BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1574—1580 (1967)

The Crystal Structure of 2-Anilino-3-bromo-tetrahydro-exo-dicyclopentadiene

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(Received January 16, 1967)

2-Anilino-3-bromo-tetrahydro-exo-dicyclopentadiene, $C_{16}H_{20}NBr$, crystallizes in the monoclinic space group $P2_1/c$, with four molecules in a unit cell of dimensions $a=9.15$, $b=17.36$, $c=9.56$ Å, $\beta=108.45°$. The structure was solved by superimposing the minimum function upon the first Fourier map based on the Br atom only. The atomic parameters were refined by the block-diagonal least-squares method. Most of bond-angles of carbon atoms forming a tricyclic system in the molecule are somewhat smaller than the ordinary tetrahedral angle, particularly on the bridged carbon atom. The Br atom is bonded to the endo side of the ring and the N atom to exo.

Recently, Funakubo, Moritani, Taniguchi, Yamamoto and Tsuchiya have investigated the decomposition of dihydro-exo-dicyclopentadieno-4,5-triazol1) as a part of the studies on the reactivity of the compounds having a tricyclic system. They obtained several derivatives of tetrahydro-dicyclopentadiene as products, some of which have the skeleton of endo isomer as a result of Wagner-Meerwein rearrangement. The small bond-angle at a bridged carbon atom has been reported in some bicyclic compounds.2–4) Appreciable bond-angle

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1) E. Funakubo, I. Moritani, H. Taniguchi, T. Yamamoto and S. Tsuchiya, *Chem. Ber.*, **96**, 2035 (1963).

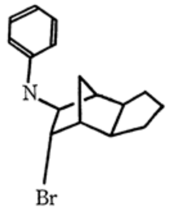
2) A. C. MacDonald and J. Trotter, *Acta Cryst.*, **18**, 243 (1965).

3) H. G. Norment, *ibid.*, **18**, 627 (1965).

4) A. C. MacDonald and J. Trotter, *ibid.*, **19**, 456 (1965).

strain at the cyclic system may have to do something with a formation of a non-classical carbonium ion or a mesomeric ion expected in such a reaction.

The present paper will describe the crystal structure of 2-anilino-3-bromo-tetrahydro-exo-dicyclopentadiene, one of the products of above mentioned reactions. The crystal was supplied by Professor Moritani who prepared it by decomposition of dihydro-exo-dicyclopentadieno-4,5-triazol with addition of hydrobromic acid.



Experimental

The crystals were obtained by recrystallization from an acetone-water solution, as colorless rods elongated along the c axis. Unit cell dimensions were determined from the equatorial Weissenberg photographs about the b and c axes, on which the Debye lines of aluminum was superposed for calibration. The unit cell dimensions are;

$$a = 9.15 \pm 0.02 \text{ Å}$$
$$b = 17.36 \pm 0.03 \text{ Å}$$
$$c = 9.56 \pm 0.02 \text{ Å}$$
$$\beta = 108.45° \pm 0.25°$$

From the systematic absence of reflections, the space group was determined to be $P2_1/c$. The density obtained by floatation in aqueous solution of zinc chloride is 1.39 g/cm^3, while the density calculated on the basis of four molecules per unit cell is 1.44 g/cm^3.

The equi-inclination Weissenberg photographs were taken for layer lines 0 to 7 about the c axis and 0 to 7 about the b axis with Cu$K\alpha$ radiation. The relative intensities, ranging between 1 and 18000, were measured visually with a standard scale. 1793 Reflections in total were observed, in which about 500 were too weak to be measured. The intensities were corrected for Lorentz and polarization factors and spot-size factors for the equi-inclination Weissenberg photographs, but the corrections for absorption and secondary extinction were neglected. A rod-shaped crystal having a cross section of 0.2 mm × 0.1 mm was used for the c axis photographs. A crystal for the b axis photographs, cut perpendicularly to the c axis, was small and ill-shaped.

The interlayer scales were at first obtained by comparing the intensities about the c axis with those about the b. Three-dimensional intensities used in the following analysis were mainly obtained from the c axis photographs and were supplemented from the b axis for the planes to which the c axis data were not accessible.

Determination and Refinement of the Structure

A three-dimensional Patterson function was calculated, $|F_o|^2$ being sharpened by the factor of $\exp\{5.0(\sin\theta/\lambda)^2\}$. Two predominant peaks were found in the section at $V=1/2$. One of them should be the Harker peak, due to the two fold screw axis and the other could be interpreted as the vector between the Br atoms related by a center of symmetry, so that the y-coordinate of the Br atom was nearly 0.25. This means that the Br atom does not have any contribution to the reflections with l odd, and the first Fourier map based on the Br atom only has an additional mirror plane at $y=0.25$. Therefore, the molecular structure could not be figured out in the map, being confused by many false peaks. A minimum function calculated by translating the origin of the Patterson function upon the most predominant peak in the section at $V=1/2$ of the same function was also uninterpretable.

The structure was finally obtained by superimposing the minimum function upon the first Fourier map and by leaving only the peaks which exist on both maps. Though this new function still has the additional mirror symmetry, some false peaks were removed by this procedure and a reasonable model consistent with the chemical acquaintance was constructed.

In order to determine the arrangement of the molecule in the cystal, it became necessary to decide which one of the predominant peaks on the section at $V=1/2$ is the Harker peak. If the higher peak of them is so, the molecules related to each other by a center of symmetry would come too close. Thus, the other was considered as the Harker peak. In fact, the structure factors calculated based on this agreed well with those observed. The second Fourier summation gave well resolved peaks for all eighteen atoms in the molecule. At this stage, it was found that one carbon atom C(9) was misplaced in the initial model.

Atomic positions and isotropic temperature factors were refined by a diagonal least-squares method, cross-terms between x and z coordinates of each atom being also taken into account. After 4 cycles, the R factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$, was reduced to 0.31.

Further refinement was made by a block-diagonal least-squares method, only the bromine atom being treated as anisotropic. The weighting scheme was as follows;

$$w = 30/|F_o| \quad \text{if} \quad |F_o| \geqq 30$$
$$w = 1 \quad \text{if} \quad 30 > |F_o| \geqq 1.5$$
$$w = 0.25 \quad \text{if} \quad 1.5 > |F_o|$$

Atomic scattering factors used were taken from the International Tables for X-ray Crystallography. The

TABLE 1. THE FINAL ATOMIC PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS IN Å

Atom	x/a	$\sigma(x)$	y/b	$\sigma(y)$	z/c	$\sigma(z)$	B
Br	0.0444	0.002	0.2546	0.002	0.4372	0.002	*
N	0.4320	0.012	0.1951	0.011	0.6927	0.012	5.46
C(1)	0.2300	0.016	0.1466	0.015	0.3245	0.016	6.03
C(2)	0.2427	0.015	0.2047	0.015	0.4500	0.015	5.82
C(3)	0.2950	0.014	0.1537	0.013	0.5965	0.014	4.76
C(4)	0.3407	0.014	0.0774	0.014	0.5344	0.014	5.13
C(5)	0.1851	0.015	0.0360	0.015	0.4648	0.015	5.73
C(6)	0.1074	0.015	0.0861	0.015	0.3223	0.015	5.73
C(7)	0.3811	0.017	0.1048	0.016	0.3941	0.017	6.80
C(8)	0.2049	0.018	−0.0484	0.017	0.4056	0.017	7.16
C(9)	0.0843	0.021	−0.0507	0.021	0.2538	0.021	9.36
C(10)	0.0887	0.018	0.0288	0.018	0.1904	0.019	7.76
C(1′)	0.5001	0.014	0.1691	0.014	0.8354	0.014	5.09
C(2′)	0.4300	0.016	0.1140	0.015	0.9014	0.016	5.98
C(3′)	0.5098	0.017	0.0945	0.017	1.0565	0.017	6.91
C(4′)	0.6449	0.018	0.1292	0.017	1.1293	0.018	7.39
C(5′)	0.7069	0.018	0.1849	0.017	1.0688	0.018	7.23
C(6′)	0.6386	0.017	0.2063	0.016	0.9100	0.017	6.69

* Anisotropic temperature factors of the form: $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$

β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
0.0318	0.0069	0.0222	0.0112	−0.0145	−0.0058

real part of the anomalous dispersion ($\Delta f'=-0.9$) of the scattering factors of Br was included in the calculations. The interlayer scales were adjusted by comparing the observed structure factors with those calculated. After 6 cycles, the R factor was reduced to 0.12. The final parameters and their estimated standard deviations are listed in Table 1, and the observed and calculated structure factors are tabulated in Table 2. The final composite electron density map is shown in Fig. 1.

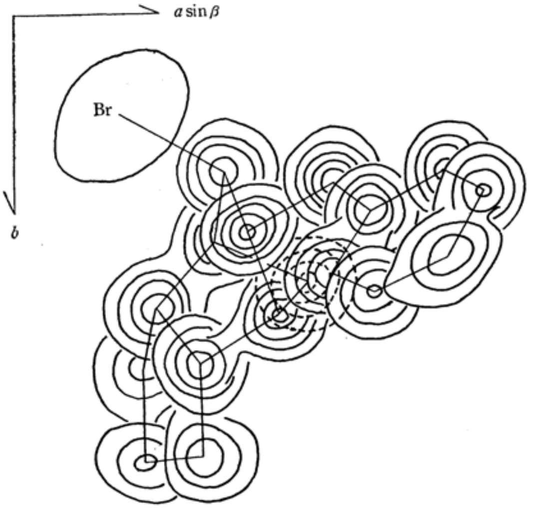


Fig. 1. Composite electron-density contour sections parallel to (001). Contours are drawn at intervals 1.0 e.Å^{-3}; those for the bromine atom are not drawn. The lowest is 1.0 e.Å^{-3}.

Discussion

The estimated standard deviations of the positional parameters of the light atoms are from 0.011 Å to 0.021 Å. Therefore, the mean value of the standard deviations of the bond lengths between the light atoms is about 0.023 Å, and that of the bond angles is about 1.1°. However, these values might be somewhat larger due to neglect of the corrections for the absorption (μ=44 cm^{-1}) and secondary extinction.

The C–C distances in the tricyclic system are in

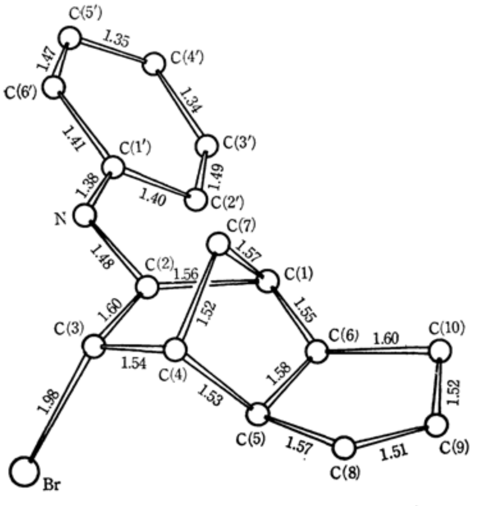


Fig. 2. Bond lengths of the molecule (Å).

Table 2. Observed and calculated structure factors

$2.5|F_o|$ and $2.5\,F_c$ are listed for each reflection.

K	FO	FC
H,L=	0	0
2	243	-279
4	116	116
6	221	-197
8	59	71
10	95	-85
12	51	50
14	64	-56
16	16	15
18	19	-25
20	18	14
H,L=	1	0
0	89	101
1	188	-198
2	82	-106
3	24	-22
4•	406	413
5	34	-38
6	201	-213
7	46	62
8	140	147
9	31	-35
10	161	-168
11	23	23
12	58	63
13	24	-25
14	39	-39
15	20	-19
16	20	20
17•	0	-1
18	21	-20
H,L=	2	0
0	154	167
1	129	-141
2	154	-186
3	185	181
4	158	169
5	93	-105
6	191	-202
7	45	54
8	132	131
9	78	-80
10	48	-45
11	20	20
12	73	78
13	23	-24
14	60	-60
15•	0	2
16	32	28
H,L=	3	0
0	117	124
1	166	-164
2	184	-195
3	73	87
4	90	91
5	154	-149
6	112	-106
7	102	111
8	90	95
9	36	-30
10	49	-49
11	28	21
12	50	44
13	42	-55
14•	0	-10
15	26	33
16	24	27
17•	0	-14
18	18	-14
H,L=	4	0
0	58	54
1	72	-79
2	116	-120
3	98	96
4	56	57
5	132	-131
6	10	2
7	103	102
8	39	32
9	70	-72
10	53	-55
11	77	82
12	36	38
13	39	-38
14	24	-21
15•	0	2
16	14	10
H,L=	5	0
0•	9	-5
1	156	-155
2	18	-19
3	134	136
4	41	36
5	51	-44
6	26	-27
7	57	60
8	32	33
9	62	-59
10•	0	-11
11	25	17
12	14	-18
13	19	-12
14	14	-13
15	23	19
16	17	14
17	16	-14
18•	0	-5
19	12	9
H,L=	6	0
0•	0	-16
1	59	-54
2	22	14
3	68	65
4•	0	-12
5	65	-59
6•	0	-1
7	55	57
8•	0	-2
9	41	-38
10•	12	-12
11	28	29
12	15	17
13	31	-29
14•	0	-5
15	22	18
16•	0	0
17	16	-10
H,L=	7	0
0	34	-43
1	39	-26
2•	0	-3
3	40	41
4	19	-12
5	39	-38
6•	0	20
7	30	21
8•	0	-3
9	35	-33
10•	0	10
11	29	26
12•	0	-2
13	18	-14
14•	0	-1
15	13	13
16•	0	3
17	13	-8
H,L=	8	0
0	16	-12
1	24	-20
2•	0	5
3	25	19
4	19	-21
5	23	-13
6•	0	6
7	20	16
8•	0	-6
9	23	-20
10	14	13
11	16	9
12•	0	1
13•	0	-7
14•	0	5
15	15	11
H,L=	9	0
0•	0	-5
1•	0	-2
2	13	12
3•	9	10
4	15	-9
5	14	-11
6•	0	1
7	15	7
8•	0	-8
9•	0	-2
10•	0	8
11•	9	9
H,L=	10	0
0•	0	0
1•	9	-10
2•	9	10
3•	0	2
4•	9	-8
5•	0	0
6	12	8
H,L=	0	1
1	132	-86
2	10	-3
3	100	-95
4	90	-94
5	35	32
6	109	105
7•	0	6
8•	0	-5
9	82	70
10•	0	-10
11•	0	-4
12	15	-21
13•	0	4
14•	0	-6
15	18	-16
16	20	-17
17	23	25
H,L=	1	1
1	179	-156
2	140	128
3	46	-35
4	12	-2
5	54	54
6	16	-10
7•	0	-7
8	13	-17
9	36	28
10•	0	3
11	17	-15
12•	0	-11
13	34	32
H,L=	2	1
1•	9	-8
2	44	-36
3	15	-27
4	50	-40
5•	0	3
6	24	-33
7	23	-24
8	50	51
9	31	37
10	12	-14
11	25	-31
12	25	23
13	25	29
14	12	-18
15	24	-25
H,L=	3	1
1	25	-31
2	51	-50
3	50	-53
4	99	92
5	111	99
6	21	-30
7•	13	-5
8•	0	-3
9	10	19
10	34	-39
11	39	-43
12	14	16
13	20	-23
14•	0	-10
15•	0	11
16	14	22
H,L=	4	1
1	12	0
2	49	49
3	13	7
4	40	41
5	65	-60
6	66	-66
7•	0	14
8	30	33
9	29	-18
10	48	-49
11•	0	19
12	19	24
13	21	18
H,L=	5	1
1	27	-36
2	40	-35
3•	0	-9
4•	0	2
5	19	-18
6	12	1
7•	0	5
8	14	10
9•	0	3
10	23	-26
11	15	20
12	26	32
13•	0	-1
14	19	-21
15•	0	11
16	15	17
H,L=	6	1
1	18	-20
2•	0	0
3•	0	1
4•	0	13
5	16	-14
6	10	-18
H,L=	7	1
1	12	17
2•	0	9
3•	0	11
4•	0	9
5	15	-25
H,L=	8	1
1•	0	13
2•	0	-17
3•	0	4
H,L=	9	1
1•	0	-3
2•	0	1
3	10	15
H,L=	-1	1
1	28	16
2	299	-276
3	129	116
4	183	149
5	37	29
6	49	-40
7	42	-40
8	26	-23
9	13	-2
10	58	56
11	31	-28
12	51	-49
13	15	19
14•	0	9
15•	0	-5
16	34	-36
H,L=	-2	1
1	361	331
2	220	209
3	15	-22
4	180	-167
5	42	-33
6	66	71
7	15	-3
8	49	-46
9	43	-39
10	12	18
11•	0	-16
12	24	-27
13•	0	-4
14•	0	9
15•	0	-5
16•	0	-9
17•	0	-14
18•	9	13
H,L=	-3	1
1	30	29
2•	0	17
3	98	110
4	59	-52
5	36	40
6	42	41
7•	0	3
8	21	-19
9	37	-34
10	38	45
11•	0	-4
12	34	-37
13	29	-31
14	29	30
H,L=	-4	1
1	26	32
2	21	-21
3	56	49
4	10	12
5	70	-70
6	21	23
7	10	-13
8•	0	-2
9	15	-20
10	27	30
11	60	70
12•	0	-1
13	27	-27
14	17	24
15•	0	4
16	16	-17
H,L=	-5	1
1	43	-40
2	15	26
3	26	25
4	46	54
5	49	-55
6	15	18
7	53	60
8	32	-40
9	31	-32
10	10	16
11•	0	6
12•	0	7
13•	0	3
14•	0	2
15	24	24
H,L=	-6	1
1•	0	7
2•	0	2
3	35	-47
4•	9	-10
5•	0	10
6•	0	3
7	26	20
8	20	22
9	22	-20
10	23	-22
11	27	25
12•	0	-7
13	23	-22
14•	0	15
15	19	16
H,L=	-7	1
1•	0	-17
2•	0	12
3	31	31
4•	0	-10
5	15	-16
6	10	-22
7•	7	11
8•	0	-5
9•	7	-16
10•	0	5
11•	0	10
12•	0	8
13	19	-18
H,L=	-8	1
1•	0	-7
2•	0	-11
3•	0	11
4•	0	7
5•	0	-6
6•	0	-5
7•	0	10
8•	0	2
9	10	-13
H,L=	0	2
0	188	264
1	287	228
2	208	-197
3	200	-193
4	159	153
5	110	125
6	181	-178
7	188	-169
8	94	94
9	58	63
10	47	-50
11	40	-39
12	43	44
13	42	43
14	28	-32
15	21	-18
16	11	15
17•	7	2
18	12	-11
H,L=	1	2
0	241	260
1	124	133
2	271	-272
3	143	-149
4	170	171
5	51	60
6	116	-115
7	76	-81
8	111	124
9	22	32
10	87	-88
11	48	-50
12	34	33
13	23	24
14	45	-51
15•	0	-8
16	29	32
17	23	22
18•	0	-10
19	11	-13
H,L=	2	2
0	127	140
1	59	63
2	224	-232
3	56	42
4	177	192
5•	9	6
6	181	-185
7	74	-67
8	114	116
9	37	36
10	95	-94
11	53	-56
12	73	77
13	29	31
14	18	-16
15•	0	-6
16	17	14
17•	0	1
18	17	-16
H,L=	3	2
0	220	201
1	15	-20
2	185	-190
3	46	-37
4	69	75
5	64	55
6	158	-165
7•	0	-1
8	127	126
9	33	-35
10	70	-68
11	33	36
12	86	84
13•	0	0
14	29	-29
15•	0	0
16	25	20
H,L=	4	2
0	124	114
1	60	-59
2	151	-155
3	20	18
4	137	141
5	55	-51
6	110	-107
7	48	48
8	59	62
9•	0	13
10	36	-32
11	20	16
12	42	41
13•	0	-4
14	26	-31
15•	0	0
16	28	24
17•	0	0
18	21	-16
H,L=	5	2
0	112	109
1	32	-33
2	63	-64
3	65	80
4	88	92
5	56	-56
6	73	-74
7	33	33
8	53	47
9	21	-18
10	43	-46
11	15	20
12	25	23
13•	0	-6
14	25	-22
15	12	11
16	14	10
H,L=	6	2
0	101	89
1	53	-66
2	20	-19
3	23	24
4	28	32
5	35	-47
6	36	-34
7	47	55
8	28	29
9	21	-16
10	42	-40
11•	0	14
12	22	17
13	15	-13
14	20	-13
H,L=	7	2
0•	6	4
1	52	-55
2•	0	-12
3	31	42
4	15	22
5	18	-23
6•	0	-2
7	10	12
H,L=	8	2
0•	0	-4
1•	0	-11
2•	0	-9
3	15	19
4	10	13
5	14	-23
6•	0	-9
7	20	28
H,L=	9	2
0•	0	-2
1	12	-15
2•	0	0
3	12	17
4•	0	-3
5•	5	-15
H,L=	10	2
0•	0	-3
1•	0	-7
2•	0	2
3•	5	8
H,L=	-1	2
0	144	-129
1	281	223
2	244	-252
3	160	-162
4	213	207
5	215	220
6•	0	3
7	149	-151
8	44	50
9	82	78
10	58	-59
11	75	-79
12	48	46
13	33	32
14	18	-16
15	15	-12
16	16	17
17	21	22
18	10	-8
19	14	-15
H,L=	-2	2
0	104	-119
1	259	265
2	12	-2
3	225	-236
4	89	-78
5	132	139
6	75	-79
7	60	-65
8	156	166
9	100	104
10	19	-20
11	69	-75
12	24	24
13	39	44
14	27	-30
15	44	-50
16	13	17
17•	7	9
H,L=	-3	2
0	54	69
1	110	89
2	85	-84
3	145	-141
4	57	62
5	187	192
6	58	70
7	148	-151
8	65	-72
9	93	86
10•	0	-3
11	57	-58
12•	0	5
13	33	33
14	11	10
15	40	-40
16•	0	12
17	13	11
18	12	-12
19•	9	-7
H,L=	-4	2
0	36	56
1	132	134
2	81	102
3	131	-130
4	33	-31
5	63	63
6•	9	8
7	63	-54
8	11	-12
9	74	75
10•	0	0
11	72	-77
12	15	-18
13	27	18
14•	0	-2
15	26	-21
16•	0	-12
17	24	24
H,L=	-5	2
0	43	-37
1	82	87
2	97	103
3	77	-73
4	20	-20
5	47	41
6	28	33
7	69	-68
8	26	-21
9	50	56
10•	0	3
11	23	-16
12	17	-20
13	27	22
14•	0	-7
15	19	-16
16•	0	-5
17	11	6
H,L=	-6	2
0	24	-20
1	40	33
2	54	63
3	59	-58
4	26	-22
5	47	49
6	14	3
7•	7	9
8	39	-46
9	17	13
10	28	35
11	16	-14
12•	0	-7
13	26	27
14	15	9
15	20	-17
16•	0	-5
17	17	10
H,L=	-7	2
0	26	-19
1•	0	-11
2	26	22
3	13	30
4	42	-48
5	37	39
6	29	33
7	30	-33
8	16	-11
9	23	26
10•	0	8
11	14	-10
12•	0	-4
13	13	10
H,L=	-8	2
0	20	-10
1	22	24
2•	0	7
3•	0	-4
4	19	-21
5•	0	-6
6	14	14
7•	0	8
8	10	-14
9•	0	3
10	15	14
11•	0	-6
12	16	-11
H,L=	-9	2
0	15	-18
1•	0	2
2	16	13
3•	0	-1
4•	0	-2
5•	0	-3
6•	0	1
7•	0	-3
8	13	-12
H,L=	0	3
1	36	-25
2•	0	-5
3	76	-49
4	23	-12
5	41	-35
6•	0	11
7	11	-8
8	12	-9
9•	0	3
10	31	31
11	16	20
12	50	-52
13•	0	5
14	30	29
H,L=	1	3
1	12	23
2	17	-7
3	102	-77
4	15	19
5	86	-67
6	78	72
7	57	41
8	43	-36
9	19	-20
10	20	19
11•	0	1
12•	0	3
13	52	46
14	17	16
H,L=	2	3
1•	0	-8
2	22	-8
3	19	18
4	79	-65
5	40	40
6	52	42
7	120	-95
8•	0	7
9	72	58
10	54	51
11•	0	-6
12•	0	17
13•	0	0
14	12	-13
H,L=	3	3
1	25	24
2	12	-8
3	37	26
4	12	13
5	48	37
6	18	-11
7	14	-18
8	29	27
9	15	14
10•	0	1
11	36	-36
12	15	-13
13•	0	1
14•	0	13
15	20	-23
H,L=	4	3
1	49	51
2•	0	-5
3•	0	-4
4	10	7
5	26	26
6	32	-24
7•	0	-12
8	28	33
9•	0	-4
10	20	-16
11	33	-33
12•	0	6
13	16	14
H,L=	5	3
1•	0	8
2	15	-11
3	19	-15
4	15	22
5	15	17
6	15	-18
H,L=	6	3
1	31	-33
2•	0	-7
3	23	23
4•	0	7
5•	0	-1
6•	0	8
7•	0	2
8•	0	11
9•	0	12
10	27	-27
H,L=	7	3
1•	0	7
2•	0	10
3	14	-15
4	17	23
5•	0	4
6	15	-29
H,L=	8	3
1•	0	0
2•	0	-8
3•	5	6
H,L=	-1	3
1	29	-16
2	64	65
3	21	21
4	78	-70
5	42	-24
6	87	-59
7	16	-18
8	50	-45
9	18	-14
10	19	18
11	13	14
12	20	-17
13	17	-14
14	28	24
H,L=	-2	3
1	15	12
2	43	-36
3	52	43
4	34	-27
5	79	-70
6	15	-7
7•	0	7
8	69	-64
9	27	-20
10•	0	-1
11	32	30
12•	0	-9
13	30	-30
14	12	16
15	21	24
16•	0	-5
17	12	-13
18	11	14
H,L=	-3	3
1	67	-79
2	44	39
3	37	-37
4	19	-28
5	45	43
6	58	59
7	61	76
8	43	-57
9	56	-57
10	22	-17
11	47	47
12•	0	6
13	27	-25
H,L=	-4	3
1	54	-61
2	26	-16
3	28	33
4	46	58
5	84	-78
6	57	-62
7	61	65
8	43	46
9•	0	8
10•	0	12
11	16	16
12	17	-8
13	19	-19
14•	0	-1
15	13	23
16•	8	-13
H,L=	-5	3
1	12	-18
2	12	2
3•	0	-7
4	19	18
5•	0	15
6•	0	10
7	24	27
8	20	12
9	38	-39
10	27	-29
11	21	21
12•	0	9
13•	0	-11
14	18	-15
15	14	21
16•	0	4
17•	7	-7
H,L=	-6	3
1•	0	10
2•	0	-7
3	13	14
4•	0	-13
5•	0	-3
6	13	-7
7•	0	6
8	16	13
9•	0	0
10	17	-16
11•	0	6
12•	0	4
13	17	-20
14	14	-15
H,L=	-7	3
1•	0	11
2•	0	-10
3•	7	9
4•	0	1
5	12	18
6	28	-34
7•	0	3
8	19	17
9	11	-20
H,L=	-8	3
1•	0	9
2	15	-18
3	12	26
4	13	3
5	19	-29
H,L=	-9	3
1•	0	5
2•	0	7
3•	0	-18
4	15	19
H,L=	0	4
0	92	-78
1	150	166
2	39	41
3	280	-237
4	84	75
5	196	184
6	26	-23
7	101	-97
8	26	-27
9	96	92
10•	0	-6
11•	0	2
12•	0	6
13	23	23
14•	0	-1
15	40	-37
16•	0	4
17	20	17
H,L=	1	4
0	169	138
1	140	150
2	48	-44
3	120	-132
4	80	65
5	121	109
6	19	-12
7	103	-107
8	22	19
9	103	104
10•	0	-5
11	90	-82
12	21	-18
13	54	58
14	38	-38
15	16	-16
16	15	12
H,L=	2	4
0	97	91
1	174	162
2	51	-55
3	130	-129
4	117	102
5	105	100
6	42	-46
7	78	-71
8	46	45
9	76	68
10	72	-68
11	66	-58
12	17	15
13•	8	15
14•	0	-5
15	18	-16
16•	0	3
17	26	23
H,L=	3	4
0	96	98
1	103	105
2	97	-91
3	69	-57
4	80	76
5	109	89
6	62	-63
7	83	-79
8	71	62
9	41	38
10	49	-50
11	26	-26
12	33	37
13	27	28
14	26	-19
15	27	-21
H,L=	4	4
0	59	65
1	15	26
2	105	-104
3	56	-52
4	95	86
5	73	69
6	75	-72
7	24	-26
8	79	76
9	26	24
10	34	-32
11	26	-25
12	26	23
13•	0	9
14	19	-19
15•	0	-6
16	15	13
H,L=	5	4
0	121	103
1	56	54
2	84	-96
3•	0	4
4	80	76
5•	7	4
6	56	-52
7•	0	-13
8	33	32
9•	0	-1
10	26	-25
11•	0	-9
12	31	27
13	17	11
14	17	-13
H,L=	6	4
0	50	55
1	24	-27
2	23	-38
3•	0	-1

TABLE 2.-2

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
4	33	47	13	14	12	11	17	22	9•	0	1	10•	0	-6	12	41	-39	H,L=	1	7	5	20	11	4	21	17
5•	0	-7	14•	5	16	H,L=	2	5	10	28	-35	11	40	-27	13•	0	3	1	18	-11	H,L=	0	8	5•	0	-2
6	40	-55	15	11	-9	1	17	-18	11	15	20	12•	0	4	14	12	14	2	21	-23	0	77	-73	6	12	-11
7•	0	-6	16•	0	-10	2	13	11	12	16	11	13	15	11	H,L=	-4	6	3	17	24	1•	0	8	H,L=	1	9
8	45	40	17	23	20	3•	0	-9	H,L=	-6	5	14•	4	-5	0	30	-35	4	16	14	2	45	53	1•	0	6
9•	0	6	H,L=	-5	4	4	16	-13	1	21	15	H,L=	5	6	1•	9	-1	5	22	-23	3•	0	-3	2•	0	-1
10	38	-40	0	111	-118	5•	0	4	2•	0	-13	0	37	32	2	59	48	6	26	-24	4	42	-43	3•	0	0
11•	0	-3	1	45	46	6	40	35	3	22	-28	1	52	44	3	15	15	7	15	-9	5•	0	-4	4•	0	0
12	26	22	2	50	52	7	13	17	4•	0	-4	2	41	-33	4	38	-33	8•	0	1	6	30	29	5•	0	-10
H,L=	7	4	3	14	-17	8	19	-21	5•	9	6	3	38	-39	5•	8	8	9•	0	-6	7	32	23	6	11	-10
0	41	37	4	43	-52	9•	0	6	6	14	-13	4	15	20	6	39	39	10•	0	10	H,L=	1	8	H,L=	-1	9
1	10	-10	5	18	-4	10	35	26	7•	0	-4	5	62	46	7•	7	5	11	23	19	0	22	-34	1•	0	3
2	23	-34	6	70	79	H,L=	3	5	8	15	-32	6	19	-20	8	22	-19	H,L=	2	7	1	26	24	2	10	11
3•	7	11	7•	0	-7	1	11	6	9•	0	0	7	32	-28	9	14	-19	1	25	-21	2	21	27	H,L=	-2	9
4	20	31	8	24	-15	2	56	40	10•	0	-6	8	27	18	10	18	10	2	20	19	3	13	5	1•	0	-3
5•	9	-10	9	12	-26	3•	8	0	11	17	4	9	26	23	11•	0	14	3•	0	0	4	31	-36	2•	0	5
6	18	-20	10•	0	-7	4	26	-17	12	34	20	10	18	-15	12	21	-20	4	50	-30	5	21	22	3•	0	8
H,L=	8	4	11	15	-8	5•	0	-5	H,L=	0	6	11	13	-15	13•	0	0	5•	0	-1	6	61	50	4•	0	12
0	22	19	12	12	-4	6•	5	9	0	73	-87	12	11	9	14	17	13	6	34	24	7	25	-17	5	10	-3
1•	0	-12	13	22	27	7	15	-10	1	47	58	13	17	12	15•	0	0	7	34	25	H,L=	2	8	H,L=	-3	9
2	12	-19	14	15	13	8	22	-23	2	58	69	H,L=	6	6	16	15	-12	8•	0	10	0	25	-33	1•	0	0
3•	0	11	15•	0	-6	9	19	19	3	75	-74	0	27	27	H,L=	-5	6	9	19	-17	1	17	20	2•	0	-2
4•	7	13	16	18	-18	H,L=	4	5	4	54	-59	1	26	21	0	61	-44	H,L=	3	7	2	37	46	3•	0	-5
H,L=	-1	4	H,L=	-6	4	1	27	19	5	49	51	2	38	-30	1•	9	-16	1•	0	2	3	16	-20	4•	0	20
0•	0	0	0	40	-29	2	82	-49	6	54	61	3	30	-24	2	21	10	2	22	15	4	34	-39	H,L=	-4	9
1	163	150	1•	9	-17	3	22	-13	7	33	-37	4	44	30	3	28	28	3•	9	-8	5	31	25	1•	8	-14
2	45	39	2	25	23	4	19	8	8	38	-39	5	31	22	4	14	-6	4	25	16	6	23	23	2•	0	-10
3	137	-130	3•	0	9	5	27	21	9	69	64	6	24	-18	5•	0	-1	5•	0	-3	H,L=	3	8	3•	0	0
4	142	-126	4	40	-38	6	15	-10	10	18	22	7	18	-17	6	43	43	6•	0	4	0	20	-27	4	17	-8
5	200	173	5•	0	0	7	39	-27	11	26	-33	8	25	15	7	22	30	7	13	8	1	19	26	5	11	6
6	31	27	6	25	24	H,L=	5	5	12•	0	-4	9	22	14	8	14	-19	H,L=	4	7	2	21	30	H,L=	-5	9
7	62	-60	7•	0	0	1•	0	-1	13•	9	9	10	18	-12	9•	0	4	1•	0	2	3	21	-33	1	13	15
8•	9	13	8	24	-22	2	23	15	14	16	14	11•	8	-5	10•	5	7	2	12	-5	4	18	-24	2•	0	0
9	94	93	9	19	26	3•	0	2	15	14	-10	H,L=	7	6	11•	0	3	3•	0	2	5	17	22	3	16	-25
10•	0	-8	10	28	35	4	34	-21	H,L=	1	6	0	22	18	12	15	-18	4•	0	-4	6	13	19	H,L=	-6	9
11	66	-64	11•	0	-11	H,L=	-1	5	0	23	-34	1•	4	9	13•	0	-1	5•	0	2	7	19	-21	1•	9	-12
12•	0	8	12	15	-16	1	10	14	1	89	95	2	30	-19	14•	9	7	6	14	12	H,L=	4	8	2•	0	-1
13	46	44	13•	0	-7	2	43	30	2	36	43	3•	0	-6	15•	0	0	7•	6	-3	0	17	-21	3	11	22
14	13	17	14	15	12	3	20	20	3	72	-74	4	48	27	16	10	-6	H,L=	-1	7	1	27	38	H,L=	0	10
15	23	-24	H,L=	-7	4	4	31	-37	4	43	-42	5	16	9	H,L=	-6	6	1•	0	7	2	11	17	0•	9	-7
16•	0	-7	0	24	-25	5	36	28	5	54	59	6	32	-21	0•	4	-1	2	29	-23	3	15	-24	1	15	-16
17	16	16	1•	0	7	6•	0	-3	6	25	34	7	16	-10	1•	9	-10	3•	0	-1	4•	8	-15	2•	0	10
18	13	3	2•	0	2	7	11	8	7	85	-80	8	15	14	2	15	16	4	17	-21	5	16	25	3•	0	7
H,L=	-2	4	3	22	38	8•	8	4	8	14	-19	H,L=	8	6	3•	0	12	5	19	-14	6	10	11	4•	9	-14
0	40	-64	4	21	-10	9•	0	-6	9	27	32	0	11	20	4	31	-29	6	18	-18	7	16	-23	5•	0	-6
1	128	127	5•	0	0	10	12	-10	10	26	27	H,L=	-1	6	5	17	-18	7	18	24	H,L=	5	8	6	10	12
2	38	39	6	20	23	11•	0	3	11	24	-28	0	49	-65	6•	5	5	H,L=	-2	7	0•	0	0	7	10	12
3	87	-92	7•	0	-1	12•	0	9	12	20	-17	1	80	93	7	30	26	1	13	13	1	17	27	H,L=	1	10
4	115	-116	8	16	-14	13	55	-51	13	34	29	2	116	104	8•	5	-7	2•	0	6	2•	0	7	0	15	-20
5	61	65	9•	0	-10	14•	0	10	14•	0	8	3•	9	-13	9	13	21	3	13	-6	3	22	-29	1•	0	-9
6	49	49	10	19	17	15	19	24	15	14	-14	4	106	-98	10	13	4	4	17	-12	4•	0	-8	2	14	18
7	76	-69	11•	0	-2	H,L=	-2	5	16	10	-13	5	64	63	11•	5	9	5•	0	13	5	20	29	3•	0	6
8	25	-38	12	14	-16	1•	0	5	H,L=	2	6	6	21	18	12•	0	0	6	18	-18	H,L=	6	8	4•	8	-11
9	93	96	13•	0	3	2	52	-63	0	33	24	7	17	-17	13•	9	-11	7•	8	-16	0•	0	2	5•	0	-1
10	34	36	14	12	10	3	42	45	1	58	64	8	14	-20	H,L=	-7	6	8	44	36	1•	5	21	6	12	14
11	46	-48	15•	0	-2	4•	6	7	2•	0	13	9•	0	-4	0	17	-12	9•	0	-7	H,L=	-1	8	7•	8	10
12•	0	-10	16•	0	-3	5	11	-11	3	137	-124	10	51	50	1	22	-18	10•	0	-12	0	52	-44	H,L=	2	10
13	36	37	17•	8	0	6	40	38	4	31	-27	11	14	-14	2•	0	0	11	16	22	1	14	-17	0	15	-19
14•	0	10	H,L=	-8	4	7	20	20	5	71	73	12	21	-22	3	22	12	H,L=	-3	7	2	32	39	1•	0	-1
15	28	-30	0	25	-27	8•	0	11	6	16	20	13	17	17	4•	0	10	1•	0	-2	3	20	21	2	12	19
16•	0	0	1	17	-22	9	36	-44	7	62	-61	14	12	14	5•	0	1	2•	1	5	4	35	-33	3•	0	6
17	14	11	2•	0	11	10•	0	3	8	36	-29	15	12	-12	6•	0	-15	3	17	30	5•	0	0	4•	0	-11
18•	0	1	3•	0	-10	11	23	23	9	24	32	16•	6	-7	7•	0	2	4	51	56	6	19	19	5•	0	-6
19	14	-11	4•	0	-1	12	15	22	10	13	14	17•	9	10	8	15	-16	5	34	-40	H,L=	-2	8	6•	8	12
H,L=	-3	4	5•	0	-1	13	11	-16	11	44	-39	H,L=	-2	6	9	10	-11	6	14	-12	0	37	-38	H,L=	3	10
0	126	-133	6	14	12	14	23	-22	12•	0	-3	0	101	-92	10	14	17	7•	0	10	1	30	-30	0	11	-13
1	76	78	H,L=	-9	4	H,L=	-3	5	13	25	20	1•	0	-14	11•	4	2	8•	0	1	2•	0	6	H,L=	-1	10
2	89	92	0	32	10	1•	0	-3	14•	0	0	2	39	40	12	10	-10	9•	0	12	3•	0	-5	0•	0	-7
3	99	-100	1•	0	9	2	29	27	15	15	-15	3	18	24	H,L=	-8	6	10•	0	-12	4•	9	-14	1	11	-10
4	28	-33	2•	0	3	3	11	-7	H,L=	3	6	4	20	-28	0•	0	2	11•	0	0	5	21	-22	2•	0	10
5	22	17	3•	0	-4	4	45	60	0	66	-47	5	17	21	1	13	-8	12•	9	13	6	39	39	3	13	14
6	28	17	4•	0	-1	5	25	-30	1	81	79	6	97	98	2•	0	-3	H,L=	-4	7	H,L=	-3	8	4•	8	-10
7	70	-68	5•	7	-17	6•	3	-6	2	27	20	7	31	-35	3	10	-15	1•	0	-3	0	14	15	5	19	-20
8	87	-92	H,L=	0	5	7	54	53	3	78	-79	8	66	-68	4	13	-10	2	15	-15	1	33	-37	6•	0	3
9	40	44	1	26	-22	8	30	34	4•	8	11	9	30	27	5•	0	-10	3•	9	-14	2	16	17	7•	8	10
10	31	38	2	13	12	9	15	-26	5	35	45	10	17	23	6•	0	6	4•	0	5	3•	0	2	H,L=	-2	10
11	41	-48	3	72	59	10•	0	-2	6	40	-26	11	24	-28	7•	0	5	5	29	29	4	39	-39	0•	0	1
12•	0	-6	4	58	40	11	15	12	7	81	-69	12	13	-17	8•	0	0	6•	0	-1	5	26	-35	1	16	-17
13	28	27	5	15	-22	12	10	10	8	12	9	13	13	17	9	12	-13	7•	0	-5	6	11	15	2•	0	-4
14	17	18	6	12	-18	H,L=	-4	5	9	60	53	14•	7	13	10•	0	-2	8	27	20	H,L=	-4	8	3•	6	9
15	11	-7	7	59	51	1	13	-9	10	12	-6	15•	9	-8	11•	8	9	9•	0	-2	0	22	-28	4•	0	-2
16•	0	-4	8•	0	-11	2	15	-8	11	38	-28	16	11	-13	H,L=	-9	6	10	14	-17	1•	0	16	5	18	-5
17	13	10	9	47	-43	3•	7	-13	12•	0	3	17•	0	3	0•	0	7	H,L=	-5	7	2	13	19	H,L=	-3	10
H,L=	-4	4	10	14	13	4•	0	-8	13	25	19	18	15	10	1•	0	0	1	17	17	3•	0	2	0•	0	2
0•	0	8	11	10	9	5•	0	-14	14•	0	0	H,L=	-3	6	2•	0	4	2•	0	11	4•	0	13	1•	0	0
1•	0	-6	12	35	-28	6	24	-14	15	25	-17	0	48	-37	3	14	1	3•	0	-10	5	21	-30	2•	0	0
2	70	64	H,L=	1	5	7•	0	10	H,L=	4	6	1•	0	3	H,L=	0	7	4•	0	3	6•	0	0	3•	7	8
3	34	-49	1	11	13	8	58	62	0	31	24	2	78	70	1•	0	-1	5•	0	0	7	22	27	H,L=	-4	10
4	90	-86	2	44	30	H,L=	-5	5	1	69	74	3	14	-15	2	23	-26	6	10	-12	H,L=	-5	8	0•	0	-3
5	46	40	3	10	-11	1•	0	-5	2	57	-41	4	43	-47	3•	7	-1	7	17	-17	0•	0	6	H,L=	-5	10
6	27	17	4	27	15	2	17	-24	3	86	-67	5•	0	-9	4•	0	-6	8•	0	-4	1	20	-32	0	11	10
7	71	-84	5•	0	-13	3	25	27	4	13	12	6	35	33	5•	9	-5	9	18	14	2•	0	8	H,L=	-6	10
8	44	-42	6	43	31	4•	8	8	5	54	52	7•	0	0	6	21	-18	H,L=	-6	7	3	15	20	0•	7	-10
9•	0	-4	7	13	7	5	20	-23	6•	0	-2	8	35	-31	7•	8	18	1•	0	-8	H,L=	0	9			
10	55	65	8	21	-17	6	21	-27	7	31	-33	9•	0	-3	8•	0	-3	2•	0	7	1•	0	0			
11	23	-13	9•	0	-9	7	22	-46	8•	9	11	10	40	40	9	23	-20	3•	0	1	2•	0	-7			
12	36	-42	10•	0	-1	8	22	26	9	47	37	11•	0	-3	10	24	-21	4•	0	10	3•	0	2			

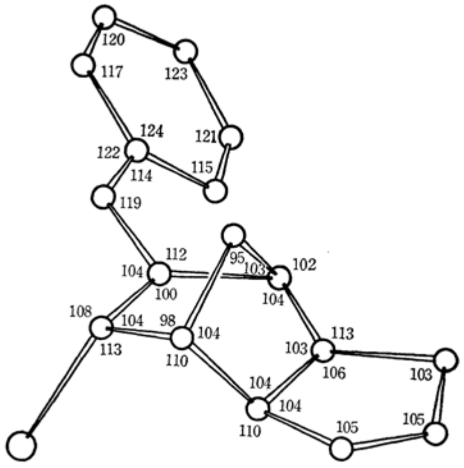


Fig. 3. Bond angles of the molecule (degree).

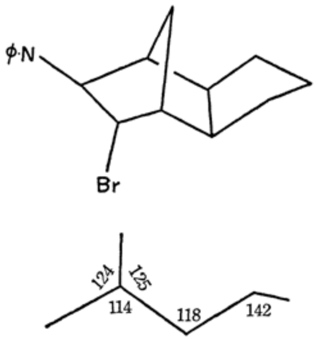


Fig. 4. Angles between the best planes in the tricyclic system (degree).

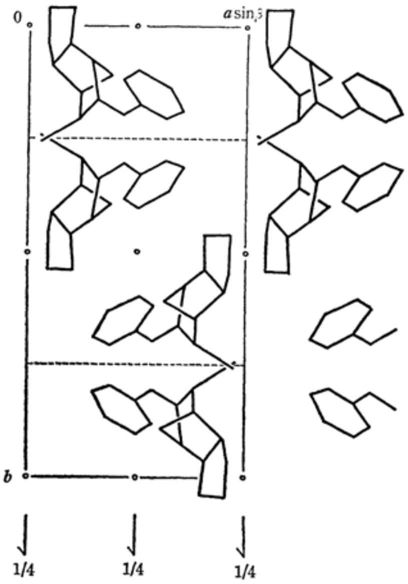


Fig. 5. The packing of the molecules viewed along the c axis.

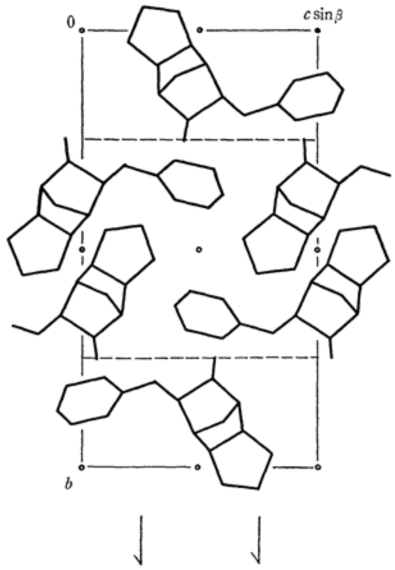


Fig. 6. The packing of the molecules viewed along the a axis.

TABLE 3. CLOSE INTERMOLECULAR CONTACTS WITHIN 4.0 Å

Atom	Nearest atom	Molecule position	Distance Å
C(5)	C(5)	i	3.86
Br	C(9)	ii	3.85
C(10)	C(10)	iii	3.62
N	C(4′)	iv	3.77
N	C(5′)	iv	3.74
C(1)	Br	iv	3.94
C(1)	N	iv	3.75
C(2)	N	iv	3.84
C(2)	C(1′)	iv	3.63
C(2)	C(2′)	iv	3.68
C(6′)	C(4′)	iv	3.93
C(6′)	C(5′)	iv	3.99
C(7)	C(3′)	v	3.77
C(4)	C(7)	vi	3.98
C(7)	C(8)	vi	3.79
C(2′)	C(3′)	vii	3.66
C(3′)	C(3′)	vii	3.44
Br	C(10)	viii	3.83

Key for molecule position

i: $-x,\ -y,\ 1-z$
ii: $-x,\ 0.5+y,\ 0.5-z$
iii: $-x,\ -y,\ -z$
iv: $x,\ 0.5-y,\ -0.5+z$
v: $x,\ y,\ -1+z$
vi: $1-x,\ -y,\ 1-z$
vii: $1-x,\ -y,\ 2-z$
viii: $-1+x,\ 0.5-y,\ -0.5+z$

the range from 1.53 Å to 1.60 Å. Bonds of C(2)–C(3) and C(5)–C(6) seem to be a little longer than the other and their elongation may be favorable to release the bond-angle strain expected at a bridged carbon atom. The fluctuation of the bond length in the benzene ring is also of the same order as that in the tricyclic system. Bonds at the ends of the molecule are somewhat short. This shortening may be due to the large thermal motion of the ends of the molecule.

The bond angles in the tricyclic system are below 107°, almost all of them being about 104°. Especially, the angle C(1)C(7)C(4), 94°, completely deviates from the usual tetrahedral angle. Similar values of the angles at the bridged carbon have been reported for *anti*-8-tricyclo-(3,2,1,$0^{2,4}$)-octyl *p*-bromobenzene sulfonate (97°),[2] *trans*-(1,4),(5,8)-dimetylene-*cis,anti,cis*-perhydroanthraquinone (97°),[3] and *anti*-7-norbonyl *p*-bromobenzoate (96°).[4]

The present molecule consists of several planar groups. The angles between their best planes are shown in Fig. 4. The deviations of the C(7) atom from the planes C(1)C(2)C(3)C(4) and C(4)C(5)C(6)C(1) respectively are significantly larger than that of C(9) from the plane C(5)C(8)C(10)C(6) or that of the corresponding atom in cyclopentane.[5] This is another indication of a great deal of the strain at the bridged carbon atom C(7).

A tricyclo-[5,2,1,$0^{5,6}$]-decane ring is of an exo-form and has an approximate mirror plane perpendicular to the C(2)–C(3) bond. The C(9) atom is in the opposite side of the ring C(5)C(6)C(10)C(8) to C(7). The Br atom is bound to the endo side of the ring and the N atom to exo.

The molecular packing are shown in Figs. 5 and 6, and intermolecular distances within 4.0 Å are listed in Table 3. No unusually short contacts are observed, suggesting that the molecules contact with each other by van der Waals forces.

The authors wish to express their deep thanks to Professor Ichiro Moritani for supplying the material and for his continued interest. Thanks are also due to the Computing Center of the University of Tokyo, through which a Hitac 5020E computer was available to the authors.

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[5] G. A. Barclay and F. S. Stephens, *J. Chem. Soc.*, **1963**, 2027.