Acta Cryst. (1983). C**39**, 910–912

γ-(2,3-Dimethylphenyl)-γ-butyrolactone,* $C_{12}H_{14}O_2$

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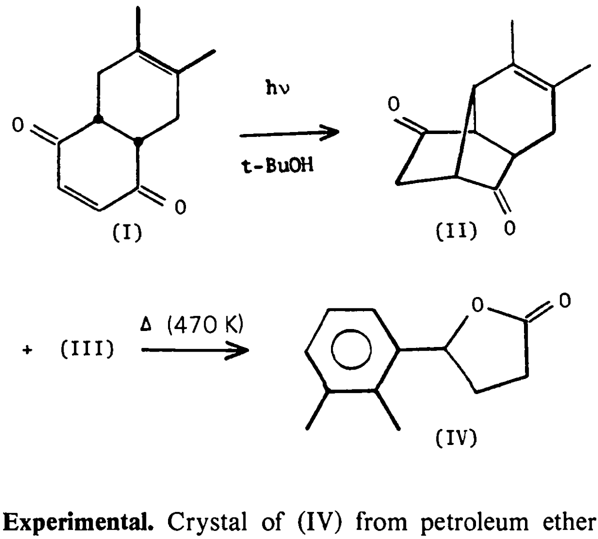
(*Received* 8 *September* 1982; *accepted* 8 *March* 1983)

Abstract. $M_r = 190{\cdot}24$, monoclinic, $P2_1/n$, $a = 10{\cdot}847\ (3)$, $b = 6{\cdot}924\ (1)$, $c = 13{\cdot}654\ (4)$ Å, $\beta = 95{\cdot}22\ (1)^\circ$, $V = 1021{\cdot}2\ (5)$ Å^3, $Z = 4$, $D_m = 1{\cdot}244$, $D_x = 1{\cdot}237$ g cm^{-3}, $T = 294$ K, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}47$ cm^{-1}, $F(000) = 408$, $R = 0{\cdot}057$ for 569 reflections. The lactone ring has a disordered envelope conformation with normal bond lengths and angles, and makes an angle of 70° with the phenyl ring.

Introduction. Further study of the photolysis of the dimethyltetrahydronaphthoquinone (I) has revealed the formation of the previously observed β-hydrogen abstraction product (II) (Scheffer, Bhandari, Gayler & Wostradowski, 1975), and in addition a new minor photoproduct (III) (Scheffer & Walsh, 1982). Chemical and spectroscopic data did not reveal the structure of (III) and crystals suitable for X-ray analysis could not be obtained. Thermolysis of (III) yielded a crystalline material, which is shown by the present X-ray study to be the γ-butyrolactone (IV).



Experimental. Crystal of (IV) from petroleum ether/ethanol bounded by six well-defined faces ±(102), ±(10$\bar{1}$) and ±(01$\bar{1}$), 0·14 × 0·04 × 0·06 mm, density by flotation; CAD-4 diffractometer, $0{\cdot}0 < \theta \leq 22{\cdot}5^\circ$ (graphite-monochromatized Mo $K\alpha$), ω–2θ scans, speeds 1·44 to 10·06° min^{-1}, ω-scan angle $(0{\cdot}90 + 0{\cdot}35\tan\theta)^\circ$ (extended by 25% on each side for background counts), horizontal aperture $(2{\cdot}00 + \tan\theta)$ mm, vertical aperture 4 mm; intensity-control reflections every 3600 s of X-ray exposure time (maximum decay 3·0%) and crystal-orientation check after every 100 reflections; cell parameters from sin θ values for 18 reflections ($\theta = 9$–16°); Lp but no absorption correction; 569 of the 1341 reflections collected had $I \geq 3\sigma(I)$, where $\sigma^2(I) = S + 2B + [0{\cdot}04(S - B)]^2$, S = scan count, B = time-averaged background. Direct methods, least-squares refinement on F, H atoms from a difference map, refined with isotropic temperature factors. Anomalies in the methylene groups, C(8) and C(9) (Fig. 1), indicated disorder (*cf.* Nowell, Rettig & Trotter, 1972), treated by use of two positions C(8)′ and C(8)″, occupancies 60:40; two half-hydrogen and two overlapping half-hydrogen peaks from a difference map, refined. $S = 3{\cdot}3$ when $w = 1/\sigma^2(F)$ (probably due to incomplete handling of the disorder); in the final cycle $w = (A + BF_o + CF_o^2 + DF_o^3)^{-1}$, $A = 0{\cdot}3957$, $B = 0{\cdot}00000$, $C = -0{\cdot}004568$ and $D = 0{\cdot}000384$ (constant averages of $w\Delta^2$ over ranges of F_o); mean and maximum [B of C(8)″] parameter shifts on the last cycle 0·23 and 1·20σ, respectively; scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965); computer programs include locally modified versions of the following: *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), *ORFLS* (Busing, Martin & Levy, 1962), *ORFFE* (Busing, Martin & Levy, 1964), *FORDAP* (A. Zalkin), and *ORTEP* II (Johnson, 1976). Final R value for 569 reflections with $I \geq 3\sigma(I)$ 0·057, R_w 0·065; for entire data set (1341 reflections) $R = 0{\cdot}141$ and $R_w = 0{\cdot}066$; difference-Fourier synthesis showed random fluctuations between 0·16 and −0·22 e Å^{-3}. A list of coordinates and temperature factors is given in Table 1.†

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* Alternative IUPAC name: 5-(2,3-dimethylphenyl)tetrahydro-2-furanone.

† Anisotropic thermal parameters, bond lengths and angles involving H atoms, torsion angles, packing diagram, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38465 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/83/070910-03$01.50

Table 1. *Final positional (fractional* $\times 10^4$, H $\times 10^3$) *and isotropic thermal parameters* ($U \times 10^3$ Å^2) *with estimated standard deviations in parentheses*

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

Primed (′) atoms are at 60% occupancy; doubly primed (″) atoms are at 40% occupancy; asterisks (*) denote atoms in calculated positions.

	x	y	z	U_{eq}/U_{iso}
C(1)	5386 (6)	−879 (7)	1867 (4)	71
C(2)	5493 (6)	813 (7)	1313 (4)	66
C(21)	4454 (11)	2262 (11)	1216 (8)	90
C(3)	6569 (7)	1174 (9)	854 (4)	74
C(31)	6724 (13)	2952 (12)	256 (7)	110
C(4)	7510 (8)	−167 (12)	944 (6)	89
C(5)	7437 (9)	−1804 (11)	1500 (6)	92
C(6)	6373 (9)	−2176 (10)	1939 (5)	87
C(7)	4233 (11)	−1263 (9)	2366 (7)	100
C(8)′	3958 (17)	−326 (17)	3301 (11)	76 (4)
C(8)″	4691 (20)	−464 (22)	3555 (12)	62 (4)
C(9)	4208 (7)	−1940 (10)	4050 (5)	102
C(10)	4101 (6)	−3764 (9)	3463 (6)	82
O(1)	3999 (5)	−5396 (7)	3737 (4)	121
O(2)	4078 (5)	−3332 (5)	2526 (4)	105
H1(21)	372 (7)	214 (10)	158 (5)	121 (31)
H2(21)	478 (7)	330 (12)	147 (6)	114 (31)
H3(21)	395 (11)	221 (14)	60 (9)	188 (49)
H1(31)	604 (7)	313 (11)	−26 (6)	120 (31)
H2(31)	742 (8)	327 (13)	−5 (7)	129 (38)
H3(31)	687 (7)	421 (12)	72 (6)	147 (27)
H(4)	820 (5)	3 (7)	68 (4)	61 (20)
H(5)	807 (7)	−280 (11)	157 (5)	106 (24)
H(6)	623 (6)	−317 (11)	236 (5)	104 (23)
H(7)	361 (6)	−86 (10)	189 (6)	98 (28)
H1(8)′	306 (9)	−32 (12)	348 (6)	77 (28)
H2(8)′ + H2(8)″	459 (7)	107 (12)	340 (5)	50 (22)
H1(8)″	547 (11)	−86 (15)	383 (7)	39 (30)
H1(9)*	496	−194	447	136
H2(9)*	353	−181	443	136

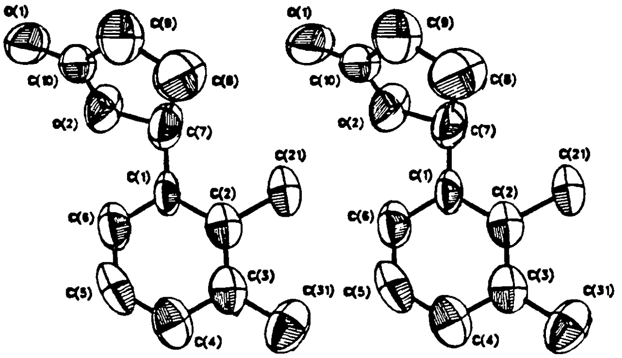

Fig. 1. Stereoview of the lactone.

Discussion. The structure of (IV) consists of a 2,3-dimethylphenyl substitutent bonded to the γ-carbon of a butyrolactone moiety. Considering only the gross conformation, the molecule may be described in terms of two ring systems, whose mean planes subtend a dihedral angle of 70° [Fig. 1, crystallographic numbering, C(8) drawn as one anisotropic atom]. A detailed description of the structure is prevented by the limited accuracy, in particular by the disorder, which was treated only for the atom most affected, C(8). Obviously other atoms of the lactone ring are affected to a lesser extent. Butyrolactone rings usually assume an envelope conformation (Jeffrey, Rosenstein & Vlasse, 1967; Harlow & Simonsen, 1976), in which the only atom deviating significantly from the plane of the remaining four is the β-carbon. The planarity of the remaining atoms in the ring stems from the carbonyl group and the partial sp^2 character of the hetero-oxygen atom. The results for the disordered ring of the present structure are consistent with an envelope conformation, with the β-carbon atom, C(8), out-of-plane, but possible smaller displacements of other atoms, particularly C(9), are obscured by the disorder.

Bond lengths and angles (Table 2) in the lactone ring are generally close to normal values (Harlow & Simonsen, 1976), except for those involving the lower occupancy C(8)″, which must be considered unreliable. In (IV) C(10)—O(2) and C(7)—O(2) differ significantly from each other, 1·31 (1) and 1·46 (1) Å, respectively, and the angles at C(10) exhibit the usual deviations from 120°. The phenyl group is close to planar with mean C—C 1·39 Å.

The molecules pack* with lactone rings back-to-back and almost parallel to (30$\bar{1}$), and phenyl rings are across centres of symmetry and parallel to (113) (both of the corresponding reflections have high E values). Packing forces are of van der Waals type.

The structure of (IV) seems quite unrelated to that of its precursor (I), but in fact a reasonable, though complex, mechanism can be proposed for its formation (Scheffer & Walsh, 1982). This mechanism is not, however, well enough established to allow a definitive statement on the structure of (III).

Table 2. *Bond lengths* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

C(1)–C(2)	1·405 (7)	C(7)–C(8)′	1·49 (2)
C(1)–C(6)	1·394 (9)	C(7)–C(8)″	1·74 (2)
C(1)–C(7)	1·502 (10)	C(7)–O(2)	1·461 (8)
C(2)–C(21)	1·505 (10)	C(8)′–C(9)	1·523 (15)
C(2)–C(3)	1·397 (8)	C(8)″–C(9)	1·357 (15)
C(3)–C(31)	1·496 (10)	C(9)–C(10)	1·495 (8)
C(3)–C(4)	1·377 (9)	C(10)–O(1)	1·199 (7)
C(4)–C(5)	1·371 (11)	C(10)–O(2)	1·312 (8)
C(5)–C(6)	1·372 (10)		
C(2)–C(1)–C(6)	118·3 (7)	C(1)–C(7)–O(2)	110·7 (6)
C(2)–C(1)–C(7)	120·3 (6)	[C(8)′–C(7)–C(8)″	28·9 (7)]
C(6)–C(1)–C(7)	121·3 (6)	C(8)′–C(7)–O(2)	105·4 (7)
C(1)–C(2)–C(21)	120·3 (7)	C(8)″–C(7)–O(2)	101·5 (8)
C(1)–C(2)–C(3)	120·2 (5)	C(7)–C(8)′–C(9)	102·7 (8)
C(21)–C(2)–C(3)	119·4 (7)	C(7)–C(8)″–C(9)	97·7 (10)
C(2)–C(3)–C(31)	122·2 (7)	[C(8)′–C(9)–C(8)″	33·5 (9)]
C(2)–C(3)–C(4)	118·9 (6)	C(8)′–C(9)–C(10)	105·0 (7)
C(31)–C(3)–C(4)	119·0 (8)	C(8)″–C(9)–C(10)	112·6 (8)
C(3)–C(4)–C(5)	121·8 (8)	C(9)–C(10)–O(1)	129·3 (7)
C(4)–C(5)–C(6)	119·3 (8)	C(9)–C(10)–O(2)	108·9 (5)
C(1)–C(6)–C(5)	121·3 (7)	O(1)–C(10)–O(2)	121·7 (6)
C(1)–C(7)–C(8)′	123·6 (11)	C(7)–O(2)–C(10)	112·1 (6)
C(1)–C(7)–C(8)″	100·8 (9)		

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* See previous footnote.

We thank the Natural Sciences and Engineering Research Council Canada for financial support, the University of British Columbia Computing Centre for assistance, and Dr J. R. Scheffer and L. Walsh for crystals and discussion.

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Acta Cryst. (1983). C**39**, 912–914

Structure of Piperazinium Succinate, $C_4H_4O_4^{2-}.C_4H_{12}N_2^{2+}$*

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(*Received* 25 *January* 1983; *accepted* 18 *February* 1983)

Abstract. $M_r = 204{\cdot}23$, triclinic, $P\bar{1}$, $a = 5{\cdot}8225$ (11), $b = 6{\cdot}0027$ (9), $c = 6{\cdot}8943$ (15) Å, $\alpha = 95{\cdot}06$ (2), $\beta = 99{\cdot}54$ (2), $\gamma = 93{\cdot}77$ (2)°, $V = 235{\cdot}91$ Å^3, $Z = 1$, $D_m = 1{\cdot}44$, $D_x = 1{\cdot}437$ Mg m^{-3}, λ(Cu $K\alpha$) = $1{\cdot}54178$ Å, $\mu = 0{\cdot}927$ mm^{-1}, $F(000) = 110$, $T = 293$ K. Final $R = 0{\cdot}037$ for 869 observed reflections. The structure consists of a completely planar succinate anion on a crystallographic center of symmetry and a piperazinium cation, in the chair conformation, also on a crystallographic center of symmetry. Each piperazinium cation forms four hydrogen bonds with four different succinate anions.

Introduction. The present study follows a report in which the densities and the melting points, in a series of piperazinium alkanedioates, were correlated to the parity of the number of C atoms in the alkanedioate chain (Vanier, 1982). The crystal structure of piperazinium glutarate, reported recently (Vanier & Brisse, 1982), revealed that the glutarate anion, with an odd number of C atoms, had a *gauche–trans* conformation. It is to find out if the above observed correlation may be linked to a structural differentiation that the structure determination of three alkanedioates, all having an even number of methylene groups, has been undertaken. We report here on the crystal structure of piperazinium succinate.

Experimental. Prepared by reaction between the diacid and a matched amount of piperazine in 2-propanol, recrystallization in dimethylformamide solution; D_m by flotation in chloroform/monochlorobenzene m.p. = 481 K; colorless thin platelets, $0{\cdot}08 \times 0{\cdot}10 \times 0{\cdot}58$ mm; Nonius CAD-4 diffractometer, graphite-monochromatized Cu $K\alpha$; intensity check every hour, orientation verified every 100 reflections using three standard reflections, largest intensity fluctuation: 2·1%; 973 unique reflections (hkl, $hk\bar{l}$, $h\bar{k}l$, $h\bar{k}\bar{l}$) with $2\theta \leq 150°$, 873 with $I \geq 1{\cdot}90\sigma(I)$, 100 unobserved; Lp correction, no absorption correction; direct methods (*MULTAN*, Main, Lessinger, Woolfson, Germain & Declercq, 1977); anisotropic full-matrix least-squares refinement based on F's; H(calculated) isotropic; final $R = 0{\cdot}037$ (four reflections given zero weight in last refinement cycle), $R_w = 0{\cdot}038$, $w = 1$, for all measured reflections $R = 0{\cdot}046$; maximum (shift/σ) = 1·0, average (shift/σ) = 0·2; final electron-density fluctuations $-0{\cdot}21$ to $+0{\cdot}26$ e Å^{-3}; scattering factors for O, N and C from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965); programs used in this work are modified versions of *NRC*-2 (data reduction), *NRC*-10 (bond distances and angles) and *NRC*-22 (mean planes) (Ahmed, Hall, Pippy & Huber, 1973), *FORDAP* (Fourier and Patterson maps, A. Zalkin), *NUCLS* (least-squares refinement, Doedens & Ibers, 1967), *MULTAN* (Main *et al.*, 1978), *ORTEP* (stereoviews, Johnson, 1965).

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[*] Structural Studies of Compounds with Aliphatic Chains. 8. For previous papers, see Vanier & Brisse (1982).

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