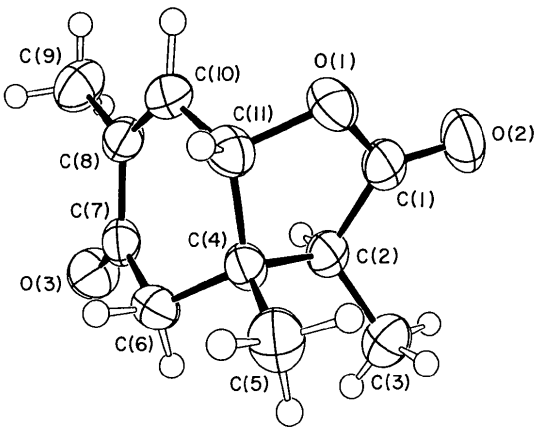

Fig. 1. Perspective drawing of the molecular structure of 3β,3aβ,6-trimethyl-3a,7aβ-dihydro-2(3*H*),5(4*H*)-benzo[*b*]furandione. The shapes of the ellipsoids of the C and O atoms correspond to 50% probability contours of atomic displacement.

chemistry was assigned on the basis of the revised structure (Norin, 1962; Cox, Koch, Whalley, Hursthouse & Rogers, 1967; Kulkarni, Eisenbraun & Marsh, 1968) of the precursor (−)-methylisopulegone.

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Structure of 3-(4-Bromophenyl)-5-*n*-butylglutaramic Acid

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Abstract. 3-(4-Bromophenyl)-5-(*n*-butylamino)-5-oxopentanoic acid, $C_{15}H_{20}BrNO_3$, $M_r = 342{\cdot}2$, monoclinic, $P2_1/c$, $a = 16{\cdot}000\ (5)$, $b = 8{\cdot}363\ (1)$, $c = 12{\cdot}713\ (9)$ Å, $\beta = 107{\cdot}55\ (5)°$, $V = 1622\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}401$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54184 Å, $\mu = 3{\cdot}527$ mm^{-1}, $F(000) = 704$, $T = 293$ K. Of the 3065 unique reflections, 1000 were observed with $F_o > 4\sigma(F_o)$ giving $R = 0{\cdot}066$. The bond distance N(1)—C(11) = 1·317 (14) Å and C(11)—O(3) = 1·259 (14) Å. The H atoms of the carboxyl group and of the amido linkage are located; they participate in the intermolecular hydrogen-bonding scheme, through hydrogen bonds N(1)—H(N1)···O(1), N···O = 2·968 (16) Å, and O(2)—H(O2)···O(3), O···O = 2·570 (11) Å.

Experimental. Colourless crystals from dilute ethanol; crystal of approximate dimensions 0·25 × 0·04 × 0·05 mm; Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54184$ Å) was used with a graphite-crystal monochromator on a Nonius CAD-4 single-crystal diffractometer. Unit-cell dimensions from the angular settings of 25 reflections with $18 < \theta < 37°$. The space group was determined from the systematic extinctions and the structure determination. The intensity data of 6219 reflections were measured (half a sphere up to $\theta = 58°$), using the ω–2θ scan technique, with a scan angle of 1·5° and a variable scan rate with a maximum scan time of 20 s per reflection. The maximum indices (*hkl*) were 19, 10 and 15, respectively. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 30 min. The final drift-correction factors were between 0·97 and 1·03. Profile analysis (Lehmann & Larsen, 1974; Grant & Gabe, 1978) was performed on all reflections. Lorentz and polarization corrections were applied and the data were reduced to F_o values. Symmetry-equivalent reflections were averaged, $R_{int} = \Sigma(|F_o - \langle F_o\rangle|)\Sigma F_o = 0{\cdot}129$ for all reflections and 0·026 for the observed reflections only, resulting in 3065 unique reflections of which 1000 were observed with $F_o > 4\sigma(F_o)$.

A *p*-bromotolyl skeleton (eight atoms) was input to the vector-search rotation-function program *ORIENT* (Beurskens, Beurskens, Strumpel &

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Nordman, 1987); the oriented fragment was positioned by the reciprocal-space translation-function program *TRACOR* (Beurskens, Gould, Bruins Slot & Bosman, 1987) and automatically expanded by *DIRDIF* (Beurskens, Bosman, Doesburg, van den Hark, Prick, Noordik, Beurskens, Gould & Parthasathi, 1983). Isotropic least-squares refinement using *SHELX* (Sheldrick, 1976) converged to $R = 0{\cdot}17$. At this stage an empirical absorption correction was applied (Walker & Stuart, 1983), resulting in a further decrease of R to 0·11. Relative absorption-correction factors were in the range 0·443–1·902.

The H atoms of the carboxyl group and of the amido linkage [N(O2) and N(N1), respectively], were found by a difference Fourier map; their positions were kept fixed and the isotropic temperature parameters were refined. The other H atoms, except for those of the methyl group [C(15)], were located on calculated positions with a C—H distance of 1·00 Å; they were allowed to ride on the parent atom, with isotropic temperature factors approximately equal to $U(\mathrm{C}) + 0{\cdot}005$ Å^2, where $U(\mathrm{C})$ is the isotropic equivalent of the parent C-atom temperature factor. [Because of the rather large temperature factors of the butyl chain, we carefully contoured a difference Fourier map but we could not trace any disorder in the chain; the H atoms of C(12), C(13) and C(14) were apparent in the map but those of C(15) were not.] The non-H atoms were refined with anisotropic temperature factors.

The final conventional agreement factors were $R = 0{\cdot}066$, $wR = 0{\cdot}082$ and $S = 1{\cdot}926$ for 1000 'observed' reflections and 183 variables. The function minimized was $w(F_o - |F_c|)^2$ with $w = 1/[\sigma^2(F_o) + 0{\cdot}002F_o^2]$ with $\sigma(F_o)$ from counting statistics. The maximum shift-over-e.s.d. ratio in the last full-matrix least-squares cycle was less than 0·052. The final difference Fourier map showed maximum peaks at 0·37 e Å^{-3} [in the neighbourhoods of Br and C(15)]. The scattering factors used were from *International Tables for X-ray Crystallography* (1974). Plots were made with *PLUTO* (Motherwell, 1976).

Final positional and thermal parameters are given in Table 1.* Bond lengths are collected in Table 2. A stereoview of the molecule, showing the molecular configuration, is given in Fig. 1. The crystallographic numbering scheme is shown in Fig. 2.

Related literature. The biological activity of thalidomide, glutarimide (De & Pal, 1975, 1977),

* Lists of structure factors, anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms, torsion angles, and geometrical and conformational parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51866 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional positional and thermal parameters with e.s.d.'s in parentheses*

The expression for the equivalent isotropic vibrational parameter is: $U_{eq} = \frac{1}{3}\sum_i\sum_j a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j U_{ij}$.

	x	y	z	$100U_{eq}$ (Å^2)
C(1)	0·1345 (7)	0·1441 (16)	0·2564 (9)	4·3 (5)
C(2)	0·2173 (7)	0·1119 (15)	0·2570 (9)	4·5 (5)
C(3)	0·2868 (6)	0·1331 (14)	0·3481 (9)	4·4 (5)
C(4)	0·2747 (6)	0·1892 (13)	0·4473 (9)	2·9 (4)
C(5)	0·1909 (7)	0·2232 (15)	0·4466 (9)	4·7 (5)
C(6)	0·1201 (7)	0·1997 (17)	0·3499 (13)	7·0 (6)
C(7)	0·3513 (6)	0·2133 (15)	0·5488 (9)	4·1 (5)
C(8)	0·4033 (7)	0·0575 (15)	0·5861 (9)	4·7 (5)
C(9)	0·4639 (8)	0·0678 (15)	0·6976 (10)	4·7 (6)
C(10)	0·4137 (6)	0·3454 (12)	0·5338 (9)	3·5 (5)
C(11)	0·3651 (7)	0·5038 (18)	0·5181 (12)	4·6 (5)
C(12)	0·2855 (9)	0·7046 (17)	0·3824 (14)	8·7 (8)
C(13)	0·1990 (10)	0·6711 (18)	0·3017 (15)	9·2 (8)
C(14)	0·1948 (14)	0·6035 (23)	0·1956 (18)	17·7 (12)
C(15)	0·1183 (16)	0·6129 (28)	0·1023 (15)	17·2 (12)
N(1)	0·3411 (6)	0·5590 (11)	0·4163 (9)	5·1 (5)
Br(1)	0·03772 (9)	0·11352 (24)	0·12982 (12)	8·64 (7)
O(1)	0·4399 (5)	0·0939 (12)	0·7797 (7)	7·1 (4)
O(2)	0·5466 (5)	0·0541 (10)	0·7056 (7)	5·8 (4)
O(3)	0·3480 (5)	0·5728 (10)	0·5972 (7)	5·7 (4)
H(N1)*	0·3589	0·4661	0·3523	12·0 (6)
H(O2)*	0·5665	0·1122	0·7821	11·0 (5)

* Atoms in fixed positions.

Table 2. *Selected bond lengths* (Å) *with e.s.d.'s in parentheses*

C(1)—C(2)	1·350 (15)	C(9)—O(1)	1·235 (13)
C(1)—C(6)	1·358 (17)	C(9)—O(2)	1·300 (14)
C(1)—Br(1)	1·884 (10)	C(10)—C(11)	1·519 (16)
C(2)—C(3)	1·353 (13)	C(11)—N(1)	1·317 (14)
C(3)—C(4)	1·413 (15)	C(11)—O(3)	1·259 (14)
C(4)—C(5)	1·369 (14)	C(12)—C(13)	1·480 (16)
C(4)—C(7)	1·501 (12)	C(12)—N(1)	1·492 (15)
C(5)—C(6)	1·412 (15)	C(13)—C(14)	1·446 (24)
C(7)—C(8)	1·542 (16)	C(14)—C(15)	1·427 (21)
C(7)—C(10)	1·539 (15)	N(1)—H(N1)	1·219 (10)
C(8)—C(9)	1·459 (13)	O(2)—H(O2)	1·047 (8)

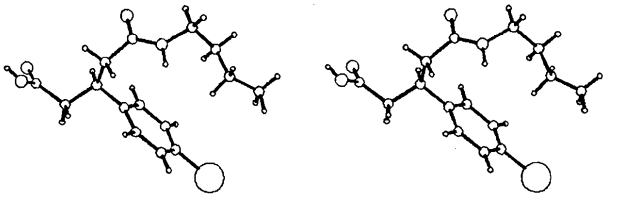

Fig. 1. Stereoview of the molecule showing the molecular configuration.

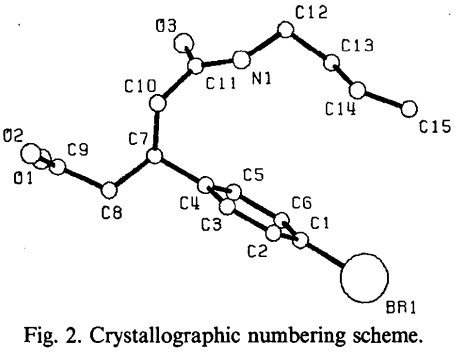

Fig. 2. Crystallographic numbering scheme.

glutaramide and glutamine analogs as possible antineoplastic agents is evident from their activities by way of glutamine and/or folic acid antagonism. Glutaramic acid analogs may be regarded as the precursors of glutaramides and may interfere with the biochemical and physiological functions of natural glutaramic acid and/or folic acid or their derivatives by taking their place or by blocking the enzymes or coenzymes involved in their metabolism (Debnath, Jha, Majumdar & De, 1987). The X-ray structural information gained from a study of 3-(4-bromophenyl)-5-*n*-butylglutaramic acid may help to reveal the effects of different substituents on antineoplastic activity. The bond distance C(1)—Br(1) = 1·884 (10) Å is quite close to the value of 1·911 Å obtained by Kosuge, Tsuji & Hirai (1981). The deviation of the Br(1) atom from the least-squares plane through the benzenoid ring [C(1)—C(6)] is −0·017 Å. Some intramolecular contacts are O(1)···O(2), 2·209 (13) and C(12)···O(3), 2·833 (18) Å [with an O···H contact of 2·41 (17) Å]. The molecules are linked through hydrogen bonds: N(1)—H(N1)···O(1), N···O = 2·968 (16) Å and O(2)—H(O2)···O(3), O···O = 2·570 (11) Å.

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Structure of N^2-*p*-Bromophenyl-N^1-methyl-N^1-phenylbenzamidine

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Abstract. $C_{20}H_{17}BrN_2$, $M_r = 365{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}267$ (1), $b = 12{\cdot}312$ (1), $c = 15{\cdot}392$ (1) Å, $V = 1754{\cdot}6$ (6) Å^3, $Z = 4$, $D_m = 1{\cdot}36$, $D_x = 1{\cdot}38$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ(Cu $K\alpha$) = 2·9 mm^{-1}, $F(000) = 744$, room temperature, $R = 0{\cdot}027$ for 1248 observed reflexions. Crystals of the title compound are isostructural with those of N^1-methyl-N^1-phenyl-N^2-(*p*-tolyl)benzamidine [Oszczapowicz, Tykarska, Jaskólski & Kosturkiewicz (1986). *Acta Cryst.* C**42**, 1816–1818], which suggests that a Br atom exerts the same steric effect as a methyl group, and which confirms the stereochemical similarity between these two molecules. In both molecules the phenyl rings are situated on one side of the amidine moiety while the other side is occupied by the methyl group alone, and the configuration around the double bond C—N^2 is *trans* (*E*). The steric hindrance is primarily relaxed by twisting of the phenyl substituents at N^1, $C_{amidine}$ and N^2 relative to the central amidine plane by 62·2 (5), 60·6 (5) and 71·1 (5)°, respectively. Two C—N bonds in the amidine moiety differ in length [1·359 (5) and 1·291 (5) Å for C—N^1 and C—N^2, respectively] and the N^1—C—N^2 angle is 118·9 (3)°. These values are similar to those found in the *p*-tolyl derivative.

Experimental. The title compound was synthesized by Oszczapowicz, Raczyńska & Orliński (1981).

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