

THE DETERMINATION OF THE CRYSTAL STRUCTURE OF
1,5-DIPHENYLTRICYCLO[2.1.0.0^{2,5}]PENT-3-YL

p-BROMOBENZOATE

BY X-RAY DIFFRACTION

by

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required standard.

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ABSTRACT

The crystal structure of 1,5-diphenyltricyclo[2.1.0.0^{2,5}]pent-3-yl p-bromobenzoate has been determined by X-ray diffraction. The crystals are triclinic, $a = 5.92$, $b = 8.98$, $c = 17.85$ Å, $\alpha = 89^\circ 17'$, $\beta = 82^\circ 46'$, $\gamma = 89^\circ 50'$, $Z = 2$, space group $P\bar{1}$. The structure was determined with visual Cu-K α data by heavy atom Patterson and Fourier methods, and the positional and thermal parameters were refined by least-squares, the final discrepancy index R , being 0.16 for 1228 observed reflections.

The tricyclopentane system is highly strained, with six C-C-C angles of 60° , three of 80° , and four of 90° , and an intramolecular non-bonded C...C distance of 1.99 Å. The C-C bond lengths are similar to those of normal single bonds, except for the bond common to the two three-membered rings, which may possibly be slightly shorter than the others.

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ACKNOWLEDGMENTS

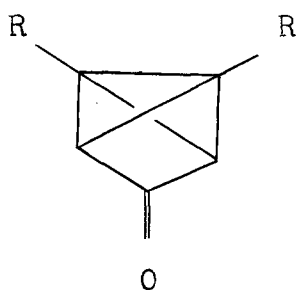
I would like to express my appreciation for the guidance and encouragement given to me by Dr. J. Trotter during the progress of this work.

I also want to thank Dr. S. Masamune for the crystal sample of the tricyclopentane derivative which he has provided.

INTRODUCTION

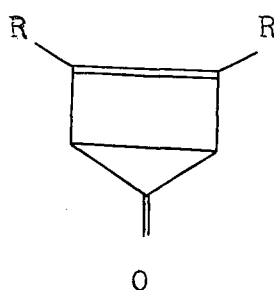
In recent years, polyhedranes have been the subject of much study by theoreticians, who have attempted to interpret the nature of bonding in such compounds, as well as by organic chemists, who have attempted to synthesize them.

One of the first successful preparations of the tricyclopentane system was carried out by Masamune (1), who by photolysis of 1,2-diphenyl-3-diazomethylketocyclopropene, obtained as product 1,5-diphenyltricyclo[2.1.0.0^{2,5}]pentanone-3* (I). This product was identified on the basis of chemical analysis, infra-red spectra, and nuclear magnetic resonance. Shortly thereafter, Doering and Pomerantz (3), using a copper catalyst instead of photolysis, prepared the dimethyl analogue, which was characterized by the same methods. However, they cast doubt on the structure of their compound as well as Masamune's by suggesting an alternative structure (II) which could fit the data equally well. The information available at that time was insufficient to distinguish between the two.



O

I



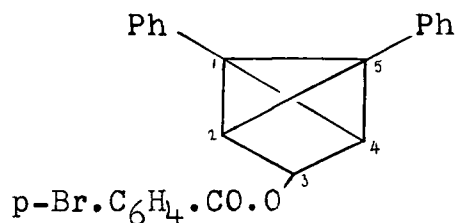
O

II

R = Ph, Me.

* The name first used for this compound, 4,5-diphenyltricyclo[1.1.1.0^{4,5}]pentanone-2, is rather arbitrarily based on the view that the compound is derived from bicyclo[1.1.1]pentane. However, Meinwald and Crandall (2) have pointed out that according to I.U.P.A.C. rules, the ring system should be named as it appears in the text above.

The interpretation of spectra could not be carried out satisfactorily, nor could the unusual chemical properties of this compound be explained without first resolving this controversy. Therefore an X-ray structure analysis of a heavy atom derivative, 1,5-diphenyltricyclo[2.1.0.0^{2,5}]pent-3-yl p-bromobenzoate (III) was undertaken to resolve this difficulty, and to obtain details of the geometry of the ring system.



III

EXPERIMENTAL

Crystals of 1,5-diphenyltricyclo[2.1.0.0^{2,5}]pent-3-yl p-bromobenzoate (III) are colorless plates elongated along a, with (001) developed, and smaller (010) faces. The density was measured by flotation in aqueous potassium iodide, and the unit cell dimensions were determined from rotation, Weissenberg, and precession photographs.

Crystal Data (λ , Cu-K $_{\alpha}$ = 1.5418 Å; λ , Mo-K $_{\alpha}$ = 0.7107 Å).

1,5-Diphenyltricyclo[2.1.0.0^{2,5}]pent-3-yl p-bromobenzoate,

C₂₄H₁₇BrO₂; mol. wt. = 417.3; m.p. = 139°.

Triclinic, a = 5.92, b = 8.98, c = 17.85 Å,

α = 89°17', β = 82°46', γ = 89°50'.

Volume of unit cell, V = 941.3 Å³.

D_x (Z = 2) = 1.47 g.cm.⁻³.

D_m = 1.43 g.cm.⁻³.

Absorption coefficient for Cu-K $_{\alpha}$ X-rays, λ = 1.5418 Å,

μ = 34 cm.⁻¹.

Absorption coefficient for Mo-K $_{\alpha}$ X-rays, λ = 0.7107 Å,

μ = 23 cm.⁻¹.

Total number of electrons per unit cell, F(000) = 424.

No absent reflections. Space group is P1 (C₁¹) or

P $\bar{1}$ (C₁¹); P $\bar{1}$ from structure analysis.

The intensities of the reflections were recorded with Cu-K $_{\alpha}$ radiation (Ni filter) on hkl equi-inclination Weissenberg films (h = 0—5), and estimated visually using the multiple film technique. The layers were scaled, and the data

supplemented from $h0\ell$ and $hk0$ precession films (Mo- K_{α} ; Zr filter). The crystal used had cross-section 0.19 x 0.13 mm., and no absorption correction was made. Lorentz and polarization factors were applied, and the structure amplitudes were derived for the 1228 observed reflections.

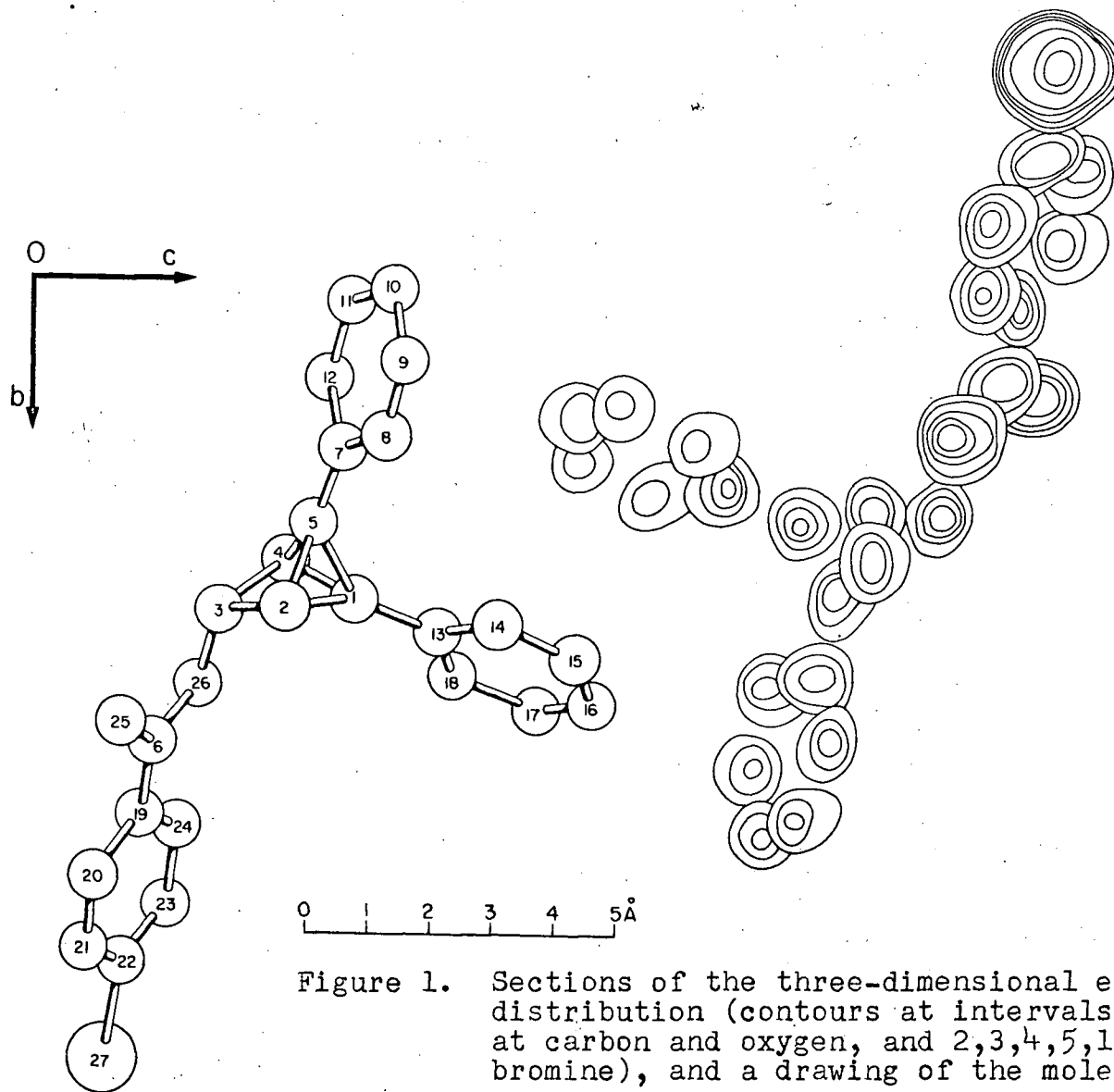
STRUCTURE ANALYSIS

The bromine atom position was determined from the three-dimensional Patterson function, and structure factors were calculated for all reflections using the scattering factors for Br from the International Tables (4) and assigning a temperature factor, B , of $4.0 \text{ \AA}^2$ ($R = 0.53$). A three-dimensional Fourier series was summed with the signs of the structure amplitudes based on the contribution from the bromine atom only. All the carbon and oxygen atoms in the molecule were located on the resulting electron density map, which could be interpreted on the basis of space group $P\bar{1}$. The structure factors for all 27 atoms were calculated ($R = 0.32$), setting $B = 4.0 \text{ \AA}^2$ for all atoms and using the C and O scattering factors from the International Tables (4).

The positional and thermal parameters and an overall scale factor were refined by block-diagonal least-squares methods, with minimization of $\sum w (F_o - F_c)^2$, where $\sqrt{w} = 1$ when $|F_o| \leq F^*$, and $\sqrt{w} = F^* / |F_o|$ when $|F_o| > F^*$. F^* was initially taken as 20. For the 257 unobserved reflections F_o was taken as $0.6 F(\text{min.})$ and $\sqrt{w}$ as 1.0. Seven cycles of least-squares reduced R to 0.172, and an analysis of the values of $w(F_o - F_c)^2$ suggested that F^* should be changed to 8. Three further cycles with anisotropic thermal parameters completed the refinement, the maximum shift in the positional parameters being 0.2σ for the final cycle. The final value of the discrepancy index, R , was 0.157 for the 1228 reflections. The final F_o and F_c values calculated from the output

parameters of the tenth cycle are listed in Table IV (Appendix I).

A final three-dimensional Fourier series was summed, and sections of the resulting electron density distribution are shown in Figure 1, together with a drawing of the molecule showing the atom numbering system used. A final difference map showed no significant spurious detail, the maximum fluctuations being $\pm 1 \text{ e } \text{\AA}^{-3}$, except in the vicinity of the bromine atom, where fluctuations of $\pm 1\frac{1}{2} \text{ e } \text{\AA}^{-3}$ were observed.



COORDINATES AND MOLECULAR DIMENSIONS

The final positional and thermal parameters are given in Table I. $\underline{x}$, $\underline{y}$ and $\underline{z}$ are the coordinates referred to the triclinic crystal axes, and the mean standard deviations of the coordinates (in $\text{\AA}$) were calculated from the least-squares residuals. B values are the isotropic temperature factors from the seventh least-squares cycle. Since the visual intensity data are of limited accuracy (in comparison with counter methods), the detailed values of the anisotropic temperature factors probably have little physical significance, so they are not listed and will not be discussed.

The bond distances and valency angles in the molecule are listed in Table II. The standard deviation for bonds is approximately $0.05 \text{ \AA}$, and for angles is approximately 3° . Equations of the mean planes through the three phenyl rings and the carboxyl group are given in Table III, together with several selected planes through the tricyclopentane system and the interplanar angles.

The packing of the molecules in the unit cell is shown in Figure 2.

TABLE I

Final positional (fractional $\times 10^3$) and isotropic thermal ($\text{\AA}^2$) parameters. Mean standard deviations are $\sigma(\underline{x}) = \sigma(\underline{y}) = \sigma(\underline{z}) = 0.004 \text{ \AA}$ for Br, $0.024 \text{ \AA}$ for O, $0.038 \text{ \AA}$ for C; $\sigma(\underline{B}) = 0.1 \text{ \AA}^2$ for Br, $0.5 \text{ \AA}^2$ for O, $0.8 \text{ \AA}^2$ for C.

Atom	<u>x</u>	<u>y</u>	<u>z</u>	<u>B</u>
C(1)	357	426	706	4.7
C(2)	158	407	769	5.2
C(3)	313	404	830	4.4
C(4)	467	493	770	4.5
C(5)	255	558	740	4.7
C(6)	293	161	888	5.2
C(7)	187	705	718	4.6
C(8)	003	725	681	5.0
C(9)	-064	867	657	6.2
C(10)	074	991	672	6.6
C(11)	258	968	709	6.3
C(12)	316	830	730	4.6
C(13)	420	366	630	4.1
C(14)	275	379	578	6.3
C(15)	327	315	506	7.2
C(16)	534	237	492	7.1
C(17)	675	222	542	7.9
C(18)	628	287	615	6.9
C(19)	418	019	899	4.8
C(20)	303	-093	940	5.3
C(21)	420	-219	950	5.4
C(22)	644	-242	916	4.9
C(23)	754	-134	874	4.7
C(24)	651	002	865	4.7
O(25)	102	188	914	5.5
O(26)	418	262	842	5.3
Br(27)	795.9	-423.0	929.6	6.6

TABLE II

Bond distances (σ = ca. 0.05 Å) and valency angles (σ = ca. 3°).

Tricyclopentane system

C(2)-C(3) = 1.50	C(2)-C(3)-C(4) = 81.7
C(3)-C(4) = 1.54	C(3)-C(4)-C(5) = 89.3
C(2)-C(5) = 1.53	C(3)-C(4)-C(1) = 92.2
C(1)-C(2) = 1.54	C(3)-C(2)-C(5) = 90.8
C(4)-C(5) = 1.53	C(3)-C(2)-C(1) = 92.9
C(1)-C(4) = 1.52	C(4)-C(5)-C(2) = 81.3
Mean = 1.53	C(4)-C(1)-C(2) = 81.4
	C(5)-C(4)-C(1) = 56.3
C(1)-C(5) = 1.44	C(5)-C(2)-C(1) = 56.1
	C(4)-C(5)-C(1) = 61.4
C(2)...C(4) = 1.99	C(4)-C(1)-C(5) = 62.3
	C(2)-C(5)-C(1) = 62.3
	C(2)-C(1)-C(5) = 61.6

External angles at C(1)

and C(5) = 134.4-142.1
(six angles), mean 138°

C(2)-C(3)-O(26) = 115.6
C(4)-C(3)-O(26) = 109.5

Substituent groups

C(3)-O(26) = 1.45	C(3)-O(26)-C(6) = 117.3
O(26)-C(6) = 1.37	O(26)-C(6)-O(25) = 121.1
C(6)-O(25) = 1.19	O(26)-C(6)-C(19) = 112.9
C(6)-C(19) = 1.50	O(25)-C(6)-C(19) = 125.9
C(5)-C(7) = 1.45	
C(1)-C(13) = 1.47	
Br(27)-C(22) = 1.88	

Aromatic rings

C-C = 1.30-1.44 (18 bonds), mean 138

Angles at C = 117-123 (26 angles), mean 120.

TABLE III

Equations of mean planes and angles between planes.

Equations of mean planes in the form $\underline{l}X' + \underline{m}Y' + \underline{n}Z' + \underline{p} = 0$, where X' , Y' , Z' are coordinates in Å referred to orthogonal axes $\underline{a}'$, $\underline{b}'$, $\underline{c}'$.

Plane	Atoms	$\underline{l}$	$\underline{m}$	$\underline{n}$	$\underline{p}$	Maximum Displ. (Å)
A	7—12	-0.459	0.136	0.878	10.790	0.017
B	13—18	0.422	0.838	-0.346	0.664	0.005
C	19—24	0.436	0.367	0.822	15.174	0.022
D	6,19,25,26	0.444	0.396	0.803	14.935	0.014
E	2,3,4	-0.364	0.855	0.369	7.335	0
F	1,4,5	-0.499	-0.561	0.661	4.173	0
G	1,2,5	0.736	-0.022	0.677	11.094	0

Angles between planes.

<u>Planes</u>	<u>Angle</u>
F-G	85°
E-F	87
E-G	88
A-F	43
A-G	75
B-F	25
B-G	87

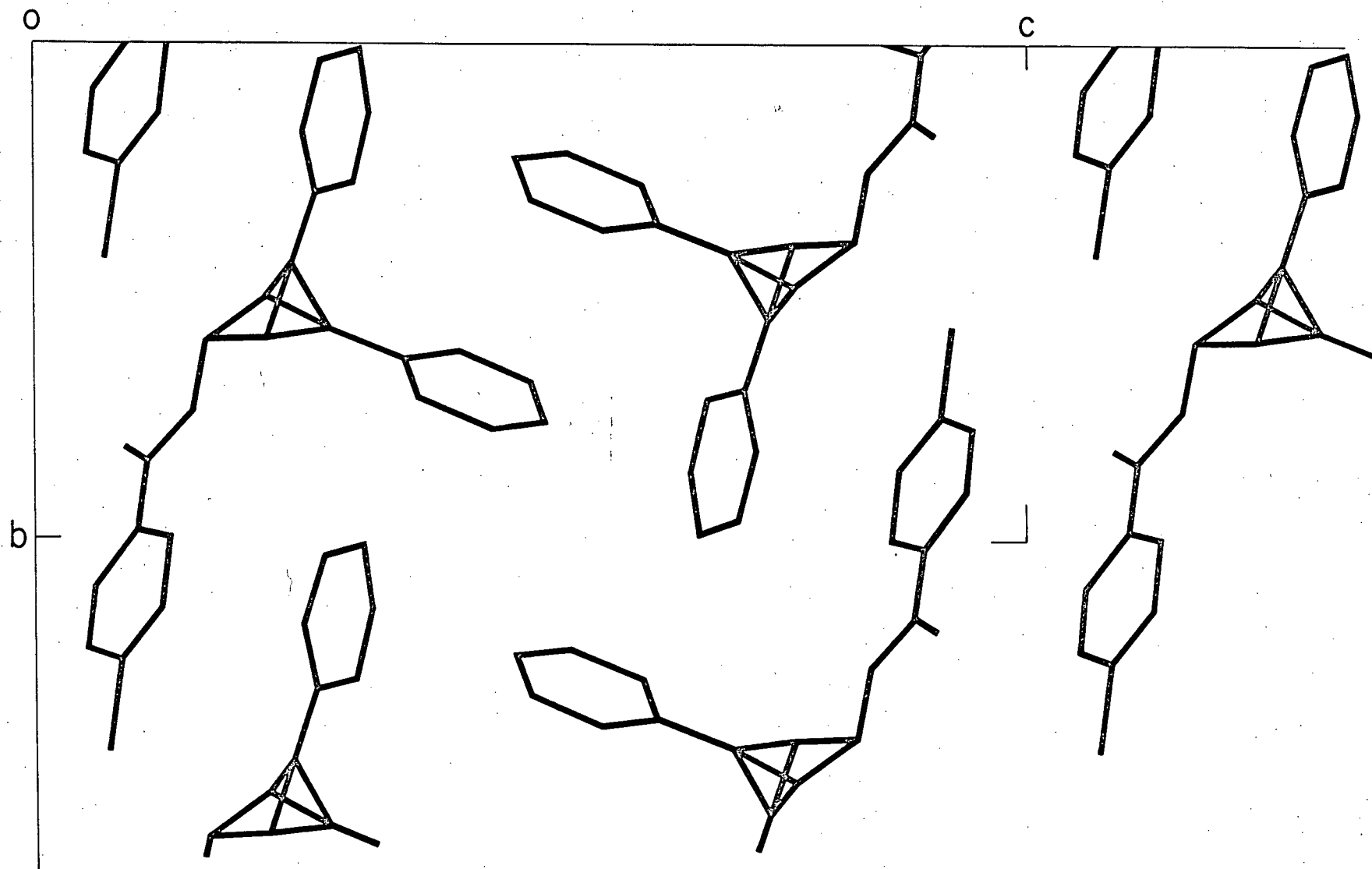


Figure 2. Packing of the molecules in the unit cell.

DISCUSSION

The crystal analysis has confirmed the formulation of the compound as a derivative of tricyclo[2.1.0.0^{2,5}]pentane. The lack of accuracy in the bond lengths and angles is due to (i) the limited accuracy of estimating the intensity data visually, (ii) the presence of the relatively heavy bromine atom, and, (to a lesser extent), (iii) possible absorption errors. However, the geometry of the ring system is now known, and some observations about bond lengths and angles can be made.

The great strain in the tricyclopentane system is indicated by the valency angles given in Table II, there being six C-C-C angles of about 60°, three of about 80°, and four of about 90°. The bond distances, however, do not appear to be greatly influenced by the strain. Six of the C-C distances are in the range of 1.50 - 1.54 Å, mean value 1.53 Å (standard deviation of the mean = 0.02 Å), close to the normal single bond length (5). The bond which is common to the two three-membered rings, C(1) - C(5), measures 1.44 ± 0.05 Å, so that this bond does seem to be shortened slightly, although the difference from the other bonds (0.09 Å = 1.8σ) cannot be claimed to be definitely statistically significant. The C(2)... C(4) non-bonded distance is only 1.99 Å.

The bond distances in the aromatic rings are in the range 1.30 - 1.44 Å, mean 1.38 Å. The root-mean-square deviation of the lengths from the mean value, 0.04 Å, is close to the standard deviation computed from the least-squares

equations, indicating that the estimations of the accuracy are reasonable. The valency angles at the aromatic carbons vary from $117 - 123^\circ$, with a mean value of 120° . The dimensions of the carboxyl group, $C=O = 1.19 \text{ \AA}$, $C-O = 1.37 \text{ \AA}$, $C-C=O = 125.9^\circ$, $C-C-O = 112.9^\circ$, $O-C=O = 121.1^\circ$, are normal (5), and the C—Br distance ($1.88 \text{ \AA}$) is close to the usual value (5).

Each of the aromatic rings is planar (Table III), and the carboxyl group is planar and, within experimental error it is coplanar with the aromatic ring to which it is bonded. The orientations of the C_6H_5 rings are quite similar (Table III), each being approximately at right angles to the plane $C(1)-C(2)-C(5)$, but are not quite identical, and are probably influenced by intermolecular interactions. Similarly the exact arrangement of the p-bromobenzoyl group probably depends on the crystal packing forces, and the two external angles at C(3) appear to differ slightly (110 and 116°).

The intermolecular distances correspond to van der Waals interactions. The shortest C...O contacts are 3.36 and $3.41 \text{ \AA}$, and the shortest C...C and C... Br distances are 3.60 and $3.73 \text{ \AA}$, respectively.

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APPENDIX I

Table IV

Observed and Calculated
Structure Factors

(Negative F_o values indicate an unobserved reflection.)

TABLE IV

h k l F _o F _c				h k l F _o F _c				h k l F _o F _c				h k l F _o F _c				h k l F _o F _c							
0 0 0	1	70.5	70.2	0 4 4	27.2	30.5	1 0 12	26.4	30.1	1 3 0	69.7	52.1	1 5 4	17.7	-16.3	-2 1 3	8.2	11.1					
0 0 2	2	7.2	11.4	0 4 5	9.6	12.7	1 0 13	11.1	13.0	1 3 1	-1	22.2	-25.6	1 5 5	-3	25.1	19.3						
0 0 4	3	8.9	9.5	0 4 6	43.6	39.4	1 0 14	-6.0	3.9	1 3 2	1	21.9	25.4	-1 5 6	9.8	-13.2	2 1 4	-4	-36.6	-25.5			
0 0 6	4	20.3	-20.1	0 4 7	19.4	16.5	1 0 15	-4.0	3.9	1 3 3	1	-2.3	6.0	-1 5 7	8.1	-6.5	-2 1 5	-4	-4.8	-41.8			
0 0 8	5	135.4	-101.4	0 4 8	1.4	2.8	1 0 16	17.3	14.6	1 3 4	3	-2	9.9	-9.5	1 5 8	10.0	-17.8	2 1 6	-5	5.5	-4.7		
0 0 10	6	60.3	-54.4	0 4 9	-1.4	1.4	1 0 17	12.0	8.7	1 3 5	3	-13.4	18.3	1 5 9	15.8	-29.9	-2 1 7	-6	3.7	7.7			
0 0 12	7	46.9	-45.0	0 4 10	4.6	4.1	1 0 18	6.9	-11.3	1 3 6	3	41.3	39.5	-1 5 10	6	-15.6	-8.0	-2 1 8	-7	-2.1	4.0		
0 0 14	8	23.1	-25.3	0 4 11	22.5	-24.0	1 0 19	15.6	-16.3	1 3 7	3	10.3	-12.1	1 5 11	5	7	6.1	-6.2	-2 1 9	-8	24.8	-21.9	
0 0 16	9	39.0	-34.3	0 4 12	28.2	-24.8	1 0 20	18.6	-18.6	1 3 8	3	-13.4	10.0	1 5 12	5	-3.2	11.9	-2 1 10	-9	5.0	-28.1		
0 0 18	10	10.2	-8.4	0 4 13	11.2	9.0	1 0 21	30.8	-46.7	1 3 9	3	-66.2	54.8	1 5 13	5	10.2	2.4	-2 1 11	-10	4.1	-6.8		
0 0 20	11	-1.5	1.9	0 4 14	12.6	9.0	1 0 22	14.4	-11.7	1 3 10	3	4.3	38.0	-1 5 14	5	15.5	17.7	-2 1 12	-11	7.8	5.8		
0 0 22	12	15.1	15.6	0 4 15	9.5	6.7	1 0 23	14.4	-11.7	1 3 11	3	-2.7	-4.3	1 5 15	5	-8	6.5	9.1	-2 1 13	-12	6.6	-8.7	
0 0 24	13	16.7	16.4	0 4 16	-1.8	2.2	1 0 24	13.3	13.6	1 3 12	3	26.4	26.2	-1 5 16	5	28.3	-28.5	-2 1 14	-13	17.5	-17.4		
0 0 26	14	5.3	5.2	0 4 17	13.5	5.4	1 0 25	13.3	13.6	1 3 13	3	5	-2.7	1 5 17	5	20.6	20.9	-2 1 15	-14	51.4	-38.8		
0 0 28	15	5.4	5.4	0 4 18	14.0	-12.3	1 0 26	13.7	15.9	1 3 14	3	5	20.2	-22.3	1 5 18	5	-9	-4.0	-2 1 16	-15	8.1	-6.8	
0 0 30	16	46.7	-46.6	0 4 19	45.5	40.8	1 0 27	100.1	-113.1	1 3 15	3	6	14.9	14.9	-1 5 19	5	9	6.7	-9.4	-2 1 17	-16	43.3	-28.3
0 0 32	17	31.2	-22.0	0 4 20	18.1	19.4	1 0 28	7.7	12.0	1 3 16	3	6	28.0	-31.2	1 5 20	5	10	16.5	14.8	-2 1 18	-17	75.7	-60.5
0 0 34	18	1.0	-0.3	0 4 21	41.8	37.4	1 0 29	8.5	-12.4	1 3 17	3	5	15.0	-16.7	1 5 21	5	-10	-7.1	2 1 19	-18	16.9	-17.3	
0 0 36	19	21.6	-21.7	0 4 22	2.3	3.4	1 0 30	10.6	97.6	1 3 18	3	6	27.8	-28.6	-1 5 22	5	10	9.7	-13.2	-2 1 20	-19	5.6	-2.8
0 0 38	20	9.8	10.7	0 4 23	2.3	22.2	1 0 31	9.7	-18.6	1 3 19	3	7	36.8	41.5	1 5 23	5	11	6.8	5.9	-2 1 21	-20	46.6	-29.2
0 0 40	21	7.0	4.4	0 4 24	30.0	-24.7	1 0 32	30.3	14.5	1 3 20	3	7	7.4	10.8	-1 5 24	5	11	-4.0	-12.1	-2 1 22	-21	10.0	75.2
0 0 42	22	7.1	-9.4	0 4 25	37.6	23.9	1 0 33	63.2	-86.0	1 3 21	3	7	5.0	-10.3	1 5 25	5	11	-4.0	-12.1	-2 1 23	-22	13.1	10.5
0 0 44	23	138.8	-117.9	0 4 26	4.6	-41.4	1 0 34	139.9	125.6	1 3 22	3	7	22.7	-25.8	1 5 26	5	12	11.2	11.2	-2 1 24	-23	14.0	-16.2
0 0 46	24	56.9	51.1	0 4 27	24.7	17.7	1 0 35	34.6	-38.0	1 3 23	3	8	21.1	25.4	1 5 27	5	12	7.1	-10.6	-2 1 25	-24	10.1	-10.6
0 0 48	25	17.3	18.8	0 4 28	9.6	-9.9	1 0 36	31.8	-34.3	1 3 24	3	8	30.2	-34.0	-1 5 28	5	13	12.6	12.6	-2 1 26	-25	15.6	18.8
0 0 50	26	20.0	18.9	0 4 29	5.4	-5.8	1 0 37	110.2	-98.8	1 3 25	3	8	17.4	-17.6	1 5 29	5	13	7.1	10.2	-2 1 27	-26	11.1	5.3
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0 0 58	30	68.0	66.5	0 4 33	15.2	-13.5	1 0 41	5.3	-10.8	1 3 29	3	9	17.8	-20.0	1 5 33	5	13	14.8	14.8	-2 1 31	-30	11.1	-3.0
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0 0 102	52	53.8	67.2	0 4 55	22.9	15.8	1 0 63	7.2	9.7	1 3 51	3	10	10.3	-15.1	1 5 55	5	13	14.8	14.8	-2 1 53	-52	11.1	-3.0
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0 0 114	58																						

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2	6	9	9.8	-6.3	3	2	11	11.6	9.7	-3	5	7	35.7	32.9	4	2	10	11.3	12.8	5	-1	7	17.2	16.7
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2	-4	10	12.2	-22.0	-3.2	3	3	0	16.3	16.0	3	5	12	8.3	-8.7	4	-3	1	21.1	-18.2	-1	10	4.8	5.9
2	-4	11	-4.0	5.6	-3.2	3	3	0	16.3	16.0	3	5	12	8.3	-8.7	4	-3	1	21.1	-18.2	-1	10	4.8	5.9
2	-4	11	11.6	-24.0	-3.2	3	3	0	16.3	16.0	3	5	12	8.3	-8.7	4	-3	1	21.1	-18.2	-1	10	4.8	5.9
2	-4	11	21.6	-21.3	-3.2	3	3	0	16.3	16.0	3	5	12	8.3	-8.7	4	-3	1	21.1	-18.2	-1	10	4.8	5.9
2	-4	12	21.6	-21.3	-3.2	3	3	0	16.3	16.0	3	5	12	8.3	-8.7	4	-3	1	21.1	-18.2	-1	10	4.8	5.9
2	-4	12	21.6	-21.3	-3.2	3	3	0																