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The Crystal and Molecular Structure of 2-Bromomethyl-2, 3-dihydrofuro[2, 3-*b*]tropone

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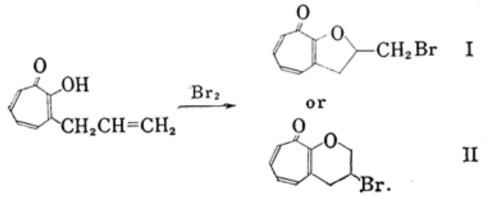
Crystals of 2-bromomethyl-2, 3-dihydrofuro[2, 3-*b*]tropone, $C_{10}H_9O_2Br$, are monoclinic, with four molecules in a unit cell of the dimensions: $a=8.34$, $b=10.23$, $c=11.26$ Å, and $\beta=96.9°$, and with the space group of $P2_1/c$. The intensities were recorded on multiple-film equi-inclination Weissenberg photographs and measured visually against a standard scale. The structure was solved by the heavy atom method. The positional and thermal parameters were refined by the least-squares method. The final R factor for (hkl) reflections is 0.095. An apparent bond alternation in the conjugated seven-membered ring is observed. The longest and the shortest bond lengths in the ring are 1.48 and 1.36 Å respectively. The C–O bond length in the carbonyl group is 1.23 Å, suggesting a considerable contribution of ionic resonance forms. The IR absorption band at 1612 cm^{-1} could be assigned to the stretching frequency of the carbonyl group. The seven carbon atoms in the tropone ring are coplanar, but the oxygen atom in the carbonyl group lies significantly out of the seven-membered ring plane. This may be interpreted as a result of short intermolecular contact. The other intermolecular distances are equal to or larger than the sum of the van der Waals radii.

Recently Funamizu has reported that 3-allyltropolone reacts with bromine in carbon tetrachloride or chloroform to form a colorless compound, $C_{10}H_9O_2Br$.[1)] Considering the reaction mechanism and the UV, IR, and NMR spectra, the structure of this compound has been supposed to be a tropone derivative with a formula of either I or II;



This compound gives a considerably stable hydrobromide, one which does not decompose in a methanol solution. An X-ray crystal analysis has been undertaken in order to determine the structure definitely and also out of our general interest in the aromatic seven-membered ring compound. As a result this compound has been found to be 2-bromomethyl-2, 3-dihydrofuro[2, 3-*b*]tropone (I).

Experimental

The compound crystallizes from a benzene solution in the form of colorless prisms elongated along the c axis.

The crystallographic and physical data obtained are: 2-Bromomethyl-2, 3-dihydrofuro[2, 3-*b*]tropone $C_{10}H_9O_2Br$, mp 123—124°C, Monoclinic, $a=8.34$ Å, $b=10.23$ Å, $c=11.26$ Å, $\beta=96.9°$. Absent spectra, $(0k0)$ when k is odd and $(h0l)$ when l is odd. Space group, $P2_1/c$. Four molecules per unit cell. Volume of the unit cell, 953.7 $Å^3$. Density (by flotation), 1.67_5 $g\cdot cm^{-3}$. Density (calculated), 1.67_9 $g\cdot cm^{-3}$. Linear absorption coefficient for $CuK\alpha$ radiation, $\mu=61.65$ cm^{-1}. Total number of electrons per unit cell, $F(000)=480$.

Equi-inclination Weissenberg photographs were taken at room temperature for the layer lines from 0 to 7 about the b axis and from 0 to 8 about c, using $CuK\alpha$ radiation. The crystals used had the following maximum and minimum dimensions at right angles to the axis of rotation:

0.03×0.03 cm for the b axis rotation,

0.02×0.02 cm for the c axis rotation.

Intensities were estimated by visual comparison with a standard scale prepared with the same crystal. The multiple-film technique was used to correlate strong and weak reflections, ranging in relative intensities from 14000 to 1. Reflections from 1479 planes were observed out of 2100 accessible (hkl) planes. The corrections for Lorentz and polarization factors were made in the usual way, but that for absorption was omitted.

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1) M. Funamizu, M. Sc. thesis submitted to Tohoku University in 1959.

Structure Determination

Bromine coordinates were located from the projections of the Patterson function on (001) and (010). A three-dimensional Fourier synthesis based on the coordinates of the bromine atom clearly revealed all twelve light atoms. The structure factors were calculated with all the non-hydrogen atoms, an isotropic temperature factor $B=4.0$ Å^2 being assigned. The second three-dimensional Fourier synthesis of electron density with the revised signs confirmed the positions of all the carbon and oxygen atoms and considerably reduced the false details which had appeared in the first map. The coordinates of all the atoms obtained from the second map gave a discrepancy factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$, of 0.27 for all the reflections after the observed structure amplitudes had been placed on the same scale as the calculated values. The third three-dimensional electron density map was scarcely different from the second one. Therefore, further refinement of the parameters was made by the block-diagonal matrix least-squares method, all (hkl) reflections being used. Anisotropic temperatures factors of the form: $\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$ were applied for the bromine atom, while the light atoms were treated as undergoing isotropic thermal motions. After four cycles of refinement, the R factor was reduced to 0.095 for the observed reflections. The atomic scattering factors used in the calculations

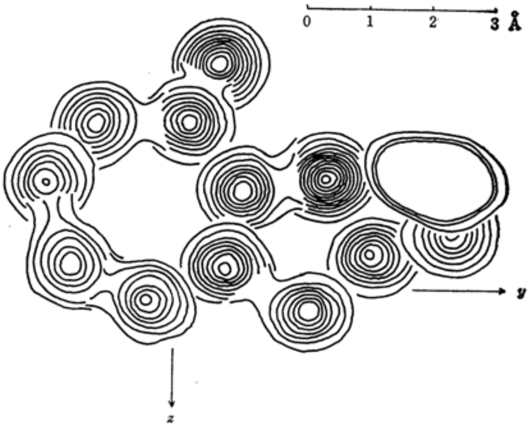

Fig. 1. Composite electron density diagram of sections parallel to (100). The contours are at intervals of 1.0 e.Å^{-3} starting with 1.0 e.Å^{-3}. The contours of the bromine atom are omitted.

TABLE 1. FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS
The anisotropic temperature factors are expressed in the form of
$\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	0.0495	0.4059	−0.1595	0.01671	0.01985	0.00747	0.00504	0.00704	0.00574

Atom	x	y	z	B(Å^2)	Atom	x	y	z	B(Å^2)
C(1)	0.3944	0.0169	−0.2025	3.01	C(7)	0.3417	0.1059	−0.1114	2.87
C(2)	0.3602	−0.1211	−0.2014	3.95	C(8)	0.2441	0.2090	0.0503	3.58
C(3)	0.2843	−0.1957	−0.1251	4.40	C(9)	0.3405	0.3058	−0.0202	3.24
C(4)	0.2185	−0.1613	−0.0171	4.51	C(10)	0.2592	0.4339	−0.0626	3.92
C(5)	0.2095	−0.0376	0.0324	3.78	O(1)	0.4685	0.0642	−0.2805	3.97
C(6)	0.2652	0.0804	−0.0117	2.87	O(2)	0.3786	0.2317	−0.1258	3.14

TABLE 2. ESTIMATED STANDARD DEVIATIONS ($\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ in Å, $\sigma(B)$ in Å^2)

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B_{11})$	$\sigma(B_{22})$	$\sigma(B_{33})$	$\sigma(B_{12})$	$\sigma(B_{13})$	$\sigma(B_{23})$
Br	0.0011	0.0015	0.0011	0.00016	0.00018	0.00008	0.00034	0.00018	0.00023

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$	Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$
C(1)	0.0082	0.0091	0.0083	0.15	C(7)	0.0077	0.0089	0.0078	0.14
C(2)	0.0094	0.0102	0.0094	0.18	C(8)	0.0091	0.0097	0.0091	0.17
C(3)	0.0102	0.0109	0.0102	0.20	C(9)	0.0085	0.0094	0.0085	0.16
C(4)	0.0104	0.0111	0.0104	0.21	C(10)	0.0094	0.0101	0.0095	0.19
C(5)	0.0093	0.0100	0.0094	0.18	O(1)	0.0062	0.0066	0.0062	0.13
C(6)	0.0078	0.0090	0.0078	0.14	O(2)	0.0056	0.0061	0.0056	0.11

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	II	FO	FC
K,L=	0	0	-1	15	-10	-9	10	12	K,L=	1	14	9	13	-14	2	122	-128	3	94	-83	-2	145	-143	1	56	-60
1	46	55	K,L=	1	0	-8	14	18	-3	8	16	K,L=	2	6	3	111	-114	4	72	-80	-1	163	-164	2•	0	-5
2	31	9	1	142	-148	-7	66	69	-2•	0	13	-9	27	-24	4	157	-159	5	53	-47	0	29	-35	3	45	48
3	224	241	2	31	25	-6	54	54	-1	18	20	-8	41	-37	5	167	-175	6	56	-64	1	141	-149	4	28	27
4	92	98	3	149	-146	-5	31	29	0	21	22	-7	40	34	6	44	-30	7•	0	-9	2	13	7	5	27	24
5	29	29	4	123	-114	-4	114	111	K,L=	2	0	-6	32	-22	7	61	-69	8	9	-6	3	16	-17	6	33	35
6	56	-51	5	75	-74	-3	79	67	0	107	119	-5	28	19	8	39	-38	K,L=	3	7	4	23	20	7	15	9
7	82	-88	6	71	-73	-2	15	16	1	91	89	-4	27	23	9	12	-15	-9•	0	-3	5	50	49	8	9	19
8	26	-16	7	35	-28	-1	42	32	2	128	128	-3	41	43	10•	0	5	-8	22	-14	6	61	61	K,L=	4	8
9	41	-43	8	21	-15	0	82	-74	3	29	-29	-2	98	102	K,L=	3	1	-7	11	-13	7	31	29	-8	23	20
10	40	-40	9	23	-29	1•	6	-1	4	51	55	-1	34	38	-9•	0	-3	-6•	0	0	8	26	26	-7	12	13
K,L=	0	2	10•	0	2	2	67	-64	5•	0	-8	0	48	46	-8	26	-26	-5	23	-19	9	21	23	-6	49	46
-10	16	13	K,L=	1	1	3	72	-75	6	31	-24	1	94	95	-7	13	-14	-4	29	-27	K,L=	4	2	-5	75	71
-9•	0	9	-10	23	23	4	52	-49	7	20	-13	2	19	-20	-6•	0	4	-3	30	-23	-9	9	11	-4	24	28
-8	18	-19	-9	27	23	5	58	-58	8	23	-26	3	9	6	-5	31	-30	-2	40	28	-8•	0	-6	-3	66	60
-7	42	-37	-8	57	60	6	24	-24	9	17	-18	4•	0	5	-4	20	-18	-1	26	-13	-7	31	32	-2	73	77
-6	143	-145	-7	61	56	7•	0	0	10•	0	-6	5•	0	-7	-3	40	-36	0•	0	7	-6	57	55	-1	45	43
-5	98	-91	-6	88	90	8	19	-23	K,L=	2	1	6	23	-17	-2	54	40	1	40	27	-5	67	71	0	20	21
-4	186	-179	-5	142	145	K,L=	1	7	-9	36	32	7	34	-40	-1	53	49	2	14	-6	-4	100	106	1	11	-11
-3	271	-256	-4	122	126	-9	33	34	-8	23	22	8•	0	10	0	51	-37	3	28	27	-3	66	73	2	14	-14
-2	303	-320	-3	12	-2	-8	40	37	-7	11	-10	K,L=	2	7	1•	6	0	4	40	42	-2	137	128	3	10	-9
-1	255	-290	-2	52	44	-7	83	80	-6	31	-28	-9	17	15	2	100	86	5•	0	-2	-1	116	108	4	26	-27
0	28	-2	-1	122	-152	-6	64	63	-5	88	-86	-8•	0	0	3	59	63	6	15	15	0	72	61	5	35	-38
1	236	242	1	122	-125	-5	44	39	-4	100	-110	-7•	0	1	4	26	-26	7•	0	0	1	14	17	6	21	-21
2	333	-343	2	351	-415	-4	108	96	-3	192	-205	-6	69	-65	5	46	43	8•	0	7	2	43	-37	7	10	-11
3	127	146	3	109	-106	-3	40	-27	-2	170	-188	-5	65	-70	6	35	32	K,L=	3	8	3	8	-3	K,L=	4	9
4	254	249	4	152	-155	-2	45	-46	-1	305	-346	-4	90	-89	K,L=	3	2	-9	24	-32	4	71	-69	-8	22	24
5	90	94	5	90	-83	-1	60	-55	0	202	-219	-3	152	-141	-10	29	-34	-8	36	-39	5	59	-59	-7•	0	15
6	103	104	6	59	-62	0	63	-63	1	145	-160	-2	145	-150	-9	28	-29	-7	40	-33	6	34	-32	-6	40	39
7	59	49	7	37	-31	1	137	-139	2•	6	-5	-1	84	-88	-8	41	-42	-6	62	-50	7	58	-62	-5	40	42
8	55	58	8•	0	-7	2	119	-117	3	81	-72	0	136	-132	-7	66	-75	-5•	0	-7	8	17	-13	-4	79	66
9	48	44	9	16	17	3	93	-97	4	21	19	1	50	-47	-6	79	-78	-4	72	54	9	17	-12	-3	12	-8
K,L=	0	4	10	10	8	4	33	-23	5	72	64	2	14	8	-5	86	-83	-3•	0	6	K,L=	4	3	-2	38	-30
-10	27	21	K,L=	1	2	5	48	-51	6	88	87	3	10	-11	-4	82	75	-2	91	88	-9	22	25	-1	24	22
-9	47	47	-10	24	-19	6	23	-22	7	68	69	4	42	45	-3•	6	9	-1	90	101	-8	9	7	0•	0	-6
-8	72	73	-9	14	-15	7•	0	-6	8	38	36	5	38	33	-2•	6	17	0	127	131	-7	36	41	1	69	-71
-7	62	63	-8	28	-28	8	14	15	9	34	32	6	30	34	-1	224	216	1	81	83	-6	54	60	2	68	-69
-6	136	141	-7	65	-71	K,L=	1	8	10	24	24	7	48	46	0	244	229	2	71	72	-5	64	71	3•	0	-7
-5	103	98	-6	40	-32	-9	16	-17	K,L=	2	2	8	19	18	1	253	251	3	47	49	-4	83	83	4	29	-26
-4	160	149	-5	17	-22	-8	38	-33	-10•	0	2	K,L=	2	8	2	120	120	4	31	37	-3	128	120	5	32	-28
-3	23	-6	-4	32	-25	-7	30	-26	-9•	0	0	-9•	0	-1	3	183	178	5•	0	0	-2	64	-39	K,L=	4	10
-2	36	-51	-3	57	48	-6•	0	4	-8•	0	-8	-8	25	-18	4	98	96	6•	0	-4	-1	80	63	-6	40	-35
-1	87	-92	-2	40	38	-5	65	-52	-7•	0	2	-7	17	-16	5	29	31	7	11	-15	0	24	-22	-5	20	-18
0	91	-93	-1	173	156	-4	14	7	-6	31	-30	-6•	0	-5	6•	0	3	K,L=	3	9	1	40	-35	-4	28	-22
1	211	-210	0	172	178	-3	88	77	-5	67	-69	-5	80	-69	7•	0	14	-8	11	14	2	119	-116	-3	28	-25
2	221	-216	1	39	41	-2	24	24	-4	49	-49	-4•	0	-16	8	37	-42	-7•	0	1	3	78	-82	-2	43	33
3	265	-253	2	238	228	-1	60	55	-3	63	-59	-3	68	-57	9	25	-19	-6•	0	2	4	72	-75	-1	24	26
4	69	-59	3	160	166	0	82	83	-2	183	-173	-2	49	-33	10	11	-16	-5•	0	11	5	53	-52	0	12	18
5	64	-54	4	44	-43	1	52	49	-1	51	47	-1	35	28	K,L=	3	3	-4	28	-21	6	30	-32	1	33	35
6	84	-86	5	75	76	2	93	98	0	131	-116	0	40	-36	-9•	0	6	-3•	0	-12	7	25	-31	2	43	40
7	13	-5	6	29	20	3	23	12	1	48	43	1	32	24	-8•	0	4	-2	22	-15	8•	0	-4	3	40	37
8	9	-3	7	11	-9	4	12	9	2•	6	16	2	36	35	-7•	0	-5	-1•	0	-3	9•	0	0	4	21	21
9	18	23	8•	0	-5	5	25	29	3	22	10	3•	0	7	-6	32	28	0	33	-31	K,L=	4	4	5	18	15
K,L=	0	6	9	22	-25	6•	0	-5	4	84	69	4	41	45	-5	25	-19	1	25	-28	-9	13	-15	K,L=	4	11
-10	25	-31	10	11	-11	7	10	-7	5	56	59	5	26	24	-4	56	-48	2	20	-23	-8	42	-42	-5	20	10
-9	36	-35	K,L=	1	3	K,L=	1	9	6	27	22	6•	0	0	-3	30	17	3	22	-11	-7	56	-56	-4	29	19
-8	53	-51	-10	31	-32	-8	19	-18	7	27	27	7•	0	10	-2	60	-61	4•	0	4	-6	36	-36	-3	31	28
-7	25	-22	-9	27	-25	-7•	0	-6	8	8	13	K,L=	2	9	-1	40	-28	5•	0	-10	-5	50	-48	-2•	0	15
-6	15	-12	-8	43	-49	-6	14	15	9•	0	4	-8	47	47	0	12	-4	6•	0	-12	-4	62	-59	-1	52	49
-5	69	56	-7	42	-40	-5	26	21	10•	0	8	-7	38	46	1	129	-115	K,L=	3	10	-3	52	-44	0	73	69
-4	62	55	-6	31	-29	-4	34	42	K,L=	2	3	-6	55	66	2	21	-21	-7	10	-13	-2	16	8	1•	0	5
-3	162	149	-5	46	45	-3	142	128	-9	30	32	-5	61	68	3•	0	0	-6	38	-37	-1	104	80	2•	0	8
-2	125	137	-4	121	109	-2	42	51	-8	54	54	-4	80	78	4	24	-22	-5	39	-50	0	38	42	3	21	18
-1	237	231	-3	59	54	-1	119	104	-7	50	52	-3	48	49	5	37	-34	-4	53	-64	1	71	69	K,L=	4	12
0	214	208	-2	151	144	0	112	103	-6	89	95	-2	13	17	6	13	19	-3	70	-81	2	95	94	-5	28	-22
1	97	126	-1	336	325	1	52	54	-5	174	172	-1•	0	0	7•	0	-3	-2	94	-94	3	93	90	-4	19	-17
2	73	77	0	215	239	2	25	19	-4	97	95	0	27	-31	8•	0	-3	-1	29	-31	4	73	85	-3	33	-30
3	61	57	1	174	179	3	23	18	-3	204	182	1	63	-62	9	12	11	0	51	-51	5	33	27	-2	31	-31
4	20	12	2	138	133	4•	0	-3	-2	105	93	2	58	-60	K,L=	3	4	1	18	-12	6	37	34	-1	22	-21
5	24	-20	3	11	-11	5•	0	-4	-1	32	37	3	56	-53	-9	27	30	2•	0	-7	7	23	21	0	49	-42
6	37	-29	4	119	125	6	38	-35	0	69	-62	4	54	-63	-8	39	37	3	27	23	8•	0	-7	1	26	-27
7	50	-47	5	39	-46	7	22	-17	1	73	-70	5	28	-30	-7	34	-31	4	34	32	K,L=	4	5	K,L=	4	13
8	23	-18	6	50	-44	K,L=	1	10	2	127	-119	6	23	-27	-6	54	-52	5	20	17	-9	14	-14	-4	22	-29
9	14	-23	7	30	-32	-7•	0	-12	3	106	-99	K,L=	2	10	-5	65	-62	6	19	21	-8	19	-21	-3	20	-22
K,L=	0	8	8	36	-36	-6	21	-20	4	190	-190	-8	10	15	-4	119	-111	K,L=	3	11	-7	70	-74	-2	27	-26
-9	11	-11	9	27	-27	-5	30	-33	5	100	-112	-7	17	20	-3	138	-138	-6•	0	8	-6	15	-12	-1	8	-9
-8	30	-26	10•	7	-12	-4	70	-67	6	37	-31	-6•	0	15	-2	255	-240	-5•	0	8	-5•	0	-7	K,L=	5	0
-7	73	-57	K,L=	1	4	-3	12	-23	7	46	-50	-5•	0	15	-1	226	-214	-4	16	15	-4	27	18	1	109	-96
-6	33	-42	-10	7	9	-2	63	-55	8	31	-35	-4•	0	-3	0	34	-43	-3•	0	8	-3•	0	4	2	52	43
-5	122	-129	-9	11	13	-1	67	-63	K,L=	2	4	-3•	0	-2	1	120	-118	-2	26	21	-2	53	56	3	39	-36
-4	131	-132	-8	12	13	0	14	-20	-10	18	17	-2	42	-34	2	63	-50	-1	14	16	-1	92	96	4	18	-10
-3	108	-97	-7•	0	0	1	21	-21	-9	15	-16	-1	13	-10	3	21	-22	0	17	21	0	157	149	5	36	-37
-2	118	-114	-6	56	-52	2•	0	0	-8	33	36	0•	0	-16	4	94	98	1•	0	-6	1	55	50	6	11	-10
-1	71	-71	-5	34	-35	3	17	18	-7	36	38	1	64	-67	5	38	32	2•	0	-4	2	81	86	7	14	17
0	11	7	-4	83	-81	4•	0	-10	-6	49	50	2•	0	-9	6	60	55	3•	0	12	3	49	47	8•	0	-2
1	10	-4	-3	134	-131	5	28	25	-5	20	18	3•	0	-14	7	58	55	4•	0	0	4	24	20	9•	0	-11
2	40	38	-2	104	-97	6	24	22	-4	32	23	4•	0	-8	8	32	31	K,L=	3	12	5	14	22	K,L=	5	1
3	79	93	-1	185	-174	K,L=	1	11	-3	61	50	K,L=	2	11	9	18	17	-6	41	49	6	19	-19	-9	23	-21
4	63	55	0	77	-72	-7	17	-20	-2	31	-20	-7	14	-19	K,L=	3	5	-5	32	35	7	15	-12	-8	40	-49
5	56	50	1	109	-102	-6	45	-46	-1	114	-100	-6	37	-30	-9•	0	-9	-4	37	30	8	18	-18	-7	33	-30
6	42	35	2	47	-36	-5	76	-64	0	32	29	-5•	0	1	-8•	0	5	-3•	0	12	K,L=	4	6	-6	86	-95
7	31	32	3	72	61	-4	49	-56	1	122	-121	-4	23	24	-7	17	15	-2•	0	3	-9	23	26	-5	61	-57
8	13	10	4	19	-16	-3	59	-55	2	66	-56	-3	26	31	-6	29	23	-1•	0	-8	-8	13	12	-4	29	-32
K,L=	0	10	5•	0	-2	-2•	0	-11	3	89	-86	-2	41	48	-5	35	29	0	15	-20	-7•	0	1	-3	83	-78
-8	34	43	6	86	90	-1	61	-52	4	32	-36	-1	55	63	-4	25	-14	1	54	-48	-6	25	24	-2	20	-19
-7	55	54	7	24	19	0•	0	10	5	9	15	0	68	72	-3	71	58	2	31	-29	-5	15	-11	-1	59	46
-6	47	51	8	15	14	1	30	31	6	45	-44	1	40	47	-2	58	53	3	26	-28	-4	62	-58	0	101	102
-5	71	57	9	19	16	2•	0	12	7•	0	3	2	34	41	-1	24	-9	4	14	-22	-3	70	-69	1	121	123
-4	33	-21	K,L=	1	5	3	40	33	8	15	13	3	23	29	0	68	62	K,L=	3	13	-2	78	-77	2	103	107
-3	14	13	-10	16	17	4	39	36	9•	0	2	4	14	18	1	7	12	-4	20	-18	-1	63	-66	3	87	87
-2	14	4	-9	11	-14	5	23	20	K,L=	2	5	K,L=	2	12	2	36	-41	K,L=	4	0	0	91	-93	4	110	119
-1	105	-113	-8	11	-7	K,L=	1	12	-10	24	-28	-5•	0	10	3	40	39	0	102	-121	1	112	-114	5	96	93
0	46	-52	-7	50	-50	-6	21	22	-9	50	-53	-4	20	22	4	12	-11	1	141	-153	2	47	-45	6	18	18
1	75	-74	-6	101	-97	-5	25	23	-8	27	-28	-3	15	20	5	20	-12	2	100	-91	3	12	-17	7	11	7
2	86	-93	-5	88	-81	-4	33	28	-7	67	-71	-2	12	18	6	21	-19	3	82	-79	4	18	-19	8	25	29
3	35	-39	-4	132	-128	-3	17	16	-6	80	-76	-1	28	28	7	8	-9	4	62	-53	5•	0	-2	9	14	-19
4	40	-38	-3	184	-175	-2•	0	9	-5	18	-10	0	12	17	8•	7	-5	5	20	22	6	9	5	K,L=	5	2
5	32	-34	-2	212	-194	-1	22	-15	-4	24	20	1•	0	0	K,L=	3	6	6	11	-10	7	14	19	-9•	0	-11
K,L=	0	12	-1	40	-35	0•	0	-3	-3	23	-7	2•	0	-10	-9•	0	7	7	26	23	8	12	12	-8•	0	13
-6	10	9	0	17	-15	1	19	-21	-2	207	183	K,L=	2	13	-8	69	68	8	25	29	K,L=	4	7	-7	29	-34
-5	11	23	1	25	-20	2	30	-29	-1	107	107	-5	25	-35	-7	55	56	9	8	7	-9	20	23	-6	25	-27
-4	51	53	2•	5	0	3•	0	-7	0	156	153	-4	30	-35	-6	36	47	10	17	26	-8•	0	0	-5	25	25
-3	40	46	3	119	112	4	20	-21	1	207	206	-3	42	-42	-5	135	143	K,L=	4	1	-7	22	-19	-4•	0	-7
-2	83	96	4	83	74	K,L=	1	13	2	140	134	-2	49	-47	-4	112	107	-9	20	17	-6	59	-51	-3	26	-22
-1	61	52	5	100	105	-3	10	2	3	114	115	-1	32	-29	-3	80	71	-8	13	12	-5	11	1	-2	13	12
0	11	16	6	30	21	-2	33	-27	4	71	66	0	9	-15	-2	26	27	-7	21	18	-4	56	-57	-1	13	14
1	78	72	7	40	47	-1	21	-23	5	8	-6	1•	0	-4	-1	14	12	-6	19	-14	-3	99	-109	0	98	84
K,L=	0	14	8	38	35	0	55	-51	6	24	24	2	9	-10	0	39	-33	-5	69	-74	-2	111	-105	1•	0	3
-3	13	-18	9•	0	1	1	23	-22	7	8	13	K,L=	3	0	1	47	-47	-4	9	-5	-1	19	-16	2	40	-32
-2	24	-27	K,L=	1	6	2	22	-20	8	40	-47	1	86	-84	2	139	-144	-3	116	-124	0	13	-15	3	83	81

TABLE 3 (Continued)

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC
4	31	-31	6	22	20	9	10	-16	-4•	0	5	-7	25	27	-4•	0	-4	-2	22	-15	K,L=	9	3	K,L=	10	3
5•	0	1	K,L=	5	8	K,L=	6	2	-3	33	29	-6	11	4	-3	14	-13	-1	50	43	-4	15	17	-3	11	-6
6	15	-17	-8•	0	-6	-9	12	15	-2	30	31	-5	13	14	-2•	0	-5	0	20	-25	-3•	0	1	-2•	0	3
7•	0	-1	-7	11	-9	-8•	0	-7	-1	21	20	-4	20	26	-1	61	-59	1•	0	3	-2	29	28	-1	16	-18
8	7	-8	-6•	0	3	-7•	0	-4	0	41	36	-3	33	-27	0	26	-29	2	20	23	-1	28	28	0	27	24
9	12	-15	-5•	0	3	-6	60	67	1	33	39	-2	17	-20	1	10	-13	3•	0	-12	0	12	-11	1•	0	6
K,L=	5	3	-4	33	25	-5	47	44	2•	0	3	-1	60	-60	2	48	-51	4•	0	-3	1	39	47	2•	0	-1
-9	29	36	-3•	0	0	-4	82	85	3	12	8	0	89	-85	3	16	-23	5•	0	-7	2•	0	8	3	15	16
-8	13	17	-2	14	15	-3	68	65	4	8	9	1	20	-23	4	11	-12	6	12	-12	3	12	12	K,L=	10	4
-7•	0	10	-1	15	19	-2	84	85	K,L=	6	8	2	55	-56	5	12	-13	K,L=	8	5	4	14	21	-5	18	22
-6	16	25	0	40	37	-1	80	80	-8	8	11	3	65	-68	K,L=	7	9	-6	22	22	K,L=	9	4	-4•	0	-4
-5	17	-12	1•	0	4	0	46	46	-7	23	18	4	46	-48	-5	13	-8	-5•	0	-2	-5	11	9	-3•	0	9
-4	37	-34	2•	0	0	1	26	-20	-6	25	27	5	11	-8	-4•	0	-15	-4•	0	0	-4	15	18	-2•	0	1
-3	102	-110	3	15	-22	2	20	17	-5	48	47	6•	0	-2	-3	29	-27	-3	21	19	-3	33	31	-1•	0	-2
-2	120	-120	4•	0	10	3	72	-67	-4	59	55	K,L=	7	3	-2	23	-24	-2	62	-62	-2	33	33	0	18	-17
-1	91	-93	5•	0	-9	4	54	-60	-3	37	41	-8	11	15	-1	15	-16	-1	40	-45	-1	9	4	1	23	-21
0	175	-171	6	11	-12	5	37	-38	-2	27	27	-7•	0	0	0•	0	-12	0	25	-24	0	12	9	2	9	-12
1	104	-98	K,L=	5	9	6	34	-34	-1	34	33	-6	22	27	1	21	-20	1	47	-50	1	45	50	3	10	-9
2	65	-94	-7	9	10	7	36	-39	0	15	-8	-5	21	-22	2	14	19	2	21	-21	2	12	-13	4	17	-15
3	64	-56	-6•	0	-3	8	22	-25	1•	0	0	-4	18	-17	3•	0	-5	3	39	-50	3	23	-23	5	15	-15
4	21	-15	-5	12	-12	K,L=	6	3	2	26	-28	-3•	0	4	4•	0	8	4	22	-26	4	9	-3	K,L=	10	5
5	28	20	-4	50	-44	-9•	7	-8	3	37	-45	-2	61	-60	5	8	12	5	11	18	5•	0	-5	-3•	0	0
6	12	14	-3	77	-69	-8	10	-13	4	14	-11	-1	45	-40	K,L=	7	10	K,L=	8	6	6	10	-11	-2	8	-7
7	9	14	-2	34	-44	-7	12	-12	5	32	-39	0	46	-48	-5	19	16	-6•	0	0	K,L=	9	5	-1	12	-12
8	27	26	-1	67	-61	-6	40	-47	6	15	-11	1	26	-18	-4	18	18	-5•	0	-10	-5	16	-15	0	12	-14
9	18	29	0	78	-73	-5	14	15	K,L=	6	9	2•	0	-12	-3	33	30	-4	12	11	-4	22	-17	1	10	11
K,L=	5	4	1	55	-56	-4	37	-37	-7	18	-18	3•	0	-14	-2	27	26	-3	20	-15	-3	15	-17	2	14	-13
-9	8	12	2•	0	-7	-3	65	-55	-6	9	-10	4•	0	-14	-1	34	32	-2•	0	5	-2•	0	-8	3	8	-12
-8•	0	-1	3	20	-19	-2	26	16	-5	14	-14	5	28	35	0•	0	11	-1•	0	-1	-1	9	-12	4	10	12
-7•	0	9	4•	0	-3	-1	11	-4	-4	18	-16	6	13	13	1	20	19	0•	0	1	0	20	-19	K,L=	10	6
-6	24	-24	5	11	10	0	62	-59	-3	28	-27	K,L=	7	4	2•	0	10	1•	0	5	1	22	-20	-4	14	14
-5	14	5	K,L=	5	10	1	56	53	-2	13	-14	-7	11	7	3	8	-12	2	10	17	2	14	23	-3•	0	1
-4	19	16	-7	9	-11	2•	0	5	-1•	0	-7	-6	21	18	K,L=	7	11	3	9	7	3•	0	-9	-2	25	22
-3	73	-56	-6	10	-9	3	20	25	0	17	-13	-5•	0	-1	1	16	-15	4	9	4	4•	0	6	-1	19	16
-2	23	-24	-5	11	2	4	19	10	1	20	16	-4	66	74	2	16	-19	5	16	18	K,L=	9	6	0	15	19
-1	22	-13	-4	27	-25	5	14	14	2•	0	3	-3	59	62	K,L=	8	0	K,L=	8	7	-6	18	-17	1	8	8
0	24	18	-3•	0	-1	6	33	41	3•	0	-5	-2	15	12	0	32	-28	-6•	0	8	-5•	0	-6	2•	0	8
1•	0	2	-2	29	-25	7	11	12	4	24	22	-1	94	88	1•	0	0	-5	36	29	-4	16	-16	3	19	21
2	10	-7	-1	13	10	K,L=	6	4	5	13	18	0	36	41	2	23	25	-4	30	22	-3	27	-20	K,L=	10	7
3•	0	4	0	19	16	-8	22	-21	K,L=	6	10	1	24	25	3	24	25	-3	40	39	-2•	0	5	-4	16	12
4	57	58	1•	0	7	-7	57	-64	-6	16	-19	2	60	63	4	40	-43	-2	42	42	-1•	0	-3	-3•	0	4
5•	0	-6	2•	0	6	-6	38	-41	-5	20	-15	3	26	-31	5	30	30	-1•	0	8	0•	0	6	-2•	0	4
6	16	23	3	11	13	-5•	0	-6	-4•	0	-6	4	12	-13	6	17	13	0	44	45	1	24	26	-1•	0	1
7	11	5	4	12	11	-4	74	-78	-3	12	8	5•	0	1	7•	0	-4	1	16	18	2	24	24	0•	0	-3
8•	0	5	5	11	19	-3	12	7	-2	21	15	6	15	-16	K,L=	8	1	2•	0	-11	3•	0	0	1•	0	3
K,L=	5	5	K,L=	5	11	-2	9	-12	-1	31	29	7	17	-17	-7	14	10	3•	0	5	4	18	21	2•	0	-1
-9	10	11	-6	25	35	-1	48	48	0	32	35	8	11	-15	-6	12	-13	4	20	-23	5	16	17	3	16	-19
-8	10	5	-5	32	35	0	84	91	1	34	35	K,L=	7	5	-5	22	13	5•	0	-6	K,L=	9	7	K,L=	10	8
-7	20	21	-4	43	44	1	52	49	2	39	37	-6	18	15	-4	44	48	K,L=	8	8	-6	14	16	-2	13	-19
-6	57	56	-3	35	29	2	85	95	3	19	19	-5	29	32	-3	56	61	-6	11	-1	-5•	0	5	K,L=	11	1
-5	82	94	-2	38	35	3	81	92	K,L=	6	11	-4•	0	3	-2	55	52	-5•	0	0	-4•	0	1	-3	17	11
-4	86	98	-1	37	34	4	23	22	-5	22	20	-3	50	51	-1	20	18	-4•	0	2	-3•	0	10	-2•	0	-4
-3	71	53	0	25	-17	5	41	43	-4•	0	3	-2	47	47	0	47	49	-3•	0	1	-2•	0	0	-1•	0	-2
-2	107	102	1	13	-11	6	22	27	-3	9	-8	-1	50	-49	1	81	81	-2	25	-23	-1	17	12	0	13	-12
-1	98	103	2•	0	0	7•	0	-8	-2•	0	-3	0	36	36	2	15	14	-1•	0	5	0	20	-22	1	8	-8
0	13	22	3	18	-20	8•	0	-7	-1	21	-12	1	13	-10	3	20	-22	0	14	-14	1	11	-12	2	10	-10
1	33	-33	4	29	-35	K,L=	6	5	0•	0	-3	2	24	-18	4•	0	-11	1	28	-21	2•	0	-1	3	19	-18
2	14	12	K,L=	5	12	-9	9	10	1	20	-18	3	29	-33	5•	0	-6	2•	0	5	3•	0	-5	4•	0	-1
3	55	-58	-3	32	-24	-8•	0	5	2	19	-17	4	32	-37	6	19	-14	3	14	-17	4	16	-24	5	11	-12
4	59	-59	-2•	0	1	-7•	0	5	3	17	-18	5	14	-9	7	17	-21	K,L=	9	0	5•	7	-5	K,L=	11	3
5	40	-46	-1	22	-18	-6	19	21	K,L=	6	12	6•	0	2	8	16	-20	1	35	38	K,L=	9	8	-3	21	19
6	34	-39	0•	0	-4	-5•	0	-1	-4	21	-24	7	17	-26	K,L=	8	2	2	27	21	-3	23	-18	-2	13	9
7	33	-29	1•	0	-11	-4	23	22	-3	22	-26	K,L=	7	6	-7•	0	1	3•	0	0	-2	24	-18	-1•	0	8
8	19	-22	2	19	-20	-3	31	-25	-2	23	-25	-8	12	-13	-6	10	-10	4	27	25	-1•	0	-10	0	10	12
K,L=	5	6	K,L=	5	13	-2	14	-16	-1	30	-30	-7	31	-28	-5•	0	2	5	24	28	0	25	-25	1	16	16
-8•	0	4	-1	28	28	-1	10	-7	0	17	-18	-6	17	-20	-4	11	13	6	17	13	1•	0	-10	2	13	13
-7•	0	1	0	15	20	0	36	-34	1	15	-14	-5	39	-39	-3	50	-52	7	15	12	2	12	-15	K,L=	11	4
-6•	0	10	K,L=	6	0	1	46	-43	K,L=	7	0	-4	52	-50	-2	53	57	K,L=	9	1	K,L=	10	0	-4	10	-11
-5	19	18	0	150	-152	2	15	-13	1	55	49	-3	15	10	-1•	0	-8	-7	12	14	0	33	36	-3•	0	1
-4	29	20	1	70	-65	3	37	-39	2	43	43	-2	46	-51	0	33	-39	-6•	0	-5	1	14	15	-2•	0	-2
-3•	0	1	2	86	-85	4	29	-31	3	17	20	-1	29	-32	1•	0	0	-5	23	24	2•	0	5	-1•	0	2
-2	45	-41	3	59	-58	5	17	-14	4	50	44	0	49	49	2•	0	8	-4	11	-10	3	35	37	0	10	-12
-1	18	12	4	29	-30	6	10	-5	5	45	43	1•	0	0	3•	0	-8	-3	9	14	K,L=	10	1	1•	0	-2
0	31	-17	5	21	19	7•	0	1	6	35	39	2	26	26	4	9	-8	-2	19	19	-5	10	6	2•	0	-4
1	9	-8	6	15	19	8•	7	-14	7	23	22	3	39	45	5	22	-24	-1	36	-41	-4•	0	-5	3•	0	1
2	53	-56	7	21	21	K,L=	6	6	8	9	11	4•	0	-1	6	11	19	0	11	11	-3	17	21	4	9	-11
3	20	-15	8	10	10	-8	25	22	K,L=	7	1	5	33	46	K,L=	8	3	1	11	-13	-2•	0	-9	K,L=	11	5
4•	0	-7	9	20	23	-7•	0	0	-8	15	-20	6	21	23	-8	11	-16	2	33	-40	-1	22	17	-3	10	-11
5•	0	6	K,L=	6	1	-6•	0	-8	-7	16	-12	K,L=	7	7	-7•	0	-7	3•	0	8	0	18	13	-2•	0	-6
6•	0	-9	-8	16	16	-5•	0	3	-6	22	-23	-7	10	-13	-6	28	-34	4	13	-16	1	9	-7	-1	10	-14
7•	0	4	-7	13	-21	-4	28	-27	-5	19	-17	-6	17	-15	-5	57	-61	5	27	-33	2•	0	5	K,L=	11	6
K,L=	5	7	-6	21	21	-3	89	-90	-4	33	-36	-5•	0	-7	-4•	0	-1	6•	0	3	3•	0	0	-2	12	11
-8	35	-36	-5	47	46	-2	38	-40	-3	14	-14	-4•	0	-5	-3	29	-25	7	13	-15	4	12	-15	-1•	0	-1
-7	52	-51	-4•	0	-5	-1	96	-98	-2•	0	3	-3•	0	-1	-2	42	-45	K,L=	9	2	5•	0	5	0	9	7
-6	36	-38	-3	49	45	0	53	-51	-1	8	7	-2	32	28	-1	12	-17	-7	16	22	6	14	-15	K,L=	11	7
-5	30	-33	-2	76	79	1	46	-47	0	20	19	-1	26	22	0•	0	-2	-6•	0	0	K,L=	10	2	-2	10	-10
-4	49	-40	-1	21	-15	2	50	-61	1	45	40	0•	0	-3	1	53	59	-5•	0	9	-5	18	-18	-1•	0	-5
-3	19	-22	0	79	73	3	13	14	2	59	57	1	64	74	2	36	36	-4•	0	2	-4	22	-22	0	11	-10
-2	27	17	1	16	17	4•	0	-8	3	27	22	2	11	9	3•	0	-1	-3•	0	12	-3•	0	-15	K,L=	12	4
-1	78	74	2	54	54	5•	0	5	4	29	25	3	12	13	4	38	44	-2	13	-8	-2•	0	-6	-1	11	-13
0	36	42	3	10	-6	6	32	35	5	13	12	4	10	6	5	34	43	-1	58	-64	-1	28	-31	0•	0	-2
1	61	51	4•	0	-5	7	12	11	6	23	38	5•	0	3	6	18	17	0	15	-14	0•	0	-5	1•	0	4
2	80	90	5	11	6	K,L=	6	7	7	14	-16	K,L=	7	8	K,L=	8	4	1	9	-3	1•	0	-3	2•	6	-8
3	70	76	6	13	-13	-7•	0	1	8•	0	-7	-7	14	16	-5•	0	0	2	37	-35	2•	0	-4	K,L=	12	5
4	28	31	7•	0	-2	-6•	0	4	K,L=	7	2	-6	15	15	-4•	0	3	3	36	-38	3	10	14	0•	6	8
5	22	26	8	11	-12	-5	27	26	-8	17	18	-5•	0	6	-3•	0	8	4	11	-8	4	12	18			

were from taken the International Tables for X-ray Crystallography (1962).[2] The final atomic coordinates and the temperature factors are given in Table 1, and their standard deviations, in Table 2. The observed and calculated structure factors are listed in Table 3. The final three-dimensional electron-density distribution calculated with signs based on these parameters is shown in Fig. 1.

The computations were done on a NEAC 2101 computer in the Institute and on a NEAC 2206 computer in the Computing Center of the University, with programs written by Tsunehiro Takano and Yoriko Nishi. The least-squares refinement was done on a HITAC 5020 computer in the University of Tokyo with a program written by one of the present authors (T. A.).

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[2] International Tables for X-ray Crystallography, Vol. 3, Kynoch Press, Birmingham, England, 1962, p. 202.

Discussion

Molecular Geometry. The intramolecular bond lengths and angles are shown in Fig. 2 and are listed in Table 4 with their standard deviations. The C(1)–O(1) distance, 1.232 Å, is significantly longer than the pure C–O double bond length, 1.21 Å.³⁾ The C(7)–O(2) distance, 1.337 Å, is apparently shorter than the C(sp^2)–O single bond length,⁴⁾ while a similar value, 1.354 Å, was reported in 1-oxa-azulan-2-one.⁵⁾ The bond alternation, as suggested from its Kekule formula, is observed in the seven-membered ring, but the C(1)–C(2) distance is shorter than the C(1)–C(7) distance. A similar difference has been also reported in the case of sodium tropolonate.⁶⁾ Figure 3(a) shows four main canonical structures for the tropone ring in this molecule. The observed bond distances can be explained quite satisfactorily by assuming that the first structure contributes approximately 70% to the resonance hybrid, the second, 20%, and the last two, 5% each. The bond distances calculated from these weights are shown in Fig. 3(b), where the C–C distances were taken from

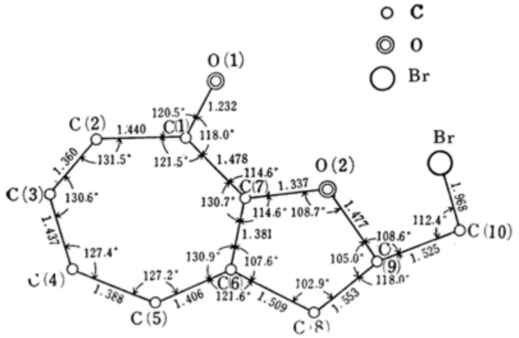

Fig. 2. Bond-lengths (Å) and angles (degrees).

TABLE 4. BOND LENGTHS AND ANGLES WITH THEIR e. s. d.'s

	Distance (Å)	e. s. d.
C(1)-O(1)	1.232	0.011
C(1)-C(2)	1.440	0.014
C(2)-C(3)	1.360	0.015
C(3)-C(4)	1.437	0.016
C(4)-C(5)	1.388	0.015
C(5)-C(6)	1.406	0.013
C(6)-C(7)	1.381	0.013
C(7)-C(1)	1.478	0.013
C(7)-O(2)	1.337	0.011
O(2)-C(9)	1.477	0.011
C(9)-C(8)	1.553	0.014
C(8)-C(6)	1.509	0.013
C(9)-C(10)	1.525	0.014
C(10)-Br	1.968	0.010

	Angle (deg.)	e. s. d.
O(1)-C(1)-C(2)	120.5	0.7
C(2)-C(1)-C(7)	121.5	0.7
O(1)-C(1)-C(7)	118.0	0.7
C(1)-C(2)-C(3)	131.5	0.7
C(2)-C(3)-C(4)	130.6	0.7
C(3)-C(4)-C(5)	127.4	0.7
C(4)-C(5)-C(6)	127.2	0.7
C(5)-C(6)-C(7)	130.9	0.7
C(5)-C(6)-C(8)	121.6	0.7
C(7)-C(6)-C(8)	107.6	0.7
C(6)-C(7)-C(1)	130.7	0.7
C(6)-C(7)-O(2)	114.6	0.7
C(1)-C(7)-O(2)	114.6	0.7
C(7)-O(2)-C(9)	108.7	0.7
O(2)-C(9)-C(8)	105.0	0.7
O(2)-C(9)-C(10)	108.6	0.7
C(8)-C(9)-C(10)	118.0	0.7
C(6)-C(8)-C(9)	102.9	0.7
C(9)-C(10)-Br	112.4	0.7

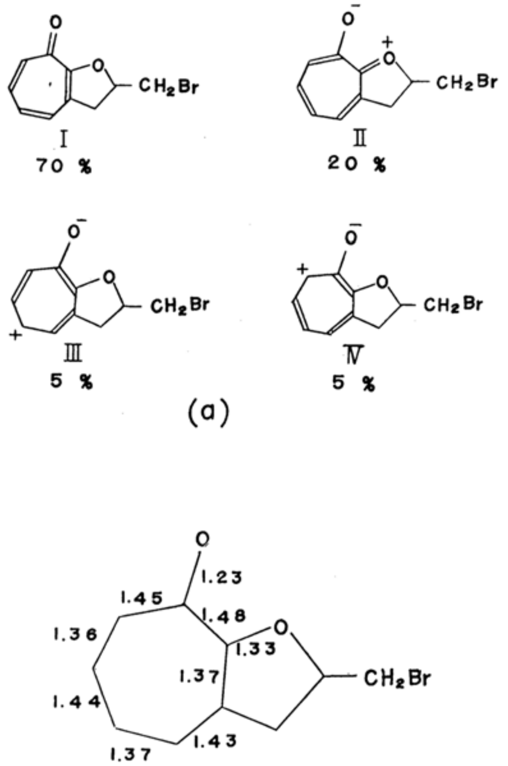

Fig. 3. Canonical structures for the tropone ring and the predicted bond distances (Å).

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3) R. E. Marsh, R. Bierstedt and E. L. Eichhorn, *Acta Cryst.*, **15**, 310 (1962).

4) I. Ambats and R. E. Marsh, *ibid.*, **19**, 942 (1965).

5) Y. Sasada and I. Nitta, *ibid.*, **9**, 205 (1956).

6) Y. Sasada, This Bulletin, **32**, 171 (1959).

Table 7-9 of Pauling,⁷⁾ and the C–O distances, from the curve drawn through points representing the observed C–O bond distances for the bond numbers 1.0, 1.5, and 2.0.³⁾

The O(2)–C(9) distance, 1.477 Å, is considerably longer than the C(sp^3)–O length, 1.43 Å.⁸⁾ This may be partly due to the errors caused by the omission of absorption corrections, and partly to the weakness of the bond; O(2), which is positively charged due to contribution of the structure II in Fig. 3, may attract the bonding electrons between C(9) and O(2).

Though C(1) is involved in the seven-membered ring, each bond angle around C(1) is nearly equal to 120°. Therefore, the C(1) atom seems to have an approximately pure sp^2 hybridized orbitals, and in the C(1)–O(1) bond the deviation from the pure C=O double bond length can be supposed to depend on the π-bond order only. It has been found that the stretching frequencies of carbon-oxygen bonds in carbonyl compounds can be correlated with the C=O bond distances when no distortion is exerted.⁹⁾ By using the correlation curve and the observed bond length, the stretching frequency of the C=O bond of this compound is derived to be about 1670 cm^{-1}. This compound, as well as the other tropone derivatives, exhibits quite a sharp band at 1612 cm^{-1} and the strongest band 1557 cm^{-1} in KBr. Therefore, the absorption at 1612 cm^{-1} can be assigned to the C=O stretching vibration within the average deviation. This seems to be supported by the fact that in tetrahydroxy-*p*-benzoquinone a strong band at 1625 cm^{-1} is interpreted as a stretching vibration of C=O whose bond length is 1.229 Å.¹⁰⁾

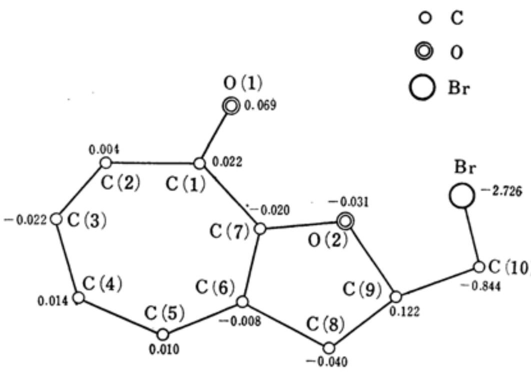

Fig. 4. The deviations (Å) of the atoms from the least-squares plane through atoms C(1)—C(7).

Planarity. The equation for the best plane of the seven carbon atoms in the seven-membered ring is:

$$5.910X + 2.972Z - 11.026 = Y$$

where $X = ax\sin\beta$, $Y = by$, and $Z = cz + ax\cos\beta$. The deviations from this plane are shown in Fig. 4. The seven ring atoms, C(1)—C(7), are coplanar within the range of experimental error, showing that these atoms make a conjugate system, but the O(1) atom, which should conjugate with the seven-membered ring, lies significantly out of the plane. This seems to be due to the intermolecular repulsive force, as will be discussed in the next paragraph. Each atom in the five-membered ring also lies nearly within this plane.

Crystal Structure. The packing diagrams of the crystal viewed along the a, b, and c axes are

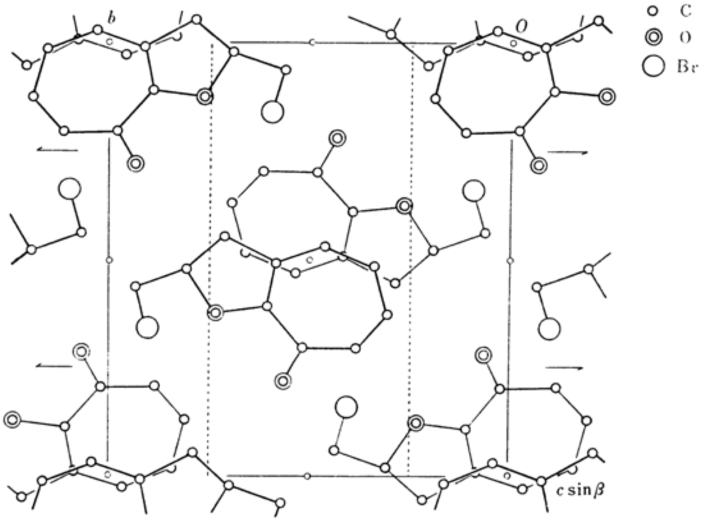

Fig. 5. The crystal structure projected along the a axis.

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7) L. Pauling, "The Nature of the Chemical Bond," 3rd ed. Ithaca, New York: Cornell University Press.

8) D. R. Lide, Jr., *Tetrahedron*, **17**, 125 (1962).

9) E. M. Layton, Jr., R. D. Kross and V. A. Fassel, *J. Chem. Phys.*, **25**, 135 (1956).

10) H. P. Klug, *Acta Cryst.*, **19**, 983 (1965).

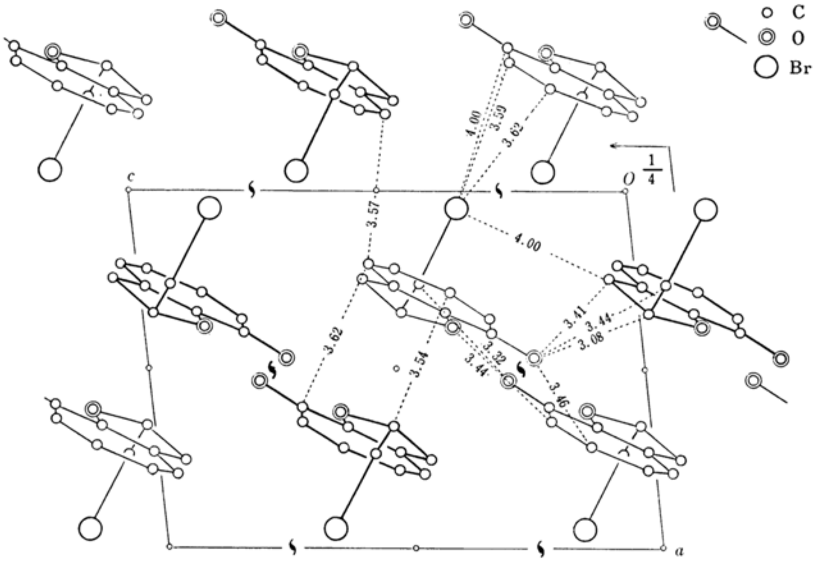

Fig. 6. The crystal structure projected along the b axis and the short intermolecular distances (Å).

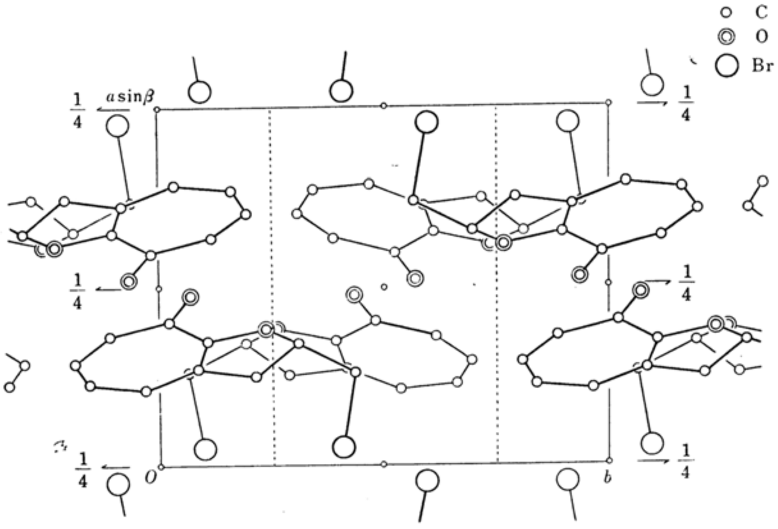

Fig. 7. The crystal structure projected along the c axis.

shown in Figs. 5, 6, and 7 respectively, together with the short intermolecular distances. The shortest carbon-oxygen distance is 3.08 Å, as is shown in Fig. 6; this is considerably less than the sum of the van der Waals radii of 3.4 Å.7) A similar short contact between C(sp^3) and O, 3.08 Å, has been reported in the crystal of barbituric acid.11) Such a short contact may suggest a strong interaction between these atoms. The direction of the deviation of the O(1) atom from the seven-membered ring plane is consistent with such an interaction.

The short contacts below 4.0 Å around the bromine atom were not observed along the b axis direction. In the electron-density map shown in Fig. 1, an elliptical peak elongated parallel to the b axis was obtained for the bromine atom. Although this may come from the omission of absorption corrections, it may be possible to be interpreted as the bromine atom easily vibrating along this direction due to no short contacts.

The authors wish to express their deep thanks to Mrs. Yoriko Nishi and Dr. Tsunehiro Takano for their assistance in the use of the electronic computer, and to Dr. Makoto Funamizu for supplying the sample.

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11) W. Bolton, *ibid.,* **16,** (166 (1963).