Temperature Dependence of the Rigid-Body Motion of Anthraquinone

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Abstract

Anthraquinone has been studied at five temperatures between 296 and 162 K. The unsatisfactory agreement factors obtained in earlier studies probably resulted from the use of data collected from twinned crystals; needle-like crystals with approximately equidimensional cross sections are usually contact twins related by reflection across $(10\bar{2})$. The temperature dependence of the **T** and **L** tensors is normal. The out-of-plane displacement parameters of the O atom indicate a large-amplitude internal vibration.

1. Introduction

The crystal structure of anthraquinone ($C_{14}H_8O_2$, 9,10-anthraquinone or 9,10-anthracenedione; see Fig. 1) has been studied by Banerjee & Sengupta (1940), Sen (1948), Murty (1955, 1960), Lonsdale, Milledge & El Sayed (1966), Prakash (1967) and Lenstra & Van Loock (1984). The best agreement factors R for anisotropic refinement at room temperature are 0.120 for photographic data (Lonsdale, Milledge & El Sayed, 1966; hereafter LME), and 0.106 for diffractometer data (Lenstra & Van Loock, 1984; hereafter LV). The effects of extinction, Renninger reflections and variable spot shapes were all invoked to explain the high agreement factors, which all authors considered to be unsatisfactory.

Rigid-body thermal-motion analyses (Cruickshank, 1956) were performed by Lonsdale, Walley & El Sayed (1966; hereafter LWE), using anisotropic displacement parameters measured at five temperatures by LME.
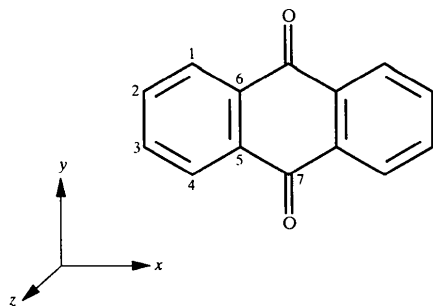

Fig. 1. Diagram of anthraquinone showing atom numbering and the location of the inertial axes.

The mean-square amplitude L^{11}_{inertial} determined from the displacement parameters of all the C and O atoms is 29 deg^2 at 294 K, but the L^{11}_{inertial} is only 10 deg^2 if the U^{ij} values of the O atom are not included in the analysis. If the LME/LWE analysis is accurate, then the O atoms must have a large intramolecular out-of-plane vibration. On the other hand, the temperature variations of the T^{33}_{inertial} and L^{11}_{inertial} values determined by LWE (see Fig. 2) are so abnormal that the reliability of the U^{ij} values is in doubt.

We reinvestigated anthraquinone to determine whether data collected with a modern diffractometer would yield a thermal-motion description that changed with temperature in the expected way (see *e.g.* Brock &
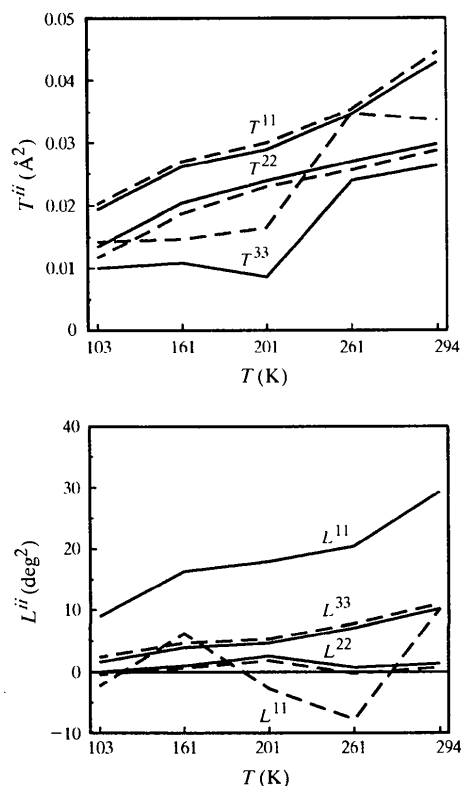

Fig. 2. Temperature dependence of the diagonal components of L_{inertial} and T_{inertial} determined by Lonsdale, Walley & El Sayed (1966). Results from the analyses that included all atoms (solid lines) and that included C atoms only (dashed lines), are both shown.

Table 1. *Experimental details*

	296 K	260 K	230 K	197 K	162 K
Crystal data					
Chemical formula	$C_{14}H_8O_2$	$C_{14}H_8O_2$	$C_{14}H_8O_2$	$C_{14}H_8O_2$	$C_{14}H_8O_2$
Chemical formula weight	208.22	208.22	208.22	208.22	208.22
Cell setting	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	7.8684 (5)	7.8642 (6)	7.8616 (7)	7.8621 (9)	7.8674 (10)
b (Å)	3.9634 (3)	3.9446 (5)	3.9280 (6)	3.9121 (7)	3.8948 (8)
c (Å)	15.7839 (13)	15.748 (2)	15.713 (3)	15.679 (4)	15.651 (4)
β (°)	102.687 (6)	102.662 (9)	102.616 (13)	102.591 (15)	102.548 (18)
V (Å^3)	480.21 (7)	476.63 (9)	473.51 (13)	470.63 (15)	468.13 (17)
Z	2	2	2	2	2
D_x (Mg m^{-3})	1.440	1.451	1.460	1.469	1.477
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	22	22	22	22	22
θ range (°)	10.3–13.0	10.4–13.1	10.4–13.1	10.4–13.1	10.6–13.2
μ (mm^{-1})	0.09	0.09	0.09	0.09	0.09
Temperature (K)	296 (1)	260 (1)	230 (1)	197 (1)	162 (1)
Crystal size (mm)	0.55 × 0.52 × 0.18	0.55 × 0.52 × 0.18	0.55 × 0.52 × 0.18	0.55 × 0.52 × 0.18	0.55 × 0.52 × 0.18
Crystal color	Yellow	Yellow	Yellow	Yellow	Yellow
Data collection					
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	None	None	None	None	None
No. of measured reflections	1096	1089	1077	1076	1061
No. of independent reflections	1096	1089	1077	1076	1061
No. of observed reflections	749	799	809	818	841
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
θ_{max} (°)	27.43	27.45	27.46	27.48	27.43
Range of h, k, l	$0 \rightarrow h \rightarrow 10$ $0 \rightarrow k \rightarrow 5$ $-20 \rightarrow l \rightarrow 19$	$0 \rightarrow h \rightarrow 10$ $0 \rightarrow k \rightarrow 5$ $-20 \rightarrow l \rightarrow 19$	$0 \rightarrow h \rightarrow 10$ $0 \rightarrow k \rightarrow 5$ $-20 \rightarrow l \rightarrow 19$	$0 \rightarrow h \rightarrow 10$ $0 \rightarrow k \rightarrow 5$ $-20 \rightarrow l \rightarrow 19$	$0 \rightarrow h \rightarrow 10$ $0 \rightarrow k \rightarrow 5$ $-20 \rightarrow l \rightarrow 19$
No. of standard reflections	3	3	3	3	3
Frequency of standard reflections (min)	120	120	120	120	120
Intensity decay (%)	−0.7	None	−0.1	−1.8	−1.1
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.038	0.042	0.051	0.047	0.055
$wR(F^2)$	0.104	0.117	0.138	0.132	0.147
S	1.14	1.07	1.10	1.08	1.10
No. of reflections used in refinement	1096	1088	1074	1076	1060
No. of parameters used	90	90	89	89	89
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0600P)^2 + 0.0800P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0850P)^2 + 0.0650P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 0.1000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 0.1000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1200P)^2 + 0.0700P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	−0.001	0.001	−0.03	−0.001	−0.001
$\Delta\rho_{max}$ (e Å^{-3})	0.19	0.19	0.24	0.27	0.33

Table 1 (cont.)

	296 K	260 K	230 K	197 K	162 K
$\Delta\rho_{min}$ (e Å^{-3})	−0.13	−0.22	−0.26	−0.26	−0.33
Extinction method	SHELXL93 (Sheldrick, 1993)	SHELXL93 (Sheldrick, 1993)	None	None	None
Extinction coefficient	0.101 (15)	0.043 (15)	−	−	−
Source of atomic scattering factors	International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs					
Data collection	CAD-4 (Enraf–Nonius, 1988)	CAD-4 (Enraf–Nonius, 1988)	CAD-4 (Enraf–Nonius, 1988)	CAD-4 (Enraf–Nonius, 1988)	CAD-4 (Enraf–Nonius, 1988)
Cell refinement	CAD-4 (Enraf–Nonius, 1988)	CAD-4 (Enraf–Nonius, 1988)	CAD-4 (Enraf–Nonius, 1988)	CAD-4 (Enraf–Nonius, 1988)	CAD-4 (Enraf–Nonius, 1988)
Structure refinement	SHELXL93 (Sheldrick, 1993)	SHELXL93 (Sheldrick, 1993)	SHELXL93 (Sheldrick, 1993)	SHELXL93 (Sheldrick, 1993)	SHELXL93 (Sheldrick, 1993)

Dunitz, 1982, 1990; Brock *et al.*, 1991 for analogous studies of naphthalene and anthracene). We also hoped to discover why previous studies were somewhat unsatisfactory.

2. Experimental

Crystals of anthraquinone (Eastman Kodak) were grown by very slow evaporation of solutions in benzene, toluene and methyl ethyl ketone (*i.e.* 2-butanone; hereafter, MEK). About half of the crystals mounted on the diffractometer showed the same monoclinic unit cell reported previously. The others appeared to be orthorhombic, but several 'orthorhombic' crystals examined proved to be twins composed of two mono-clinic individuals. The best crystals were grown from MEK. Crystals grown from benzene (the solvent used by LME) and toluene were found to have mosaic spreads about twice as large as those of crystals grown from MEK.

The heat capacity of the crystals grown from benzene was measured with a Perkin–Elmer DSC-7 from 108 to 308 K.† The temperature dependence of C_p is normal. No phase transition was observed.

Details of the data collections are given in Table 1. During data collection the temperature was monitored using a thermocouple inside the low-temperature device. The temperature rise between that thermo-couple and the crystal was measured later with a second thermocouple wound from *ca.* 10 cm of very fine copper-constantan wire into a 2.5 mm diameter coil which was placed at the position of the crystal. The second thermocouple was calibrated with a series of slush baths (Rondeau, 1966).

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* $(\overset{\circ}{A}{}^2)$ *at 162 K*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O	−0.20894 (15)	0.0239 (4)	0.11487 (7)	0.0358 (4)
C1	0.3427 (2)	0.2714 (4)	0.04877 (10)	0.0242 (4)
C2	0.4032 (2)	0.4165 (5)	0.13054 (10)	0.0273 (4)
C3	0.2955 (2)	0.4302 (5)	0.19011 (10)	0.0280 (4)
C4	0.1281 (2)	0.2993 (4)	0.16787 (9)	0.0247 (4)
C5	0.0655 (2)	0.1544 (4)	0.08558 (9)	0.0202 (4)
C6	0.1745 (2)	0.1408 (4)	0.02541 (9)	0.0204 (4)
C7	−0.1141 (2)	0.0138 (4)	0.06272 (9)	0.0222 (4)
H1	0.419 (3)	0.256 (5)	0.0070 (13)	0.031 (5)
H2	0.520 (3)	0.512 (5)	0.1461 (14)	0.032 (5)
H3	0.332 (3)	0.529 (6)	0.2450 (17)	0.047 (6)
H4	0.050 (3)	0.313 (6)	0.2109 (15)	0.038 (5)

The atomic positions and isotropic displacement parameters of LV's study were used as starting para-meters for the least-squares refinement. The structure was refined with the program *SHELXL*93 (Sheldrick, 1993). Atomic coordinates and displacement para-meters at 162 (1) K are listed in Tables 2 and 3; bond lengths and angles at this temperature are given in Table 4. Ellipsoid plots are shown in Fig. 3.

3. Twinning

Lath-shaped anthraquinone crystals (see Fig. 4), which are substantially wider than they are thick, are usually single. The longest dimension parallels **b**. Crystal faces {001} (largest), {100} and {111} are nearly always present, {10$\bar{2}$} faces are often present and {011} faces are occasionally developed. These are the same faces that Sen (1948) identified.

Approximately equidimensional anthraquinone crystals grown from MEK, benzene and toluene are usually twinned. Re-entrant angles involving {*h*0*l*} faces are sometimes obvious, but often are not. Careful

Table 3. *Anisotropic displacement parameters for the atoms of anthraquinone at 162 K*

The form of the anisotropic displacement expression is: $\exp[-2\pi^2(U^{11}h^2a^{*2} + U^{22}k^2b^{*2} + U^{33}l^2c^{*2} + 2U^{12}hka^*b^* + 2U^{13}hla^*c^* + 2U^{23}klb^*c^*)]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O	0.0274 (7)	0.0617 (10)	0.0222 (6)	−0.0083 (5)	0.0138 (5)	−0.0065 (5)
C1	0.0201 (7)	0.0297 (9)	0.0230 (7)	0.0030 (6)	0.0047 (5)	0.0008 (6)
C2	0.0221 (8)	0.0308 (9)	0.0261 (8)	0.0025 (6)	−0.0016 (6)	−0.0025 (6)
C3	0.0319 (8)	0.0317 (9)	0.0173 (7)	0.0005 (6)	−0.0019 (6)	−0.0013 (6)
C4	0.0290 (8)	0.0301 (9)	0.0147 (7)	0.0005 (6)	0.0042 (5)	0.0003 (6)
C5	0.0205 (7)	0.0255 (8)	0.0144 (7)	0.0024 (6)	0.0032 (5)	0.0017 (5)
C6	0.0194 (7)	0.0262 (9)	0.0157 (7)	0.0034 (5)	0.0042 (5)	0.0022 (5)
C7	0.0211 (7)	0.0307 (9)	0.0158 (7)	0.0025 (6)	0.0064 (5)	0.0015 (6)

Table 4. *Bond lengths (Å) and and angles (°) for anthraquinone at 162 K*

Distances corrected for the effects of thermal motion using the model determined using all atoms and then for the model determined by the C atoms only.

	Uncorrected distance	Corrected distances	
O−C7	1.221 (2)	1.225	1.223
C1−C2	1.385 (2)	1.388	1.387
C1−C6	1.390 (2)	1.392	1.392
C2−C3	1.391 (2)	1.396	1.394
C3−C4	1.384 (2)	1.386	1.386
C4−C5	1.394 (2)	1.397	1.396
C5−C6	1.406 (2)	1.411	1.408
C5−C7	1.485 (2)	1.487	1.486
C6−C7	1.485 (2)	1.488	1.487
C1−H1	0.98 (2)		
C2−H2	0.97 (2)		
C3−H3	0.93 (3)		
C4−H4	1.01 (2)		
O−C7−C5	121.00 (14)	O−C7−C6^i	121.01 (13)
C6−C1−C2	120.60 (14)	C6−C5−C7	120.77 (13)
C1−C2−C3	119.82 (14)	C1−C6−C5	119.61 (14)
C2−C3−C4	120.17 (15)	C1−C6−C7^i	119.15 (13)
C3−C4−C5	120.47 (15)	C5−C6−C7^i	121.23 (13)
C4−C5−C6	119.32 (14)	C5−C7−C6^i	118.00 (12)
C4−C5−C7	119.90 (13)	C2−C1−H1	120.2 (12)
C2−C3−H3	121.6 (14)	C6−C1−H1	119.2 (12)
C4−C3−H3	118.2 (14)	C1−C2−H2	120.4 (13)
C3−C4−H4	119.9 (12)	C3−C2−H2	119.8 (13)
C5−C4−H4	119.7 (12)		

Symmetry code: (i) $-x, -y, -z$.

examination of the small faces at the ends of the crystal may reveal interfacial angles, both re-entrant and not, of ca. 16° between {111} faces of two individuals (see Fig. 4). The twin boundaries are not usually obvious when the crystals are viewed through a polarizing microscope, perhaps because the **b** axes of the individuals are parallel and usually lie approximately perpendicular to the view direction.

Twinned crystals have cell dimensions $a \simeq c \simeq 15.76$, $b \simeq 3.96$ Å, $\alpha \simeq \gamma \simeq 90$ and $\beta \simeq 102.8°$, *i.e.* dimensions similar to those of the $P2_1/c$ structure, except for a doubled a axis. The reflection conditions (hkl, $h = 2n$ or $l = 2n$, $h0l$, $h = 2n$ and $l = 2n$, and $0k0$, $k = 2n$) do not

correspond to any monoclinic space group. This cell can be transformed $(0\bar{1}\bar{1}/01\bar{1}/100)$ into a C-centered orthorhombic unit cell ($Z = 8$) with dimensions $a \simeq 19.68$, $b \simeq 24.61$, $c \simeq 3.96$ Å, $\alpha \simeq 90.0$, $\beta \simeq 90.0$, $\gamma \simeq 90.0°$, but the resulting reflection conditions ($0kl$, $k = 4n$, $h0l$, $h = 2n$, and $hk0$, $h = 2n$, $h + k = 4n$) do not correspond to any orthorhombic space group.
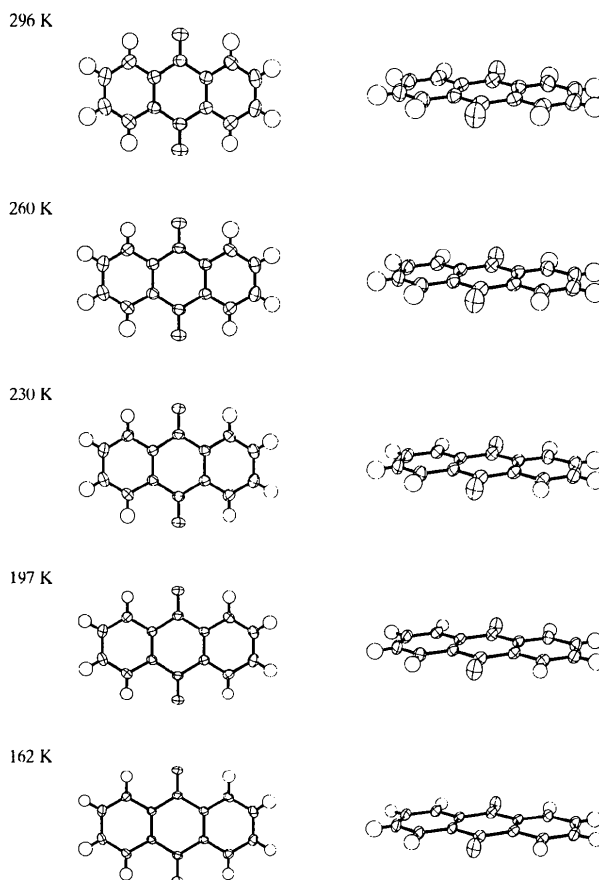

Fig. 3. Perspective drawings of anthraquinone at five temperatures. The ellipsoids correspond to 50% probability contours of atomic displacement. The orientation of the molecules on the left is the same as in Fig. 1; the molecules on the right have been rotated clockwise by 90° around the **x** inertial axis.

Since the **c** axis in the $P2_1/c$ cell is almost twice as long as the **a** axis, it seemed possible that these axes could be interchanged without disrupting crystal growth. Contact twinning resulting from reflection across the $(10\bar{2})$ plane leads to a switch of the **a** and **c** axes and explains the observed extinction conditions and crystal morphology (see Fig. 4). Sen (1948) and Murty (1955, 1960) both reported having observed weak $h0l$, $h = 2n + 1$, reflections which should be absent because of the glide plane. (Early authors used the setting $P2_1/a$ rather than $P2_1/c$.) Murty (1955) pointed out that these 'forbidden' reflections are 'sharper than normal reflections'. His observation is consistent with a twin model in which two individuals contribute to many of the 'allowed' reflections, which are therefore widened slightly.

To test the twin hypothesis data $(h, k, l$ all > 0; $\theta_{max} = 27.5°$ for Mo $K\alpha$ radiation) originally collected at 293 (2) K from an 'orthorhombic' crystal [$a = 19.678$ (2), $b = 24.613$ (8), $c = 3.963$ (1) Å, $\alpha = 89.99$ (2), $\beta = 90.03$ (1), $\gamma = 89.96$ (2)°] were transformed $\frac{1}{2}\frac{1}{2}$ 0/0 0 $1/\frac{1}{2}$ $-\frac{1}{2}$ 0) to a monoclinic cell ($a = 15.761$, $b = 3.963$, $c = 15.751$ Å, $\beta = 102.72°$) and then refined using a twin model (Sheldrick, 1993). Coordinates and U^{ij} values were taken from the 296 K determination and were held fixed; an overall scale factor and a volume fraction for one of the individuals [final value 0.576 (4)] were varied. The agreement factors R_1 and wR_2 were 0.054 ($I > 2\sigma I$) and 0.160 (all data) for 815 observations (of which 530 have $I > 2\sigma I$) and only two variables. Of the 815 observations (about half of the unique data), 318 corresponded to one individual, 312 corresponded to the other and 348 included contributions from both individuals.

The two individuals of the twin are related by the mirror plane $(10\bar{2})$, which includes the single crystal vectors **b** and 2**a** + **c**. The structure of the single crystal can be thought of as composed of layers (see darkened atoms in Figs. 5 and 6), which include the directions

Fig. 5. Projection of the anthraquinone structure viewed along the **b** axis. The atoms in a layer (see text) have been darkened.
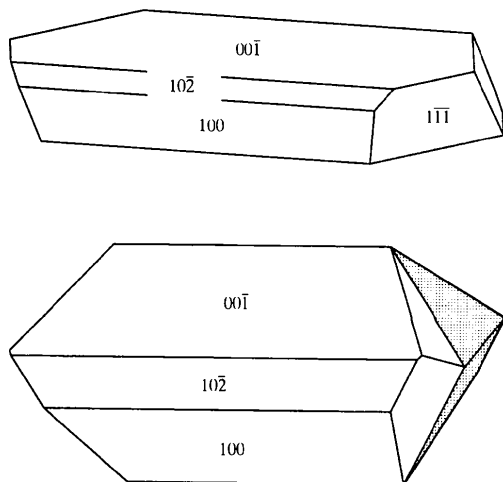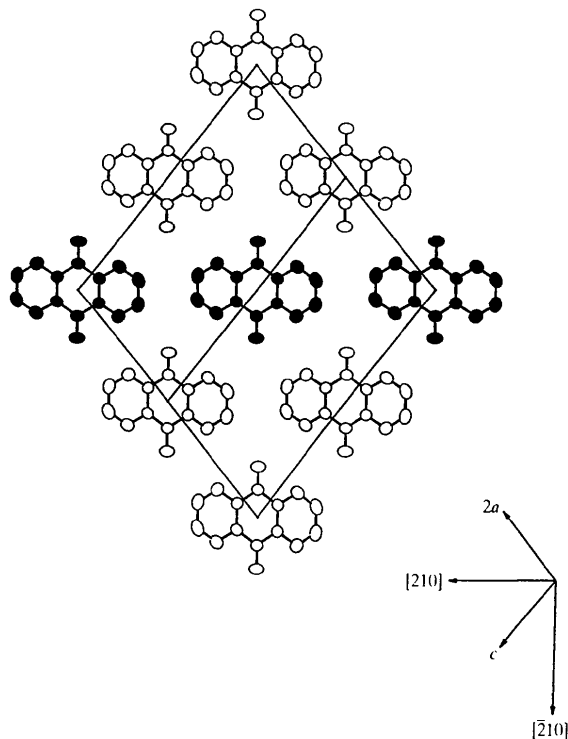

Fig. 4. Drawings of typical single (above) and twinned (below) anthraquinone crystals grown by evaporation of solutions in methyl ethyl ketone. The faces of the second individual (lower drawing) are stippled. The angle between the upper pair of end faces is re-entrant.
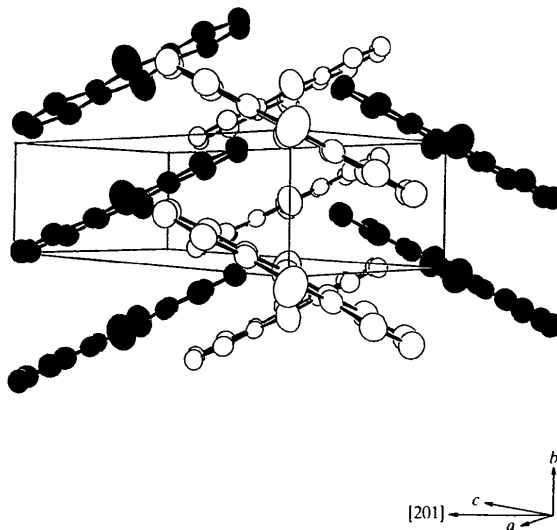

Fig. 6. Drawing of molecules from three of the layers (see text); the atoms of the middle layer have been darkened. This figure is related to Fig. 5 by a 90° rotation around [201].

Table 5. *Models for the thermal motion of anthraquinone at 296 K (inertial coodinate system; see Fig. 1)*

$\langle\sigma^2(U^{ij})\rangle^{1/2}$ (Å²)			0.0008	
$\langle\Delta^2(A,B)\rangle^{1/2}$ (Å²)	Bonded pairs (9)		0.0015	
	All pairs (56)		0.0021	
			C1—C7 and O	C1—C7 only
wR†			0.060	0.041
$\langle\Delta U^2\rangle^{1/2}$ (Å²)			0.0019	0.0012
GOF‡			3.0	2.0
T (Å²):	T^{11}		0.0440 (14)	0.0440 (9)
	T^{22}		0.0331 (18)	0.0331 (12)
	T^{33}		0.0252 (28)	0.0315 (22)
	T^{12}		0.0008 (14)	0.0008 (8)
	T^{13}		0.0037 (16)	0.0037 (9)
	T^{23}		−0.0013 (18)	−0.0015 (12)
L (deg²):	L^{11}		40 (2)	21 (4)
	L^{22}		4.4 (10)	4.1 (6)
	L^{33}		9.7 (7)	9.7 (5)
	L^{12}		0.3 (10)	0.4 (6)
	L^{13}		0.6 (15)	1.9 (11)
	L^{23}		0.8 (8)	0.8 (5)

† $wR = [\Sigma w(U_o^{ij} - U_c^{ij})^2/\Sigma w U_o^{ij2}]^{1/2}$, where $w = \langle\sigma(U^{ij})\rangle^{-2}$.   ‡ $GOF = \Sigma[(U_o^{ij} - U_c^{ij})/\sigma(U_o^{ij})]^{1/2}/(N_o - N_v)^{1/2}$, where $N_o - N_v = (6)(8) - 12 = 36$ or $N_o - N_v = (6)(7) - 12 = 30$.

Table 6. *Models for the thermal motion of anthraquinone at 162 K (inertial coodinate system; see Fig. 1)*

$\langle\sigma^2(U^{ij})\rangle^{1/2}$ (Å²)			0.0007	
$\langle\Delta^2(A,B)\rangle^{1/2}$ (Å²)	Bonded pairs (9)		0.0008	
	All pairs (56)		0.0012	
			C1—C7 and O	C1—C7 only
wR†			0.074	0.047
$\langle\Delta U^2\rangle^{1/2}$ (Å²)			0.0011	0.0007
GOF‡			2.0	1.2
T (Å²):	T^{11}		0.0211 (8)	0.0213 (4)
	T^{22}		0.0146 (10)	0.0147 (6)
	T^{33}		0.0152 (17)	0.0197 (11)
	T^{12}		0.0018 (8)	0.0017 (4)
	T^{13}		0.0052 (9)	0.0052 (5)
	T^{23}		−0.0018 (11)	−0.0020 (6)
L (deg²):	L^{11}		20.5 (14)	8.1 (21)
	L^{22}		2.1 (6)	1.8 (3)
	L^{33}		4.4 (4)	4.4 (3)
	L^{12}		0.3 (6)	0.3 (3)
	L^{13}		0.3 (8)	1.2 (6)
	L^{23}		0.5 (5)	0.4 (3)

† $wR = [\Sigma w(U_o^{ij} - U_c^{ij2})/\Sigma w U_o^{ij2}]^{1/2}$, where $w = \langle\sigma(U^{ij})\rangle^{-2}$.   ‡ $GOF = \{\Sigma[(U_o^{ij} - U_c^{ij})/\sigma(U_o^{ij})]\}^{1/2}/(N_o - N_v)^{1/2}$, where $N_o - N_v = (6)(8) - 12 = 36$ or $N_o - N_v = (6)(7) - 12 = 30$.

[010] (*i.e.* **b**) and [201] (*i.e.* 2**a** + **c**) and are almost perpendicular [89.3 (1)°] to [$\bar{2}$01] (*i.e.* −2**a** + **c**). Each layer is composed of molecular stacks which parallel **b**, the direction that grows most rapidly. The layers have approximate mirror symmetry and can be thought of as being stacked in the [$\bar{2}$01] direction. The angle between the intramolecular O−O′ vector and [$\bar{2}$01] is 2.2 (1)°. The approximate mirror plane within a layer would interchange the **a** and **c** axes if it also related adjacent layers.

4. Analysis of atomic displacement parameters

The program *THMA*14 (Trueblood, 1978) was used for the rigid-body motion analysis. The screw rotation tensor S vanishes because the anthraquinone molecule is located on an inversion center (Schomaker & Trueblood, 1968). The values of $\Delta_{A,B}$ (Hirshfeld, 1976; see Tables 5 and 6) both for bonded pairs and for all pairs of atoms (Rosenfield *et al.*, 1978) are a little smaller than those found for anthracene (Brock & Dunitz, 1990).

The effects of internal motion were ignored. Calculations (Criado, 1989) suggest that the separation of internal and external modes is a valid approximation for naphthalene, and a reasonable approximation for anthracene. The U^{ij} values of both naphthalene and anthracene fit rigid-body models to within their e.s.d.'s whether or not corrections for internal motion are made (Brock & Dunitz, 1982, 1990) because the rigid-

body model can absorb a considerable amount of internal motion. In the absence of any reliable method of correcting for the internal motion, the C-atom skeleton, which is very similar to anthracene, has been assumed to be rigid and an analysis without the O atom, which is most affected by the internal motion, was made.

The results of the analyses are shown in Fig. 7; details of the analyses for the 296 and 162 K data are shown in Tables 5 and 6. Complete information for the analyses at the other three temperatures are given in the supplementary material.†

5. Discussion

The agreement factors in this study are substantially lower than those obtained previously. No anomaly was encountered. The change with temperature of the T^{ii} and L^{ii} values is normal. The bond lengths corrected for thermal motion (Table 4) are similar to those found in the gas-phase electron diffraction study [Ketkar *et al.*, 1981; $r(C{=}O) = 1.220$ (2), $r(C{-}C) = 1.400$ (2) Å within the benzene rings; $r(C{-}C) = 1.499$ (2) Å for the ketone bridge; $r(C{-}H) = 1.087$ (4) Å; $C{-}C{-}C$ 117.4 (4)° for the ketone bridge].

It seems likely that many, if not most, of the previous studies used data collected from crystals that contained at least a small volume of a second individual. The 'forbidden' reflections observed by Sen (1948) and

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† See deposition footnote on p. 310.

Fig. 7. The temperature variation of the T^{ii} and L^{ii} values as calculated from the U^{ij} values for all atoms (T^{ii} and L^{ii}) and for the C atoms only (T_c^{ii} and L_c^{ii}). E.s.d.'s for the values at 296 and 162 K are shown in Tables 5 and 6; standard deviations at other temperatures can be estimated by interpolation.

Murty (1955) are consistent with the proposed twin model. In our experience an attempt to find crystals that are at least approximately equidimensional essentially guarantees the choice of a twinned crystal. The drawing given by Sen (1948) of a typical crystal grown from benzene shows a needle (rather than a lath) that has point-group symmetry 2 rather than 2/*m*; furthermore, the rotation axis is perpendicular, rather than parallel, to the unique monoclinic **b** axis. Lonsdale, Milledge & El Sayed (1966) pointed out that crystals grown from $CHCl_3$ were usually twinned, but might not have noticed that crystals grown from benzene are also twinned. Early authors had to use data sets (usually recorded on zero-level Weissenberg photographs) that were limited both in extent and intensity range. If the volume fraction of a second individual was quite low its presence could easily have been missed.

The near equality of 2*a* and *c* [ratio 1.003 (1)] caused some confusion about the space group; several early reports described the crystals as orthorhombic (Banerjee & Sengupta, 1940; Sen, 1948), a mistake that we repeated (see above). An accidental relationship between cell dimensions greatly increases the probability of twinning. If such a relationship is combined with unsatisfactory agreement factors, then twin models should probably be tried, especially if some classes of reflections are wider than others.†

The 'mistakes' that result in twinning (see Fig. 6) would seem to be more likely when the crystals are extremely small (*i.e.* just past the nucleation stage) and the long-range interactions not yet well established. If the growing crystal was lying on a surface so that growth in one direction was hindered, a twinned crystal composed of two individuals having quite different volumes might result. If two 'mistakes' were made then a twinned crystal might appear single. Either type of growth could explain the almost, but not quite, satisfactory agreement factors obtained by LME and LV.

Cooling generated substantial strain in the crystal, even though the temperature was lowered by increments of 3° at intervals of at least 30 min. Strain is apparent in the widths of the peaks used for determining cell constants. These widths increased by as much as 50% between 296 and 197 K, then dropped slightly at 162 K. When the crystal was removed from the diffractometer an internal plane that reflected light was obvious. A few months later the reflecting plane was no longer visible, but a very small wedge-shaped chip had fallen out of one of the corners of the crystal, leaving re-entrant angles.
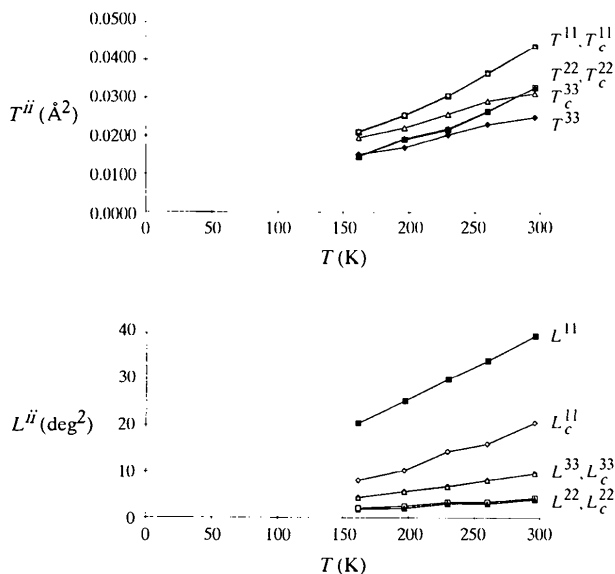
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† For one 'orthorhombic' crystal we investigated 11 reflections for which both *h* and *l* were even with peak widths in the range 0.54–1.05° [average 0.77 (5)°], while 13 reflections having either *h* or *l* odd had peak widths in the range 0.53–0.65° [average 0.57 (1)°]. The corresponding values for a second crystal were 0.54–0.99° [13 reflections; average 0.71 (4)°] and 0.43–0.70° [12 reflections; average 0.53°].

We find the out-of-plane amplitude of the O atom to be even larger than LME/LWE did. The O-atom U^{ij} values almost certainly indicate a low-frequency internal motion.† That possibility was discussed by Shmueli & Kroon (1974), who used semi-empirical nonbonded potential functions to calculate energy profiles for the librations about the inertial axes (14 deg^2 for the x axis) and to estimate the associated librational frequencies, which agreed well with those observed by Raman spectroscopy (Miyazaki & Ito, 1973). Shmueli & Kroon (1974) ascribed the discrepancy between the observed and calculated libration about the inertial x axis to neglect of the out-of-plane O-atom motion, which may be coupled to a 'butterfly' bending motion of the anthracene core.‡

Removing the O atoms from the TL analyses lowers $L^{11}_{inertial}$ substantially and raises $T^{33}_{inertial}$ (see Fig. 7). It is difficult to say which is the better model for the overall motion, but in any event the choice of model makes little difference to the bond-length corrections (see Table 4). The model determined by only the C atoms is consistent with the models determined for anthracene itself (Brock & Dunitz, 1990; Brock et al., 1991).

† Hummel et al. (1990) have shown that replacement of spherical atoms with multipoles in the refinement of boron nitrilotriacetate has little effect on the out-of-plane displacement parameters for the O atoms of the carbonyl groups.

‡ Capelli & Buergi (1997) have analyzed our results with their new algorithm that accounts explicitly for the temperature dependence of the ADP's. The program attempts to determine low-energy internal motions in addition to the usual overall translational and librational oscillations. Their preliminary analysis of the five sets of anthraquinone ADP's indicates a low-frequency (ca. 60 cm^{-1}) internal motion, in which a butterfly deformation of the C-atom skeleton is coupled to the out-of-plane bending of the O atoms.

References

Banerjee, K. & Sengupta, S. N. (1940). Z. Kristallogr. 102, 415–416.

Brock, C. P. & Dunitz, J. D. (1982). Acta Cryst. B38, 2218–2228.

Brock, C. P. & Dunitz, J. D. (1990). Acta Cryst. B46, 795–806.

Brock, C. P., Dunitz, J. D. & Hirshfeld, F. L. (1991). Acta Cryst. B47, 789–797.

Capelli, S. C. & Buergi, H. B. (1997). Unpublished results.

Criado, A. (1989). Acta Cryst. A45, 915–923.

Cruickshank, D. W. J. (1956). Acta Cryst. 9, 754–756.

Enraf-Nonius (1988). CAD-4 Manual. Version 5.0. Enraf-Nonius, Delft, The Netherlands.

Hirshfeld, F. L. (1976). Acta Cryst. A32, 239–244.

Hummel, W., Raselli, A. & Buergi, H.-B. (1990). Acta Cryst. B46, 683–692.

Ketkar, S. N., Kelley, M., Fink, M. & Ivey, R. C. (1981). Mol. Struct. 77, 127–138.

Lenstra, A. T. H. & Van Loock, J. F. J. (1984). Bull. Soc. Chim. Belg. 93, 1053–1055.

Lonsdale, K., Milledge, H. J. & El Sayed, K. (1966). Acta Cryst. 20, 1–13.

Lonsdale, K., Walley, D. & El Sayed, K. (1966). Acta Cryst. 20, 13–17.

Miyazaki, Y. & Ito, M. (1973). Bull. Chem. Soc. Jpn, 46, 103–106.

Murty, B. V. R. (1955). Acta Cryst. 8, 113–114.

Murty, B. V. R. (1960). Z. Kristallogr. 113, 445–465.

Prakash, A. (1967). Acta Cryst. 22, 439–440.

Rondeau, R. E. (1966). J. Chem. Eng. Data, 11, 124.

Rosenfield, R. E. Jr, Trueblood, K. N. & Dunitz, J. D. (1978). Acta Cryst. A34, 828–829.

Schomaker, V. & Trueblood, K. N. (1968). Acta Cryst. B24, 63–76.

Sen, S. N. (1948). Indian J. Phys. 22, 347–378.

Sheldrick, G. M. (1993). SHELXL93. Program for the Refinement of Crystal Structures. University of Göttingen, Germany.

Shmueli, U. & Kroon, P. A. (1974). Acta Cryst. A30, 768–771.

Trueblood, K. N. (1978). Acta Cryst. A34, 950–954.