nettement plus de l'enveloppe pure ($\Delta = 36°$; Altona, Geise & Romers, 1968).

Le Tableau 4 montre les distances intermoléculaires les plus courtes. L'édifice cristallin est uniquement assuré par des liaisons de van der Waals dont les deux plus fortes font intervenir la molécule d'acétone.

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Structure of 5,5-Diallyl-1-(*p*-bromophenyl)barbituric Acid

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Abstract. $C_{16}H_{15}BrN_2O_3$, $M_r = 363{\cdot}3$, monoclinic, $P2_1/c$, $a = 11{\cdot}338$ (2), $b = 17{\cdot}688$ (3), $c = 7{\cdot}899$ (1) Å, $\beta = 92{\cdot}78$ (1)°, $Z = 4$, $D_m = 1{\cdot}52$, $D_c = 1{\cdot}52$ Mg m^{-3}, $V = 1582{\cdot}3$ Å^3, μ(Cu $K\alpha$) = 4·0 mm^{-1}. The structure was solved by Patterson and Fourier methods and refined to $R = 0{\cdot}050$. The pyrimidine ring is not planar. The dihedral angle between the pyrimidine and phenyl rings is 107·3°. The molecules are centrosymmetrically linked together by N—H···O [2·877 (5) Å] hydrogen bonds to form dimers.

Introduction. We present the structure of the title compound as part of the studies on the factors responsible for the easy isomerization of 5-allyl-*N*-aryl-5-(β-hydroxypropyl)barbituric acids.

The easy isomerization of 5-(β-hydroxypropyl)-barbituric acid substituted with a phenyl group at N(1) might be explained by the electron-acceptor character of this group. However, it was further found that *para* substitution of an electron-donor group into the aromatic ring has practically no influence on the isomerization rate, which consequently indicated that there is little or no conjugation between the aromatic ring and the lone electron pair at the N atom. These results led to the hypothesis that the easy isomerization is a consequence of the steric inhibition of the resonance within the barbituric ring.

It was thus expected that the barbituric ring in 5,5-diallyl-1-(*p*-bromophenyl)barbituric acid should be non-planar and that the plane of the phenyl group should be nearly perpendicular to it (Bobrański, Michniak, Przytocka & Wagner, 1971).

An X-ray analysis of the title compound has been undertaken to prove this hypothesis and to compare the results with some already solved derivatives of 5,5-diallylbarbituric acid.

Single crystals were grown by cooling a hot methanol solution of the compound. Precession photographs showed the space group to be $P2_1/c$. Cell parameters for use in the intensity-data collection were calculated by a least-squares analysis of the angular settings of 15 counter reflexions. 2356 unique intensity data with $2\theta \leq 114°$ were collected for a crystal with dimensions 0·3 × 0·35 × 0·4 mm on a Syntex $P2_1$ diffractometer by the use of graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54178$ Å), the θ–2θ scan technique and a variable scan rate. 2150 reflexions with $I \geq 1{\cdot}96\sigma(I)$ were included in the calculations. The data were corrected for Lorentz and polarization effects, but not for absorption. Extinction corrections were also neglected; instead, the two most intense reflexions (130 and 141) judged to suffer seriously from this effect were excluded from the final stages of refinement.

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The Br atom was located from the Patterson map and a Fourier synthesis based on its contribution revealed the positions of all non-hydrogen atoms. Refinement of the trial structure was carried out with a full-matrix least-squares method. Coordinates of all the H atoms were obtained from a difference Fourier map which was calculated at the final stage of refinement. The H atoms were assigned B values of 4·5 Å^2 and their parameters were included in the structure factor calculation, but they were not refined. The full-matrix least-squares refinement was considered converged when all the shift/σ values for positional parameters were less than 0·03. The final $R = 0{\cdot}050$, and $R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2} = 0{\cdot}059$. In the least-squares refinement, the function $\sum w(F_o - F_c)^2$ was minimized, where $w = (F_o/F_{low})^2$ if $|F_o| < F_{low}$, $w = 1$ if $F_{low} \leq |F_o| \leq F_{high}$, $w = (F_{high}/F_o)^2$ if $|F_o| > F_{high}$, with $F_{low} = 8$ and $F_{high} = 35$.

Table 1. *Final fractional atomic coordinates* ($\times 10^4$, $\times 10^3$ *for* H *atoms*) *and* B_{eq} (Å^2) *for non-hydrogen atoms*

B_{iso} for all H atoms is 4·5 Å^2.

	x	y	z	B_{eq}
Br	8159 (1)	7739 (1)	−44 (1)	4·01 (1)
C(1)	4457 (4)	8694 (3)	991 (5)	1·9 (1)
C(2)	4551 (4)	7993 (3)	252 (6)	2·5 (1)
C(3)	5661 (5)	7698 (3)	−82 (7)	3·1 (1)
C(4)	6643 (4)	8120 (3)	399 (6)	2·5 (1)
C(5)	6555 (4)	8822 (3)	1145 (6)	2·8 (1)
C(6)	5451 (4)	9115 (3)	1428 (6)	2·5 (1)
C(7)	2995 (4)	8979 (2)	3041 (6)	1·9 (1)
C(8)	1167 (4)	8837 (3)	4634 (6)	2·9 (1)
C(9)	732 (5)	8157 (4)	3728 (7)	3·9 (2)
C(10)	1089 (9)	7466 (4)	3962 (9)	5·2 (2)
C(11)	1864 (4)	9377 (3)	3509 (5)	2·1 (1)
C(12)	2601 (4)	9273 (3)	25 (6)	2·0 (1)
C(13)	1084 (4)	9624 (3)	2013 (6)	2·2 (1)
C(14)	2249 (4)	10103 (3)	4520 (6)	3·0 (1)
C(15)	2886 (6)	10666 (3)	3511 (7)	3·8 (2)
C(16)	4012 (6)	10809 (3)	3629 (8)	4·5 (2)
N(1)	3311 (3)	8991 (2)	1367 (4)	1·8 (1)
N(2)	1509 (3)	9552 (2)	442 (4)	2·2 (1)
O(1)	2896 (3)	9276 (2)	−1412 (4)	3·2 (1)
O(2)	3636 (3)	8686 (2)	4126 (4)	2·8 (1)
O(3)	104 (3)	9887 (2)	2187 (4)	3·5 (1)
H(21)	390	770	6	
H(31)	579	721	−68	
H(51)	720	917	135	
H(61)	535	966	182	
H(20)	107	976	−37	
H(81)	55	912	509	
H(82)	165	870	571	
H(91)	15	828	311	
H(101)	73	691	340	
H(102)	141	741	480	
H(141)	277	996	556	
H(142)	170	33	492	
H(151)	250	1077	269	
H(161)	448	1058	446	
H(162)	445	1112	271	

All calculations were carried out using original (*Syntex XTL Operation Manual*, 1973) and locally modified *XTL* structure determination programs on a Nova minicomputer.

Final positional parameters are given in Table 1.*

Discussion. Geometrical aspects of the structure are summarized in Figs. 1 and 2 and in Table 2. The bond lengths and angles in the oxopyrimidine ring are similar to those found in other barbiturates (Craven, Cusatis, Gartland & Vizzini, 1973). Asymmetry in substitution and in hydrogen bonding [O(3) is hydrogen bonded but O(2) is not] with respect to the C(11)···C(12) line induces small differences in bond lengths and angles between corresponding values. The greatest difference (0·029 Å) occurs for N(1)–C(7) (elongated by steric hindrance) and its equivalent N(2)–C(13) [shortened due to acceptance of a hydrogen bond by O(3) associated with C(13)]. The former effect is also accompanied by a decrease of the internal ring angle C(12)–N(1)–C(7), which is 3·2° less than the corresponding angle C(12)–N(2)–C(13).

The bond lengths next to C(11) in the aliphatic chains are slightly elongated, probably by steric stress, whereas the terminal bonds are shortened by high thermal motion. A similar trend has been noted in other 5,5-diallylbarbituric acid derivatives (Dideberg, Dupont & Pyżalska, 1975; Dupont, Dideberg & Pyżalska, 1974; Escobar, 1975).

The average bond length of 1·383 (7) Å in the aromatic ring agrees at the 2σ level with the literature value of 1·395 (3) Å (Bowen, 1958). The C(4)–Br bond length, 1·894 (5) Å, is consistent with the value found in other *para*-substituted bromobenzenes (Sutton, 1965). The N(1)–C(1) bond distance [1·445 (5) Å] between the pyrimidine and phenyl rings differs significantly from those found in 5,5-diallyl-1-cyclohexylbarbituric acid [1·496 (5) Å] and in 5,5-diallyl-1,3-dicyclohexylbarbituric acid [1·489 (4) Å], indicating some conjugation between the N lone pair and the phenyl group.

The χ^2 test used as a measure of planarity showed that the pyrimidine ring is not planar. The torsion angles (Fig. 2) and the deviations of atoms from the least-squares planes (Table 2) describe its conformation. The displacements of C(7) and C(11) from the least-squares plane through N(1), C(12), N(2), C(13) are 0·056 (4) and −0·084 (5) Å, respectively. The pseudo twofold axis (which is characteristic of a half-chair conformation) is indicated by the small magnitude of the $\Delta C_2^{2,12} = 0{\cdot}14$ asymmetry parameter (Duax & Norton, 1975).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35121 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The phenyl ring forms an angle of 107·3° with the least-squares plane of the pyrimidine ring.

Comparison with non-substituted barbituric acids shows that the substitution at the N atom causes strain, changing the symmetry and conformation of the oxopyrimidine ring. In monosubstituted derivatives the dominant symmetry (*i.e.* the symmetry having the lowest asymmetry-parameter value) in the ring is located about a line joining the mid-points of the N(2)—C(12) and C(7)—C(11) bonds, in contrast to the symmetry located along C(11)···C(12) dominating in the non-substituted or symmetrically substituted cases. These geometrical and conformational variations indicate a change in the resonance of the barbituric ring that must influence the isomerization potential of the 5-allyl-5-(β-hydroxypropyl)barbituric acid derivatives (Bobrański & Matczak, 1975). In order to assess the influence of the individual variations in the oxopyrimidine ring geometry and conformation on the isomerization rate of appropriate derivatives, the HOMA indexes of aromaticity (Kruszewski & Krygowski, 1972; Krygowski & Kruszewski, 1973) based on bond lengths have been calculated and compared. They are: 0·347, 0·340, 0·328 and 0·318 for 5,5-diallylbarbituric acid (I), 5,5-diallyl-1,3-dicyclohexylbarbituric acid (II), 5,5-diallyl-1-(*p*-bromophenyl)barbituric acid (III) and 5,5-diallyl-1-cyclohexylbarbituric acid (IV), respectively. These results indicate that the isomerization rate depends on

Table 2. *Weighted mean planes*

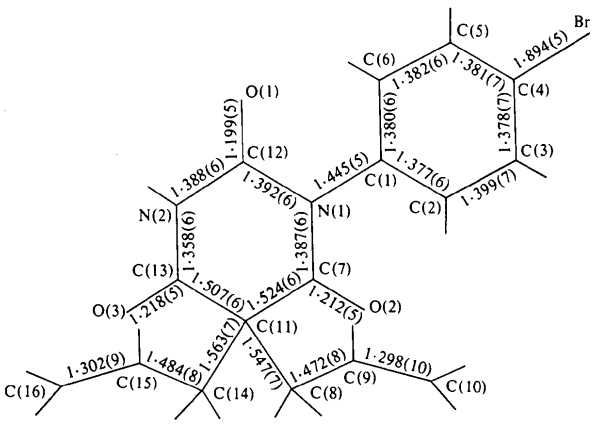
Plane (1): [N(1),C(12),N(2),C(13),C(11),C(7)]

$-0{\cdot}4273x - 0{\cdot}8985y - 0{\cdot}1002z + 15{\cdot}96 = 0, \chi^2 = 470{\cdot}9$

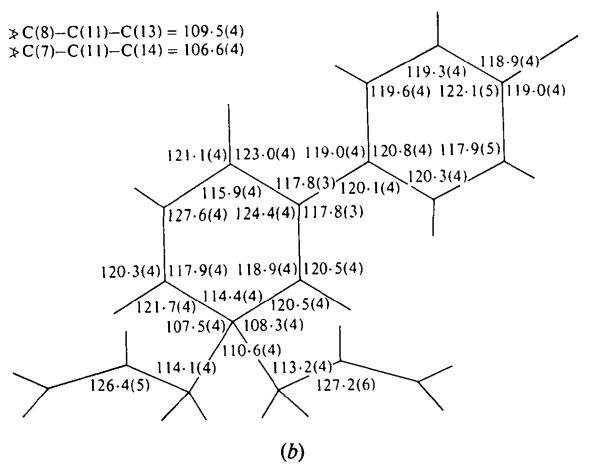
Plane (2): [N(1),C(12),N(2),C(13)]

$-0{\cdot}4126x - 0{\cdot}9043y - 0{\cdot}1097z + 16{\cdot}03 = 0, \chi^2 = 47{\cdot}8$

	Deviation (Å) from plane (1)	Deviation (Å) from plane (2)
N(1)	−0·012 (3)	0·008 (3)
C(12)	−0·033 (4)	−0·017 (4)
N(2)	0·027 (4)	0·018 (4)
C(13)	0·020 (5)	−0·009 (5)
C(11)	−0·059 (5)	−0·084 (5)
C(7)	0·056 (4)	0·056 (4)
O(1)	−0·090 (4)	
O(2)	0·142 (3)	
O(3)	0·066 (4)	



(*a*)



(*b*)

Fig. 1. (*a*) Bond lengths (Å) and (*b*) bond angles (°) involving the non-hydrogen atoms.

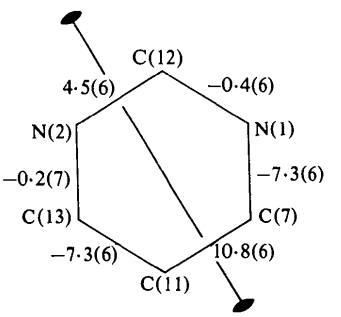


Fig. 2. Torsion angles (°) for the pyrimidine ring.

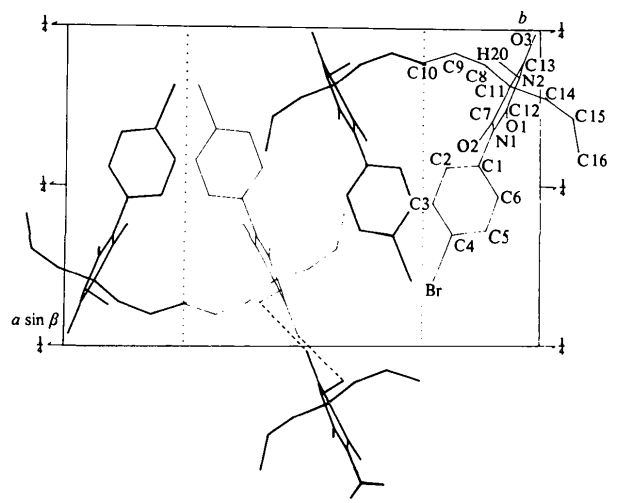


Fig. 3. The (001) projection showing the packing of the molecules.

the aromaticity of the oxopyrimidine ring. Experiments have shown that only (III) and (IV) undergo isomerization (Bobrański, 1977), which means that substantial differences in the isomerization rate are due to small changes in the aromaticity of the oxopyrimidine ring. The greater value of HOMA for (III) than for (IV) shows that a cyclohexyl substituent crowds the adjacent carbamido groups more than a *p*-bromophenyl group does and that it also has a stronger influence on the oxopyrimidine-ring conformation and resonance.

It is worth noting that the *p*-bromophenyl group in (III) is not only a hindrance, but that it is also partially conjugated with the lone pair at N(1). This is evident from the shortening of the N(1)–C(1) bond. However, as can be seen from a comparison of the HOMA indexes for compounds (III) and (IV), this conjugation influences the oxopyrimidine-ring resonance much less than the *p*-bromophenyl-group steric effect.

The molecules are hydrogen bonded into dimers across centers of symmetry. The N(2)–H(20)···O(3^{i}) hydrogen bond is characterized by the following parameters: N(2)···O(3^{i}) = 2·877 (5), N(2)–H(20) = 0·874, H(20)···O(3^{i}) = 2·010 Å; N(2)–H(20)–O(3) = 171·2°. The symmetry operation relating O(3) to O(3^{i}) is $-x$, $2-y$, $-z$. The packing of the molecules in the unit cell is shown in Fig. 3.

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(±)-*erythro*-Methyl 3-*tert*-Butoxy-2-iodo-3-(*p*-methoxyphenyl)propionate

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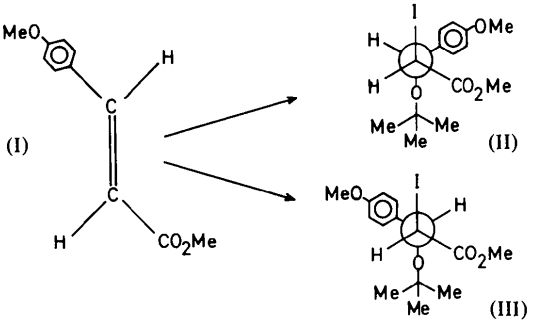
Abstract. $C_{15}H_{21}IO_4$, triclinic, $P\bar{1}$, $a = 8{\cdot}49\ (1)$, $b = 10{\cdot}07\ (1)$, $c = 10{\cdot}94\ (1)$ Å, $\alpha = 113{\cdot}36\ (5)$, $\beta = 101{\cdot}23\ (5)$, $\gamma = 83{\cdot}45\ (5)°$, $V = 841{\cdot}3$ Å^3, $M_r = 392{\cdot}2$, $Z = 2$, $D_c = 1{\cdot}548$, $D_m = 1{\cdot}46$ Mg m^{-3} (flotation in aqueous KI); μ(Mo $K\alpha$) = 0·177 mm^{-1}. The compound, synthesized by the ionic addition of *tert*-butyl hypoiodite to (*E*)-methyl *p*-methoxycinnamate, is in the *erythro* form. This establishes the mode of addition to the olefin as *trans*.

Introduction. The aim of this analysis was to determine the mode of ionic addition of *tert*-butyl hypoiodite (Bu^{t}OI) to the olefin (*E*)-methyl *p*-methoxycinnamate (I). The scheme below illustrates the two alternative configurations, *threo* (II) or *erythro* (III), expected on the basis of *cis* or *trans* addition respectively.



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