

4-Methylthio-2-phthalimido- γ -butyrolactone

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Abstract. $C_{13}H_{11}NO_4S$, monoclinic, $P2_1/c$, $a = 13.657$ (4), $b = 10.655$ (2), $c = 8.720$ (5) Å, $\beta = 95.28$ (2)°, $Z = 4$, $M_r = 277.29$, $V = 1263.5$ Å³, $D_c = 1.457$, $D_m = 1.45$ Mg m⁻³, $\lambda(Cu K\alpha) = 1.5418$ Å. The structure was solved with the aid of a direct-methods computer program (*MULTAN*) and refined to $R = 0.040$ for 1838 reflexions. The molecular conformation of the title compound may be described in terms of four planes: the phthalimido group, two planes of the γ -butyrolactone ring and the methylthio side chain. The phthalimido and methylthio planes make angles of 72.4 and 58.3° with respect to the main plane of the γ -butyrolactone ring. The γ -butyrolactone ring containing substituents in positions 2 and 4, *cis* to each other, has an envelope form with a folding angle of 29.0°.

Introduction. This work is part of a research program which we have undertaken in order to elucidate the crystal and molecular structures of different 2,4-disubstituted γ -butyrolactones.

The pyrolysis of 2-phthalimido-4-methylsulfinyl-4-methylthiobutyric acid (Štefanac, Deljac & Balenović, 1967) results in two substances. Both have the same chemical composition but different melting points, 453 K (title compound) and 438 K respectively.

The cell parameters were determined and refined from diffractometer data. The intensities were collected at room temperature on a Philips PW 1100 four-circle diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å) using a θ - 2θ scanning technique. 1886 independent reflections were measured within the range $13.2^\circ < 2\theta < 140.0^\circ$. Lorentz and polarization corrections were applied, but no absorption correction was made [$\mu(Cu K\alpha) = 2.323$ mm⁻¹].

The structure was solved by means of the *MULTAN* system of computer programs (Declercq, Germain, Main & Woolfson, 1973). 200 reflections with $|E| > 1.57$ and 2000 Σ_2 relationships were used in the phase-determining procedure. An *E* map computed

with the phases from the set with the highest combined figure of merit revealed peaks for the complete molecule except for one C atom from the six-membered ring. All non-hydrogen atoms were then refined isotropically and anisotropically by means of the full-matrix least-squares method using the XRAY 72 system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The function minimized was $\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$ where w was defined as $w = 1/\sigma^2(F_o)$. A subsequent difference synthesis revealed the

Table 1. Fractional atomic coordinates ($\times 10^4$, for H $\times 10^3$) and isotropic temperature factors ($\times 10^3$) with *e.s.d.*'s in parentheses

$$U_{eq} = \frac{1}{3}(U_1 + U_2 + U_3).$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U (Å ²)
S	4903 (1)	1502 (1)	681 (1)	59
C(1)	3736 (2)	1853 (5)	-355 (5)	72
C(2)	5342 (2)	3037 (2)	1177 (3)	42
C(3)	6343 (2)	2990 (3)	2081 (3)	48
C(4)	6826 (1)	4183 (2)	1558 (3)	39
C(5)	6338 (1)	4397 (2)	-52 (3)	40
C(6)	8429 (2)	3382 (2)	720 (3)	41
C(7)	9476 (1)	3671 (2)	1198 (3)	41
C(8)	10323 (2)	3202 (3)	654 (4)	55
C(9)	11213 (2)	3663 (3)	1323 (4)	60
C(10)	11250 (2)	4552 (3)	2470 (4)	58
C(11)	10398 (2)	5023 (3)	3017 (3)	51
C(12)	9515 (2)	4565 (2)	2349 (3)	41
C(13)	8491 (2)	4896 (2)	2638 (3)	42
O(1)	5491 (1)	3751 (2)	-225 (2)	41
O(2)	6610 (1)	5042 (2)	-1050 (2)	54
O(3)	8077 (1)	2634 (2)	-210 (2)	59
O(4)	8199 (1)	5630 (2)	3537 (3)	63
N	7889 (1)	4165 (2)	1610 (2)	39
H(C1)A	330 (3)	219 (5)	30 (6)	135 (18)
H(C1)B	349 (3)	109 (5)	-65 (5)	138 (19)
H(C1)C	381 (3)	245 (4)	-124 (5)	126 (17)
H(C2)	483 (2)	353 (2)	171 (3)	45 (7)
H(C3)A	629 (2)	297 (3)	318 (4)	56 (8)
H(C3)B	673 (2)	218 (3)	178 (3)	57 (8)
H(C4)	667 (2)	493 (2)	216 (3)	44 (7)
H(C8)	1027 (2)	259 (3)	-15 (4)	64 (9)
H(C9)	1182 (2)	334 (3)	92 (4)	70 (9)
H(C10)	1187 (2)	485 (3)	289 (3)	62 (8)
H(C11)	1043 (2)	568 (3)	386 (4)	62 (8)

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positions of the H atoms, which were then isotropically refined together with the anisotropic refinement of all the other non-hydrogen atoms. The refinement was terminated at $R = 0.040$ (corresponding $R_w = 0.059$) for 1838 reflexions with $I > 3\sigma(I)$; reflexions 100, 600 and 102 were not included in the refinement owing to the evident influence of secondary extinction.* Positional parameters and isotropic thermal parameters are in Table 1.

Discussion. The crystal structure of the title compound is built up from isolated molecules and the overall configuration is determined by a combination of intramolecular repulsion and crystal-packing factors. There is no interaction between the phthalimido and methylthio groups of different molecules. The molecular conformation (Fig. 1) is best described in terms of four planes: the phthalimido group, the γ -butyrolactone ring, which appears in this structure in two planes, and the methylthio side chain. The distances and angles within the phthalimido group (Figs. 2, 3) are very symmetrical and the group itself is almost planar within e.s.d.'s ($\sigma = 0.17$). The six-membered ring of the phthalimido group, with a mean value for the C—C bond lengths of 1.383 Å, is strictly planar.

The N atom is almost coplanar with C(6), C(13) and C(4), being only 0.024 Å out of their plane. The imido C(12)—C(13)(O4)—N and C(7)—C(6)(O3)—N groups centered on the sp^2 C(13) and C(6) carbon atoms are also planar within e.s.d.'s of 0.001 and 0.003 respectively. The γ -butyrolactone ring is defined by two planes, the main one formed by

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35721 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

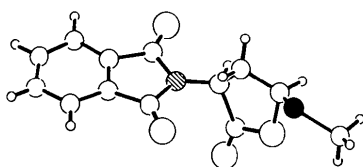


Fig. 1. A perspective view of the molecule.

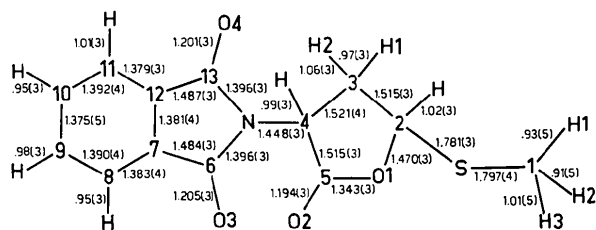


Fig. 2. Atom labeling scheme and bond distances (Å) with e.s.d.'s in parentheses.

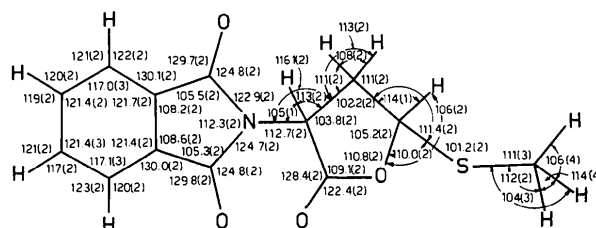


Fig. 3. Valence angles ($^\circ$) with e.s.d.'s in parentheses.

C(4)—C(5)(O2)—O(1)—C(2) and the other by C(2), C(3) and C(4). The ring may be considered as having an envelope form with a folding angle of 29.0° . C(3) is -0.462 Å out of the main γ -butyrolactone plane. These results are in good agreement with literature data (Bryan & Shen, 1978). The plane of the phthalimido group and the main plane through the γ -butyrolactone ring make angles of 49.6 and 58.3° , respectively, with the plane of the methylthio side chain, while the angle between the phthalimido group and the main plain through the γ -butyrolactone ring is 72.4° .

The γ -butyrolactone substituents are in positions 2 and 4 and are *cis* to each other according to the generally accepted opinion that the *cis* isomers are more stable than the corresponding *trans* isomers. The present structure analysis also confirms that the difference in free energies between the *cis* and *trans* isomers of the γ -butyrolactone envelope conformers is rather small as suggested by Hussain, Ollis, Smith & Stoddart (1975). All bond lengths and angles are within the expected values and agree well with those found in other γ -butyrolactone structures (Sikirica, Vicković & Viterbo, 1979).

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References

- BRYAN, R. F. & SHEN, M. S. (1978). *Acta Cryst.* B34, 327–329.
- DECLERCQ, J. P., GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1973). *Acta Cryst.* A29, 231–234.
- HUSSAIN, S. A. M. T., OLLIS, W. D., SMITH, C. & STODDART, J. F. (1975). *J. Chem. Soc. Perkin Trans.* 1, pp. 1480–1492.
- SIKIRICA, M., VICKOVIĆ, I. & VITERBO, D. (1979). *Acta Cryst.* B35, 1735–1737.
- ŠTEFANAC, Z., DELJAC, A. & BALENOVIĆ, K. (1967). *Bull. Sci. Cons. Acad. Sci. Arts RSF Yougosl. Sect. A*, 12, Nos. 11–12.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.