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Refinement and Thermal Expansion Coefficients of the Structure of Anthrone (20, -90 degrees C) and Comparison with Anthraquinone

H. D. Flack

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I. REFINEMENT AND THERMAL EXPANSION COEFFICIENTS OF THE STRUCTURE OF ANTHRONE (20, −90 °C) AND COMPARISON WITH ANTHRAQUINONE

By H. D. FLACK

CONTENTS

	PAGE		PAGE
Introduction	561	Thermal parameters of anthrone	569
Refinement of the structure of anthrone	562	Thermal expansion	572
		References	574

The crystal structure of anthrone at 20 and −90 °C has been refined and is found to possess long-range disorder, with a statistical distribution of anthrone molecules among two centrosymmetrically-related orientations. The anisotropic thermal-vibration parameters have been analysed. There is a large independent out-of-plane vibration of the oxygen atom, with which is associated considerable anisotropy of the thermal-expansion coefficients. These are also affected by molecular reorientation with change of temperature and by the short-range order to be discussed in parts II and III.

Introduction

The crystal structure of anthrone at room temperatures has been studied by Srivastava (1957, 1959, 1961, 1962, 1964) and by Banerjee & Srivastava (1960). In table 1 the unit-cell dimensions and other basic information are given and compared with those found for anthraquinone (Sen 1948; El Sayed 1965; Lonsdale, Milledge & El Sayed 1966) with which it is isomorphous and can form mixed crystals (Harris 1965), although not, apparently, over the whole composition range (Flack 1968). The unit-cell parameters given in table 1 were measured at 20 °C from photographs using the Straumanis and inclined-beam oscillation techniques. Those at −90 °C were estimated using the thermal-expansion coefficients given later, on the assumption of linear expansion over the 20 to −130 °C range.

Table 1. Comparison of anthrone and anthraquinone (Flack 1968)

property	anthrone		anthraquinone
formula (figure 1)	$C_{14}H_{10}O$		$C_{14}H_8O_2$
melting point/°C	155		286
space group	$P2_1/a$		$P2_1/a$
	20 °C	−90 °C	20 °C
unit-cell dimensions a/Å	15.79 ± 0.01	15.60	15.83 ± 0.04
unit-cell dimensions b/Å	3.994 ± 0.005	3.92	3.97 ± 0.01
unit-cell dimensions c/Å	7.904 ± 0.008	7.89	7.89 ± 0.01
unit-cell dimensions β	101.4° ± 0.3°	100.8°	102.5°
D (meas.) (22 °C)/g cm^{-3}	1.33 ± 0.01		1.438
D (calc.)/g cm^{-3}	1.320 ± 0.007		1.430
molecules/unit cell	2		2
molecular symmetry	$(\bar{1})$		$\bar{1}$
dipole moment in solution (Angyal & Le Fèvre 1950)/D	3.46		0

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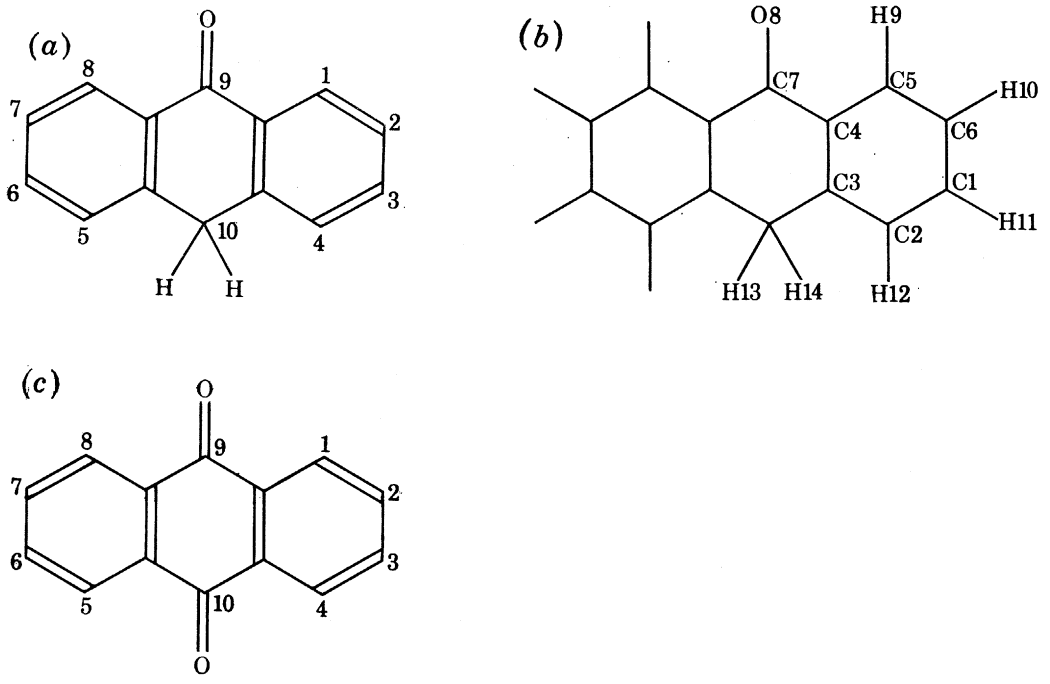

FIGURE 1. Formulae and numbering of atoms: (*a*) anthrone: chemical numbering; (*b*) anthrone: crystallographic numbering; (*c*) anthraquinone: chemical numbering.

REFINEMENT OF THE STRUCTURE OF ANTHRONE

Crystallization from various solvents by slow evaporation or by slow cooling and from the melt showed that those crystals grown by evaporation of a diethyl ether solution were the most suitable for X-ray diffraction studies. These were acicular along [010], very pale yellow, melted sharply at 155 to 156 °C and showed, before melting, a pale blue-green fluorescence, probably due to a trace of the enol-form 9-anthranol. Crystallization from glacial acetic acid and from ethanol gave, in addition to anthrone, crystals of 10-10′-dianthronyl (Ehrenberg 1967).

Attempts to cut equidimensional crystal blocks only resulted in splitting or distorting: the crystals were therefore used uncut but with only part of the needle irradiated. Cross-sections were $0.17 \times 0.17\,\mathrm{mm}^2$ (20 °C) and $0.12 \times 0.12\,\mathrm{mm}^2$ (-90 °C), prism faces being $\{20\bar{1}\}$, $\{100\}$, $\{001\}$. No well-developed end face was found. Oscillation photographs using the Straumanis technique and Cu Kα radiation (Cu Kα_1, $\lambda = 1.54051$ Å; Cu Kα_2, $\lambda = 1.54433$ Å) gave high-angle reflexions $20\,0\,\bar{2}$, $20\,0\,\bar{1}$, $\bar{2}\,0\,10$, $\bar{1}\,0\,10$ for the calculation of a, c and β (using a least-squares program written for the Pegasus computer by Mrs M. Walley). The inclined-beam oscillation technique (Milledge 1963) with Co Kα (Co Kα, $\lambda = 1.79021$ Å) radiation gave b from layer-line spacings, the film-holder radius and the inclination angle being calibrated by means of a small crystal of lead nitrate, mounted about [110]. Intensity measurements were made from Cu Kα Weissenberg photographs $h0l$, $h1l$, $h2l$ and $h3l$. The absence of $0k0$, k odd, was checked from a Mo Kα $0kl$ Weissenberg photograph, on which up to $0\,11\,0$ should have been observable; and Weissenberg photographs $hk0$, $hk1$, although not used in the structure refinement, helped to confirm the assignment of lattice. For the low-temperature studies the crystal was bathed in a stream of cold nitrogen gas, surrounded by a sheath of dry air. Full details of the experimental methods and least-squares refinement at both temperatures are given by Flack (1968). The final R-value at

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20 °C for 480 reflexions, not including those unobserved, was 7.0 %; that at −90 °C was 5.2 % for 357 reflexions.

A list of F_{obs} and F_{calc} values is given in table 2. Projections of the structure of both anthraquinone and anthrone along [010] and [001] are similar to those illustrated in part IV, figures 5 (*a*) and 5 (*b*) for *N*-oxyphenazine, with which they are isostructural.

TABLE 2. OBSERVED AND CALCULATED STRUCTURE FACTORS

Values marked with an asterisk were omitted from least squares refinement.

			20 °C		−90 °C	
h	*k*	*l*	F_{obs}	F_{calc}	F_{obs}	F_{calc}
2	0	0	*13.92	16.84	*14.56	16.84
4	0	0	10.77	−11.27	11.27	−11.19
6	0	0	1.51	−1.22	—	—
8	0	0	9.92	−9.92	8.79	−8.49
10	0	0	2.02	−1.71	2.53	−0.93
14	0	0	1.32	−1.28	3.00	−2.89
−20	0	1	1.76	−1.93	—	−5.79
−12	0	1	6.06	5.98	11.05	11.22
−10	0	1	1.41	1.25	2.96	2.80
−8	0	1	3.11	3.00	3.78	3.49
−6	0	1	6.45	5.64	*8.34	7.28
−4	0	1	10.07	−10.03	9.80	−9.95
−2	0	1	*15.83	25.48	—	24.97
0	0	1	*12.17	15.01	13.04	13.94
2	0	1	8.79	−9.32	8.84	−9.15
4	0	1	7.60	7.69	7.07	7.20
6	0	1	14.93	−15.64	19.01	−19.12
8	0	1	14.21	−13.83	16.02	−16.28
10	0	1	2.14	2.23	2.63	2.79
12	0	1	2.30	2.16	2.92	2.72
14	0	1	0.81	−1.31	—	—
16	0	1	2.53	−2.89	4.01	−4.18
−20	0	2	1.56	−1.36	—	—
−14	0	2	9.05	10.03	15.84	16.70
−12	0	2	7.95	8.39	10.82	11.24
−10	0	2	3.82	−2.89	5.06	−4.92
−8	0	2	3.58	3.57	4.30	4.10
−6	0	2	2.23	−2.07	3.68	−3.85
−4	0	2	*12.47	−14.93	14.36	−15.72
−2	0	2	9.07	−9.91	9.82	−10.56
0	0	2	9.42	−9.60	10.24	−9.94
2	0	2	7.85	8.37	9.51	9.56
4	0	2	2.96	3.40	3.61	3.41
6	0	2	2.95	−2.73	5.84	−5.48
12	0	2	1.14	−1.29	—	—
14	0	2	3.51	−3.86	6.57	−7.09
−20	0	3	—	—	—	3.10
−18	0	3	1.57	−1.68	2.28	−1.97
−14	0	3	5.96	6.07	5.94	5.33
−12	0	3	0.73	0.99	—	—
−8	0	3	4.86	−4.31	6.74	−6.13
−6	0	3	*12.76	−14.31	15.55	−16.41
−4	0	3	1.10	0.76	3.48	3.13
−2	0	3	6.71	5.66	*7.59	6.52
0	0	3	2.55	−2.27	4.37	−3.85
2	0	3	*14.67	−15.97	16.35	−17.02
4	0	3	2.44	−2.14	—	—
6	0	3	5.48	5.00	6.55	6.53
8	0	3	2.40	−1.85	3.19	−2.76
10	0	3	—	—	2.93	−1.76
12	0	3	—	—	3.00	−3.04
14	0	3	1.60	−1.45	—	—
16	0	3	1.33	1.42	3.05	3.09
−18	0	4	1.78	−1.80	4.15	−3.50
−16	0	4	1.21	−1.60	*2.75	−3.25
−14	0	4	0.81	−1.22	2.99	−3.13
−10	0	4	2.12	2.01	2.78	1.83
−8	0	4	4.13	−3.66	*5.91	−4.45
−6	0	4	2.59	−2.30	—	—
−4	0	4	2.90	2.66	2.92	2.84
−2	0	4	2.10	2.02	2.10	1.99
0	0	4	10.62	−10.89	14.88	−14.92
2	0	4	12.84	−12.71	14.99	−14.41
6	0	4	1.61	−1.32	2.67	−1.74
8	0	4	6.19	6.40	9.97	9.74
10	0	4	9.99	10.37	12.32	12.34
12	0	4	—	—	2.89	−1.80
−14	0	5	1.67	−1.31	—	—
−12	0	5	2.91	−2.95	5.84	−5.93
−8	0	5	2.66	2.16	4.66	4.18
−6	0	5	1.15	−1.05	2.60	−2.57
−4	0	5	2.36	−2.15	2.50	−2.33
−2	0	5	2.11	2.01	2.46	2.65
0	0	5	1.31	−1.26	—	—
2	0	5	2.62	2.35	3.73	3.03
4	0	5	—	—	2.76	−2.53
6	0	5	1.67	1.33	4.15	4.29
8	0	5	9.86	10.41	18.70	18.72
10	0	5	2.55	2.35	2.90	3.01
12	0	5	1.89	−2.14	3.63	−3.32
−16	0	6	1.21	1.35	—	—
−14	0	6	1.56	−1.43	2.73	−2.75
−12	0	6	4.74	−5.03	8.04	−8.17
−10	0	6	2.42	−2.25	—	—
−6	0	6	2.63	2.43	4.40	4.30
−4	0	6	9.32	9.70	14.86	15.37
−2	0	6	4.65	4.37	3.57	3.12
2	0	6	1.88	1.71	2.90	3.01
4	0	6	*0.49	−1.45	2.98	−2.66
6	0	6	—	—	3.00	2.05
10	0	6	1.71	−1.75	*3.80	−3.03
12	0	6	—	—	1.97	2.19
−16	0	7	1.15	1.17	2.61	2.65
−6	0	7	6.95	7.09	13.48	13.63
−4	0	7	7.01	7.27	8.65	8.48
−2	0	7	0.81	−1.38	4.06	−4.11

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TABLE 2 (*cont.*)

			20 °C		−90 °C					20 °C		−90 °C	
h	*k*	*l*	F_{obs}	F_{calc}	F_{obs}	F_{calc}	*h*	*k*	*l*	F_{obs}	F_{calc}	F_{obs}	F_{calc}
2	0	7	1.90	−1.91	4.07	−3.96	−15	1	2	3.49	3.52	3.85	4.08
4	0	7	3.15	−3.44	5.14	−4.97	−14	1	2	3.23	3.34	4.04	3.96
6	0	7	0.76	−0.86	—	—	−13	1	2	2.43	2.21	*3.57	2.69
−14	0	8	1.03	0.98	—	—	−12	1	2	4.60	−4.60	8.54	−8.48
−12	0	8	1.21	1.30	3.24	3.17	−11	1	2	4.40	4.53	7.90	7.94
−8	0	8	1.49	−1.49	2.76	−2.15	−10	1	2	3.31	−3.14	4.79	−4.76
2	0	8	2.40	−2.67	5.24	−5.36	−8	1	2	3.02	−2.87	4.33	−3.74
6	0	8	1.32	1.27	2.80	2.72	−7	1	2	4.82	−4.95	6.85	−6.38
−10	0	9	0.53	−0.77	3.04	−2.55	−6	1	2	7.88	−8.74	9.62	−9.50
−8	0	9	1.33	−1.26	—	—	−5	1	2	0.84	0.70	—	—
−6	0	9	1.23	−1.01	2.36	−1.91	−3	1	2	3.85	−3.95	4.30	−4.22
−4	0	10	—	−1.57	4.95	−4.72	−2	1	2	2.30	2.10	2.50	2.30
−2	0	10	—	−1.55	3.54	−3.24	−1	1	2	1.23	1.14	—	—
1	1	0	*8.94	13.03	—	12.94	0	1	2	2.52	−2.54	3.02	−2.92
2	1	0	*14.94	−29.34	—	−28.94	1	1	2	5.27	−5.38	6.16	−5.98
3	1	0	*15.05	18.37	17.13	18.08	2	1	2	2.10	1.98	*2.63	3.23
4	1	0	4.47	−4.66	4.67	−4.78	3	1	2	1.15	−0.99	—	—
5	1	0	9.50	−10.83	11.83	−11.55	5	1	2	5.78	5.64	6.75	6.57
6	1	0	8.44	−8.62	9.59	−9.42	6	1	2	2.10	1.72	1.93	2.19
7	1	0	6.78	−6.80	6.69	−6.61	7	1	2	4.51	−4.36	6.54	−6.30
8	1	0	4.99	−4.61	5.73	−5.53	8	1	2	3.24	2.63	4.78	4.31
10	1	0	2.98	2.61	—	—	9	1	2	4.26	−4.12	6.58	−6.25
12	1	0	—	—	2.72	−2.35	12	1	2	2.46	−2.52	4.24	−4.61
13	1	0	—	—	2.07	2.32	16	1	2	1.89	1.97	2.98	3.08
14	1	0	0.99	−1.23	—	—	17	1	2	1.21	−1.29	2.79	−2.78
15	1	0	0.98	−1.51	2.40	−2.37	−19	1	3	1.16	−1.15	—	—
−19	1	1	—	—	*1.17	−2.42	−16	1	3	1.66	1.37	—	—
−15	1	1	3.72	3.62	7.56	7.36	−14	1	3	2.45	−2.39	4.33	−4.66
−14	1	1	4.56	4.56	8.05	8.21	−13	1	3	4.89	5.12	7.88	7.68
−13	1	1	2.34	2.33	*1.96	3.52	−12	1	3	4.67	−4.95	5.76	−5.88
−12	1	1	2.21	2.17	3.22	3.62	−11	1	3	4.17	4.10	4.95	4.56
−10	1	1	1.45	−1.03	2.12	−2.12	−10	1	3	0.90	−1.08	1.87	−0.59
−9	1	1	2.61	2.25	3.38	3.57	−9	1	3	4.48	−4.39	6.38	−6.25
−8	1	1	3.83	3.69	3.52	3.62	−8	1	3	3.80	−3.67	*4.65	−4.00
−7	1	1	1.48	−1.39	—	—	−7	1	3	2.40	−2.03	—	—
−6	1	1	3.42	−3.43	4.74	−4.71	−6	1	3	1.38	1.07	2.63	2.79
−5	1	1	2.33	−2.56	2.18	−2.34	−5	1	3	0.95	−0.94	1.40	−1.64
−4	1	1	1.69	−1.40	2.78	−2.77	−4	1	3	8.18	9.12	10.94	10.52
−3	1	1	4.72	−4.81	6.38	−6.20	−3	1	3	3.06	−3.09	2.92	−3.09
−1	1	1	1.94	2.26	1.97	2.31	−2	1	3	1.56	1.53	—	—
0	1	1	*13.74	−26.93	—	−27.40	−1	1	3	7.05	−7.66	9.52	−9.50
1	1	1	*17.23	32.74	—	34.40	0	1	3	9.05	−9.99	11.43	−11.32
2	1	1	8.31	−9.27	10.03	−10.24	1	1	3	9.14	−9.89	11.17	−10.65
3	1	1	3.21	3.24	2.29	2.52	2	1	3	4.53	−4.32	3.89	−3.32
4	1	1	1.62	0.94	—	—	3	1	3	—	—	2.49	2.31
5	1	1	7.95	−8.55	11.26	−10.81	4	1	3	2.76	2.65	2.46	2.26
6	1	1	5.79	−5.40	7.35	−6.73	5	1	3	1.10	−0.84	—	—
7	1	1	3.26	−2.86	3.95	−3.32	7	1	3	2.12	2.03	1.81	2.36
8	1	1	4.95	5.06	6.62	6.15	8	1	3	2.75	2.88	2.42	2.82
9	1	1	4.46	−4.27	3.55	−3.74	9	1	3	4.53	4.52	3.68	4.22
10	1	1	4.92	4.54	5.93	5.80	10	1	3	2.40	2.39	—	—
12	1	1	0.92	−1.45	—	—	12	1	3	—	—	2.06	0.23
13	1	1	*0.87	−1.54	3.10	−3.48	14	1	3	1.61	1.61	4.07	4.27
14	1	1	2.22	−2.28	—	−2.97	−9	1	4	1.29	1.14	3.48	3.11
15	1	1	—	—	—	−2.20	−7	1	4	2.25	−2.08	3.14	−3.16
−19	1	2	1.81	−1.88	3.41	−3.59	−6	1	4	3.62	3.31	*4.74	3.61
−16	1	2	3.02	2.98	5.18	4.88	−5	1	4	5.50	−5.64	7.08	−6.71

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TABLE 2 (*cont.*)

			20 °C		−90 °C	
h	k	l	F_{obs}	F_{calc}	F_{obs}	F_{calc}
−4	1	4	2.32	2.20	1.56	1.73
−3	1	4	—	—	2.07	2.19
−2	1	4	4.31	−4.19	6.07	−5.95
−1	1	4	1.45	−1.22	—	—
0	1	4	4.19	−4.06	4.90	−4.50
1	1	4	2.25	−1.80	2.43	−2.80
2	1	4	5.11	5.27	6.98	6.59
3	1	4	6.54	−6.73	9.40	−9.15
4	1	4	3.21	3.05	3.52	2.84
5	1	4	1.23	−0.90	—	—
6	1	4	3.58	3.73	5.49	6.11
7	1	4	7.91	8.53	11.71	13.23
8	1	4	6.89	7.44	9.63	9.92
9	1	4	2.98	2.78	*3.81	2.98
11	1	4	—	—	—	−0.41
12	1	4	2.92	−2.74	—	—
15	1	4	1.39	−1.33	2.10	−1.93
16	1	4	1.01	−1.11	2.32	−2.36
−15	1	5	1.62	−1.60	—	−2.53
−14	1	5	—	—	—	−2.77
−13	1	5	2.95	−2.99	5.10	−5.16
−6	1	5	0.90	1.10	—	—
−5	1	5	3.08	2.93	5.55	5.66
−4	1	5	3.43	3.46	4.71	4.71
−3	1	5	1.81	1.51	—	—
−2	1	5	1.22	1.28	—	—
0	1	5	3.07	2.71	4.60	4.26
2	1	5	3.61	3.39	4.38	4.38
3	1	5	3.07	−2.97	4.23	−4.24
5	1	5	1.65	1.79	3.38	3.73
6	1	5	2.97	2.72	5.92	6.05
7	1	5	—	—	2.07	2.36
8	1	5	—	—	2.48	−2.60
9	1	5	1.94	1.89	4.35	4.02
10	1	5	5.08	−5.37	8.97	−8.95
11	1	5	3.91	3.94	6.22	6.31
13	1	5	—	—	2.67	−2.84
14	1	5	—	—	2.23	−2.18
15	1	5	—	−1.30	—	−2.76
−14	1	6	1.43	−1.44	—	—
−13	1	6	1.81	−1.64	—	—
−11	1	6	2.96	−2.68	4.55	−4.54
−10	1	6	0.99	1.52	—	2.85
−9	1	6	0.99	−1.25	—	—
−8	1	6	1.20	1.62	—	—
−7	1	6	4.52	4.71	8.66	8.94
−6	1	6	5.28	5.54	9.10	8.99
−5	1	6	4.95	4.91	5.48	5.51
−4	1	6	3.08	2.59	—	—
−2	1	6	3.17	−2.96	4.81	−4.57
−1	1	6	1.75	1.62	—	—
2	1	6	1.40	−1.72	2.60	−2.96
4	1	6	2.14	−2.17	—	—
8	1	6	2.54	−2.30	5.65	−5.57
9	1	6	2.44	2.41	6.05	5.72
13	1	6	—	—	1.74	−2.03
−12	1	7	0.88	1.25	—	2.68
−11	1	7	2.07	−1.94	—	−3.08
−9	1	7	0.92	−1.09	—	—
−8	1	7	1.61	1.61	3.19	3.13
−7	1	7	*0.86	1.76	—	—
−6	1	7	*0.87	1.39	—	—
−5	1	7	2.12	2.02	*3.35	2.72
−4	1	7	4.24	−4.33	8.37	−8.57
−3	1	7	4.31	4.12	7.49	7.32
−2	1	7	3.90	−3.85	4.71	−4.72
−1	1	7	1.42	1.12	—	—
0	1	7	0.94	−1.21	—	—
1	1	7	2.12	−2.37	4.02	−4.23
2	1	7	1.81	−1.72	2.63	−2.86
6	1	7	1.45	1.50	—	—
9	1	7	1.36	−1.26	3.14	−2.97
−10	1	8	1.33	−1.15	—	—
−6	1	8	0.86	−1.15	2.59	−2.78
−5	1	8	*0.81	1.42	3.58	3.64
−4	1	8	1.68	−1.81	*1.96	−2.62
−3	1	8	1.68	1.76	—	—
4	1	8	*0.69	1.72	3.65	3.64
7	1	8	0.95	−0.68	—	—
8	1	8	–	−1.25	3.61	−3.19
−5	1	9	1.44	−1.15	2.82	−2.86
−3	1	9	1.34	−1.04	2.12	−2.07
1	2	0	—	5.93	—	5.70
2	2	0	1.60	−1.53	2.01	−2.09
3	2	0	6.27	−6.42	7.05	−6.88
4	2	0	2.14	−1.91	4.72	−4.50
5	2	0	9.60	−9.42	10.47	−9.78
6	2	0	3.15	−2.90	4.34	−4.15
7	2	0	2.05	1.97	3.04	2.63
8	2	0	1.89	1.80	3.09	2.88
10	2	0	1.59	1.78	2.36	2.79
12	2	0	*0.58	−1.68	—	—
13	2	0	2.60	−2.78	4.50	−4.55
14	2	0	0.92	0.91	2.84	2.59
15	2	0	2.49	−2.36	—	−4.66
16	2	0	1.65	1.64	3.96	3.79
−17	2	1	2.07	2.13	4.69	4.94
−16	2	1	2.92	3.18	5.15	5.30
−15	2	1	2.99	2.91	4.70	4.44
−11	2	1	0.92	1.08	—	—
−9	2	1	1.73	−1.46	—	—
−8	2	1	3.36	−3.30	4.59	−4.36
−7	2	1	1.68	−1.53	2.38	−2.22
−6	2	1	7.05	−6.89	7.49	−7.61
−5	2	1	3.50	3.37	3.13	2.99
−4	2	1	3.78	−3.72	4.38	−4.26
−3	2	1	1.97	−1.88	2.03	−2.24
−2	2	1	0.66	−0.67	—	—
−1	2	1	4.05	4.25	4.59	4.68
0	2	1	0.77	−0.64	0.71	−0.71
1	2	1	4.90	−4.62	4.99	−4.72
2	2	1	*10.59	13.15	14.06	15.00
3	2	1	*10.48	−16.11	17.34	−17.74
4	2	1	9.09	9.45	10.37	10.40

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PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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TABLE 2 (*cont.*)

			20 °C		−90 °C	
h	k	l	F_{obs}	F_{calc}	F_{obs}	F_{calc}
5	2	1	0.92	−0.88	—	—
6	2	1	1.65	−1.57	1.88	−2.02
8	2	1	—	—	1.61	−0.00
10	2	1	2.83	−2.66	*1.79	−3.38
12	2	1	3.29	−3.11	4.08	−3.98
−18	2	2	—	—	2.42	−2.24
−17	2	2	2.22	2.20	3.57	3.68
−9	2	2	6.11	−5.94	8.32	−8.61
−8	2	2	2.11	−1.68	—	—
−7	2	2	1.06	−0.69	—	—
−6	2	2	0.65	1.00	2.03	2.08
−5	2	2	1.05	0.95	—	—
−4	2	2	3.82	3.57	4.59	4.53
−3	2	2	1.00	−1.02	—	—
−2	2	2	3.86	−3.82	5.63	−5.79
−1	2	2	5.28	−5.42	6.05	−6.01
0	2	2	2.36	−2.24	2.23	−2.22
1	2	2	9.33	−10.72	11.47	−10.85
2	2	2	8.29	8.81	11.40	11.51
4	2	2	0.68	−0.82	—	—
5	2	2	1.40	1.19	—	—
6	2	2	0.73	−0.93	—	—
9	2	2	3.84	3.64	4.27	3.73
10	2	2	4.29	−4.22	7.06	−6.94
11	2	2	1.35	1.35	—	2.33
14	2	2	*0.51	1.21	—	—
−18	2	3	0.86	−1.15	2.53	−2.57
−12	2	3	2.48	2.40	4.17	4.15
−11	2	3	5.44	−5.45	8.95	−8.89
−10	2	3	4.37	4.41	7.52	7.86
−9	2	3	3.58	−3.55	4.04	−3.79
−7	2	3	1.03	1.14	—	—
−5	2	3	1.03	−1.09	—	—
−3	2	3	1.70	−1.67	1.68	−2.07
−2	2	3	8.07	−8.33	10.26	−10.16
−1	2	3	2.74	−2.53	2.97	−2.89
0	2	3	3.63	−3.25	3.61	−3.53
1	2	3	1.21	1.43	1.80	1.83
2	2	3	1.58	−1.36	3.01	−2.87
5	2	3	1.99	2.13	2.95	2.99
6	2	3	7.04	7.34	10.43	11.09
7	2	3	7.68	7.69	8.72	9.01
8	2	3	2.72	2.68	—	—
9	2	3	1.80	1.48	—	—
10	2	3	1.96	−1.79	3.19	−3.03
−14	2	4	1.58	−1.44	3.60	−3.39
−13	2	4	2.22	−2.22	3.79	−3.92
−12	2	4	2.51	2.65	4.10	3.84
−11	2	4	2.66	−2.67	—	—
−10	2	4	2.21	2.00	1.84	1.85
−8	2	4	0.90	−1.03	1.75	−2.24
−5	2	4	3.18	2.96	4.73	4.57
−4	2	4	3.04	−2.77	4.49	−4.18
−3	2	4	3.94	3.82	4.96	4.44
−2	2	4	2.99	−2.67	2.16	−2.43
−1	2	4	1.97	1.73	1.94	1.76
0	2	4	2.30	2.13	2.83	2.82
1	2	4	0.76	−0.75	—	—
3	2	4	—	—	1.65	1.07
4	2	4	1.24	1.22	3.64	3.58
5	2	4	7.29	7.44	10.84	11.08
6	2	4	2.89	2.99	5.28	5.78
7	2	4	2.65	2.20	—	—
9	2	4	2.12	−1.99	3.25	−3.31
13	2	4	1.87	−1.52	—	—
14	2	4	1.23	−1.17	4.00	−3.84
−16	2	5	1.25	−1.39	2.64	−2.86
−14	2	5	2.26	−2.21	3.85	−3.87
−8	2	5	3.17	3.23	6.19	6.69
−7	2	5	4.16	4.24	6.79	7.08
−6	2	5	3.94	4.01	4.84	5.33
−5	2	5	4.21	4.26	4.35	4.41
−4	2	5	—	—	2.35	−2.20
−2	2	5	—	—	2.20	2.24
2	2	5	2.76	−2.81	3.96	−4.24
3	2	5	2.61	2.24	4.28	4.26
4	2	5	3.52	−3.52	4.96	−4.90
5	2	5	1.53	1.78	—	—
6	2	5	1.83	−1.63	2.20	−2.48
7	2	5	1.32	−1.51	—	−2.64
11	2	5	1.74	−1.66	3.83	−3.70
12	2	5	1.24	1.46	—	—
13	2	5	2.61	−2.73	5.02	−4.66
−9	2	6	2.89	2.94	5.99	6.15
−8	2	6	2.65	2.88	4.17	4.32
−7	2	6	3.53	3.37	4.08	4.10
−6	2	6	1.34	1.48	—	—
−5	2	6	—	—	3.19	−3.16
0	2	6	1.53	−1.71	—	−3.24
1	2	6	1.53	−1.93	—	—
2	2	6	2.23	−2.05	3.08	−3.16
9	2	6	1.52	−1.57	3.20	−3.05
10	2	6	1.38	1.50	4.52	4.63
11	2	6	2.63	−2.80	5.85	−5.70
−10	2	7	2.00	−2.02	4.40	−4.27
−9	2	7	1.21	1.55	2.46	2.59
−8	2	7	1.42	−1.29	2.74	−2.93
−2	2	7	1.31	1.09	—	—
−1	2	7	3.88	−3.95	7.05	−7.03
0	2	7	1.64	1.25	—	—
1	2	7	1.45	−1.42	—	—
6	2	7	—	—	2.88	−2.53
7	2	7	1.01	−1.10	2.78	−2.56
8	2	7	1.17	−1.30	2.32	−2.19
9	2	7	0.70	−1.33	3.08	−3.16
−4	2	8	0.75	1.03	2.84	2.61
−3	2	8	2.62	−2.60	5.92	−5.66
−2	2	8	2.61	2.60	5.69	5.62
−1	2	8	1.66	−1.72	1.53	−1.74
0	2	8	0.77	0.83	—	—
6	2	8	—	−1.23	3.41	−3.53
−6	2	9	1.14	−1.22	2.99	−3.46
−5	2	9	—	—	2.26	−2.28
2	3	0	2.57	−2.55	3.42	−3.50

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TABLE 2 (*cont.*)

			20 °C		−90 °C	
h	*k*	*l*	F_{obs}	F_{calc}	F_{obs}	F_{calc}
3	3	0	2.99	−3.06	3.41	−3.50
4	3	0	0.92	1.05	—	—
8	3	0	1.22	1.34	—	—
9	3	0	2.47	−2.40	3.21	−3.44
10	3	0	1.48	−1.61	—	—
11	3	0	0.85	−1.19	—	—
12	3	0	1.24	−1.71	—	—
15	3	0	1.03	1.23	—	—
16	3	0	1.67	−1.90	—	−4.32
−11	3	1	1.75	−1.85	—	—
−10	3	1	2.32	−2.22	3.24	−3.51
−9	3	1	2.45	−2.24	—	—
−8	3	1	2.35	−2.09	—	—
−5	3	1	2.05	−1.99	—	—
−4	3	1	4.49	4.54	5.97	5.58
−3	3	1	3.94	−4.31	5.82	−6.32
−1	3	1	1.89	−1.81	1.77	−1.92
0	3	1	1.68	−1.62	—	—
1	3	1	1.46	−1.35	—	—
2	3	1	2.72	2.85	3.56	3.77
3	3	1	1.96	1.57	2.14	2.15
4	3	1	4.79	−4.74	5.83	−5.57
5	3	1	5.24	4.90	5.53	5.02
6	3	1	4.32	−4.13	5.34	−4.81
10	3	1	1.75	−1.88	—	−3.14
−12	3	2	—	−1.16	—	—
−11	3	2	1.47	−1.53	—	—
−7	3	2	1.19	1.01	—	—
−6	3	2	1.30	1.45	—	—
−5	3	2	2.28	−2.04	—	—
−3	3	2	4.09	−4.08	5.62	−5.27
−2	3	2	4.49	−4.75	6.05	−5.94
−1	3	2	2.09	−2.01	2.37	−2.42
0	3	2	1.02	1.11	2.39	2.28
1	3	2	1.06	0.94	—	—
2	3	2	4.39	−4.15	5.92	−5.36
3	3	2	5.91	6.44	9.08	8.59
4	3	2	6.21	−6.34	8.40	−8.14
5	3	2	6.28	6.63	9.03	9.10
6	3	2	4.16	4.27	5.36	4.96
7	3	2	2.18	1.88	—	—
11	3	2	0.80	−1.00	—	—
12	3	2	2.22	2.11	3.15	3.54
13	3	2	1.27	−1.37	—	—
−10	3	3	0.86	−1.00	—	—
−9	3	3	2.72	2.34	3.97	3.70
−8	3	3	3.35	−3.16	5.74	−5.79
−7	3	3	2.23	2.00	—	—
−5	3	3	0.77	−0.67	—	—
−4	3	3	2.30	−2.23	—	—
0	3	3	0.77	0.86	—	—
2	3	3	2.36	−2.19	—	—
3	3	3	3.88	3.90	6.65	6.68
4	3	3	5.30	5.56	9.14	9.04
5	3	3	4.49	4.46	6.61	6.74
6	3	3	3.96	3.78	4.87	4.45
8	3	3	1.52	−1.61	—	−3.00
9	3	3	1.49	−1.52	—	—
10	3	3	1.61	1.55	—	—
11	3	3	1.66	−1.71	*2.37	−3.64
13	3	5	1.36	−1.27	—	—
−15	3	4	0.78	−1.15	—	—
−11	3	4	1.58	1.75	—	—
−10	3	4	3.51	−3.56	6.13	−6.27
−9	3	4	4.08	4.33	6.86	7.34
−7	3	4	3.19	3.04	3.70	3.77
−6	3	4	2.45	2.33	—	—
−2	3	4	3.04	2.73	4.61	4.39
−1	3	4	2.30	−2.07	2.95	−2.79
0	3	4	1.55	1.36	—	—
1	3	4	1.42	−1.58	—	—
3	3	4	1.46	1.35	—	—
4	3	4	0.86	1.33	—	—
6	3	4	1.27	−1.36	—	—
7	3	4	1.59	−1.41	—	—
11	3	4	1.06	−0.94	—	—
12	3	4	1.14	−1.22	2.77	−2.99
−11	3	5	1.14	1.34	—	—
−10	3	5	0.79	1.03	—	3.81
−9	3	5	3.25	3.46	5.50	5.53
−8	3	5	3.39	3.56	5.46	5.57
−7	3	5	2.12	1.79	—	—
−3	3	5	1.76	−1.82	—	—
−2	3	5	1.48	1.48	—	—
−1	3	5	2.13	−2.15	—	—
0	3	5	1.63	−1.84	—	—
2	3	5	1.62	−1.37	—	—
5	3	5	2.14	−1.94	—	−3.54
6	3	5	1.88	1.94	—	—
−10	3	6	0.46	1.16	—	—
−2	3	6	1.43	−1.51	—	—
−1	3	6	0.82	−1.28	—	—
4	3	6	1.77	1.63	—	—
5	3	6	1.59	−1.73	3.33	−3.84
7	3	6	1.35	−1.19	—	—
8	3	6	1.06	−1.13	—	—
−7	3	7	0.66	−0.95	—	—
1	3	7	1.01	1.11	—	—
6	3	7	—	−1.21	—	—
−7	3	8	—	−1.21	—	—
−2	3	8	0.46	−0.71	—	—
−1	3	8	1.29	1.63	2.89	3.55
0	3	8	1.79	−1.97	3.89	−4.34
1	3	8	—	1.65	—	—

The molecule used in the trial structure refined assumes a statistical arrangement of two orientations of the anthrone molecules (figure 1) to account for the pseudo-centrosymmetry. That is to say, the half-molecule unit has ($\frac{1}{2}$H + $\frac{1}{2}$O + $\frac{1}{2}$H) attached to the C7 position

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(crystallographic numbering). The possibility of a non-overlap of the two carbon skeletons has been considered, but in fact overlapping seems to be almost exact except possibly in the direction of the C 9 (aromatic) and C 10 (aliphatic) atoms (chemical numbering).

Table 3 gives the fractional coordinates for all atoms at 20 and −90 °C, with standard deviations for all except the H atoms, which were adjusted to be at 1.08 Å (1 Å = 10^{-10} m) from the appropriate C atoms and which were given isotropic temperature factors of 3.5 Å² at 20 °C

Table 3. Fractional coordinates and estimated standard deviations
(c.s.d.s given in parentheses)

atom	x (20 °C)	x (−90 °C)
C 1	0.13574 (27)	0.13193 (25)
C 2	0.05485 (24)	0.04958 (23)
C 3	0.02785 (22)	0.02531 (22)
C 4	0.08552 (21)	0.08620 (23)
C 5	0.16747 (22)	0.16980 (21)
C 6	0.19225 (25)	0.19202 (24)
C 7	0.06066 (24)	0.06383 (23)
O 8	0.10684 (31)	0.11232 (30)
H 9	0.21165	0.21741
H 10	0.25606	0.25574
H 11	0.15577	0.15259
H 12	0.01061	0.00246
H 13	0.06601	0.07021
H 14	0.10671	0.10996

	y (20 °C)	y (−90 °C)
C 1	0.40243 (91)	0.40962 (113)
C 2	0.26837 (84)	0.26518 (106)
C 3	0.13740 (73)	0.13812 (96)
C 4	0.14456 (73)	0.14734 (97)
C 5	0.28623 (84)	0.28870 (100)
C 6	0.41202 (84)	0.41819 (102)
C 7	0.00892 (92)	0.01027 (106)
O 8	0.01910 (160)	0.02438 (171)
H 9	0.30132	0.30275
H 10	0.51561	0.52962
H 11	0.49967	0.51226
H 12	0.26831	0.25826
H 13	0.21148	0.21696
H 14	−0.18387	−0.18664

	z (20 °C)	z (−90 °C)
C 1	0.39425 (50)	0.40109 (47)
C 2	0.34181 (47)	0.34149 (44)
C 3	0.17316 (41)	0.17362 (43)
C 4	0.05959 (44)	0.06572 (44)
C 5	0.11533 (49)	0.12444 (47)
C 6	0.28095 (55)	0.29080 (50)
C 7	−0.11870 (48)	−0.11563 (44)
O 8	−0.21053 (67)	−0.20439 (58)
H 9	0.02715	0.04150
H 10	0.32319	0.33744
H 11	0.52443	0.52782
H 12	0.43074	0.42440
H 13	−0.20698	−0.20364
H 14	−0.13148	−0.12890

and 2.0 Å² at −90 °C. These parameters for H were not refined, but for all other atoms anisotropic temperature factors were used in the later stages of refinement. At both temperatures the molecule is essentially planar, except for H 13 and H 14. Tables 4 and 5 give the bond lengths (uncorrected for thermal libration) and bond angles. The differences shown at 20 and −90 °C in the bond lengths and angles are unlikely to be real; these differences may be reduced by the correction

Table 4. Bond lengths with e.s.d. uncorrected for thermal libration.
Crystallographic numbering of atoms

	bond length/Å	
	at 20 °C	at −90 °C
C 1–C 2	1.370 (6)	1.402 (5)
C 2–C 3	1.409 (5)	1.400 (5)
C 3–C 4	1.399 (5)	1.390 (5)
C 3–C 7	1.496 (5)	1.498 (5)
C 4–C 5	1.400 (5)	1.413 (5)
C 4–C 7	1.480 (5)	1.507 (5)
C 5–C 6	1.376 (6)	1.390 (5)
C 6–C 1	1.383 (6)	1.394 (5)
C 7–O 8	1.125 (9)	1.125 (6)

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for thermal libration, since this is large for C 1 and C 6 and for disorder, which affects C 7 mostly; or they may be partly due to the neglect in the refinement of a number of intensities affected by extinction. Intermolecular contact distances are given by Flack (1968). In view of the disorder to be discussed later, it is unlikely that the accuracies of the *individual* bond lengths, etc. in tables 3 and 4 (and in Flack's thesis) are as good as the derived e.s.d.s would imply.

Thermal parameters of anthrone

The values of b_{ij} for the anisotropic temperature factors given in the form

$$\exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{31}lh + b_{12}hk)$$

are given in table 6. Values of the mean square displacements $\langle u^2 \rangle$ have been calculated for the principal axes of the ellipsoid of thermal vibration for each atom. Figures 2 and 3 show projections of $\langle u^2 \rangle$ along the molecular axes, N and L respectively.

Table 5. Bond angles

	20 °C	−90 °C
C 1–C 2–C 3	121.0°	122.0°
C 2–C 3–C 4	118.7	118.4
C 3–C 4–C 5	119.3	120.3
C 4–C 5–C 6	120.8	120.3
C 5–C 6–C 1	120.1	120.2
C 6–C 1–C 2	120.1	118.8
C 7–C 3–C 2	120.1	119.9
C 7–C 4–C 5	119.7	119.1
C 3–C 7–C 4	117.9	117.7
C 3–C 7–O 8	121.4	121.5
C 4–C 7–O 8	120.7	120.7

Table 6. Thermal parameters, $10^4\, b_{ij}$ and their e.s.d.

	temp. °C	C 1	C 2	C 3	C 4	C 5	C 6	C 7	O 8
$b_{11}(\sigma)$	20	65 (2)	53 (2)	40 (1)	34 (1)	37 (1)	44 (2)	39 (1)	41 (2)
$b_{11}(\sigma)$	−90	27 (2)	22 (1)	14 (1)	19 (1)	17 (1)	18 (1)	20 (1)	17 (2)
$b_{22}(\sigma)$	20	561 (27)	541 (24)	393 (21)	447 (21)	507 (23)	552 (24)	655 (24)	1542 (52)
$b_{22}(\sigma)$	−90	355 (31)	296 (28)	295 (32)	315 (29)	244 (29)	350 (32)	293 (29)	712 (48)
$b_{33}(\sigma)$	20	206 (8)	167 (7)	147 (5)	164 (6)	240 (8)	270 (8)	183 (6)	189 (9)
$b_{33}(\sigma)$	−90	92 (6)	74 (6)	73 (6)	63 (5)	118 (6)	109 (6)	84 (6)	66 (7)
$b_{23}(\sigma)$	20	−22 (24)	24 (22)	60 (18)	18 (20)	10 (24)	−41 (24)	12 (22)	−164 (42)
$b_{23}(\sigma)$	−90	−6 (26)	−7 (24)	−5 (22)	−20 (22)	4 (25)	−43 (26)	49 (23)	−90 (35)
$b_{31}(\sigma)$	20	−44 (7)	7 (6)	12 (5)	7 (4)	−11 (6)	−36 (7)	30 (5)	100 (6)
$b_{31}(\sigma)$	−90	−20 (6)	4 (4)	1 (5)	−7 (4)	−5 (5)	−13 (5)	−9 (5)	43 (6)
$b_{12}(\sigma)$	20	−10 (12)	32 (12)	43 (9)	33 (9)	7 (11)	−10 (12)	−2 (11)	−86 (21)
$b_{12}(\sigma)$	−90	−7 (14)	2 (14)	23 (10)	3 (12)	−6 (13)	−10 (12)	7 (13)	−32 (20)

A rigid-body analysis of the thermal data has been made, with and without the oxygen atom; and the results are shown in table 7 with those of anthraquinone for comparison. The differences between the observed and calculated atomic mean square amplitudes are shown in table 8 for the T, ω with and without the oxygen atom.

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A similar analysis has been carried out for the −90 °C data (Flack 1968). In both cases there is clear evidence, from the change in ω_{11} for the 8-atom and 7-atom analyses, that there is a strong independent oxygen vibration normal to the molecular plane. This is also apparent from

TABLE 7. T AND ω TENSORS FOR ANTHRONE AND ANTHRAQUINONE (BOTH AT 20 °C)

	$T/10^2$ Å^2	ω/degree^2
anthrone		
whole molecule	$\begin{pmatrix} 4.23 & -0.23 & 0.09 \\ & 4.48 & 0.20 \\ & & 1.69 \end{pmatrix}$	$\begin{pmatrix} 51.2 & -0.39 & -0.16 \\ & 4.24 & 0.13 \\ & & 13.0 \end{pmatrix}$
carbons only	$\begin{pmatrix} 4.30 & -0.22 & 0.10 \\ & 4.91 & 0.15 \\ & & 2.75 \end{pmatrix}$	$\begin{pmatrix} 23.0 & -0.30 & 4.37 \\ & 3.31 & -0.03 \\ & & 11.9 \end{pmatrix}$
anthraquinone (Lonsdale *et al.* 1966)		
whole molecule	$\begin{pmatrix} 4.30 & 0.07 & 0.46 \\ & 2.98 & -0.81 \\ & & 2.64 \end{pmatrix}$	$\begin{pmatrix} 29.1 & -0.20 & 4.04 \\ & 1.35 & -0.20 \\ & & 14.1 \end{pmatrix}$
carbons only	$\begin{pmatrix} 4.46 & 0.19 & 0.47 \\ & 2.88 & -0.86 \\ & & 3.37 \end{pmatrix}$	$\begin{pmatrix} 10.1 & 0.13 & 5.88 \\ & 0.69 & -0.20 \\ & & 11.0 \end{pmatrix}$

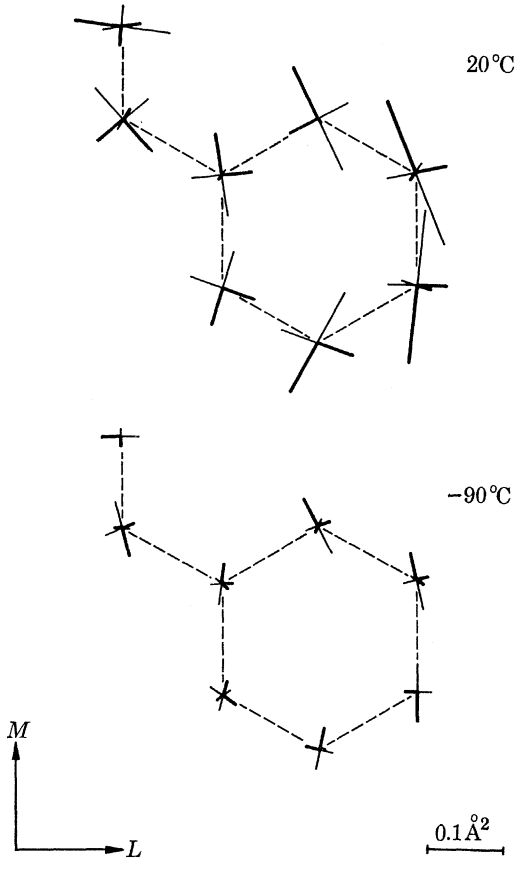

FIGURE 2. Projection along molecular normal N showing the mean square displacements ($\langle u^2 \rangle$) in the directions of the principal axes of the atomic thermal vibration ellipsoids at 20 and −90 °C.

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figure 3. There is some evidence also for a translational movement of the carbon skeleton along the M direction, in phase with the large out-of-plane vibration of the O 8 atom. However, the results would also be consistent with a 0.09 Å displacement of the pseudo-symmetric molecules relative to one another, as shown in figure 4. This, together with the fact that C 10 is aliphatic,

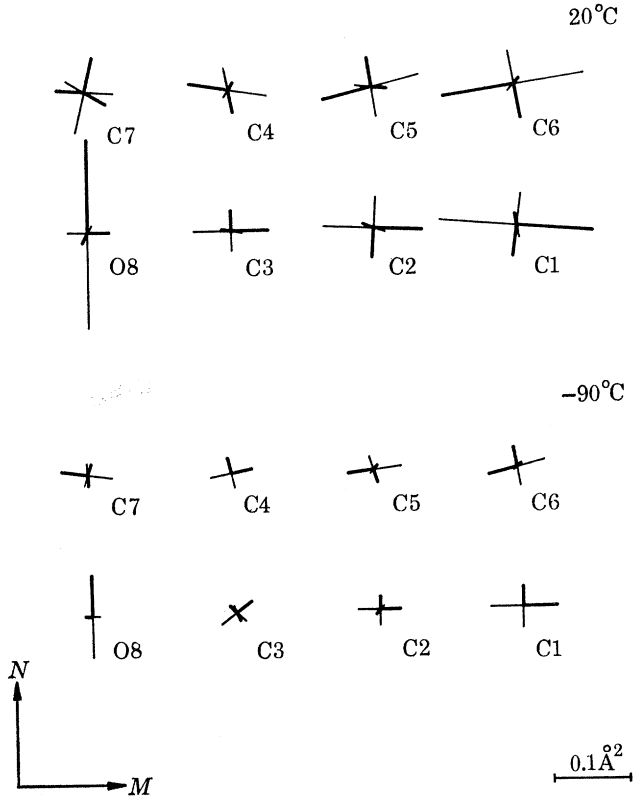

FIGURE 3. Projection along L showing the mean square displacements ($\langle u^2 \rangle$) in the directions of the principal axes of the thermal vibration ellipsoids for individual atoms, at 20 and −90° C.

TABLE 8. DIFFERENCES BETWEEN THE OBSERVED AND CALCULATED ATOMIC MEAN SQUARE AMPLITUDES FOR THE T, ω IN TABLE 7; ANTHRONE AT 20 °C; UNIT 10^{-2} Å²

		C 1	C 2	C 3	C 4
with oxygen	L	0.086	0.164	0.124	−0.233
	M	0.586	−0.082	0.247	0.266
	N	0.608	−1.283	0.146	0.646
without oxygen	L	0.036	0.160	0.074	−0.283
	M	0.593	−0.307	−0.126	−0.110
	N	0.336	−0.533	−0.451	0.053
		C 5	C 6	C 7	O 8
with oxygen	L	0.063	0.008	−0.004	−0.208
	M	−0.078	−0.093	0.757	−1.604
	N	−1.339	0.502	0.164	0.555
without oxygen	L	0.057	−0.043	0.000	−0.058
	M	−0.299	−0.082	0.330	−2.031
	N	−0.586	0.226	0.955	5.274

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would explain the short C7—O distance of 1.12 Å shown in table 4, which is to be compared with 1.24 Å in anthraquinone (Lonsdale, Milledge & El Sayed 1966) and in dianthronyl (Ehrenberg 1967) all uncorrected for thermal libration. Other differences in the anthrone, anthraquinone data shown in table 7 are consistent with the fact that intermolecular contacts in

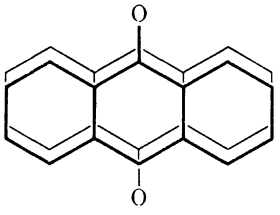

FIGURE 4. Possible displacement of the pseudosymmetric anthrone molecules relative to each other.

the [010] direction are consistently longer for anthrone than for anthraquinone, presumably because of the out-of-plane hydrogen atoms. (See Flack (1968) for a complete discussion of the analysis.)

THERMAL EXPANSION

Measurement of the variation of angle θ ($> 20°$) values for as many planes as possible were made from doubly-exposed Weissenberg photographs taken at 20 and -130 °C, a small shift of film position relative to the rotating crystal being made between the two temperatures.

Figures 5 (*a*) to (*c*) show the sections of the thermal-expansion figures corresponding to the three zones $\{h0l\}$, $\{hk0\}$ and $\{0kl\}$. Values of the observed $\alpha(hkl)$ were obtained from

$$\alpha(hkl) = \frac{1}{t_1 - t_2}\frac{\Delta d}{d}(hkl)$$

for the temperature range $t_1 - t_2$, $d(hkl)$ being the interplanar spacing at temperature $t_2 (< t_1)$, and

$$\frac{\Delta d}{d} = \frac{\operatorname{cosec}(\theta - \Delta\theta)}{\operatorname{cosec}\theta} - 1 = \frac{\sin\theta}{\sin(\theta - \Delta\theta)} - 1.$$

Rough values of α_1, α_2, α_3, the principal thermal-expansion coefficients (α_2 being along [010]) and of ϕ, the angle between [100] and the direction of α_1, positive in obtuse β, could be obtained from the sections (figure 5) and these were refined by a standard least-squares iterative procedure.

The final values are given in table 9. A comparison with anthraquinone is not possible because of the different temperature ranges used. The general explanations put forward by El Sayed (1965) and by Lonsdale *et al.* (1966) to account for the anisotropy of anthraquinone in terms of molecular reorientations, thermal-vibration amplitudes and types of intermolecular contacts apply also in the case of anthrone. In short, the large thermal expansion along [010] is due mainly to the large out-of-plane vibration of the oxygen atom, while the expansion properties in (010) are due mainly to the reorientations of intermolecular contacts.

TABLE 9. THERMAL-EXPANSION COEFFICIENTS FOR ANTHRONE/K^{-1}

	$10^6\alpha_1$	$10^6\alpha_2$	$10^6\alpha_3$	ϕ	temp. range
anthrone	95·3	162·6	−38·6	−1·50°	20 to −130°C

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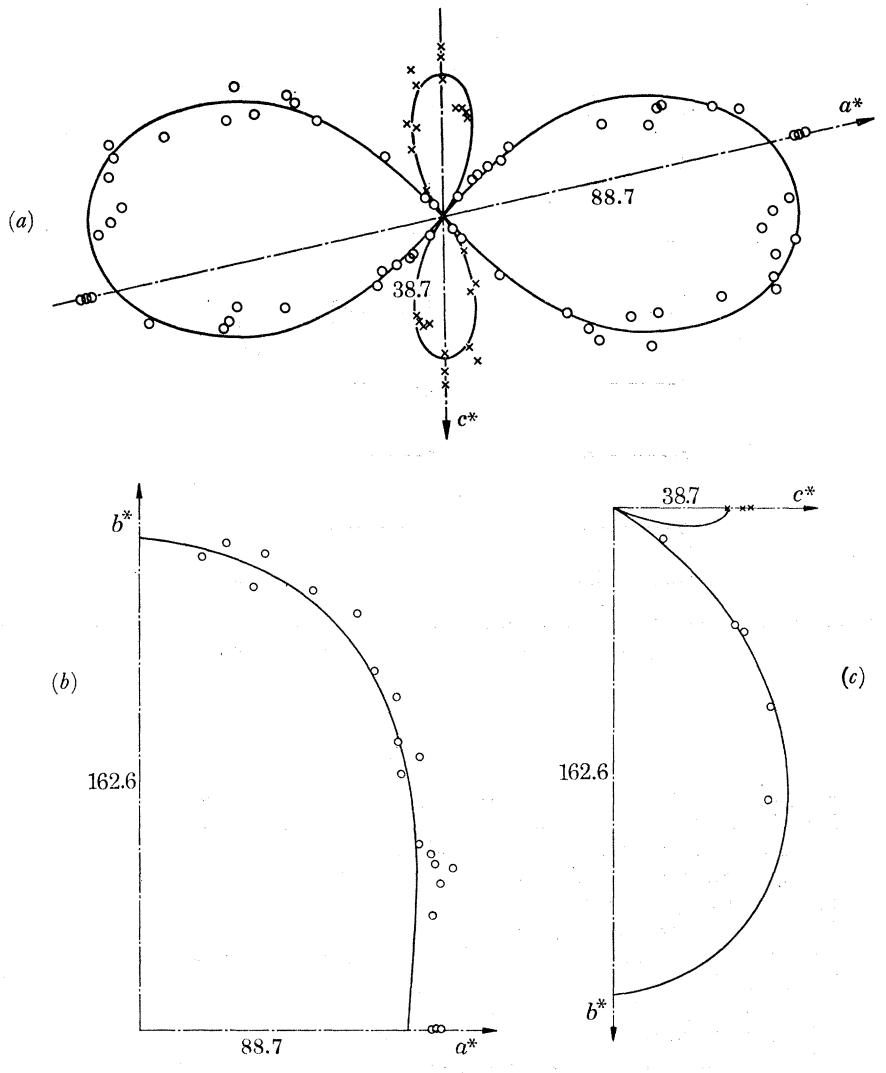

FIGURE 5. (*a*) Thermal expansion coefficients normal to the {*h*0*l*} planes (20 to −130 °C). (*b*) Thermal expansion coefficients normal to the {*hk*0} planes (20 to −130 °C). (*c*) Thermal expansion coefficients normal to the {0*kl*} planes (20 to −130 °C). The units on all three figures are in 10^{-6} °C^{-1}.

The converse is also true: the very large thermal expansion along [010] in anthrone confirms the existence of an out-of-plane libration of the oxygen atom which is found to be larger for anthrone than for anthraquinone, at least at the higher temperature. Figure 6 shows why such a difference might exist, on the hypothesis (confirmed by the short-range order shown later to occur) that there is a partial alternation of orientation of the asymmetric anthrone molecules, and that the stabilizing effect of H 13 and H 14 is not sufficient to inhibit the out-of-plane oxygen libration.

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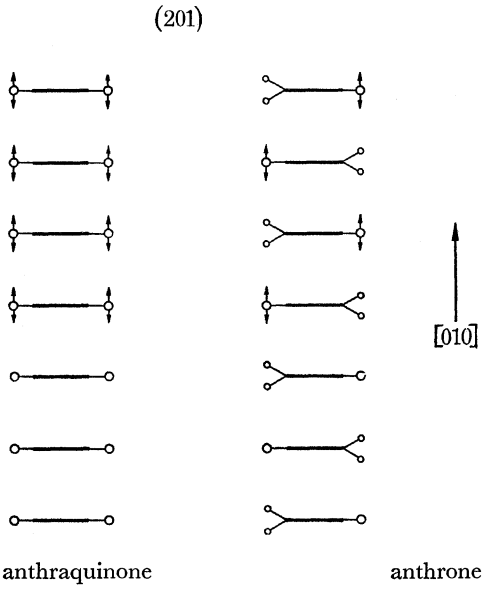

FIGURE 6. Diagrammatic representation of the anthraquinone and anthrone molecules showing the out-of-plane oxygen movements, as seen in a (201) section.

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