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The Crystal and Molecular Structure of 4,10b-Methano-8*H*-benzo[*ab*]cyclodecen-8-one

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4,10b-Methano-8*H*-benzo[*ab*]cyclodecen-8-one ($C_{14}H_{10}O$), a stable derivative of so-called 1,6-methano[10]-annulene, forms reddish orange crystals of the space group Pbca, with eight molecules in a unit cell with dimensions of $a=16.567$, $b=14.090$, and $c=8.418$ Å. The structure was solved by the symbolic addition method and refined by the block-diagonal least-squares method. The final R factor was 0.080 for the 1386 independent observed reflections. The lengths of the peripheral bonds of the [10]annulene nucleus do not exhibit any apparent alternation. The peripheral eight atoms are approximately coplanar. The C–O distance (1.236 Å) is longer than those in quinones and tropones, and it is consistent with the large dipole moment and high basicity of the present molecule.

Contrary to the prediction by Hückel's(4n+2)rule, so-called [10]annulene does not show aromaticity. This is because [10]annulene is not likely to take a stable planar conformation.[1] The bridged analogs (I) of the [10]annulene,[2-4] however, are aromatic, and the X-ray analyses of several derivatives have indicated that the [10]annulene nucleus has the structural characteristics of the aromatic compound. Recently, 4,10b-methano-8*H*-benzo[*ab*]cyclodecen-8-one (II),[5b] a derivative of 1,6-methano[10]annulene (Ia), has been synthesized by Murata *et al.*[5a] Although it was anticipated that the condensed six-membered ring would result in a strain in the molecule, the aromatic character is retained in the ten-membered ring of II; for instance, a diamagnetic ring current has been observed.[5]

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1) S. Masamune, K. Hojo, K. Hojo, G. Biogam, and D. L. Rabenstein, *J. Amer. Chem. Soc.*, **93**, 4966 (1971).

2) E. Vogel, "Aromaticity," Special publication No. 21, The Chemical Society, London (1967) p. 113.

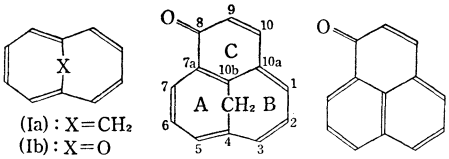
3) F. Sondheimer and A. Shani, *J. Amer. Chem. Soc.*, **86**, 3168

4) E. Vogel, W. Pretzer, and W. A. Böll, *Tetrahedron Lett.*, **1965**, 3613.

5) a) I. Murata, T. Nakazawa, and T. Tatsuoka, *ibid.*, **1971**, 1789. b) In reference 5a this compound was called 1*H*-cyclohexa[4,5,6-*de*]methano[10]annulen-1-one.

II can also be regarded as a bridged analog of phenalenone (III), which is a highly polarized ketone.[6] It is interesting that II is more polar than III.[5a]

The present work has been undertaken in order to examine the effect of the condensed ring on the aromaticity of the [10]annulene system and to ascertain the structural basis of the highly-polarized nature of II.



Experimental

Crystals of II, kindly supplied by Professor I. Murata, were recrystallized from the ether–petroleum ether mixture. They were reddish-orange mass crystals. The unit-cell dimensions were determined from zero-layer Weissenberg photographs about the *b* and *c* axes. Spacings of about 40 reflections, calibrated with superimposed aluminum powder lines, were subjected to the least-squares treatment. The density of the crystals was measured by the flotation method. Since the systematic absences of reflections are *hk*0 for *h* odd, *h*0*l* for *l* odd, and 0*kl* for *k* odd, the space group was determined to be Pbca. The crystal data of II are summarized in Table 1.

Table 1. Crystal data

Formula	$C_{14}H_{10}O$
MW	194.2
Crystal system	Orthorhombic
Space group	Pbca
a	16.567±0.004 Å
b	14.090±0.003 Å
c	8.418±0.002 Å
Volume of a unit cell	1965.0 Å^3
Density calculated	1.312 g·cm^{-3}
Density measured	1.316 g·cm^{-3}
F(000)	816
μ(Cu$K\alpha$)	6.51 cm^{-1}
Number of molecules per unit cell	8

The reflections were recorded, using Cu$K\alpha$ radiation, on equi-inclination multiple-film Weissenberg photographs for 0—10 layers around the *b* axis and 0—6 layers around *c*. The dimensions of the crystals used were 0.35×0.2×0.7 mm and 0.6×0.2×1.3 mm for the *b* and *c* axis rotations respectively.

The intensities were first estimated by visual comparison with a standard scale prepared with the same crystal. Since then a TV-densitometer has become available, and it has been proved that the TV-densitometer method is more accurate and time-saving than the visual method.[7] Therefore, the intensities were remeasured by means of the TV-densitometer.

The intensity data of 2019 independent reflections (90.0% within the Cu$K\alpha$ sphere) were collected; 632 of them were

Table 2. Final atomic coordinates and temperature factors and their standard deviations
All quantities are multiplied by 10^4 except temperature factors of hydrogen atoms. E.s.d.'s are in parentheses. The anisotropic temperature factors are expressed in the form of exp $\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$.

	x/*a*	*y*/*b*	*z*/*c*	*B*(Å^2)	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	−0716(2)	0963(2)	2269(4)		464(12)	1464(30)	3183(68)	−745(32)	−948(48)	1357(76)
C(1)	−0256(2)	1440(3)	3103(4)		289(12)	1065(31)	1882(66)	−143(32)	80(46)	1104(76)
C(2)	−0365(2)	2451(3)	3380(5)		396(14)	1065(31)	2258(75)	619(39)	410(55)	842(85)
C(3)	0158(2)	2983(3)	4181(4)		663(20)	792(27)	1782(68)	794(39)	651(61)	421(71)
C(4)	0875(2)	2562(3)	4887(4)		467(14)	567(19)	1375(50)	168(31)	399(45)	55(54)
C(5)	0915(2)	1563(2)	4885(4)		263(10)	537(18)	1253(48)	53(23)	370(36)	285(49)
C(6)	0483(2)	1010(2)	3811(4)		291(11)	582(20)	1601(55)	−148(25)	94(40)	507(55)
C(7)	0777(2)	0141(2)	3269(5)		591(19)	487(21)	2094(69)	−304(32)	−286(62)	119(61)
C(8)	1592(3)	−0127(3)	3215(5)		718(22)	468(21)	2270(75)	233(35)	195(72)	−163(65)
C(9)	2243(2)	0397(3)	3724(5)		462(16)	665(24)	2076(70)	539(32)	329(54)	323(67)
C(10)	2188(2)	1122(3)	4837(4)		292(11)	704(22)	1722(59)	175(26)	−3(43)	492(62)
C(11)	2658(2)	1953(3)	4875(4)		338(13)	1007(29)	1744(63)	−178(34)	−78(49)	264(74)
C(12)	2376(2)	2805(3)	5304(5)		601(19)	903(31)	1880(69)	−585(39)	−213(62)	2(76)
C(13)	1545(3)	3114(3)	5316(4)		881(24)	538(22)	1466(60)	−148(37)	183(67)	−309(60)
C(14)	1486(2)	1093(2)	5979(4)		335(12)	617(21)	1378(52)	3(26)	131(41)	429(54)
H(1)	−0781(23)	2756(29)	2908(49)	6.7(1.2)						
H(2)	0065(22)	3750(26)	4344(41)	4.7(0.9)						
H(3)	0387(22)	−0260(28)	2683(50)	6.2(1.1)						
H(4)	1708(21)	−0718(24)	2642(44)	4.6(0.9)						
H(5)	2738(24)	0280(29)	3052(47)	6.6(1.2)						
H(6)	3241(25)	1914(30)	4501(53)	7.8(1.3)						
H(7)	2787(27)	3348(32)	5615(55)	9.2(1.5)						
H(8)	1426(24)	3834(30)	5535(49)	6.7(1.2)						
H(9)	1577(18)	1473(21)	7028(34)	2.5(0.7)						
H(10)	1327(20)	0410(24)	6360(41)	4.2(0.9)						

6) S. Hunig and E. Wolff, *Chimia*, **22**, 33 (1968).

7) H. Shimanouchi, K. Ibata, and Y. Sasada, (1972) Unpublished work.

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS (×5).

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
K,L= 0 0			2	56	-52	18	0	-4	2	28	-27	10	22	24	4	82	78	12	26	-31	13	71	69	K,L= 8 3			5	51	-51
2	208	178	4	0	-6	19	19	23	3	70	71	11	23	-25	5	241	-231	13	21	17	14	36	37	0	70	-70	6	0	-8
4	343	333	6	79	78	20	0	-1	4	18	-16	K,L= 16		1	6	97	-99	14	40	-43	15	61	61	1	28	27	7	18	15
6	388	-372	8	32	-24	K,L= 4		1	5	45	-42	0	0	6	7	34	-32	15	0	-13	16	17	-5	2	28	-28	8	0	-1
8	54	-49	10	76	-75	0	160	-160	6	27	-28	1	25	-22	8	29	25	16	0	12	17	14	-13	3	121	123	9	14	14
10	200	-205	12	0	-2	1	257	253	7	23	-16	2	0	-12	9	0	-10	17	13	-16	18	37	-41	4	32	33	10	0	-3
12	107	106	14	51	55	2	131	-126	8	31	-26	3	17	14	10	0	1	K,L= 10		2	19	0	-1	5	0	7	11	0	0
14	61	73	16	23	23	3	27	28	9	89	88	4	0	11	11	41	-38	0	23	14	20	7	-7	6	18	-26	12	0	4
16	162	-163	K,L= 11		0	4	127	-118	10	0	3	5	0	8	12	72	74	1	0	-3	K,L= 3		3	7	0	10	K,L= 15		3
18	27	-23	2	29	-24	5	55	57	11	73	82	6	0	13	13	28	24	2	84	-79	1	34	53	8	15	-17	1	0	1
20	16	-21	4	32	27	6	181	176	12	21	-21	7	22	-21	14	28	-28	3	91	88	2	102	101	9	22	20	2	0	2
K,L= 1	0		6	120	-116	7	162	151	13	19	15	8	0	7	15	86	91	4	117	117	3	102	-99	10	25	-22	3	19	-17
2	514	-539	8	82	-76	8	80	79	14	0	9	K,L= 17		1	16	43	46	5	81	87	4	79	74	11	0	-8	4	21	16
4	196	180	10	88	-89	9	118	112	15	24	-23	1	0	7	17	20	25	6	108	106	5	172	-161	12	42	-44	5	0	0
6	224	216	12	29	34	10	0	-8	16	0	12	2	0	3	18	33	-35	7	86	86	6	0	-14	13	60	65	6	27	29
8	143	132	14	20	20	11	0	4	17	0	10	3	0	0	19	0	13	8	54	59	7	142	-135	14	43	-49	7	14	7
10	38	39	16	0	-2	12	0	-6	18	13	7	4	0	0	20	12	-15	9	25	20	8	0	3	15	0	3	8	0	-6
12	52	48	K,L= 12		0	13	56	-55	K,L= 10		1	5	20	-21	K,L= 5		2	10	56	-56	9	28	25	16	0	6	9	11	8
14	56	-59	0	0	15	14	38	-42	0	25	-11	K,L= 0		2	1	41	46	11	40	36	10	56	-57	17	12	3	10	0	10
16	26	-19	2	87	89	15	0	17	1	21	20	0	492	514	2	25	25	12	72	-70	11	107	105	18	9	10	K,L= 16		3
18	58	57	4	104	-103	16	24	-28	2	0	-12	1	185	189	3	40	-35	13	18	17	12	0	3	K,L= 9		3	0	0	4
K,L= 2	0		6	43	-39	17	0	-9	3	20	-7	2	599	-635	4	18	16	14	0	-2	13	43	45	1	95	92	K,L= 0		4
0	328	-357	8	69	-76	18	16	-22	4	42	-44	3	41	46	5	23	24	15	19	-16	14	0	-1	2	19	17	0	235	228
2	178	-185	10	0	8	19	0	16	5	26	-26	4	131	130	6	16	-13	K,L= 11		2	15	26	25	3	20	-8	1	172	-177
4	324	-326	12	24	20	20	0	6	6	67	66	5	352	329	7	63	-61	1	0	3	16	0	0	4	57	-61	2	177	-176
6	59	53	14	22	-26	K,L= 5		1	7	52	50	6	203	-193	8	0	-14	2	0	15	17	23	-25	5	91	-92	3	21	18
8	223	-215	K,L= 13		0	1	245	241	8	33	23	7	41	-41	9	0	17	3	70	70	18	0	-7	6	64	-71	4	78	-76
10	45	-35	2	40	-48	2	312	-313	9	0	14	8	263	259	10	25	27	4	101	103	19	19	21	7	9	-16	5	237	221
12	49	-46	4	59	-61	3	113	-114	10	27	-25	9	196	-184	11	32	-38	5	0	9	K,L= 4		3	8	28	22	6	315	-301
14	115	109	6	0	-12	4	0	-14	11	0	15	10	64	64	12	42	39	6	22	-16	0	27	28	9	48	-49	7	80	78
16	35	33	8	27	24	5	250	234	12	0	17	11	59	-60	13	29	31	7	64	-62	1	74	-66	10	0	-6	8	0	7
18	46	51	10	29	27	6	68	56	13	39	-41	12	50	56	14	31	33	8	50	-50	2	120	-114	11	42	44	9	54	56
20	0	-2	12	0	1	7	23	11	14	0	6	13	56	-55	15	0	-2	9	27	27	3	99	-93	12	0	-11	10	114	108
K,L= 3	0		14	12	18	8	45	42	15	25	27	14	0	11	16	24	21	10	38	-44	4	168	-165	13	0	1	11	173	165
2	49	-51	K,L= 14		0	9	74	75	16	0	11	15	0	-14	17	0	8	11	19	12	5	252	-245	14	24	24	12	118	122
4	201	206	0	62	-62	10	116	110	17	0	-9	16	62	-63	18	14	-14	12	33	35	6	47	-49	15	16	-19	13	57	60
6	195	-181	2	0	13	11	143	-141	K,L= 11		1	17	17	-16	19	0	6	13	0	-10	7	36	35	16	17	18	14	20	14
8	90	-81	4	0	8	12	57	58	1	0	-8	18	25	18	K,L= 6		2	14	0	9	8	31	-31	17	11	-10	15	0	11
10	204	-208	6	0	9	13	63	68	2	39	-43	19	31	39	0	0	3	15	21	22	9	22	20	K,L= 10		3	16	28	-30
12	95	98	8	17	18	14	60	-62	3	26	-22	20	19	22	1	89	92	K,L= 12		2	10	35	-38	0	25	21	17	17	-4
14	38	37	10	25	29	15	45	-48	4	0	-16	K,L= 1		2	2	54	67	0	33	-29	11	0	8	1	20	-12	18	14	-23
16	68	73	12	33	40	16	56	-62	5	28	25	1	387	400	3	18	17	1	0	13	12	49	47	2	31	25	19	0	-3
18	54	64	K,L= 15		0	17	0	11	6	0	-1	2	624	-668	4	18	-15	2	40	39	13	0	-2	3	0	-9	K,L= 1		4
20	18	15	2	33	33	18	0	-16	7	0	4	3	532	536	5	79	-70	3	39	42	14	28	29	4	31	-28	1	43	-39
K,L= 4	0		4	42	-46	19	0	3	8	40	-42	4	333	-326	6	30	-27	4	51	-54	15	22	8	5	50	-48	2	111	-68
0	53	54	6	0	-6	20	0	-9	9	0	10	5	166	162	7	0	0	5	35	-37	16	0	6	6	41	39	3	89	75
2	108	-117	8	46	42	K,L= 6		1	10	0	17	6	112	-108	8	32	-35	6	31	-30	17	0	9	7	58	61	4	21	-21
4	75	74	10	0	18	0	56	53	11	25	-28	7	67	-63	9	17	12	7	0	0	18	7	-15	8	0	16	5	68	-58
6	76	-76	K,L= 1		1	1	180	-178	12	0	-17	8	51	40	10	22	-11	8	0	-11	19	0	4	9	33	36	6	50	47
8	54	46	1	361	-366	2	226	229	13	0	7	9	38	31	11	0	-6	9	31	-29	K,L= 5		3	10	18	10	7	67	-61
10	0	15	2	144	-131	3	109	-107	14	0	8	10	20	23	12	0	-5	10	35	34	1	143	150	11	21	-3	8	89	83
12	67	70	3	217	202	4	20	18	15	17	-16	11	0	-10	13	31	31	11	36	-39	2	46	48	12	25	26	9	25	20
14	51	-49	4	166	158	5	53	51	16	0	6	12	32	-29	14	0	-9	12	0	13	3	214	-206	13	24	-25	10	17	15
16	39	36	5	0	0	6	55	59	K,L= 12		1	13	80	-77	15	36	41	13	0	-6	4	240	232	14	0	11	11	75	78
18	0	-4	6	52	-46	7	68	-58	0	0	-7	14	93	-91	16	0	5	14	0	-5	5	66	64	15	0	-14	12	75	-70
20	0	-4	7	158	150	8	22	-1	1	37	40	15	35	-36	17	0	2	15	0	-4	6	165	151	16	0	0	13	16	24
K,L= 5	0		8	59	56	9	32	-33	2	20	-20	16	51	-52	18	0	3	K,L= 13		2	7	133	-133	K,L= 11		3	14	36	-41
2	125	115	9	19	-12	10	37	39	3	28	-26	17	0	-18	19	0	-14	1	20	19	8	30	-27	1	28	24	15	47	49
4	21	-15	10	0	3	11	0	11	4	0	-4	18	37	38	K,L= 7		2	2	38	-44	9	39	40	2	0	0	16	14	-17
6	73	-62	11	66	61	12	0	13	5	65	68	19	0	-13	1	46	-39	3	27	29	10	0	-9	3	33	-34	17	16	12
8	152	155	12	39	31	13	0	7	6	55	56	20	0	12	2	98	91	4	0	0	11	55	-55	4	15	-18	18	32	33
10	40	-35	13	41	-41	14	0	-25	7	0	-13	K,L= 2		2	3	73	-69	5	0	-16	12	26	26	5	0	-8	19	11	11
12	0	0	14	0	2	15	33	-36	8	37	40	0	711	-861	4	78	81	6	20	20	13	91	94	6	24	8	K,L= 2		4
14	34	-33	15	27	23	16	0	-4	9	0	2	1	405	410	5	0	-11	7	64	-64	14	0	-7	7	23	19	0	321	-326
16	21	-16	16	48	49	17	27	29	10	27	-25	2	145	155	6	109	109	K,L= 14		2	15	25	-25	8	0	0	1	105	-106
18	50	-52	17	33	41	18	22	-24	11	0	-5	3	68	68	7	0	-8	0	44	-49	16	0	-2	9	33	-34	2	205	207
K,L= 6	0		18	0	19	19	16	19	12	0	0	4	42	38	8	135	-127	1	0	0	17	19	14	10	38	37	3	237	-234
0	0	-9	19	20	-24	K,L= 7		1	13	30	-37	5	222	216	9	56	56	2	0	5	18	17	20	11	13	9	4	46	38
2	122	-125	20	0	3	1	233	-233	14	0	-20	6	234	231	10	0	3	3	20	20	19	12	-11	12	0	9	5	104	-100
4	111	-115	K,L= 2		1	2	94	-93	15	0	-4	7	87	85	11	0	15	4	19	23	K,L= 6		5	13	0	7	6	195	189
6	128	124	0	466	-492	3	61	51	K,L= 13		1	8	30	-25	12	58	-59	5	54	-52	0	116	-120	14	26	33	7	108	-104
8	64	64	1	422	425	4	44	-42	1	20	-27	9	33	30	13	68	68	6	0	-10	1	143	-136	15	0	0	8	30	-26
10	88	87	2	298	-295	5	24	-23	2	25	-21	10	22	16	14	24	22	K,L= 15		2	2	158	149	K,L= 12		3	9	0	2
12	52	55	3	11	7	6	0	9	3	0	-4	11	37	-36	15	21	18	1	0	14	3	29	23	0	0	-4	10	23	24
14	0	-15	4	235	-220	7	41	39	4	0	5	12	148	-150	16	18	12	2	20	17	4	54	57	1	0	6	11	0	8
16	44	-45	5	206	202	8	27	25	5	0	21	13	21	-23	17	11	-12	K,L= 1		3	5	88	-92	2	0	-5	12	62	-60
18	0	-17	6	289	284	9	79	-74	6	30	33	14	22	-21	18	17	12	1	262	267	6	25	24	3	84	-87	13	23	-16
K,L= 7	0		7	143	-135	10	79	82	7	0	-18	15	0	0	K,L= 8		2	2	69	-72	7	51	49	4	23	-19	14	0	-6
2	17	-1	8	167	158	11	31	-33	8	0	-6	16	0	10	0	105	-115	3	97	-92	8	22	-22	5	10	-18	15	31	-32
4	142	-139	9	88	-76	12	34	36	9	0	18	17	30	-36	1	0	4	4	172	-162	9	38	33	6	10	-10	16	24	24
6	0	-29	10	25	28	13	67	-73	10	22	24	18	0	13	2	24	-10	5	78	79	10	43	45	7	35	-36	17	0	-4
8	24	18	11	52	-51	14	28	17	11	30	-37	19	0	0	3	35	33	6	201	-189	11	52	-51	8	24	17	18	0	-3
10	39	30	12	0	21	15	44	47	12	0	-12	20	0	2	4	0	-5	7	89	79	12	33	-29	9	20	16	19	0	5
12	70	-66	13	66	-67	16	0	-5	13	0	6	K,L= 3		2	5	49	-52	8	126	113	13	0	-13	10	0	-2	K,L= 3		4
14	0	-20	14	12	2	17	22	16	14	0	-18	1	126	-136	6	75	-76	9	85	-74	14	25	-23	11	0	0	1	26	33
16	31	-30	15	32	39	18	0	2	K,L= 14		1	2	82	-80	7	24	-22	10	0	7	15	54	-60	12	26	29	2	248	253
18	25	-30	16	0	1	19	16	20	0	0	-17	3	20	10	8	0	-19	11	53	-56	16	19	22	13	12	6	3	28	-24
K,L= 8	0		17	57	-62	K,L= 8		1	1	0	-8	4	70	64	9	89	-97	12	35	36	17	0	4	14	7	3	4	201	188
0	223	215	18	0	4	0	0	5	2	34	-42	5	39	41	10	34	37	13	29	23	18	14	14	15	6	-2	5	23	19
2	146	135	19	22	-14	1	47	38	3	48	56	6	106	-101	11	35	-34	14	0	8	19	0	-20	K,L= 13		3	6	60	55
4	90	-86	20	22	28	2	22	23	4	17	-10	7	204	-194	12	20	-14	15	33	-32	K,L= 7		3	1	0	-7	7	112	-104
6	47	-45	K,L= 3		1	3	22	12	5	0	-4	8	39	41	13	24	-17	16	23	18	1	44	48	2	0	3	8	58	59
8	63	-71	1	102	-107	4	62	-58	6	28	32	9	57	62	14	22	24	17	0	1	2	21	23	3	0	15	9	26	-27
10	21	18	2	411	-397	5	53	54	7	23	25	10	26	-15	15	16	-8	18	15	-13	3	39	37	4	0	-13	10	43	-44
12	20	15	3	158	148	6	28	-31	8	23	28	11	38	-40	16	0	11	19	17	-13	4	26	-22	5	0	5	11	59	-56
14	0	14	4	76	-74	7	120	-120	9	18	-23	12	78	78	17	0	-6	K,L= 2		3	5	23	25	6	0	10	12	38	-37
16	42	-54	5	215	-207	8	66	-68	10	0	-1	13	0	-12	18	17	15	0	58	55	6	0	3	7	0	-7	13	0	-9
18	26	-31	6	121	-120	9	73	-73	11	0	13	14	0	-3	K,L= 9		2	1	19	32	7	84	79	8	24	-23	14	7	8
K,L= 9	0		7	59	-54	10	62	-66	12	0	9	15	21	-23	1	47	49	2	236	236	8	20	-12	9	0	-5	15	21	-17
2	17	-17	8	67	-62	11	0	6	K,L= 15		1	16	24	-15	2	22	-14	3	94	-92	9	74	-71	10	0	-3	16	14	2
4	53	-55	9	22	-23	12	0	-12	1	26	33	17	36	40	3	0	-3	4	91	-79	10	18	-17	11	18	5	17	21	26
6	25	19	10	0	-5	13	57	62	2	0	-10	18	18	-14	4	49	-46	5	95	92	11	35	29	12	10	-9	18	18	-14
8	251	246	11	56	58	14	0	-12	3	0	-7	19	0	4	5	0	2	6	84	72	12	55	-55	13	11	-13	K,L= 4		4
10	86	87	12	0	2	15	0	19	4	0	10	20	16	-18	6	0	-4	7	89	-83	13	0	-17	K,L= 14		3	0	78	-75
12	58	58	13	67	-69	16	26	28	5	25	24	K,L= 4		2	7	70	-69	8	22	18	14	21	-19	0	0	-7	1	104	-105
14	0	-17	14	76	-78	17	0	5	6	26	26	0	64	-53	8	55	50	9	30	-28	15	35	40	1	0	7	2	19	-1
16	0	-3	15	0	6	18	12	17	7	0	-7	1	187	192	9	27	19	10	14	12	16	23	-22	2	19	-19	3	27	30
K,L= 10	0		16	32	-36	K,L= 9		1	8	0	0	2	119	118	10	29	-24	11	113	108	17	18	-21	3	0	5	4	49	-50
0	156	147	17	51	-56	1	0	-17	9	0	2	3	18	-13	11	33	-13	12	51	50	18	0	2	4	0	-8	5	41	-39

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
6	27	27	0	24	-23	3	44	-40	16	11	-11	K,L=	0	6	15	19	19	1	14	-19	10	0	12	2	0	-6	K,L=	2	9
7	22	8	1	71	-66	4	61	62	K,L=	8	5	0	229	217	16	11	-14	2	14	-11	11	0	-12	3	46	-47	0	68	-70
8	27	28	2	104	-102	5	80	82	0	36	40	1	26	-11	K,L=	6	6	3	13	-10	12	0	-2	4	0	19	1	49	52
9	0	10	3	66	-73	6	61	59	1	23	17	2	51	-49	0	83	82	4	25	-26	13	0	-5	5	24	19	2	28	27
10	96	-94	4	73	76	7	112	-114	2	47	-50	3	70	67	1	19	-8	5	0	0	14	0	13	6	49	-47	3	19	19
11	19	-5	5	27	27	8	23	6	3	78	79	4	22	18	2	18	-11	6	10	-3	K,L=	7	7	7	0	7	4	0	8
12	17	10	6	17	5	9	124	-127	4	55	53	5	26	-24	3	17	-6	7	9	-9	1	0	8	8	21	-20	5	22	20
13	34	-34	7	21	-21	10	22	-19	5	0	-2	6	131	-133	4	58	-56	8	26	29	2	33	-33	9	20	17	6	0	11
14	38	-35	8	29	30	11	19	11	6	41	-38	7	38	-36	5	29	30	K,L=	14	6	3	36	37	10	35	-41	7	0	2
15	23	-21	9	7	0	12	51	-50	7	23	-24	8	16	-11	6	16	7	0	9	3	4	25	-23	11	0	-13	8	0	-5
16	31	34	10	13	-17	13	18	11	8	20	10	9	77	-76	7	19	-19	1	9	1	5	0	25	12	19	18	9	0	9
17	15	2	11	32	33	14	33	-36	9	24	-23	10	32	25	8	0	1	2	9	0	6	0	10	13	27	36	10	0	7
18	11	-6	12	22	-24	15	19	19	10	21	12	11	26	-28	9	16	9	3	11	8	7	24	24	K,L=	4	8	11	0	-7
19	0	-10	13	16	-14	16	15	10	11	25	-28	12	18	14	10	18	-6	4	10	-11	8	0	20	0	37	-37	K,L=	3	9
K,L=	5	4	14	15	11	17	0	0	12	0	0	13	0	1	11	17	-12	5	0	-2	9	18	-25	1	28	-31	1	33	32
1	26	23	15	18	-22	18	5	6	13	16	13	14	26	-31	12	35	38	K,L=	1	7	10	29	35	2	0	0	2	37	43
2	27	24	K,L=	11	4	K,L=	3	5	14	17	15	15	33	46	13	17	10	1	47	-46	11	0	-12	3	27	24	3	23	-20
3	18	-17	1	0	2	1	39	32	15	13	-10	16	43	-55	14	18	20	2	82	-79	12	0	14	4	0	22	4	0	9
4	50	-53	2	82	82	2	109	106	16	0	-4	17	13	20	15	19	-25	3	0	-8	13	0	-13	5	0	6	5	0	-20
5	31	27	3	47	40	3	125	127	K,L=	9	5	K,L=	1	6	16	0	-7	4	32	32	K,L=	8	7	6	0	4	6	0	0
6	15	15	4	92	84	4	46	-47	1	27	28	1	11	-4	K,L=	7	6	5	0	0	0	0	12	7	0	0	7	0	-5
7	64	64	5	50	48	5	39	34	2	53	46	2	61	-53	1	0	-1	6	51	50	1	25	25	8	23	23	8	0	25
8	75	-73	6	0	5	6	0	8	3	0	2	3	41	34	2	19	-17	7	68	68	2	65	-72	9	35	-39	9	0	-11
9	18	1	7	37	36	7	24	-24	4	50	50	4	19	-15	3	79	88	8	0	13	3	29	30	10	0	13	10	0	2
10	0	13	8	8	-5	8	19	-15	5	60	-63	5	45	-39	4	14	-5	9	0	-11	4	0	14	11	0	-12	K,L=	4	9
11	0	5	9	7	10	9	82	80	6	0	-12	6	70	69	5	36	-40	10	40	42	5	0	0	12	0	1	0	23	23
12	30	-28	10	18	-14	10	22	-17	7	0	2	7	16	-1	6	32	31	11	0	2	6	29	30	13	0	-6	1	0	-8
13	20	8	11	0	-10	11	38	42	8	30	29	8	148	146	7	19	-9	12	0	20	7	29	-33	K,L=	5	8	2	0	-3
14	19	10	12	16	15	12	30	-31	9	29	-30	9	18	9	8	48	-47	13	0	-7	8	33	37	1	16	18	3	0	-4
15	8	6	13	27	-29	13	32	-35	10	35	-36	10	87	86	9	38	-43	14	27	-29	9	25	-26	2	0	4	4	0	1
16	15	-9	14	20	25	14	26	26	11	0	3	11	45	44	10	19	14	15	0	0	10	0	-12	3	28	14	5	0	-9
17	0	-1	K,L=	12	4	15	20	-18	12	24	24	12	19	-7	11	18	14	16	0	-31	11	0	-7	4	0	6	6	0	0
18	0	2	0	30	30	16	0	8	13	16	-12	13	21	-4	12	15	10	K,L=	2	7	12	0	-2	5	0	2	7	0	7
K,L=	6	4	1	8	-6	17	25	-28	14	0	7	14	12	-14	13	41	-46	0	103	-104	13	9	6	6	0	-1	8	0	11
0	34	35	2	19	11	18	0	-5	15	12	-12	15	22	5	14	20	21	1	41	48	K,L=	9	7	7	0	-10	9	13	0
1	44	-44	3	11	-12	K,L=	4	5	K,L=	10	5	16	12	-12	15	9	9	2	36	35	1	0	14	8	0	11	10	0	1
2	25	24	4	38	-37	0	102	96	0	0	1	17	29	-39	K,L=	8	6	3	0	-8	2	28	-27	9	19	-15	K,L=	5	9
3	23	-18	5	11	3	1	51	-53	1	31	-29	K,L=	2	6	0	51	54	4	0	1	3	0	-5	10	0	8	1	29	30
4	10	-8	6	0	-13	2	108	-103	2	9	7	0	71	-69	1	47	52	5	72	70	4	33	38	11	0	-13	2	0	9
5	38	40	7	0	-6	3	27	24	3	33	-31	1	30	34	2	37	35	6	32	-37	5	27	-29	12	16	19	3	0	-5
6	51	51	8	0	5	4	0	3	4	0	-10	2	15	11	3	16	8	7	0	-8	6	0	1	K,L=	6	8	4	0	-1
7	0	-7	9	0	0	5	25	-16	5	0	-11	3	0	-1	4	17	16	8	35	-37	7	0	3	0	38	-44	5	0	9
8	24	28	10	23	25	6	34	-33	6	21	-9	4	15	-6	5	38	-45	9	0	5	8	0	8	1	0	-3	6	0	1
9	35	40	11	9	3	7	37	39	7	14	-7	5	56	-57	6	18	-12	10	0	3	9	0	8	2	27	-27	7	0	-2
10	52	-54	12	23	24	8	0	8	8	23	-18	6	83	81	7	18	-13	11	40	42	10	0	-14	3	0	5	8	0	-4
11	0	11	13	12	-9	9	28	-24	9	23	-22	7	0	4	8	18	-15	12	21	-17	11	0	12	4	0	-6	9	0	-7
12	33	-26	K,L=	13	4	10	29	-34	10	18	15	8	22	-18	9	18	-12	13	24	23	12	0	18	5	35	40	K,L=	6	9
13	14	9	1	0	-10	11	0	0	11	0	-2	9	25	19	10	26	31	14	14	-22	K,L=	10	7	6	0	-3	0	15	-21
14	28	-36	2	0	-8	12	13	12	12	16	-2	10	26	18	11	27	-28	15	0	15	0	22	-6	7	0	-9	1	0	-4
15	0	-1	3	22	-17	13	26	-27	13	17	-14	11	29	-26	12	12	6	K,L=	3	7	1	0	9	8	0	17	2	0	6
16	14	-18	4	0	5	14	12	7	14	15	18	12	12	-4	13	11	-4	1	0	24	2	0	-4	9	0	-13	3	22	-25
17	18	17	5	0	8	15	15	-12	15	0	-4	13	0	1	14	9	-5	2	0	14	3	0	-18	10	0	14	4	28	-31
18	0	5	6	21	19	16	0	-3	K,L=	11	5	14	28	33	15	6	24	3	29	24	4	0	-15	11	0	-9	5	0	3
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2	55	-59	9	7	-2	K,L=	5	5	3	21	21	17	7	2	2	29	-28	6	28	-29	7	0	14	1	29	-31	8	17	-18
3	18	13	10	0	-2	1	134	-142	4	31	39	K,L=	3	6	3	18	3	7	0	0	8	0	-8	2	0	13	K,L=	8	9
4	55	-50	11	0	-9	2	24	-21	5	20	12	1	37	-30	4	30	-31	8	29	-26	9	17	9	3	37	43	0	18	21
5	30	21	K,L=	14	4	3	56	-56	6	0	14	2	24	22	5	22	-21	9	0	7	10	0	3	4	0	21	1	0	-2
6	77	80	0	16	12	4	40	-43	7	0	14	3	57	-53	6	0	-1	10	0	-3	11	0	8	5	0	-11	2	0	0
7	90	93	1	0	-7	5	63	62	8	0	9	4	27	-21	7	15	-7	11	28	36	K,L=	0	8	6	25	25	3	0	0
8	122	-121	2	0	-1	6	0	14	9	17	-19	5	48	52	8	54	58	12	0	-20	0	68	69	7	22	-14	4	14	18
9	14	-14	3	0	5	7	56	-57	10	16	-12	6	86	-87	9	23	-25	13	0	-8	1	29	27	8	0	8	5	0	-9
10	79	76	4	0	12	8	35	-35	11	18	-18	7	68	67	10	14	10	14	13	14	2	49	-46	9	0	1	6	9	13
11	19	-14	5	22	-22	9	115	115	12	12	-3	8	28	26	11	15	5	15	0	-4	3	0	10	10	0	2	7	9	-18
12	0	-1	6	0	1	10	23	20	13	0	-2	9	53	53	12	13	1	K,L=	4	7	4	0	-5	11	17	18	K,L=	0	10
13	26	-26	7	0	1	11	24	-20	K,L=	12	5	10	34	-35	13	16	15	0	109	106	5	0	-15	K,L=	8	8	0	52	55
14	27	29	8	0	0	12	23	17	0	0	-5	11	18	7	14	10	-23	1	0	-13	6	89	-90	0	0	6	1	0	13
15	22	-19	9	11	11	13	0	4	1	9	-9	12	13	-6	K,L=	10	6	2	0	-6	7	31	-32	1	38	35	2	0	7
16	0	-7	10	26	-28	14	19	21	2	26	28	13	16	15	0	54	-58	3	28	-25	8	0	2	2	0	11	3	0	12
17	17	-22	K,L=	15	4	15	26	-30	3	20	-27	14	16	-1	1	15	11	4	33	35	9	34	-41	3	0	22	4	0	-11
K,L=	8	4	1	0	0	16	0	11	4	21	14	15	17	-19	2	74	-76	5	0	-16	10	21	18	4	0	-7	5	36	44
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1	20	-17	3	27	-27	K,L=	6	5	6	25	-26	17	16	-20	4	18	14	7	0	10	12	0	13	6	0	-3	1	0	-2
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3	13	12	5	8	6	1	42	-40	8	0	-7	0	125	128	6	11	-1	9	0	-3	14	0	6	8	0	-10	3	0	-1
4	27	30	6	0	8	2	49	47	9	0	-4	1	46	-48	7	17	-14	10	0	-21	K,L=	1	8	9	13	-2	4	0	-16
5	37	31	7	30	34	3	61	58	10	0	3	2	30	26	8	14	-3	11	0	1	1	0	19	10	7	7	5	23	-26
6	78	-77	8	0	-2	4	19	14	11	22	23	3	81	81	9	12	15	12	0	14	2	56	-55	K,L=	9	8	6	0	13
7	25	26	K,L=	16	4	5	19	12	12	8	-5	4	74	-69	10	18	-11	13	23	-27	3	0	3	1	29	31	7	19	-26
8	0	5	0	19	19	6	60	-55	K,L=	13	5	5	17	14	11	13	9	14	0	-5	4	40	-41	2	23	-28	K,L=	2	10
9	0	3	1	5	-4	7	63	65	1	35	-37	6	30	-29	12	12	-8	15	0	-12	5	40	-41	3	0	-2	0	0	-13
10	64	68	2	0	-2	8	35	-34	2	16	9	7	63	62	13	0	2	K,L=	5	7	6	0	-5	4	0	6	1	0	5
11	22	22	3	11	-4	9	57	62	3	25	25	8	37	-38	K,L=	11	6	1	0	-9	7	33	-30	5	0	-1	2	0	-5
12	19	18	4	9	6	10	38	39	4	17	-20	9	24	24	1	23	-20	2	32	-27	8	0	16	6	0	-5	3	22	-25
13	21	-13	K,L=	1	5	11	0	1	5	15	8	10	60	-63	2	39	38	3	0	-15	9	0	-18	7	0	-9	4	0	1
14	0	10	1	22	-26	12	0	-2	6	17	-19	11	24	25	3	0	0	4	0	-20	10	0	5	8	0	9	5	0	-5
15	13	-7	2	91	81	13	14	13	7	16	-8	12	30	27	4	13	3	5	0	-4	11	0	10	K,L=	10	8	6	0	19
16	0	-4	3	34	-25	14	22	23	8	0	8	13	20	21	5	0	3	6	0	-6	12	0	-14	0	0	-15	K,L=	3	10
17	0	-12	4	69	65	15	10	-6	9	14	13	14	0	2	6	36	-38	7	54	-49	13	0	3	1	0	3	1	16	16
K,L=	9	4	5	14	-4	16	15	-13	10	15	-17	15	16	-19	7	18	19	8	29	-29	14	0	-8	2	0	4	2	0	-8
1	46	-46	6	49	51	17	14	21	K,L=	14	5	16	14	1	8	0	4	9	0	1	K,L=	2	8	3	0	-23	3	0	-4
2	46	-45	7	0	-9	K,L=	7	5	0	15	19	17	9	3	9	0	2	10	20	21	0	27	-30	4	30	30	4	19	22
3	112	-119	8	19	-15	1	95	-94	1	0	-3	K,L=	5	6	10	14	-16	11	26	-26	1	31	36	5	0	-7	5	22	23
4	88	-90	9	53	-54	2	25	23	2	0	10	1	42	-44	11	11	-2	12	0	-8	2	0	5	6	0	13	6	0	4
5	21	-23	10	34	-27	3	46	43	3	17	16	2	19	7	K,L=	12	6	13	0	8	3	0	-9	7	0	3	K,L=	4	10
6	21	-20	11	87	-82	4	46	-47	4	0	-9	3	19	-17	0	52	56	14	0	8	4	47	45	K,L=	1	9	0	27	-30
7	26	24	12	31	-30	5	33	39	5	0	-6	4	24	-20	1	22	22	K,L=	6	7	5	0	-5	1	0	-10	1	19	-19
8	23	14	13	0	12	6	0	-9	6	0	-2	5	36	-36	2	46	48	0	22	-22	6	32	36	2	32	-28	2	0	0
9	20	-8	14	0	1	7	68	66	7	14	-13	6	19	-8	3	0	0	1	0	7	7	27	29	3	0	8	3	0	-6
10	22	17	15	0	21	8	0	-8	8	13	-15	7	21	18	4	24	-22	2	0	-23	8	0	-4	4	0	2	4	0	-3
11	17	1	16	0	-1	9	9	-7	K,L=	15	5	8	15	-7	5	22	19	3	0	-18	9	32	39	5	0	-6	5	12	-11
12	11	-11	17	31	34	10	20	-16	1	22	-22	9	23	-22	6	0	0	4	26	-24	10	0	-16	6	24	-24			
13	33	33	18	13	5	11	0	3	2	13	-10	10	16	4	7	0	-3	5	0	2	11	0	9	7	0	0			
14	18	-20	K,L=	2	5	12	19	-16	3	0	-1	11	23	24	8	0	-5	6	0	19	12	29	-38	8	0	-7			
15	7	-2	0	77	-78	13	29	-31	4	0	2	12	11	1	9	11	-8	7	0	1	13	0	5	9	0	-6			
16	0	7	1	0	9	14	7	-9	5	0	-5	13	17	-10	10	14	15	8	0	13	K,L=	3	8	10	20	-21			
K,L=	10	4	2	98	94	15	33	42	6	0	0	14	0	3	K,L=	13	6	9	15	17	1	0	14	11	0	15			

found to have zero intensity. Lorentz and polarization corrections were made as usual, but the absorption correction was omitted. The intensities of elongated reflections on upper-layer photographs were corrected for spot size by a method proposed by Takenaka.[8]

Structure Determination and Refinement

In the earlier stage of the structure determination, visual data were used. The symbolic addition procedure was used for sign-determination. As a starting set, the signs of the following strong reflections were chosen;

h	k	l	$\|E\|$	sign
8	1	6	3.26	+
9	5	5	2.78	+
15	4	2	2.77	+
13	7	6	2.65	A
4	11	4	2.55	B

where A and B were symbols.

Using the triple-product sign relationships, the signs of 160 reflections out of 275 with $|E|\geq 1.5$ were determined in terms of A and B. From a further investigation of the list of the triple-product sign relations, it seemed most probable that A is − and B is +. The *E*-map computed with these signs clearly showed all fifteen non-hydrogen atoms.

The structure factors were calculated using these fifteen atoms, the *R* factor being 0.425 for the observed reflections. A Fourier refinement and the block-diagonal least-squares refinement were carried out successively. Four cycles of calculations using isotropic temperature factors reduced the *R* factor to 0.231. Anisotropic temperature factors were then introduced, and the *R* factor dropped to 0.155. At this stage, the coordinates of the hydrogen atoms were given by assuming a suitable geometry. The strongest reflection, 022, was excluded because it seemed to suffer from secondary extinction. The *R* factor decreased to 0.135 after four cycles; the isotropic hydrogen atoms were also shifted. Since the intensity data measured by means of the TV-densitometer became available at this stage, they were used for further refinement. After six cycles, the *R* factor was reduced to 0.080 for the observed reflections, excluding the 022 reflection. When this was included, $R=0.081$.

The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[9] The final coordinates and temperature factors are given in Table 2. The observed and calculated structure factors are listed in Table 3.

The thermal ellipsoids of atoms are shown in Fig. 1. It seems that the entire molecule undergoes a rigid-body libration around the center of gravity. Then, the thermal motion of the molecule was analysed, assuming that all atoms form a rigid body.[10]

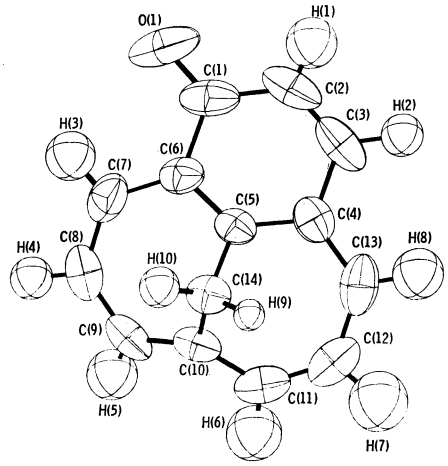


Fig. 1. Thermal ellipsoid of the molecule at the 50% probability level, viewed along the normal to its mean plane.

Table 4. Rigid-body thermal motion

(a) Principal axes of the molecule relative to the crystal axes (*a*, *b*, *c*)

Moment of inertia (Atomic weight·Å²)		Direction cosines of eigen vectors l	m	n
1	434.0	0.922	0.114	0.370
2	665.5	0.215	−0.945	−0.246
3	1024.7	−0.322	−0.307	0.896

(b) Rigid-body vibration tensors

$$\mathbf{T} = \begin{pmatrix} 0.0047 & -0.0068 & 0.0035 \\ & 0.0450 & -0.0010 \\ & & 0.0341 \end{pmatrix}$$

$$\sigma(\mathbf{T}) = \begin{pmatrix} 0.0029 & 0.0026 & 0.0031 \\ & 0.0033 & 0.0034 \\ & & 0.0054 \end{pmatrix} \text{ in Å}^2$$

$$\boldsymbol{\omega} = \begin{pmatrix} 17.74 & 0.50 & 2.66 \\ & 14.43 & 4.24 \\ & & 34.92 \end{pmatrix}$$

$$\sigma(\boldsymbol{\omega}) = \begin{pmatrix} 4.24 & 2.15 & 2.62 \\ & 2.78 & 2.11 \\ & & 1.91 \end{pmatrix} \text{ in deg}^2$$

(c) Principal axes of the **T** and $\boldsymbol{\omega}$ tensors relative to the crystal axes

	R.m.s. amplitude	Direction cosines of eigen vectors l	m	n
T	0.181 Å	−0.644	−0.215	0.735
	0.197	−0.623	0.705	−0.339
	0.229	0.445	0.676	0.558
$\boldsymbol{\omega}$	3.7 deg	0.281	−0.866	−0.414
	4.2	−0.950	−0.189	−0.249
	6.0	−0.137	−0.463	0.876

The anisotropic temperature factors, B_{ij}, were transformed to *U* tensors referred to the three principal axes of the moment of inertia of the molecule, the origin of the coordinate system being at the center of gravity (Table 4(a)). The translation and libration tensors, **T** and $\boldsymbol{\omega}$, of the rigid molecule were derived from *U*'s. Since the agreement between the *U*'s observed and those calculated from **T** and $\boldsymbol{\omega}$ was good (Table 5), the rigid-body model was justified.

The positions of the electron-density peaks are shifted

8) A. Takenaka, to be published.

9) "International Tables for X-ray Crystallography," Vol. III. Birmingham, Kynoch Press, (1962).

10) D. W. J. Cruickshank, *Acta Crystallogr.*, **9**, 754 (1956).

TABLE 5. OBSERVED AND CALCULATED U_{ij}'s IN Å^2

Atom		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O (1)	Obsd	0.044	0.182	0.101	0.013	0.004	−0.038
	Calcd	0.049	0.163	0.086	0.014	−0.003	−0.016
C (1)	Obsd	0.048	0.120	0.047	−0.016	0.011	−0.014
	Calcd	0.045	0.101	0.057	−0.009	0.003	−0.008
C (2)	Obsd	0.079	0.098	0.066	−0.051	0.005	0.003
	Calcd	0.069	0.097	0.068	−0.042	0.004	−0.007
C (3)	Obsd	0.115	0.064	0.057	−0.044	−0.008	0.010
	Calcd	0.096	0.057	0.065	−0.032	0.002	−0.002
C (4)	Obsd	0.075	0.052	0.045	−0.009	0.002	0.006
	Calcd	0.071	0.045	0.047	−0.004	0.001	0.000
C (5)	Obsd	0.048	0.054	0.033	−0.010	0.010	0.001
	Calcd	0.047	0.047	0.034	−0.007	0.003	−0.000
C (6)	Obsd	0.045	0.068	0.044	−0.002	0.010	−0.012
	Calcd	0.048	0.057	0.041	−0.001	0.004	−0.004
C (7)	Obsd	0.070	0.062	0.074	0.020	−0.003	−0.018
	Calcd	0.086	0.053	0.059	0.012	−0.002	−0.004
C (8)	Obsd	0.104	0.043	0.082	−0.004	−0.004	−0.002
	Calcd	0.121	0.047	0.072	−0.016	−0.001	0.004
C (9)	Obsd	0.081	0.058	0.067	−0.034	0.001	0.002
	Calcd	0.094	0.073	0.067	−0.042	0.007	0.004
C (10)	Obsd	0.047	0.072	0.054	−0.020	0.002	−0.005
	Calcd	0.052	0.084	0.054	−0.024	0.004	−0.005
C (11)	Obsd	0.046	0.105	0.060	−0.001	0.005	0.003
	Calcd	0.046	0.131	0.068	−0.006	0.009	−0.012
C (12)	Obsd	0.069	0.104	0.069	0.031	0.000	−0.005
	Calcd	0.066	0.121	0.076	0.032	0.002	−0.016
C (13)	Obsd	0.114	0.056	0.060	0.024	−0.013	0.002
	Calcd	0.093	0.066	0.068	0.025	−0.004	−0.007
C (14)	Obsd	0.052	0.066	0.041	−0.008	0.004	−0.005
	Calcd	0.053	0.067	0.041	−0.010	−0.003	−0.005

by the molecular libration. Therefore, the bond lengths and angles were corrected for this effect using the eigen values and vectors of ω (Table 4(b) and 4(c)).

The computations were done on a HITAC 5020E computer at the University of Tokyo and on a HITAC 8500 computer at Tokyo Institute of Technology. The programs in the Universal Crystallographic Computation Program System[11] were used with some modifications. Three programs, TLSU for the determination of the cell dimensions, TDRW for the data reduction, and DEAM for plotting the thermal ellipsoid, all written by Takenaka, were used.

Results and Discussion

Molecular Geometry. The bond lengths and angles are illustrated in Fig. 2. The lengths corrected for thermal motion are listed in Table 6. Since these corrections are fairly small, the following discussion is based on the uncorrected values. The corrected bond

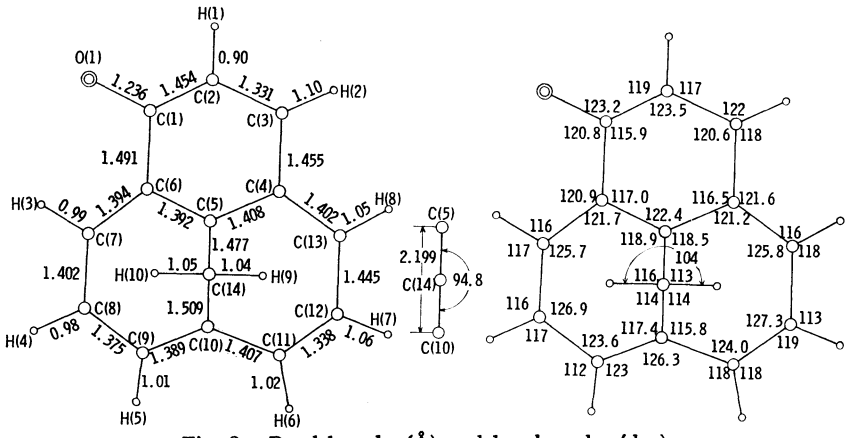


Fig. 2. Bond lengths (Å) and bond angles (deg).

11) "Universal Crystallographic Computation Program System," ed. by T. Sakurai, Published by Crystallographic Society of Japan, (1967).

TABLE 6. BOND LENGTHS (Å) AND BOND ANGLES (deg) E.s.d.'s are in parentheses.

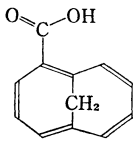
		Corrected for thermal motions		
O(1)–C(1)	1.236 (5)	1.237	C(2)–H(1)	0.90 (4)
C(1)–C(2)	1.454 (6)	1.459	C(3)–H(2)	1.10 (4)
C(2)–C(3)	1.331 (6)	1.335	C(7)–H(3)	0.99 (4)
C(3)–C(4)	1.455 (5)	1.459	C(8)–H(4)	0.98 (4)
C(4)–C(5)	1.408 (5)	1.416	C(9)–H(5)	1.01 (4)
C(5)–C(6)	1.392 (4)	1.401	C(11)–H(6)	1.02 (5)
C(6)–C(1)	1.491 (5)	1.495	C(12)–H(7)	1.06 (5)
C(6)–C(7)	1.394 (5)	1.399	C(13)–H(8)	1.05 (4)
C(7)–C(8)	1.402 (6)	1.407	C(14)–H(9)	1.04 (3)
C(8)–C(9)	1.375 (6)	1.380	C(14)–H(10)	1.05 (4)
C(9)–C(10)	1.389 (5)	1.395		
C(10)–C(11)	1.407 (5)	1.411		
C(11)–C(12)	1.338 (6)	1.342		
C(12)–C(13)	1.445 (6)	1.449		
C(13)–C(4)	1.402 (6)	1.406		
C(5)–C(14)	1.477 (4)	1.484		
C(10)–C(14)	1.509 (5)	1.515		

O(1)–C(1)–C(2)	123.2 (4)	C(1)–C(2)–H(1)	119 (3)
O(1)–C(1)–C(6)	120.8 (4)	C(3)–C(2)–H(1)	117 (3)
C(6)–C(1)–C(2)	115.9 (4)	C(2)–C(3)–H(2)	122 (2)
C(1)–C(2)–C(3)	123.5 (4)	C(4)–C(3)–H(2)	118 (2)
C(2)–C(3)–C(4)	120.6 (4)	C(6)–C(7)–H(3)	116 (2)
C(3)–C(4)–C(5)	116.5 (3)	C(8)–C(7)–H(3)	117 (2)
C(3)–C(4)–C(13)	121.6 (4)	C(7)–C(8)–H(4)	116 (2)
C(13)–C(4)–C(5)	121.2 (3)	C(9)–C(8)–H(4)	117 (2)
C(4)–C(5)–C(6)	122.4 (3)	C(8)–C(9)–H(5)	112 (2)
C(4)–C(5)–C(14)	118.5 (3)	C(10)–C(9)–H(5)	123 (2)
C(6)–C(5)–C(14)	118.9 (3)	C(10)–C(11)–H(6)	118 (3)
C(5)–C(6)–C(1)	117.0 (3)	C(12)–C(11)–H(6)	118 (3)
C(5)–C(6)–C(7)	121.7 (3)	C(11)–C(12)–H(7)	119 (3)
C(1)–C(6)–C(7)	120.9 (3)	C(13)–C(12)–H(7)	113 (3)
C(6)–C(7)–C(8)	125.7 (4)	C(12)–C(13)–H(8)	118 (2)
C(7)–C(8)–C(9)	126.9 (4)	C(4)–C(13)–H(8)	116 (2)
C(8)–C(9)–C(10)	123.6 (4)	C(5)–C(14)–H(9)	113 (2)
C(9)–C(10)–C(11)	126.3 (4)	C(10)–C(14)–H(9)	114 (2)
C(9)–C(10)–C(14)	117.4 (3)	C(5)–C(14)–H(10)	116 (2)
C(11)–C(10)–C(14)	115.8 (3)	C(10)–C(14)–H(10)	114 (2)
C(10)–C(11)–C(12)	124.0 (4)	H(9)–C(14)–H(10)	104 (3)
C(11)–C(12)–C(13)	127.3 (4)		
C(12)–C(13)–C(4)	125.8 (4)		
C(5)–C(14)–C(10)	94.8 (3)		

angles are not listed; the maximum correction is 0.2°.

The lengths of the peripheral bonds of the [10]-annulene nucleus do not exhibit any apparent alternation, and all the C–C bond lengths except for C(11)–C(12) and C(12)–C(13) are quite close to that in benzene (1.392±0.004 Å).[12]

The eight atoms, C(4), C(6), C(7), C(8), C(9), C(11), C(12), and C(13), are approximately coplanar; the displacements of these atoms from their mean plane are given in Table 7. Similar characteristics are found in 1,6-methano-cyclodecapentaene-2-carboxylic acid (IV);[13] the root-mean-square deviations of the



(IV)

eight atoms are 0.025 Å for the present compound and 0.034 Å for IV.[13] It seems that the planarity of the nucleus and, therefore, the aromaticity are not affected by the condensation of the six-membered ring(C). The torsion angles of the bonds, C(4)–C(5), C(5)–C(6), C(9)–C(10), and C(10)–C(11), which inevitably have large values in the [10]annulene nucleus, as is shown in Fig. 3(a), are also nearly equal to the corresponding angles in IV.[13]

In the methylene bridge, the C(10)–C(14) bond

12) L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions. Supplement." Special publication No. 18, The Chemical Society, London (1965).

13) M. Dabler and J. D. Dunitz, *Helv. Chim. Acta*, **48**, 1429 (1965).

TABLE 7. LEAST-SQUARES PLANES

The equations of the planes are expressed in the form $Ax+By+Cz+D=0$.

Plane	A	B	C	D
1	0.0918	0.3616	−0.9278	2.365
2	0.5053	0.1950	−0.8406	2.016
3	0.0890	0.3866	−0.9180	2.327
4	0.0892	0.3157	−0.9447	2.616
5	0.1821	0.6712	−0.7186	1.203
6	−0.0046	0.0143	−0.9999	4.076
7	0.7355	0.0604	−0.6749	1.500
8	−0.6022	0.4724	−0.6437	4.009
9	−0.2699	−0.8913	−0.3644	3.871
10	0.5093	0.1929	−0.8387	2.012

Deviations of atoms from the planes in Å

1		2		3		4	
*C- 4	−0.014	*C- 1	0.002	*C- 6	0.004	*C- 4	−0.001
*C- 6	−0.023	*C- 2	−0.008	*C- 7	−0.008	*C-11	0.001
*C- 7	0.002	*C- 3	0.009	*C- 8	0.008	*C-12	−0.003
*C- 8	0.032	*C- 4	−0.005	*C- 9	−0.004	*C-13	0.002
*C- 9	−0.000	*C- 6	0.002	C- 4	0.075	C- 5	−0.438
*C-11	−0.043	C- 5	−0.245	C- 5	−0.461	C- 6	0.107
*C-12	0.013	C- 7	0.392	C-10	−0.477	C- 7	0.194
*C-13	0.035	C-13	0.403	C-11	0.016	C- 8	0.239
C- 5	−0.514	C-14	−0.670	C-12	0.107	C- 9	0.163
C-10	−0.508	O- 1	0.075	C-13	0.143	C-10	−0.408
C-14	−1.522			C-14	−1.479	C-14	−1.433
5		7		8		10	
*C- 5	0.002	*C- 4	0.009	*C- 9	0.019	*C- 1	−0.004
*C- 6	−0.002	*C- 5	−0.026	*C-10	−0.048	*C- 3	0.004
*C- 9	0.002	*C- 6	0.011	*C-11	0.016	*C- 4	−0.004
*C-10	−0.002	*C-14	0.008	*C-14	0.014	*C- 6	0.004
		C- 1	−0.452	C- 8	0.595	C- 2	−0.017
		C- 3	−0.428	C-12	0.632	C- 5	−0.240
6		C- 7	0.602			C- 7	0.397
*C- 4	0.008	C-13	0.627	9		C-13	0.408
*C- 5	−0.011			*C- 5	0.000	C-14	−0.658
*C-10	0.011			*C-10	0.000	O- 1	0.067
*C-11	−0.008			*C-14	−0.000		

(* Asterisks indicate atoms included in the plane calculations.)

Dihedral angles between the planes

1 ∧ 2	26.3°	3 ∧ 4	175.7°	5 ∧ 6	136.7°	7 ∧ 8	91.2°
3 ∧ 5	20.7°	4 ∧ 6	18.4°	5 ∧ 9	67.3°	6 ∧ 9	69.3°

length (1.509 Å) is in good agreement with the typical value for the C(sp^3)–C(sp^2) bond (1.505±0.005 Å),[12] while the C(5)–C(14) length (1.477 Å) is significantly shorter. The C(4)–C(5)–C(6) angle is smaller than C(9)–C(10)–C(11). This is consistent with the C–C-length difference in the bridge. These changes may reasonably be interpreted as a result of the strain by the ring (C). The same explanation may also apply to the significant decrease in the internal angles at C(7) and C(13) in comparison with those in IV.[13]

The C(5)–C(14)–C(10) angle (94.8°) is significantly smaller than the corresponding angles in 1,6-methanocyclodecapentaene-2-carboxylic acid (IV) (99.6°)[13] and 11,11-difluoro-1,6-methano-[10]annulene (101°),[14] and is larger than that in tricarbonyl-1,6-methanocyclodecapentaenechromium (92.4°).[15]

The spatial approaches of the bridged methylene protons to the [10]annulene nucleus are shown in Fig. 4.

The C(1)–O(1) bond distance (1.236 Å) is significantly longer than the C=O double-bond lengths in quinones (1.222 Å in *p*-benzoquinone,[16] 1.223 Å in 2,5-dimethyl-*p*-benzoquinone,[17] 1.224 Å in 2,2-di(1,4-naphthoquinone)[18]) and in tropones (1.228 Å in 4,5-benzotropone,[19] 1.227 Å in 2,7-dimethyl-4,5-benzotropone,[20] 1.225 Å in 5,7-dibromo-2,3-benzotropone,[21] 1.227 Å in 5-chloro-2,3-benzotropone[21]). The elonga-

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17) F. L. Hirshfeld and D. Rabinovich, *ibid.*, **23**, 989 (1967).

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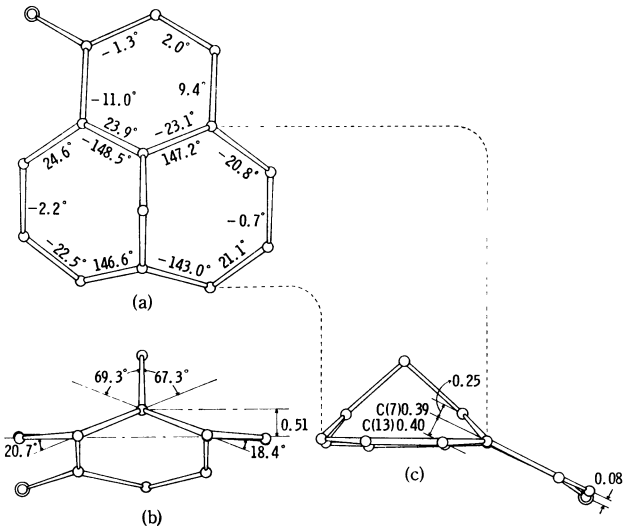


Fig. 3. (a) The molecule viewed along the normal to the mean plane 1 in Table 7. The torsion angles of the bonds are shown. (b) The molecule viewed along C(10)–C(5). 0.51Å is a deviation of C(5) and C(10) from the mean plane 1 in Table 7. (c) The molecule viewed along the normal to the plane 9 in Table 7. 0.25 Å, 0.08 Å, 0.39 Å, and 0.40 Å are the deviations of C(5), O(1), C(7), and C(13), respectively from the plane 2 in Table 7.

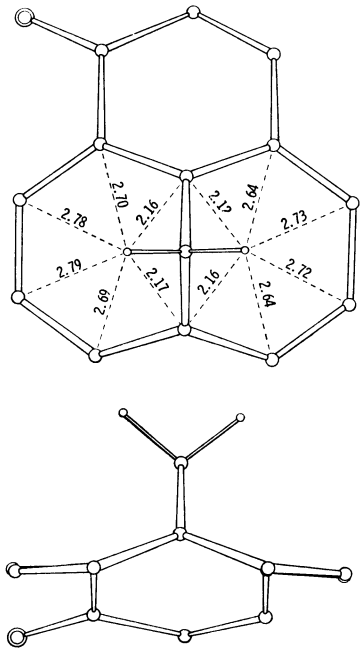


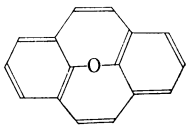
Fig. 4. The spatial approaches (Å) of the bridged methylene protons to the [10]annulene nucleus.

tion of the C=O bond is consistent with the low carbonyl stretching frequency (1605 cm^{-1}).[5] This observation suggests the highly polarized nature of the C=O bond in the present compound, which explains the large dipole moment (4.36 D)[5] and the high basicity (pK_b= −2.6).[5]

The C(1)–C(6) bond (1.491 Å) is slightly longer than the typical C(sp^2)–C(sp^2) single bond,[22] suggesting that its double-bond nature is negligibly small. On the other hand, the C(1)–C(2) and C(3)–C(4) bond lengths are almost equal to one another and are significantly shorter than C(1)–C(6). This may indicate the resonance interaction of the carbonyl group with the [10]annulene nucleus through C(1)–C(2)–C(3)–C(4), not through the C(1)–C(6) bond. This interaction may perturb the π-electron system of the [10]annulene nucleus so as to result in the longer C(12)–C(13) and shorter C(11)–C(12) bonds. It is interesting that the effect of the carbonyl group emerges in the most distant portion of the molecule. This explains well the large dipole moment of the present molecule.

The C(2)–C(3) length (1.331 Å) seems not to favor the above hypothesis, since it is as short as the C=C distance in ethylene.[23] Cruickshank suggests, however, that the ethylene distance might not be used as the standard value for double bonds in a different environment.[24] A possible explanation for the shortening is that the polarization of the C=O group may lead to an increase in the p character in the C(1)–C(2) bond and to a concomitant increase in the s component in the C(2)–C(3), which reduces the length.[25] This reasoning is supported by the values of the C(6)–C(1)–C(2) angle (115.9°) and C(1)–C(2)–C(3) (123.5°). It should be added that, although a contraction of the internal angles at the carbonyl carbons has been observed, the present angle is the smallest among the various quinones.[16–18]

In the six-membered ring (C), five atoms, C(1), C(2), C(3), C(4), and C(6), are coplanar within the limits of error (Plane 2 in Table 7), while only the C(5) atom deviates (by 0.25 Å) (Fig. 3(c)). The mutual displacements of C(5) and C(7) from Plane 2 result in the twist of the C(1)–C(6) bond. If this bond were of double-bond character, it should cause a displacement of C(2) from the reference plane to form a slight boat conformation, as has been reported for the case of the benzene ring in 8,16-oxido-*cis*[2,2]metacyclophane-1,9-diene (V).[26] This is not the case; the C(2)



(V)

atom does not deviate significantly; this is consistent with the view of the bond nature of C(1)–C(6) presented above.

The three-dimensional feature of the molecule is shown in Fig. 3. The dihedral angle between Plane 7 and Plane 8 is 91.2°, and the non-bonded distance between C(5) and C(10) is 2.199 Å. The overlap integral, *S*, between the 2p-orbitals of C(5) and C(10) is estimated using the tables by Mulliken, Rieke,

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23) L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **31**, 400 (1959).

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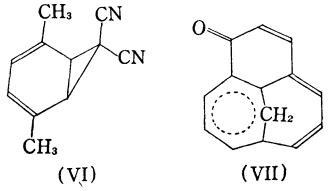
25) H. L. Ammon, M. R. Smith, and E. Kelso, *Acta Crystallogr.*, **B28**, 246 (1972).

26) A. W. Hanson and K. Huml, *ibid.*, **B25**, 2310 (1969).

Orloff, and Orloff,[27] where the 2p-orbitals are assumed to be normal to the above planes. The calculated value of 0.142 for $S_{5,10}$ is twice as large as the $S_{1,6}$ of 0.072 reported for the cycloheptatriene ring of thujic acid.[28] In connection with this, the conformation of the seven-membered ring(A) has been examined. As may be seen in Fig. 3(b), the ring is in a boat conformation, with angles of 67.3 and 20.7° between Plane 5 and Plane 9, and between Plane 5 and Plane 3, respectively. These values lie between the corresponding values in the norcaradiene structure (VI) (71.9 and



(VI) (VII)

4.2°)[29] and those in the cycloheptatriene structure in thujic acid (47.9 and 24.4°).[28] This suggests some contribution from the (VII) structure to the ground-state structure of the molecule.

Crystal Structure. The packing diagram of the crystal viewed along the *c* axis is shown in Fig. 5. The shortest C···C, O···H, and H···H contacts are 3.468, 2.47, and 2.32 Å respectively. The packing appears to be fairly efficient, but there are no abnormally short intermolecular contacts. Therefore, the distortions of the molecule, which do exist, may be ascribed to intramolecular rather than to intermolecular effects. The molecules are so arranged that the large dipole moments cancel each other out by means of the center of symmetry.

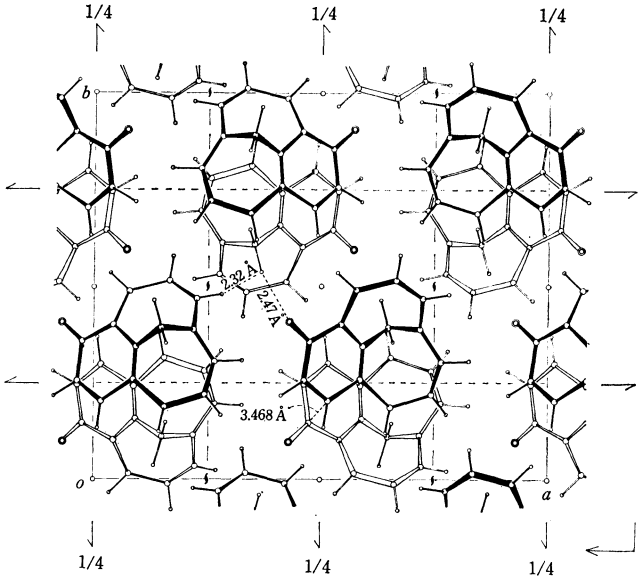


Fig. 5. The crystal structure projected along the *c* axis with some short intermolecular contacts (Å).

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