C-Torsionswinkel von nur 34,8 (1)°. Diese Einschränkung des Torsionswinkels um die N—N-Bindung führt auch zu einem relativ kleinen P—N—N—P-Torsionswinkel im anorganischen Heterocyclus: 55,3 (2)°, was erwartungsgemäß zur Stabilisierung der Sessel-Konformation dieses Ringes beiträgt. Der P···P-Abstand über den Ring hinweg ist mit 3,221 (1) Å wie in anderen Phosphor-Hydrazin-Ringen deutlich kürzer als die Summe der van der Waals-Radien nach Bondi (1964) [man vergleiche die ausführliche Diskussion bei Engelhardt & Stromburg (1985)]. Die übrigen Bindungsabstände im Molekül entsprechen den Erwartungen und sind denen in den Verbindungen mit annellierten Sechsringen sehr ähnlich (Engelhardt & Stromburg, 1985, 1987). Besonders kurze intermolekulare Kontaktabstände finden sich in der Struktur nicht.

Wir danken Herrn Kollegen J. Fuchs für die freundliche Hilfe bei den Messungen. Dem Fonds der Chemischen Industrie gilt unser Dank für finanzielle Unterstützung.

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* Die Liste der Atomkoordination der H-atome und ihrer isotropen Temperaturfaktoren, der Bindungsabstände und -winkel im Phenylring und in den CH_2-Gruppen, der Koeffizienten der anisotropen Temperaturfaktoren, und der beobachteten und berechneten Strukturfaktoren sind bei der British Library Document Supply Centre (Supplementary Publication No. SUP 54836: 15 pp.) hinterlegt. Kopien sind erhältlich durch: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF Aktenzeichen: BX0558]

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Structure of 3-(2-Hydroxyphenyl)propionic Acid

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Abstract. $C_9H_{10}O_9$, $M_r = 166$, monoclinic, $P2_1/c$, $a = 8.248\,(1)$, $b = 5.145\,(2)$, $c = 19.724\,(2)$ Å, $\beta = 90.67\,(1)°$, $V = 836.7\,(3)$ Å^3, $Z = 4$, $D_m = 1.304$, $D_x = 1.317$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.93$ cm^{-1}, $F(000) = 352.0$, $T = 293$ K, $R = 0.051$ for 1117 significant reflections. The crystal structure analysis of the title compound was undertaken in order to determine the proximity of the reacting groups, namely the —OH at C(1) and the —COOH at C(9), and to rationalize the intramolecular lactonization reaction taking place in solution. However, the geometry in the solid state is not favourable for the observed reactivity.

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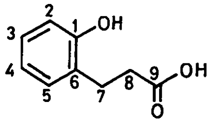
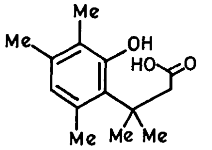
Introduction. Intramolecular reactions have been used as models for enzymic catalysis. These reactions proceed at a much faster rate than intermolecular reactions, a fact which can be explained by entropy effects (Kirby, 1980). Thus, if the reactants are held together intramolecularly, there is less change in entropy on going to the transition state; this is termed the 'proximity or propinquity effect'. Such a decrease in entropy of activation would result in a decrease in free energy of activation, leading to an increase in reaction rate. The favourable entropic effects in intramolecular reactions are due both to the reactants not needing to diffuse towards each other and also to their mutually favourable alignment. However, it has been suggested (Menger, 1985) that entropy effects do not account for the rate enhancements of intramolecular reactions, and that the important factor is the distance at which the reacting groups are held together for a certain length of time, the spatio-temporal hypothesis. It is well known that the binding interaction energy between two groups increases exponentially with decreasing distance (Bürgi, Dunitz, Lehn & Wipff, 1974). Hence, it was considered worthwhile to study some lactonization reactions of various γ-hydroxy acids whose reaction rates have been reported (Kirby, 1980). These lactonizations are all intramolecular reactions, and the variation in rates has been explained as being due to strain relief, stereo population control *etc.*

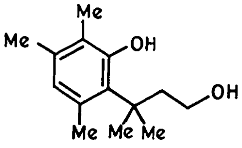
In our attempts (SC and MJ) to prepare some of the hydroxy acids and to correlate the rates and effective molarities with the intramolecular distances of the reacting groups, the title compound (I) was synthesized. The crystallographic results are presented in this paper.



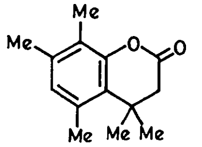
(I)



(II)



(III)



(IV)

Experimental. The title compound was prepared from coumarin by hydrogenation followed by hydrolysis. The compound was extracted with ethyl acetate and crystallized from chloroform.

Single crystals were obtained by slow evaporation using chloroform. Crystal size approximately 0.35 × 0.13 × 0.2 mm. Density measured by flotation. Preliminary oscillation and Weissenberg photographs indicated the space group $P2_1/c$. Lattice parameters refined using 25 reflections in the θ range 7–15°. Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. $\theta \leq 25°$, $\omega/2\theta$ mode. Three standard reflections ($1\bar{1}3$, $52\bar{1}$, 116) monitored every 100 reflections showed only statistical variations. 1928 unique reflections collected. *hkl* range, h 0 to 6, k 0 to 9, l −18 to 18. 1117 significant reflections $[|F_o| \geq 3\sigma(|F_o|)]$. Data corrected for secondary-extinction effects ($g = 2.3 \times 10^{-4}$) but not for absorption effects. Structure solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The best E map with ABSFOM = 1.11, PSIZERO = 0.907, RESID = 13.83, CFOM = 3.00, gave all non-H atoms. Full-matrix least-squares refinement program *SHELX*76 (Sheldrick, 1976) with F's used for refinement of a scale factor, positional and anisotropic thermal parameters for non-H atoms, and positional and isotropic thermal parameters for H atoms. All the H atoms were located from a difference map. The function $\sum w(|F_o| - |F_c|)^2$ was minimized; $w = 1.00/[\sigma^2(|F_o| + 0.005695|F_o|^2]$. At the end of the final refinement cycle $R = 0.051$, $wR = 0.054$, $S = 0.866$, $\Delta/\sigma_{\max} = 0.07$. The final difference map was featureless ($\Delta\rho \leq 0.2$ e Å^{-3}). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149).

Discussion. Final atomic positional and thermal parameters are given in Table 1. A perspective *ORTEP*II (Johnson, 1976) diagram for the title compound with the numbering is given in Fig. 1. Bond distances, bond angles and selected torsion angles are presented in Table 2.*

The phenyl group is essentially coplanar with atom C(7) deviating by 0.112 (2) Å from the plane of the ring. In the molecule the side chain has an extended conformation, but it is approximately perpendicular to the plane of the phenyl group with the torsion angle C(1)—C(6)—C(7)—C(8) = 75.1 (3)°.

For lactonization to take place, the conformation about the C(7)—C(8) bond should be *cisoid* which would bring the —OH at C(1) and the —C═O at C(9) closer. But in the crystalline state only the energetically more stable *trans* conformation is

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* Lists of structure factors, anisotropic thermal parameters, least-squares-planes data, H-atom parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54805 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI0100]

Table 1. *Fractional atomic coodinates and equivalent isotropic temperature factors* (× 10^4) *for 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} (Å^2)
C(1)	0.2989 (3)	0.1943 (4)	0.8861 (1)	531 (7)
C(2)	0.1779 (3)	0.0727 (5)	0.8486 (1)	624 (9)
C(3)	0.1516 (3)	0.1411 (5)	0.7819 (1)	618 (8)
C(4)	0.2435 (3)	0.3314 (5)	0.7525 (1)	573 (8)
C(5)	0.3644 (3)	0.4513 (5)	0.7901 (1)	514 (7)
C(6)	0.3954 (2)	0.3842 (4)	0.8573 (1)	460 (7)
C(7)	0.5351 (3)	0.5012 (4)	0.8963 (1)	518 (7)
C(8)	0.6766 (3)	0.3100 (5)	0.8997 (2)	613 (9)
C(9)	0.8154 (3)	0.3947 (5)	0.9439 (1)	543 (8)
O(1)	0.3310 (3)	0.1343 (4)	0.9528 (1)	775 (8)
O(2)	0.8600 (2)	0.2755 (4)	0.9945 (1)	689 (6)
O(3)	0.8861 (2)	0.6079 (3)	0.9248 (1)	716 (7)

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *involving non*-H *atoms with e.s.d.'s in parentheses*

C(1)—C(2)	1.385 (3)	C(5)—C(6)	1.390 (3)
C(1)—C(6)	1.386 (3)	C(6)—C(7)	1.504 (3)
C(1)—O(1)	1.374 (3)	C(7)—C(8)	1.527 (3)
C(2)—C(3)	1.377 (3)	C(8)—C(9)	1.496 (4)
C(3)—C(4)	1.371 (3)	C(9)—O(2)	1.224 (3)
C(4)—C(5)	1.381 (3)	C(9)—O(3)	1.300 (3)
C(6)—C(1)—O(1)	116.5 (2)	C(5)—C(6)—C(7)	121.3 (2)
C(2)—C(1)—C(6)	120.9 (2)	C(1)—C(6)—C(7)	120.8 (2)
C(2)—C(1)—O(1)	122.6 (2)	C(6)—C(7)—C(8)	110.2 (2)
C(2)—C(3)—C(4)	120.3 (2)	C(7)—C(8)—C(9)	114.7 (2)
C(1)—C(2)—C(3)	120.0 (2)	C(8)—C(9)—O(9)	114.8 (2)
C(3)—C(4)—C(5)	119.4 (2)	C(8)—C(9)—O(2)	123.3 (2)
C(4)—C(5)—C(6)	121.6 (2)	O(2)—C(9)—O(3)	121.8 (2)
C(1)—C(6)—C(5)	117.7 (2)		
O(1)—C(1)—C(2)—C(3)	− 179.9 (2)	C(5)—C(6)—C(7)—C(8)	− 101.1 (2)
O(1)—C(1)—C(6)—C(7)	4.4 (3)	C(6)—C(7)—C(8)—C(9)	− 173.5 (2)
O(1)—C(1)—C(6)—C(5)	− 179.2 (2)	C(7)—C(8)—C(9)—O(2)	117.6 (3)
C(1)—C(6)—C(7)—C(8)	75.1 (3)	C(7)—C(8)—C(9)—O(3)	− 62.1 (3)

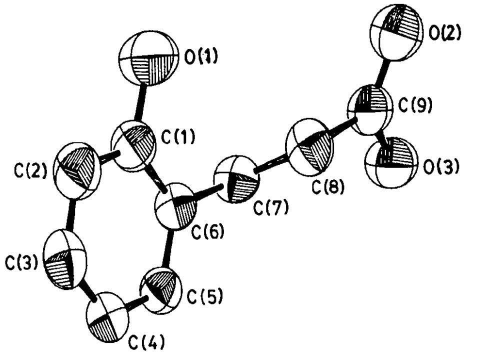

Fig. 1. A perspective view of the molecule with the atom-numbering scheme and thermal ellipsoids at the 50% probability level.

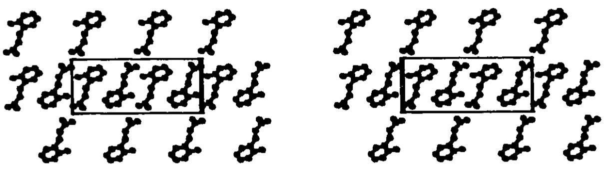

Fig. 2. Stereoscopic view of packing of the molecules in the unit cell viewed down the *b* axis.

present. The torsion angle about this bond [C(6)—C(7)—C(8)—C(9)] is − 173.5 (2)°. The intramolecular distance between the hydroxyl O(1) and the carbonyl O(2) atoms is 4.48 Å. Atoms C(9) and O(1) are at a distance of 4.22 Å. The *trans* orientation of the side chain indicates that the reacting groups are not in a favourable position for lactone formation. However, the observed reaction in the solution phase indicates the probability of the occurrence of the *cisoid* conformation to a small degree.

The reaction rates of *o*-hydroxyphenylpropionic acid and its methyl derivatives have been studied (Milstein & Cohen, 1972). They proposed that the interlocking of the methyl groups at positions 5 and 7 restricts the conformation bringing the carboxyl group proximal to the —OH group and that this is a major factor in promoting the rapid lactonization. Since (II) is a reactive acid and was too unstable for X-ray diffraction analysis, the structure of the alcohol analog of (II) *i.e.* (III) and of the lactone (IV) were established (Karle & Karle, 1972). The O(1)···C(8) distance in the lactone (IV) is 2.42 Å as compared with 2.8 Å in (II) and 3.18 Å in (I).

The crystal packing is depicted in Fig. 2. The crystal structure is stabilized through intermolecular O—H···O hydrogen bonding. O(1) donates a proton to O(2) [O(1)···O(2) = 2.84 (1) Å, O(1)—H(O1)···O(2) = 176 (2)°, H(O1)···O(2) = 1.98 (3) Å] and O(2) accepts a proton from the O(3) atom of the inversion-symmetry-related molecule [O(2)···O(3) = 2.68 (1) Å, O(3)—H(O3)···O(2) = 170 (2)°, H(O3)···O(2) = 1.80 (3) Å]. Two other intermolecular contacts are observed, C(9)···O(1) = 3.39 (1) and C(9)···O(2) = 3.38 (1) Å.

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