Table 3. *Distances* (Å) *of atoms from the least-squares plane of the five-membered ring with e.s.d.'s in parentheses*

$$-0{\cdot}8554X + 0{\cdot}4592Y - 0{\cdot}2397Z + 10{\cdot}4735 = 0.$$

C(1)	−0·029 (16)	C(4)	0·019 (14)
C(2)	0·039 (18)	N(1)	0·004 (12)
C(3)	−0·032 (16)		

five-membered ring confirm this delocalization which furthermore may explain the stability of such a compound. Indeed, isomerization of 2(*b*) is impossible (Ketari & Foucaud, 1978).

The interatomic distances and bond angles of the phenyl rings do not differ significantly from the expected values. Their mean values are 1·387 Å and 120° respectively. Indeed these five rings are coplanar within 0·018 Å. The closest intermolecular non-H atom contact of the structure is 3·33 Å. The shortest intermolecular O···H or N···H distance is 2·54 Å and is too long to be considered a hydrogen-bonding interaction. The packing of the molecules is thus determined by van der Waals forces.

We thank Dr Ketari and Professor A. Foucaud who suggested this work.

References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Ketari, R. & Foucaud, A. (1978). *Tetrahedron Lett.* **46**, 4515–4518.

Willis, B. T. M. & Pryor, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 101–102. Cambridge Univ. Press.

Acta Cryst. (1981). B**37**, 1462–1465

Structure of *trans*-3-(Diphenylmethylene)-4-morpholinocarbonyl-5-(*p*-nitrophenyl)tetrahydro-2-furanone

By John Aupers and Peter F. Lindley

Department of Crystallography, Birkbeck College, Malet Street, London WC1E 7HX, England

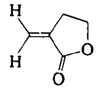
and Ahmet E. Baydar and Gerhard V. Boyd

Department of Chemistry, Chelsea College, Manresa Road, London SW3 6LX, England

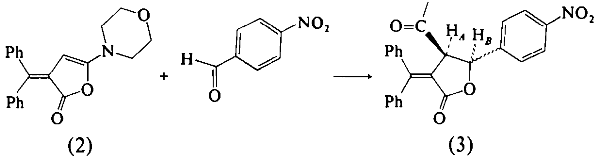
(*Received* 8 *January* 1981; *accepted* 17 *February* 1981)

Abstract. $C_{28}H_{24}N_2O_6$, orthorhombic, *Pbca*, a = 11·093 (2), b = 16·728 (4), c = 25·537 (6) Å, Z = 8, D_c = 1·36 Mg m^{-3}, μ(Cu $K\alpha$) = 0·805 mm^{-1}. The structure was solved by multisolution direct methods and refined by a full-matrix least-squares method to R = 0·049 for 2989 reflections. The compound formed by the 'acyl-ene' reaction between morpholinobutenolide and *p*-nitrobenzaldehyde has a *trans* configuration of protons across the C(4)–C(5) bond.

Introduction. The discovery that various naturally occurring sesquiterpene α-methylene-γ-lactones (1) possess tumour-inhibiting properties has stimulated the search for simpler lactones with physiological activity [for leading references see Kupchan, Hemingway, Werner & Karim (1969) and Lee, Ibuka, Kim, Vestal & Hall (1975)]. General syntheses of α-methylene-γ-lactones continue to be developed, one of which is the 'acyl-ene' reaction (Boyd, Monteil, Lindley & Mahmoud, 1978). An example of this is the formation of a mixture of the substituted *cis*- and *trans*-lactones (3) when the morpholinobutenolide (2) is treated with *p*-nitrobenzaldehyde (Baydar & Boyd, 1978). The isomers were separated by fractional crystallization



(1)



(2) (3)

© 1981 International Union of Crystallography

from ethanol–acetic acid. The minor, more soluble, component was tentatively assigned the *trans* configuration by applying the Karplus equation (Sternhell, 1969), since its ^{1}H NMR spectrum showed a lower coupling constant (J_{AB} = 7·0 Hz) of the methine protons H_A and H_B than that (J_{AB} = 7·3 Hz) of the other. As a contribution to our knowledge of α-methylene-γ-lactones we determined the exact geometry of one of these compounds and we now report on the X-ray structure of the *trans* isomer.

The compound forms colourless prismatic crystals (m.p. 537–538 K) elongated along the *c* axis. Preliminary cell dimensions and space-group information were obtained from precession photographs. Refined cell parameters were obtained by the least-squares refinement of the θ values of the Cu $K\alpha_1$ (λ = 1·5405 Å) components of 20 reflections measured on a Hilger & Watts Y290 automated four-circle diffractometer. Intensity data were also collected on this instrument using Ni-filtered Cu radiation and the $\omega/2\theta$ step-scanning technique. The scan width was 0·90°, using steps of 0·01° in ω with a count time of 1 s step^{-1}, plus a dispersion correction. Stationary background counts were taken at both ends of each scan for one-tenth of the scan time. Three reference reflections were measured after every 50 reflections and the reference-intensity sums were used to scale the observed intensities by interpolation between groups of references.

Table 1. *Positional parameters and equivalent isotropic thermal parameters*

	x	y	z	$\bar{U}$* (Å^2)
O(1)	−0·1496 (2)	0·5879 (1)	−0·0207 (1)	51
C(2)	−0·1150 (2)	0·5219 (1)	−0·0480 (1)	44
C(3)	−0·0398 (2)	0·5463 (1)	−0·0932 (1)	36
C(4)	−0·0091 (2)	0·6333 (1)	−0·0833 (1)	35
C(5)	−0·1189 (2)	0·6590 (1)	−0·0501 (1)	41
O(21)	−0·1398 (2)	0·4564 (1)	−0·0315 (1)	59
C(31)	−0·0062 (2)	0·5006 (1)	−0·1339 (1)	35
C(311)	0·0878 (2)	0·5297 (1)	−0·1708 (1)	39
C(312)	0·1969 (2)	0·5588 (1)	−0·1520 (1)	48
C(313)	0·2833 (3)	0·5871 (2)	−0·1866 (2)	69
C(314)	0·2609 (3)	0·5876 (2)	−0·2394 (2)	79
C(315)	0·1545 (4)	0·5577 (2)	−0·2587 (1)	77
C(316)	0·0682 (3)	0·5277 (2)	−0·2244 (1)	56
C(321)	−0·0624 (2)	0·4230 (1)	−0·1473 (1)	36
C(322)	0·0090 (2)	0·3602 (1)	−0·1651 (1)	45
C(323)	−0·0438 (3)	0·2883 (2)	−0·1801 (1)	54
C(324)	−0·1664 (3)	0·2791 (2)	−0·1783 (1)	59
C(325)	−0·2377 (3)	0·3409 (2)	−0·1611 (1)	58
C(326)	−0·1867 (2)	0·4128 (2)	−0·1458 (1)	50
C(41)	−0·0036 (2)	0·6851 (1)	−0·1323 (1)	34
O(42)	−0·0817 (2)	0·6774 (1)	−0·1657 (1)	47
N(43)	0·0833 (2)	0·7409 (1)	−0·1360 (1)	40
C(44)	0·1801 (2)	0·7578 (2)	−0·0989 (1)	50
C(45)	0·1855 (3)	0·8465 (2)	−0·0892 (1)	62
O(46)	0·2031 (2)	0·8887 (1)	−0·1364 (1)	70
C(47)	0·1075 (3)	0·8744 (2)	−0·1715 (1)	69
C(48)	0·0948 (3)	0·7871 (2)	−0·1842 (1)	57
C(51)	−0·0908 (2)	0·7276 (1)	−0·0140 (1)	38
C(52)	−0·0060 (3)	0·7195 (1)	0·0256 (1)	45
C(53)	0·0291 (3)	0·7855 (2)	0·0544 (1)	50
C(54)	−0·0218 (2)	0·8583 (2)	0·0434 (1)	46
C(55)	−0·1098 (3)	0·8679 (2)	0·0062 (1)	50
C(56)	−0·1431 (2)	0·8016 (2)	−0·0230 (1)	46
N(57)	0·0199 (3)	0·9284 (2)	0·0727 (1)	66
O(58)	0·1040 (3)	0·9202 (2)	0·1031 (1)	102
O(59)	−0·0302 (3)	0·9915 (2)	0·0654 (1)	112

* $\bar{U}$ is the spherical average of the three anisotropic thermal parameters U_{ii} (×10^3). Estimated standard deviations are less than 0·003 (Å^2).

Intensity data were collected for the hkl reflections over the range 0 ≤ θ ≤ 70° and for the $hk\bar{l}$ reflections over the range 0 ≤ θ ≤ 40°. Merging of the two sets of data gave 3827 independent reflections, of which 2989 had $I \geq 3\sigma(I)$ and were thereby classified as significant; the overall residual for the 748 reflections measured more than once was 0·7%. No correction was made for absorption.

The structure was solved using a weighted multisolution tangent-formula refinement (Germain, Main & Woolfson, 1974) and refined by the method of full-matrix least squares. Initially all atoms were treated isotropically using only the significant reflections to give an R value of 0·149. A difference Fourier synthesis revealed the H atoms as diffuse electron density maxima and in subsequent calculations these atoms were placed in calculated positions assuming a C—H bond length of 1·0 Å; no attempts were made to refine the positional or thermal parameters of the H atoms. Further refinement proceeded by a partial full-matrix technique in which all the non-hydrogen atoms were treated anisotropically but no more than 21 atoms were refined in any one cycle; an overall scale factor was refined in each cycle to give a maximum number of variable parameters of 190. A systematic examination of the strong low-angle reflections showed that $|F_o|$ was consistently smaller than $|F_c|$; an extinction coefficient, g, was refined in the expression $(1 + g|F_c'|)^{-1/2}$ to give a final value $g = 1{\cdot}26 \times 10^{-5}$, where $|F_c'|$ is the modulus of the uncorrected calculated structure factor. The refinement was terminated when all the positional-parameter shifts were less than half the corresponding estimated standard deviations to give a final R value of 0·049.* The weighting scheme $w = 7 \times 10^{-4}$ if $|F_o| \leq 100$ else $w = [1 - \exp(-20{\cdot}0 \times \sin^2\theta/\lambda^2)]/(100 + |F_o| + 10^{-5}|F_o|^2)$ was used to make the average values of $\sum w\Delta^2$ constant when analysed in terms of batches of increasing $|F_o|$ and $\sin\theta/\lambda$. A final difference Fourier synthesis revealed the correctness of the refinement and structure factor calculations for the

---

* Lists of structure factors, anisotropic thermal parameters, calculated H-atom positions, and least-squares-planes and torsion-angle data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36021 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

insignificant reflections revealed no outstanding discrepancies.

Throughout the structure factor calculations the atomic scattering factors listed by Hanson, Herman, Lee & Skillman (1964) were used and computations were performed on the IBM 360 computer at University College, London, and the CDC 6600 computer at the University of London Computer Centre. The final positional parameters of the non-hydrogen atoms are listed in Table 1.

Discussion. Fig. 1 is a stereodrawing of a molecule of the title compound viewed perpendicular to the lactone ring. The intramolecular bond lengths and angles together with the associated estimated standard deviations are shown in Fig. 2. Least-squares-planes and torsion-angle data have been deposited.*

The conformation of the lactone ring is given by the pseudorotational phase parameters (Altona, Geise & Romers, 1968), $\Delta = 7{\cdot}9°$ and $\varphi_m = 31{\cdot}9°$; the torsion angle C(3)–C(4)–C(5)–O(1) is taken as φ_0. These parameters indicate that the half-chair conformation in which C(4) and C(5) are displaced by 0·335 (4) and −0·193 (4) Å respectively out of the plane defined by O(1), C(2) and C(3) is dominant over the envelope conformation with C(4) at the apex. The compound is a *trans* adduct with respect to H(4) and H(5) and the torsion angle H(4)–C(4)–C(5)–H(5) is 159°. The geometry at C(3) is planar but the phenyl-ring carbon atoms C(311) and C(321) bonded to C(31) are displaced by 0·264 (5) and −0·316 (5) Å respectively out of the plane through C(2), C(3), C(4) and C(31); the dihedral angles between this plane and the phenyl rings are 56·1 (7)° for C(311) – C(316) inclusive and 52·1 (7)° for C(321) – C(326) inclusive. The configuration at C(31) and the opening out of the C(3)–C(2)–O(21) angle to 130·6 (2)° relative to the O(1)–C(2)–O(21) angle of 119·6 (2)° will mainly result from the steric effects of the bulky phenyl groups.

In the equatorial nitrophenyl group at C(5) the phenyl ring defined by C(51) – C(56) inclusive is planar and makes a dihedral angle of 78·5° with the plane defined by O(1), C(2) and C(3) in the lactone ring. However, the nitro group N(57), O(58) and O(59) is twisted with respect to the phenyl ring by 5·4 (5)°, thus minimizing repulsive forces between the O atoms and the *ortho* H atoms in the ring.

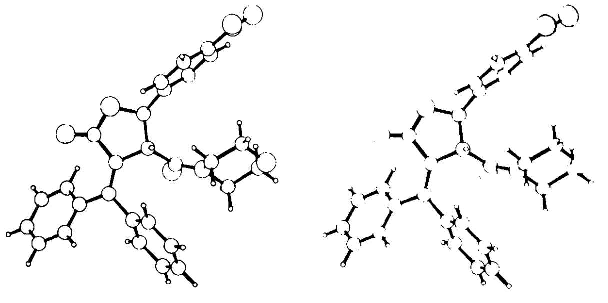


Fig. 1. A stereodrawing of the molecule of the title compound viewed perpendicular to the plane defined by the lactone-ring atoms O(1), C(2) and C(3).

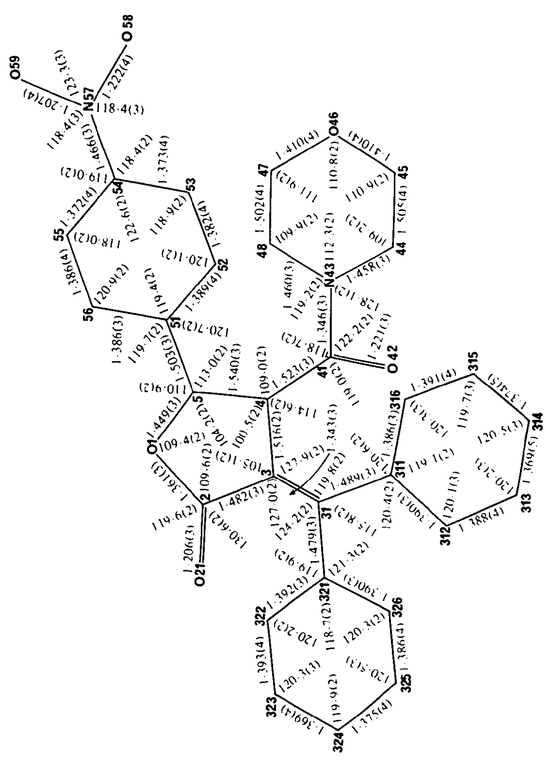


Fig. 2. A schematic drawing of the molecule showing the atom labelling and the intramolecular bond lengths (Å) and angles (°) with their associated estimated standard deviations.

The morpholinocarbonyl group at C(4) is also equatorial so that C(41) is synclinal with respect to C(51); the torsion angle C(41)–C(4)–C(5)–C(51) is −84·7 (6)°. The morpholino ring adopts the expected chair conformation in which N(43) and O(46) are displaced by −0·63 (1) and 0·67 (1) Å respectively out of the plane defined by C(44), C(45), C(47) and C(48); the asymmetry parameter (Duax & Norton, 1975) $\Delta_s^{N(43)} = 1{\cdot}96°$. The geometry in the vicinity of C(41) and N(43) is planar and the length of the C(41)–N(43) bond, 1·346 (3) Å, indicates considerable double-bond character. The opening out of the C(41)–N(43)–C(44) bond angle to 128·1 (2)° relative to the C(41)–N(43)–C(48) angle of 119·2 (2)° can be explained in terms of steric effects between O(42) and the C(44) methylene group.

There are no intermolecular separations that are significantly less than the sum of the corresponding van der Waals radii.

References

Altona, C., Geise, H. J. & Romers, C. (1968). *Tetrahedron*, **24**, 13–22.

Baydar, A. E. & Boyd, G. V. (1978). *J. Chem. Soc. Perkin Trans.* 1, pp. 1360–1366.

---

* See previous footnote.

Boyd, G. V., Monteil, R. L., Lindley, P. F. & Mahmoud, M. M. (1978). *J. Chem. Soc. Perkin Trans.* 1, pp. 1351–1360.

Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structure.* London and New York: Plenum.

Germain, G., Main, P. & Woolfson, M. M. (1974). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040–1044.

Kupchan, S. M., Hemingway, R. J., Werner, D. & Karim, A. (1969). *J. Org. Chem.* **34**, 3903–3908.

Lee, K.-H., Ibuka, T., Kim, S.-H., Vestal, B. R. & Hall, I. H. (1975). *J. Med. Chem.* **18**, 812–817.

Sternhell, S. (1969). *Q. Rev. Chem. Soc.* **23**, 236–270.

Acta Cryst. (1981). B**37**, 1465–1467

Methyl 1-Thio-β-D-galactopyranoside at 123 K

By A. Atkinson, J. R. Ruble and G. A. Jeffrey

Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260, USA

(*Received* 25 *September* 1980; *accepted* 17 *February* 1981)

Abstract. $C_7H_{14}O_5S$, orthorhombic, $P2_12_12_1$, at 123 K [293 K] a = 7·759 (4) [7·810 (2)], b = 8·952 (4) [9·010 (2)], c = 13·172 (5) [13·223 (4)] Å, V = 914·9 [930·4] Å^3, Z = 4, D_x = 1·524 [1·498] Mg m^{-3}, D_m = [1·494] Mg m^{-3}. The intensities of 3134 symmetry-independent reflections were measured with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·7107 Å), of which 2821 have $I > 2\sigma$. The structure was solved using *MULTAN* and refined anisotropically for the non-hydrogen atoms and isotropically for H atoms to R = 0·046, R_w = 0·049 by full-matrix least squares. The pyranose ring is a normal $^4C_1$ chair. The thioglycosidic torsion angle of −99° is larger than that observed in the methyl β-pyranosides. The ring C—O bond lengths are 1·429 (2) and 1·440 (2) Å. The C—S bond lengths are 1·806 (1) and 1·811 (3) Å. The hydrogen bonding consists of an infinite chain with a side-loop, which involves an intermolecular and two bifurcated interactions.

Introduction. Methyl 1-thio-β-D-galactopyranoside, from Sigma Chemical Co., was recrystallized from an ethanol–water solution at room temperature. A CAD-4 diffractometer was used for data collection with a crystal 0·72 × 0·48 × 0·24 mm, cut from a larger specimen. The unit-cell parameters were determined by a least-squares fit of $\sin^2\theta$ values for 34 reflections with 34° < 2θ < 48°. No corrections were made for absorption ($\mu_{\mathrm{Mo}K\alpha}$ = 0·53 mm^{-1}) or extinction. The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971) from 152 reflections with $|E| >$ 1·78. The 14 non-hydrogen atoms were revealed on the E map and refined isotropically to R = 0·09. The methylene H atoms were then placed at calculated positions and the remaining H atom positions were obtained from a difference map. C, O and S atomic parameters were refined anisotropically, and H atom parameters isotropically by full-matrix least squares (Busing, Martin & Levy, 1962) to final agreement factors of R = 0·046, R_w = 0·049, S = 1·66. H(4) and the methyl hydrogens H(71), H(72) and H(73) were poorly defined and their parameters were not refined. The function refined was $\sum w||F_o| - k|F_c||^2$, with $w^{-1} = \sigma_c^2$ from counting statistics. Only the strongest reflection, 013, appeared to be strongly affected by extinction, with $F_o = 0{\cdot}81F_c$. The atomic scattering factors used for C, O and S were those of Cromer & Waber (1965) and for H those of Stewart, Davidson & Simpson (1965). The atomic parameters are given in Table 1.* The atomic notation and thermal ellipsoids are shown in Fig. 1 and the molecular dimensions are given in Fig. 2. Fig. 3 gives a stereoview of the unit-cell contents.

Discussion. The pyranose ring has the normal $^4C_1$ conformation, with Cremer & Pople (1975) puckering parameters of Q = 0·598 Å, θ = 4·86°, φ = 16·4°. The thioglycosidic torsion angle, O(5)—C(1)—S—C(7), of −99·4 (2)° is larger than that in methyl β-galacto-

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35912 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/81/071465-03$01.00 © 1981 International Union of Crystallography