

- GO, K. & KARTHA, G. (1981). *Cryst. Struct. Commun.* **10**, 1323–1327, 1329–1334.
- GO, K. & KARTHA, G. (1982). *Cryst. Struct. Commun.* **11**, 279–284, 285–290.
- GO, K. & KARTHA, G. (1983). *Acta Cryst.* **C39**, 376–378.
- GO, K. & KARTHA, G. (1984). *Acta Cryst.* **C40**, 1866–1869.
- GO, K., KARTHA, G. & CHEN, J. P. (1980). *Acta Cryst.* **B36**, 1811–1819.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- KARLE, I. L. & KARLE, J. (1969). *Acta Cryst.* **B29**, 428–442.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- NORDMAN, C. E. (1966). *Trans. Am. Crystallogr. Assoc.* **2**, 65–74.
- PRZYBYLSKA, M. & AHMED, F. R. (1979). *Acta Cryst.* **B35**, 2436–2440.
- ROHRER, D. C. & FULLERTON, D. S. (1980). *Acta Cryst.* **B36**, 1565–1568.
- ROHRER, D. C., FULLERTON, D. S., YOSHIOKA, K., FROM, A. H. L. & AHMED, K. (1979). *Computer Assisted Drug Design*, edited by E. C. OLSEN & R. E. CHRISTOFFERSEN, pp. 259–279. Washington, DC: American Chemical Society.
- ROHRER, D. C., KIHARA, M., DEFFO, T., RATHORE, H., AHMED, K., FROM, A. H. L. & FULLERTON, D. S. (1984). *J. Am. Chem. Soc.* **106**, 8269–8276.
- SATOH, D. & AOYAMA, K. (1970). *Chem. Pharm. Bull.* **18**(1), 94–99.
- Tripos Associates Inc. (1988). *SYBYL/MENDYL Molecular Modelling Software*. Tripos Associates Inc., St Louis, Missouri 63144, USA.
- YODA, A., YODA, S. & SARRIF, A. M. (1973). *Mol. Pharmacol.* **9**, 766–773.

Acta Cryst. (1989). **B45**, 312–323

Conformational Polymorphism of Dimethyl 3,6-Dichloro-2,5-dihydroxyterephthalate. I. Structures and Atomic Displacement Parameters between 100 and 350 K for Three Crystal Forms

BY QING-CHUAN YANG,* MARY FRANCES RICHARDSON† AND JACK D. DUNITZ

Organic Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland

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Abstract

Atomic coordinates and displacement parameters have been obtained for the previously described crystal structures [Byrn, Curtin & Paul (1972). *J. Am. Chem. Soc.* **94**, 890–898] of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate at 105, 180, 230, 296 and 353 K for the yellow form [Y-(I)], and at 98, 296 and 353 K for the white form [W-(I)]. Crystals of Y-(I) deuterated at the hydroxyl groups have been studied at 230 and 289 K. We have also determined the structure at 97, 179, 226, 296 and 343 K of a third, light-yellow [LY-(I)] crystal form that seems to have escaped detection up till now. The molecules have different conformations in the three polymorphic forms: the twist angle of the ester grouping with respect to the mean plane of the benzene ring is about 5° in Y-(I), about 40° in LY-(I), and about 85° and 70° for the two symmetry-independent molecules in W-(I). These differences are associated with different hydrogen-bonding patterns. Analysis of the anisotropic displacement

parameters shows that the molecules do not behave as rigid bodies in the crystals. The ester groups have an additional librational motion with respect to the rest of the molecule. The temperature dependence of $\langle \omega^2 \rangle$, the mean-square amplitude of this libration, is much larger for Y-(I) than for the other two forms. The results are discussed in terms of a mean-field potential model. Crystal data at 296 K [$C_{10}H_8Cl_2O_6$, $M_r = 295.1$, $\lambda(\text{Mo K}\alpha) = 0.7107 \text{ \AA}$]: Y-(I) form, $a = 9.582$ (2), $b = 4.292$ (1), $c = 7.950$ (2) \AA , $\alpha = 114.23$ (2), $\beta = 94.93$ (2), $\gamma = 106.22^\circ$, $V = 278.67 \text{ \AA}^3$, $R = 0.028$ for 940 observed reflections; W-(I) form, $a = 9.843$ (1), $b = 7.847$ (2), $c = 10.573$ (2) \AA , $\alpha = 116.40$ (2), $\beta = 124.18$ (1), $\gamma = 88.96$ (2)°, $V = 574.76 \text{ \AA}^3$, $R = 0.026$ for 1832 observed reflections; LY-(I) form, $a = 3.8980$ (4), $b = 8.034$ (2), $c = 9.491$ (2) \AA , $\alpha = 70.42$ (2), $\beta = 89.09$ (1), $\gamma = 86.68^\circ$, $V = 279.57 \text{ \AA}^3$, $R = 0.026$ for 1039 observed reflections.

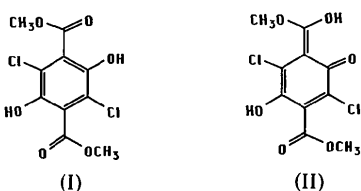
Introduction

The work to be described here and in a forthcoming paper (Richardson, Yang, Bregger & Dunitz, 1989) is a contribution towards the solution of a problem that is more than 100 years old, the problem of the colour

* On leave from Department of Chemistry, Peking University, Beijing, People's Republic of China.

† On leave from Department of Chemistry, Brock University, St Catharines, Ontario, Canada.

changes in solution and in the solid state of derivatives of 2,5-dihydroxyterephthalic acid. Briefly, this acid, its 3,6-dihalo derivatives, and their esters, frequently occur in yellow (or green) and white modifications and also yield solutions whose colour depends on the nature of the solvent. The most thorough studies have been made for dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate (I). Hantzsch (1915) reported that this compound exists in a yellow [Y-(I)] and a white [W-(I)] form, the former transforming to the latter on heating to about 410 K; both types of crystal gave identical solutions, colourless in methanol and yellow in chloroform. Hantzsch proposed that the two forms were tautomers, the white form being the dihydroxy isomer (I), the yellow form the quinonoid enol tautomer (II). From a careful study of the solvent dependence of the UV spectrum, Curtin & Byrn (1969*a,b*) interpreted the colour changes in terms of differences in hydrogen



bonding, rather than keto–enol isomerism; they proposed that the solutions consisted of an equilibrium mixture of three species, one (yellow) with intramolecular hydrogen bonds to the carbonyl O atoms, another (white) with the hydrogen bonds directed to the Cl atoms, and a third hybrid species with one hydrogen bond to a carbonyl group, the other to a Cl atom. Crystal structure analyses of Y-(I) and W-(I) by X-ray diffraction (Byrn, Curtin & Paul, 1972; BCP) then showed that the molecules in the two forms are actually conformational isomers of (I). In Y-(I) the molecules are almost coplanar (with intramolecular hydrogen bonds to carbonyl O atoms, as proposed from the spectral studies); in W-(I) the methoxycarbonyl groups are rotated nearly perpendicular to the plane of the other atoms (with hydrogen bonds to carbonyl O atoms of different molecules). BCP also made detailed observations (mainly by optical microscopy and differential scanning calorimetry) on the solid-state transformation of Y-(I) to W-(I).

In the course of a systematic study of anisotropic displacement parameters (ADP's) in polymorphic compounds, Venkatesan (1982) noted that the values published by BCP led to a large mean-square amplitude (*ca* 145 deg²) for the libration of the ester group about the exocyclic C–C bond in Y-(I), whereas the corresponding amplitudes for the two independent molecules in W-(I) were not significantly different from zero. Since the Y-(I)→W-(I) transformation is associated with a considerable change in the orientation of the ester groups, this observation led us to

wonder whether the large apparent internal motion of the ester group in Y-(I) at room temperature (the temperature of the BCP analysis) might be, so to say, a kind of harbinger of the transformation to W-(I) at around 410 K. Generally, one might ask about possible relationships between large-amplitude atomic motions in molecular crystals and phase transitions. One approach to this question would be to measure the ADP's as functions of temperature and look for relationships between these quantities (and quantities derived therefrom) and the onset of the phase transition. We therefore decided to redetermine the crystal structures of Y-(I) and W-(I) by X-ray diffraction over as wide a temperature range as possible, with particular emphasis on the measurement and interpretation of the ADP's. [For recent reviews of the potentialities and limitations of deriving information about atomic motions from ADP's see Dunitz, Schomaker & Trueblood (1988) and Dunitz, Maverick & Trueblood (1988).] During the course of this work, we have discovered a third crystal modification of (I) which has apparently been overlooked by all previous investigators; we call this the light-yellow form [LY-(I)] and have determined its structure at several temperatures along with those of the other two polymorphs.

In this paper we give results of the X-ray diffraction studies of Y-(I), LY-(I) and W-(I), with emphasis on the details of the molecular structures and the interpretation of the ADP's. In a following paper we shall discuss the relevance of these and other observations to structural, thermodynamic, kinetic and mechanistic aspects of the phase transformation. A preliminary report of this work has already appeared (Yang, Richardson & Dunitz, 1985).

Experimental

(I) was recrystallized from ethanol and from ether to obtain the Y-(I) and W-(I) polymorphs respectively, as described by BCP. However, we found that slow cooling from either solvent frequently yields a mixture of crystals of both polymorphs together with crystals of a third, pale-yellow polymorph which we designate as LY-(I). Crystals of each polymorph could easily be separated by hand according to colour and morphology. Since the LY-(I) form is obtained so easily under conditions used by earlier investigators, it seems very likely that they did actually obtain it but failed to distinguish it from the more deeply coloured Y-(I). [For example, the crystal of Y-(I) whose rearrangement to W-(I) is depicted in Fig. 2 of BCP looks suspiciously similar to crystals that we can identify unambiguously as LY-(I)]. Crystals with deuterated hydroxyl groups [DY-(I)] were obtained by crystallization from deuterioethanol/D₂O solution in a dry N₂ atmosphere, repeated until the NMR spectra of the redissolved crystals showed that exchange was complete.

Table 1. Summary of experimental data

(a) Y-(I)	353 K	296 K	230 K	180 K	105 K
Crystal dimensions (mm)	0.4 × 0.3 × 0.2	0.4 × 0.4 × 0.2	0.4 × 0.3 × 0.1	0.4 × 0.4 × 0.2	0.4 × 0.4 × 0.2
No. of reflections measured	1240	1224	1164	1192	1172
No. of observed reflections, $I \geq 3\sigma(I)$	1010	940	955	1021	1029
$P \ln w = (\sigma^2 + \rho F^2)^{-1}$	0.00040	0.00016	0.0010	0.00050	0.00040
Extinction coefficient x $F^* = F(1 - 10^{-4} x F^2 / \sin^2 \theta)$	0.024	0.0068	0.0059	0.0030	0.0023
$(\Delta/\sigma)_{\max}$	0.43	0.082	0.26	0.057	0.003
Highest peak on final difference map (e Å ⁻³)	0.3	0.2	0.3	0.3	0.4
Deepest trough on final difference map (e Å ⁻³)	0.3	0.2	0.2	0.2	0.5
R	0.036	0.028	0.027	0.025	0.029
wR	0.046	0.032	0.029	0.030	0.032
(b) LY-(I)					
	343 K	296 K	226 K	179 K	97 K
Crystal dimensions (mm)	0.4 × 0.3 × 0.2	0.3 × 0.3 × 0.2	0.3 × 0.3 × 0.2	0.3 × 0.3 × 0.2	0.3 × 0.3 × 0.2
No. of reflections measured	1220	1208	1192	1180	1172
No. of observed reflections, $I \geq 3\sigma(I)$	995	1039	1070	1074	1078
$P \ln w = (\sigma^2 + \rho F^2)^{-1}$	0.00040	0.00040	0.00040	0.0013	0.0032
Extinction coefficient x $F^* = F(1 - 10^{-4} x F^2 / \sin^2 \theta)$	0.051	0.046	0.040	0.040	0.046
$(\Delta/\sigma)_{\max}$	0.56	0.77	0.64	0.60	0.83
Highest peak on final difference map (e Å ⁻³)	0.3	0.3	0.4	0.4	0.5
Deepest trough on final difference map (e Å ⁻³)	0.3	0.2	0.2	0.2	0.3
R	0.030	0.026	0.025	0.024	0.033
wR	0.035	0.032	0.029	0.030	0.041
(c) W-(I) and DY-(I)					
	353 K	W-(I) 296 K	98 K	DY-(I) 289 K	230 K
Crystal dimensions (mm)	0.3 × 0.3 × 0.4	0.2 × 0.2 × 0.4	0.2 × 0.2 × 0.4	0.4 × 0.3 × 0.2	0.4 × 0.3 × 0.2
No. of reflections measured	2532	2516	2436	1221	1201
No. of observed reflections, $I \geq 3\sigma(I)$	1841	1832	2082	1046	1071
$P \ln w = (\sigma^2 + \rho F^2)^{-1}$	0.00025	0.00080	0.0027	0.00040	0.00016
Extinction coefficient x $F^* = F(1 - 10^{-4} x F^2 / \sin^2 \theta)$	0.016	0.017	0.016	0.0099	0.0089
$(\Delta/\sigma)_{\max}$	0.17	0.06	0.10	0.72	0.81
Highest peak on final difference map (e Å ⁻³)	0.3	0.3	0.4	0.3	0.3
Deepest trough on final difference map (e Å ⁻³)	0.2	0.2	0.6	0.3	0.2
R	0.029	0.026	0.029	0.031	0.027
wR	0.034	0.031	0.036	0.037	0.031

X-ray diffraction measurements were made with an Enraf–Nonius CAD-4 diffractometer (graphite monochromator, Mo $K\alpha$ radiation, $\lambda = 0.7107 \text{ \AA}$) equipped with a locally adapted Enraf–Nonius cooling device. Complete data sets were measured within a limiting radius of $\sin\theta/\lambda \approx 0.65 \text{ \AA}^{-1}$ for Y-(I) and LY-(I), each at five temperatures, for W-(I) at three temperatures as well as for DY-(I) at two temperatures; ω - θ scan, three standard reflections, no absorption correction. For each set of measurements the temperature was held constant within 1 K. Further experimental details are given in Table 1. Unit-cell dimensions, obtained in each case by a least-squares fit to setting angles of 25 automatically centred reflections in the range $6 < \theta < 12^\circ$, are listed in Table 2, together with the relevant temperatures.

Starting parameters for Y-(I) and W-(I) from BCP; structure of LY-(I) solved by direct methods. Full-matrix least-squares analysis with *SHELX76* (Sheldrick, 1976) on F values with weights initially assigned as $[\sigma^2(F) + 0.0003F^2]^{-1}$; anisotropic displacement parameters for C, Cl and O, isotropic for H atoms. Atomic scattering factors for C, Cl and O from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). Other experimental details are given in Table 1.

Results

Atomic coordinates and displacement parameters are listed in Table 3 for Y-(I) at five temperatures, in Table 4 for LY-(I) at five temperatures, in Table 5 for W-(I) at three temperatures, and in Table 6 for DY-(I) at two temperatures.* The atomic numbering is shown in Fig. 1.

* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51618 (127 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Unit-cell dimensions (Å, °) of W-(I), LY-(I), Y-(I) and deuterated Y-(I) at several temperatures with e.s.d.'s in parentheses

Compound	T (K)	a	b	c	α	β	γ	V (Å ³)
W-(I)	98	9.798 (2)	7.758 (3)	10.497 (3)	116.81 (3)	124.36 (2)	88.83 (2)	557.48
	296	9.843 (1)	7.847 (2)	10.573 (2)	116.40 (2)	124.18 (1)	88.96 (2)	574.76
	353	9.861 (4)	7.875 (3)	10.593 (3)	116.26 (3)	124.08 (3)	89.05 (3)	580.62
LY-(I)	97	3.812 (2)	8.037 (2)	9.363 (2)	70.83 (2)	89.23 (3)	87.22 (3)	270.63
	179	3.841 (1)	8.038 (1)	9.403 (1)	70.70 (1)	89.24 (2)	87.07 (2)	273.63
	226	3.862 (1)	8.037 (1)	9.432 (1)	70.61 (1)	89.21 (2)	86.94 (2)	275.76
	296	3.8980 (4)	8.034 (2)	9.491 (2)	70.42 (2)	89.09 (1)	86.68 (2)	279.57
	343	3.928 (2)	8.042 (3)	9.536 (2)	70.30 (3)	89.10 (4)	86.55 (4)	283.08
Y-(I)	105	9.497 (2)	4.248 (1)	7.740 (2)	112.85 (2)	95.58 (2)	106.23 (2)	268.70
	180	9.526 (2)	4.260 (1)	7.814 (2)	113.35 (2)	95.38 (2)	106.20 (1)	271.96
	230	9.535 (2)	4.2759 (4)	7.869 (1)	113.74 (1)	95.24 (1)	106.16 (1)	274.44
	296	9.582 (2)	4.292 (1)	7.950 (2)	114.23 (2)	94.93 (2)	106.22 (2)	278.67
	353	9.616 (2)	4.314 (1)	8.036 (2)	114.83 (2)	94.73 (2)	106.18 (2)	282.85
DY-(I)	230	9.540 (3)	4.270 (1)	7.861 (2)	113.71 (2)	95.19 (2)	106.15 (2)	274.06
	289	9.577 (2)	4.293 (1)	7.949 (1)	114.29 (1)	94.98 (1)	106.13 (2)	278.52

Table 3. Atomic coordinates ($\times 10^4$) and displacement parameters ($\text{\AA}^2 \times 10^4$) for Y-(I) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> or <i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
(a) 353 K									
C(1)	-836 (2)	1584 (5)	1272 (2)	334 (9)	364 (8)	323 (8)	146 (7)	113 (7)	127 (7)
C(2)	660 (2)	3564 (5)	1473 (2)	349 (9)	315 (7)	329 (8)	99 (7)	88 (7)	99 (6)
C(3)	1472 (2)	1965 (5)	217 (2)	297 (8)	366 (9)	353 (9)	93 (7)	100 (7)	132 (7)
C(7)	-1631 (2)	3477 (5)	2678 (3)	392 (10)	423 (9)	367 (9)	166 (8)	145 (7)	134 (8)
C(8)	-3761 (3)	3464 (8)	3873 (4)	472 (12)	684 (15)	647 (15)	232 (12)	307 (12)	125 (12)
O(1)	1385 (2)	6989 (4)	2830 (2)	422 (8)	367 (7)	452 (8)	79 (6)	141 (6)	17 (6)
O(2)	-1066 (2)	6628 (5)	3822 (3)	576 (11)	538 (9)	766 (13)	74 (8)	350 (10)	-139 (9)
O(3)	-2971 (2)	1577 (5)	2579 (3)	475 (9)	522 (8)	657 (10)	177 (7)	341 (8)	108 (7)
Cl	3297.6 (5)	4662 (1)	647.2 (8)	331 (4)	525 (4)	554 (4)	9 (2)	159 (2)	53 (3)
H(1)	723 (37)	7545 (88)	3425 (45)	629 (78)					
H(2)	-4704 (85)	1685 (177)	3750 (96)	1661 (232)					
H(3)	-3776 (62)	5471 (159)	3479 (80)	1424 (180)					
H(4)	-3291 (45)	4070 (114)	5231 (61)	939 (108)					
(b) 296 K									
C(1)	-841 (2)	1573 (4)	1273 (2)	260 (8)	287 (8)	259 (8)	116 (6)	87 (6)	105 (7)
C(2)	658 (2)	3556 (4)	1469 (2)	279 (8)	256 (7)	261 (8)	83 (6)	66 (6)	82 (6)
C(3)	1476 (2)	1966 (4)	214 (2)	219 (7)	296 (8)	296 (9)	76 (6)	80 (6)	124 (7)
C(7)	-1635 (2)	3466 (5)	2684 (3)	306 (9)	332 (8)	281 (8)	126 (7)	103 (7)	103 (7)
C(8)	-3775 (3)	3461 (7)	3877 (4)	372 (12)	542 (13)	530 (14)	193 (10)	255 (10)	92 (11)
O(1)	1382 (1)	6991 (3)	2827 (2)	328 (7)	286 (6)	362 (7)	56 (5)	105 (6)	11 (6)
O(2)	-1060 (2)	6614 (4)	3842 (2)	439 (9)	426 (8)	603 (10)	52 (7)	265 (8)	-101 (7)
O(3)	-2987 (2)	1551 (4)	2581 (2)	368 (8)	404 (7)	530 (9)	128 (6)	273 (7)	73 (6)
Cl	3303.8 (7)	4683 (2)	640.4 (9)	256 (3)	420 (3)	443 (3)	10 (2)	128 (2)	41 (2)
H(1)	694 (30)	7602 (69)	3447 (36)	519 (70)					
H(2)	-4827 (41)	1968 (91)	3491 (47)	947 (113)					
H(3)	-3763 (41)	5490 (106)	3684 (52)	1047 (126)					
H(4)	-3268 (40)	4179 (98)	5119 (58)	1026 (121)					
(c) 230 K									
C(1)	-849 (2)	1556 (4)	1279 (2)	194 (8)	217 (8)	199 (8)	87 (6)	71 (6)	93 (6)
C(2)	662 (2)	3555 (4)	1471 (2)	217 (8)	180 (7)	187 (8)	61 (6)	57 (6)	63 (6)
C(3)	1479 (2)	1980 (4)	210 (2)	168 (8)	220 (8)	224 (9)	64 (6)	64 (6)	96 (7)
C(7)	-1640 (2)	3452 (5)	2691 (3)	233 (8)	256 (8)	221 (9)	102 (6)	73 (7)	90 (7)
C(8)	-3793 (2)	3473 (6)	3874 (3)	262 (10)	400 (11)	352 (12)	146 (9)	162 (9)	51 (9)
O(1)	1384 (1)	6997 (3)	2827 (2)	233 (7)	202 (6)	271 (7)	39 (5)	82 (5)	16 (5)
O(2)	-1061 (2)	6603 (4)	3858 (2)	315 (8)	313 (7)	435 (9)	45 (6)	188 (7)	-63 (6)
O(3)	-3006 (1)	1523 (4)	2584 (2)	262 (7)	298 (6)	383 (8)	95 (5)	202 (6)	55 (6)
Cl	3310.7 (5)	4713 (1)	630.1 (7)	186 (2)	307 (2)	327 (3)	8 (2)	97 (2)	37 (2)
H(1)	724 (25)	7577 (56)	3431 (30)	295 (56)					
H(2)	-4806 (32)	1924 (73)	3462 (38)	632 (83)					
H(3)	-3782 (31)	5593 (80)	3679 (40)	701 (88)					
H(4)	-3306 (32)	4058 (74)	5102 (44)	672 (85)					
(d) 180 K									
C(1)	-849 (1)	1553 (4)	1285 (2)	160 (7)	183 (7)	161 (6)	75 (5)	55 (5)	80 (5)
C(2)	662 (2)	3553 (4)	1468 (2)	178 (6)	149 (6)	147 (6)	49 (5)	29 (5)	51 (5)
C(3)	1482 (2)	1990 (4)	208 (2)	126 (6)	188 (7)	181 (6)	39 (5)	45 (5)	85 (6)
C(7)	-1649 (2)	3430 (4)	2694 (2)	186 (7)	205 (7)	177 (7)	74 (5)	62 (5)	81 (5)
C(8)	-3802 (2)	3464 (5)	3875 (3)	216 (8)	320 (8)	290 (9)	124 (7)	137 (6)	68 (7)
O(1)	1386 (1)	6999 (3)	2830 (2)	181 (5)	165 (5)	218 (6)	31 (4)	58 (4)	12 (4)
O(2)	-1060 (1)	6598 (3)	3871 (2)	245 (6)	249 (6)	333 (7)	32 (5)	141 (5)	-47 (5)
O(3)	-3016 (1)	1507 (3)	2583 (2)	213 (6)	235 (5)	306 (6)	79 (4)	159 (5)	55 (5)
Cl	3315.5 (4)	4732 (1)	621.5 (5)	141 (2)	245 (2)	251 (2)	7 (2)	74 (1)	31 (2)
H(1)	653 (32)	7583 (73)	3481 (36)	514 (72)					
H(2)	-4880 (30)	1972 (67)	3501 (34)	476 (68)					
H(3)	-3770 (31)	5482 (75)	3662 (37)	545 (73)					
H(4)	-3288 (34)	4203 (77)	5090 (45)	665 (83)					
(e) 105 K									
C(1)	-854 (2)	1540 (4)	1293 (2)	91 (8)	120 (7)	131 (7)	32 (6)	34 (6)	60 (6)
C(2)	663 (2)	3555 (4)	1473 (2)	110 (7)	91 (7)	114 (7)	14 (5)	6 (5)	43 (5)
C(3)	1483 (2)	1999 (4)	201 (2)	75 (7)	123 (7)	141 (7)	8 (6)	29 (6)	71 (6)
C(7)	-1651 (2)	3421 (4)	2704 (2)	110 (7)	145 (7)	119 (7)	35 (6)	25 (6)	69 (6)
C(8)	-3820 (2)	3466 (5)	3881 (3)	129 (8)	184 (8)	189 (8)	57 (6)	77 (6)	51 (7)
O(1)	1385 (1)	6996 (3)	2826 (2)	106 (6)	110 (6)	154 (6)	9 (4)	38 (5)	14 (5)
O(2)	-1061 (1)	6592 (3)	3886 (2)	134 (6)	153 (6)	203 (6)	15 (5)	69 (5)	-8 (5)
O(3)	-3035 (1)	1478 (3)	2593 (2)	105 (6)	141 (6)	201 (6)	32 (4)	86 (5)	42 (5)
Cl	3322.2 (4)	4760 (1)	608.4 (5)	76 (2)	152 (2)	169 (2)	-3 (2)	42 (2)	31 (2)
H(1)	695 (30)	7569 (68)	3455 (35)	294 (62)					
H(2)	-4891 (27)	1801 (62)	3526 (32)	265 (59)					
H(3)	-3785 (29)	5516 (71)	3670 (35)	329 (63)					
H(4)	-3301 (31)	4118 (72)	5193 (39)	375 (65)					

Discussion

In all three crystal modifications the molecules lie on crystallographic inversion centres [in W-(I) the two molecules in the unit cell lie on symmetry-independent centres]. Views of the molecules in the individual

crystals are shown in Fig. 1. As noted by BCP, in Y-(I) the molecules are approximately planar [the torsion angle C(2)–C(1)–C(7)–O(2) is about 5°] and in W-(I) the ester groups are tilted with their planes nearly perpendicular to the plane through the benzene ring [the

Table 4. Atomic coordinates ($\times 10^4$) and displacement parameters ($\text{\AA}^2 \times 10^4$) for LY-(I) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> or <i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
(a) 343 K									
C(1)	-1540 (4)	1646 (2)	-833 (2)	303 (8)	213 (8)	287 (8)	35 (6)	9 (6)	-49 (6)
C(2)	-754 (4)	1289 (2)	672 (2)	354 (9)	229 (8)	299 (8)	28 (6)	10 (7)	-81 (7)
C(3)	835 (4)	-348 (2)	1478 (2)	349 (9)	230 (8)	257 (8)	34 (6)	-10 (6)	-51 (6)
C(7)	-3083 (4)	3457 (2)	-1658 (2)	339 (9)	219 (8)	302 (8)	32 (6)	-41 (6)	-66 (6)
C(8)	-3163 (6)	5991 (3)	-3802 (2)	562 (13)	248 (9)	381 (11)	54 (8)	-60 (10)	23 (8)
O(1)	-1328 (4)	2460 (2)	1396 (2)	660 (9)	296 (7)	349 (7)	173 (6)	-76 (6)	-151 (6)
O(2)	-5139 (4)	4196 (2)	-1090 (2)	637 (10)	324 (7)	413 (8)	201 (6)	78 (7)	-66 (6)
O(3)	-1885 (3)	4186 (2)	-3018 (1)	496 (8)	267 (7)	338 (7)	98 (5)	34 (6)	2 (5)
Cl	2029 (1)	-644.1 (6)	3289.9 (5)	669 (4)	323 (3)	295 (3)	74 (2)	-122 (2)	-90 (2)
H(1)	-2856 (72)	3237 (37)	980 (29)	673 (80)					
H(2)	-2005 (73)	6833 (44)	-3390 (33)	730 (78)					
H(3)	-5439 (80)	6050 (41)	-3920 (32)	761 (92)					
H(4)	-2236 (60)	6226 (34)	-4749 (29)	555 (69)					
(b) 296 K									
C(1)	-1549 (4)	1647 (2)	-838 (2)	242 (7)	179 (7)	250 (8)	19 (5)	6 (6)	-51 (6)
C(2)	-767 (4)	1285 (2)	677 (2)	281 (8)	198 (7)	256 (8)	18 (5)	5 (6)	-77 (6)
C(3)	827 (4)	-346 (2)	1487 (2)	274 (7)	208 (7)	217 (7)	15 (5)	-15 (6)	-55 (6)
C(7)	-3097 (4)	3452 (2)	-1661 (2)	279 (7)	184 (7)	246 (8)	13 (5)	-33 (6)	-55 (6)
C(8)	-3188 (5)	5985 (2)	-3804 (2)	451 (10)	201 (8)	320 (10)	46 (7)	-46 (8)	17 (7)
O(1)	-1346 (4)	2458 (2)	1405 (1)	533 (8)	245 (6)	293 (6)	127 (5)	-60 (5)	-129 (5)
O(2)	-5163 (3)	4196 (2)	-1084 (1)	519 (8)	268 (6)	345 (7)	156 (5)	55 (6)	-57 (5)
O(3)	-1902 (3)	4177 (1)	-3027 (1)	412 (7)	221 (6)	274 (6)	74 (5)	28 (5)	-5 (5)
Cl	2035 (1)	-638.5 (5)	3303.3 (4)	545 (3)	266 (2)	241 (3)	55 (2)	-107 (2)	-75 (2)
H(1)	-2886 (64)	3252 (35)	870 (28)	647 (75)					
H(2)	-2423 (62)	6720 (38)	-3273 (28)	637 (72)					
H(3)	-5597 (63)	5987 (34)	-3864 (27)	589 (70)					
H(4)	-2215 (52)	6237 (30)	-4755 (26)	452 (59)					
(c) 226 K									
C(1)	-1560 (3)	1643 (2)	-840 (1)	172 (6)	136 (6)	192 (7)	17 (5)	0 (5)	-34 (5)
C(2)	-786 (3)	1286 (2)	682 (2)	205 (6)	141 (6)	197 (7)	11 (5)	5 (5)	-61 (5)
C(3)	830 (3)	-345 (2)	1498 (1)	197 (6)	149 (6)	160 (6)	15 (5)	-15 (5)	-36 (5)
C(7)	-3114 (3)	3448 (2)	-1667 (2)	196 (6)	138 (6)	189 (7)	12 (5)	-33 (5)	-44 (5)
C(8)	-3207 (4)	5976 (2)	-3810 (2)	312 (8)	146 (6)	228 (8)	34 (5)	-29 (6)	14 (6)
O(1)	-1370 (3)	2456 (1)	1420 (1)	383 (6)	178 (5)	218 (5)	102 (4)	-57 (4)	-96 (4)
O(2)	-5187 (3)	4194 (1)	-1078 (1)	360 (6)	198 (5)	254 (6)	116 (4)	30 (5)	-46 (4)
O(3)	-1916 (3)	4170 (1)	-3040 (1)	286 (6)	155 (5)	196 (5)	62 (4)	20 (4)	2 (4)
Cl	2030.4 (9)	-634.0 (4)	3324.8 (4)	386 (3)	195 (2)	174 (2)	45 (1)	-78 (1)	-56 (1)
H(1)	-2875 (60)	3249 (31)	895 (26)	499 (63)					
H(2)	-2343 (52)	6713 (31)	-3305 (24)	426 (54)					
H(3)	-5652 (54)	5982 (28)	-3874 (23)	383 (52)					
H(4)	-2300 (46)	6243 (25)	-4797 (22)	294 (47)					
(d) 179 K									
C(1)	-1564 (3)	1642 (2)	-842 (1)	134 (6)	116 (6)	172 (6)	19 (4)	-1 (4)	-33 (5)
C(2)	-789 (3)	1284 (2)	688 (1)	159 (6)	123 (6)	170 (6)	15 (4)	-3 (5)	-50 (5)
C(3)	828 (3)	-344 (2)	1504 (1)	148 (6)	135 (6)	133 (6)	11 (4)	-22 (4)	-38 (5)
C(7)	-3119 (3)	3443 (2)	-1666 (1)	146 (6)	119 (5)	151 (6)	9 (4)	-30 (4)	-34 (4)
C(8)	-3225 (4)	5973 (2)	-3814 (2)	240 (7)	115 (6)	182 (7)	33 (5)	-28 (5)	14 (5)
O(1)	-1381 (3)	2452 (1)	1427 (1)	301 (5)	149 (5)	170 (5)	84 (4)	-46 (4)	75 (4)
O(2)	-5203 (3)	4190 (1)	-1074 (1)	283 (6)	156 (5)	214 (5)	89 (4)	21 (4)	-40 (4)
O(3)	-1920 (2)	4166 (1)	-3048 (1)	230 (5)	129 (5)	166 (5)	48 (4)	16 (4)	-7 (4)
Cl	2041.6 (8)	-631.6 (4)	3336.3 (3)	297 (3)	157 (2)	142 (2)	37 (1)	-64 (1)	-47 (1)
H(1)	-2838 (58)	3229 (30)	937 (25)	402 (57)					
H(2)	-2355 (52)	6702 (30)	-3304 (23)	373 (50)					
H(3)	-5673 (54)	5975 (27)	-3899 (22)	349 (50)					
H(4)	-2197 (45)	6238 (25)	-4761 (22)	252 (43)					
(e) 97 K									
C(1)	-1589 (4)	1643 (2)	-845 (2)	78 (7)	85 (7)	126 (8)	9 (5)	0 (5)	-31 (6)
C(2)	-805 (4)	1286 (2)	690 (2)	97 (7)	90 (7)	110 (8)	16 (5)	-4 (5)	-33 (6)
C(3)	832 (4)	-343 (2)	1517 (2)	86 (7)	104 (7)	93 (7)	15 (5)	-13 (5)	-24 (6)
C(7)	-3138 (4)	3440 (2)	-1666 (2)	98 (7)	74 (7)	94 (7)	8 (5)	-40 (5)	-14 (5)
C(8)	-3245 (4)	5972 (2)	-3823 (2)	143 (8)	80 (7)	122 (8)	27 (6)	-37 (6)	7 (6)
O(1)	-1395 (3)	2451 (2)	1439 (1)	184 (7)	93 (6)	117 (6)	62 (5)	-38 (5)	-45 (5)
O(2)	-5229 (3)	4188 (1)	-1067 (1)	160 (6)	97 (6)	146 (6)	51 (4)	-1 (5)	-27 (5)
O(3)	-1939 (3)	4161 (1)	-3060 (1)	135 (6)	89 (6)	110 (6)	38 (4)	3 (4)	8 (5)
Cl	2053.4 (9)	-627.6 (4)	3352.6 (4)	171 (3)	100 (3)	86 (3)	27 (2)	-43 (3)	-27 (2)
H(1)	-2473 (76)	3156 (37)	1022 (30)	269 (72)					
H(2)	-2438 (64)	6701 (35)	-3307 (27)	236 (57)					
H(3)	-5454 (65)	5856 (31)	-3817 (25)	206 (55)					
H(4)	-1913 (58)	6177 (33)	-4713 (27)	207 (54)					

torsion angles are about 85° for molecule *a* and about 70° for molecule *b* – note that the two symmetry-independent molecules in W-(I) are distinctly different]. In LY-(I) the ester groups are neither coplanar with the

benzene ring as in Y-(I), nor nearly perpendicular to it as in W-(I), but in an intermediate orientation (torsion angle about 40°), in keeping with the intermediate colour of this crystal form.

Table 5. Atomic coordinates ($\times 10^4$) and displacement parameters ($\text{\AA}^2 \times 10^4$) for *W*-(I) with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> or <i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	
(a) 353 K										
C(1a)	-341 (2)	480 (2)	1196 (2)	377 (8)	307 (8)	346 (9)	130 (6)	246 (7)	181 (7)	
C(2a)	-1605 (2)	219 (2)	-466 (2)	345 (8)	326 (8)	404 (9)	133 (7)	254 (8)	207 (7)	
C(3a)	-1248 (2)	-261 (2)	-1659 (2)	364 (9)	343 (8)	321 (8)	132 (7)	204 (7)	197 (7)	
C(7a)	-725 (2)	1121 (3)	2496 (2)	394 (9)	386 (9)	393 (9)	149 (7)	268 (8)	231 (8)	
C(8a)	-1990 (4)	1 (5)	3438 (4)	754 (17)	782 (18)	758 (18)	239 (15)	611 (16)	461 (16)	
O(1a)	-3149 (2)	396 (2)	-852 (2)	390 (7)	567 (8)	580 (9)	268 (6)	342 (7)	392 (7)	
O(2a)	-511 (2)	2825 (2)	3449 (2)	995 (12)	387 (7)	736 (10)	241 (8)	717 (10)	240 (7)	
O(3a)	-1351 (2)	-402 (2)	2418 (2)	688 (9)	417 (7)	544 (8)	151 (6)	471 (8)	255 (6)	
Cl(a)	-2825.1 (6)	-632.7 (8)	-3743.6 (6)	438 (3)	626 (3)	360 (3)	196 (2)	207 (2)	291 (2)	
H(1a)	-3424 (35)	1064 (39)	-1247 (36)	647 (81)						
H(2a)	-3049 (55)	183 (57)	2855 (52)	1384 (167)						
H(3a)	-1126 (40)	1080 (43)	4604 (41)	860 (94)						
H(4a)	-2216 (37)	-1341 (44)	3293 (37)	861 (88)						
C(1b)	1690 (2)	5158 (2)	637 (2)	283 (8)	323 (8)	398 (9)	106 (6)	219 (7)	205 (7)	
C(2b)	495 (2)	4902 (2)	-1035 (2)	323 (8)	327 (8)	379 (9)	114 (6)	240 (7)	203 (7)	
C(3b)	-1202 (2)	4752 (2)	-1660 (2)	291 (8)	339 (8)	334 (8)	98 (6)	183 (7)	196 (7)	
C(7b)	3534 (2)	5438 (3)	1358 (2)	289 (8)	423 (9)	362 (9)	134 (7)	207 (7)	230 (7)	
C(8b)	5752 (3)	3972 (5)	2000 (4)	470 (12)	808 (18)	837 (19)	406 (13)	445 (13)	542 (16)	
O(1b)	1034 (2)	4725 (2)	-2006 (2)	415 (7)	586 (8)	489 (8)	207 (6)	341 (7)	346 (7)	
O(2b)	4456 (2)	6946 (2)	1861 (2)	313 (6)	541 (8)	756 (10)	142 (6)	298 (7)	434 (7)	
O(3b)	4005 (2)	3893 (2)	1381 (2)	402 (7)	493 (7)	703 (9)	243 (6)	361 (7)	383 (7)	
Cl(b)	-2713.0 (6)	4362.0 (8)	-3768.1 (6)	378 (3)	669 (3)	390 (3)	165 (2)	207 (2)	322 (2)	
H(1b)	578 (33)	5223 (37)	-2539 (35)	631 (83)						
H(2b)	5886 (41)	2866 (45)	1897 (41)	933 (101)						
H(3b)	6018 (37)	4347 (43)	1351 (38)	888 (89)						
H(4b)	6569 (44)	5104 (48)	3244 (45)	991 (109)						
(b) 296 K										
C(1a)	-332 (2)	484 (2)	1207 (2)	317 (8)	243 (7)	292 (8)	100 (6)	216 (7)	149 (7)	
C(2a)	-1610 (2)	222 (2)	-464 (2)	271 (8)	251 (8)	305 (8)	96 (6)	190 (7)	156 (7)	
C(3a)	-1256 (2)	-257 (2)	-1666 (2)	297 (8)	255 (8)	257 (8)	90 (6)	169 (7)	145 (7)	
C(7a)	-723 (2)	1120 (3)	2503 (2)	293 (8)	319 (9)	289 (8)	115 (7)	193 (7)	183 (7)	
C(8a)	-1987 (4)	-11 (4)	3447 (4)	588 (14)	615 (15)	602 (15)	190 (12)	484 (13)	362 (13)	
O(1a)	-3157 (2)	397 (2)	-852 (2)	308 (6)	437 (8)	460 (8)	201 (6)	274 (6)	302 (7)	
O(2a)	-513 (2)	2835 (2)	3461 (2)	803 (11)	301 (7)	592 (9)	188 (7)	579 (9)	189 (7)	
O(3a)	-1343 (2)	-417 (2)	2427 (2)	542 (8)	331 (7)	431 (8)	115 (6)	375 (7)	205 (6)	
Cl(a)	-2840.6 (6)	-633.2 (7)	-3759.1 (6)	345 (3)	495 (3)	283 (2)	149 (2)	163 (2)	229 (2)	
H(1a)	-3387 (39)	1146 (43)	-1213 (38)	635 (83)						
H(2a)	-2912 (51)	424 (57)	3055 (50)	1132 (135)						
H(3a)	-1063 (37)	1047 (39)	4722 (38)	634 (75)						
H(4a)	-2154 (39)	-1269 (46)	3389 (38)	773 (88)						
C(1b)	1693 (2)	5156 (2)	641 (2)	221 (7)	251 (8)	307 (8)	77 (6)	172 (7)	156 (7)	
C(2b)	490 (2)	4899 (2)	-1043 (2)	267 (8)	247 (7)	313 (8)	87 (6)	202 (7)	161 (7)	
C(3b)	-1203 (2)	4754 (2)	-1664 (2)	236 (8)	258 (8)	269 (8)	73 (6)	146 (7)	152 (7)	
C(7b)	3544 (2)	5434 (3)	1360 (2)	240 (8)	321 (9)	289 (8)	107 (7)	171 (7)	177 (7)	
C(8b)	5764 (3)	3953 (4)	2006 (4)	373 (11)	678 (15)	670 (16)	325 (11)	366 (12)	446 (14)	
O(1b)	1034 (2)	4722 (2)	-2015 (2)	318 (7)	478 (8)	384 (7)	158 (6)	263 (6)	284 (7)	
O(2b)	4464 (2)	6937 (2)	1847 (2)	249 (6)	431 (7)	599 (9)	116 (5)	238 (6)	349 (7)	
O(3b)	4012 (2)	3876 (2)	1387 (2)	331 (7)	385 (7)	575 (8)	198 (5)	304 (7)	313 (6)	
Cl(b)	-2724.8 (6)	4362.2 (7)	-3783.1 (6)	296 (2)	532 (3)	309 (2)	128 (2)	164 (2)	257 (2)	
H(1b)	602 (34)	5217 (39)	-2533 (35)	522 (80)						
H(2b)	5923 (38)	2817 (44)	1980 (39)	732 (86)						
H(3b)	5966 (36)	4211 (43)	1331 (38)	748 (86)						
H(4b)	6680 (43)	5121 (46)	3368 (43)	789 (91)						
(c) 98 K										
C(1a)	-331 (2)	471 (2)	1214 (2)	128 (7)	63 (7)	127 (7)	31 (5)	94 (6)	54 (6)	
C(2a)	-1624 (2)	216 (2)	-465 (2)	104 (7)	65 (7)	132 (7)	30 (5)	78 (6)	57 (6)	
C(3a)	-1275 (2)	-257 (2)	-1686 (2)	116 (7)	63 (7)	94 (7)	27 (6)	59 (6)	48 (6)	
C(7a)	-717 (2)	1107 (2)	2532 (2)	95 (7)	110 (7)	128 (7)	46 (5)	73 (6)	79 (6)	
C(8a)	-1958 (2)	-56 (3)	3498 (2)	186 (8)	179 (8)	200 (8)	67 (6)	155 (7)	124 (7)	
O(1a)	-3182 (1)	392 (2)	-850 (2)	112 (5)	138 (6)	173 (6)	72 (4)	103 (5)	113 (5)	
O(2a)	-526 (1)	2865 (2)	3498 (2)	246 (6)	95 (5)	183 (6)	52 (4)	165 (5)	66 (4)	
O(3a)	-1317 (1)	-469 (2)	2458 (1)	199 (6)	101 (5)	157 (5)	40 (4)	139 (5)	76 (4)	
Cl(a)	-2876.6 (4)	-630.6 (5)	-3802.1 (5)	120 (2)	145 (2)	98 (2)	45 (2)	59 (2)	78 (2)	
H(1a)	-3476 (31)	1184 (34)	-1235 (32)	257 (58)						
H(2a)	-3019 (27)	308 (29)	2901 (28)	235 (52)						
H(3a)	-1089 (24)	1026 (27)	4772 (25)	94 (41)						
H(4a)	-2166 (26)	-1335 (31)	3435 (26)	186 (47)						
C(1b)	1703 (2)	5145 (2)	645 (2)	104 (7)	62 (7)	141 (7)	29 (5)	84 (6)	58 (6)	
C(2b)	492 (2)	4897 (2)	-1053 (2)	125 (7)	67 (7)	123 (7)	29 (5)	91 (6)	50 (6)	
C(3b)	-1217 (2)	4756 (2)	-1688 (2)	108 (7)	58 (7)	103 (7)	25 (5)	61 (6)	51 (6)	
C(7b)	3559 (2)	5406 (2)	1363 (2)	103 (6)	118 (7)	101 (7)	45 (6)	71 (6)	68 (6)	
C(8b)	5795 (2)	3899 (3)	2019 (2)	136 (7)	197 (9)	234 (8)	99 (6)	133 (7)	146 (7)	
O(1b)	1037 (1)	4714 (2)	-2037 (1)	122 (5)	149 (6)	139 (5)	53 (4)	104 (5)	99 (5)	
O(2b)	4495 (1)	6915 (2)	1816 (1)	109 (5)	128 (5)	202 (6)	38 (4)	89 (5)	117 (5)	
O(3b)	4037 (1)	3833 (2)	1432 (2)	115 (5)	110 (5)	206 (6)	68 (4)	107 (5)	110 (5)	
Cl(b)	-2750.4 (4)	4359.9 (5)	-3829.6 (5)	106 (2)	155 (2)	106 (2)	40 (2)	58 (2)	85 (2)	
H(1b)	492 (26)	5141 (28)	-2772 (28)	131 (44)						
H(2b)	5867 (26)	2626 (32)	1861 (27)	201 (48)						
H(3b)	5900 (28)	4036 (31)	1261 (30)	284 (55)						
H(4b)	6699 (30)	5119 (32)	3320 (31)	264 (54)						

Table 6. Atomic coordinates ($\times 10^4$) and displacement parameters ($\text{\AA}^2 \times 10^4$) for DY-(I) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> or <i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
(a) 289 K									
C(1)	-842 (2)	1574 (4)	1276 (2)	253 (8)	272 (7)	258 (7)	105 (6)	79 (6)	105 (6)
C(2)	662 (2)	3557 (4)	1471 (2)	278 (8)	240 (7)	256 (7)	78 (6)	61 (6)	84 (6)
C(3)	1475 (2)	1970 (4)	215 (2)	216 (7)	278 (7)	290 (8)	67 (6)	73 (6)	114 (6)
C(7)	-1636 (2)	3458 (5)	2683 (2)	293 (8)	319 (8)	290 (8)	115 (6)	90 (6)	109 (7)
C(8)	-3774 (3)	3462 (7)	3877 (4)	362 (11)	526 (12)	502 (12)	192 (9)	229 (9)	101 (11)
O(1)	1384 (1)	6991 (3)	2826 (2)	315 (7)	267 (6)	358 (7)	50 (5)	97 (5)	12 (5)
O(2)	-1065 (2)	6615 (4)	3840 (2)	432 (8)	417 (7)	582 (9)	54 (6)	245 (7)	-103 (7)
O(3)	-2989 (2)	1548 (4)	2582 (2)	364 (7)	394 (7)	514 (8)	124 (6)	265 (6)	75 (6)
Cl	3304.2 (5)	4685 (1)	639.5 (7)	245 (3)	402 (3)	434 (3)	0 (2)	118 (2)	43 (2)
H(1)	716 (24)	7559 (57)	3437 (29)	316 (51)					
H(2)	-4825 (46)	1916 (100)	3542 (53)	1067 (126)					
H(3)	-3825 (45)	5389 (116)	3679 (56)	1163 (136)					
H(4)	-3282 (40)	4124 (99)	5172 (56)	1032 (113)					
(b) 230 K									
C(1)	-849 (2)	1559 (4)	1279 (2)	195 (8)	207 (7)	211 (7)	77 (6)	63 (6)	98 (6)
C(2)	662 (2)	3554 (4)	1471 (2)	207 (7)	181 (7)	205 (7)	47 (5)	36 (6)	69 (6)
C(3)	1478 (2)	1984 (4)	214 (2)	156 (7)	221 (7)	233 (7)	46 (6)	52 (6)	97 (6)
C(7)	-1641 (2)	3444 (4)	2691 (2)	224 (7)	248 (7)	239 (8)	87 (6)	68 (6)	101 (6)
C(8)	-3791 (2)	3462 (6)	3875 (3)	269 (9)	392 (10)	389 (11)	138 (8)	173 (8)	77 (8)
O(1)	1386 (1)	6993 (3)	2828 (2)	231 (6)	203 (6)	284 (6)	30 (5)	81 (5)	20 (5)
O(2)	-1064 (2)	6603 (4)	3857 (2)	316 (7)	315 (7)	447 (8)	39 (5)	173 (6)	-66 (6)
O(3)	-3005 (1)	1525 (3)	2583 (2)	260 (6)	300 (6)	408 (7)	87 (5)	198 (6)	64 (5)
Cl	3310.6 (4)	4710 (1)	630.2 (6)	177 (2)	304 (2)	341 (3)	-5 (2)	87 (2)	38 (2)
H(1)	712 (22)	7548 (52)	3452 (27)	247 (47)					
H(2)	-4824 (33)	1922 (72)	3560 (39)	689 (85)					
H(3)	-3809 (31)	5431 (79)	3673 (39)	715 (86)					
H(4)	-3313 (31)	4206 (74)	5153 (44)	713 (84)					

As the temperature is increased, there are quite perceptible changes in the twist angle of the ester group [defined here as the mean of the C(2)–C(1)–C(7)–O(2) and C(3')–C(1)–C(7)–O(3) torsion angles]. In Y-(I) these angles (e.s.d. 0.4°) are 4.1, 4.4, 4.8, 5.1 and 5.7° at the five measurement temperatures; in LY-(I) they are 38.2, 38.7, 38.9, 39.4 and 40.0°; and in W-(I) they are 85.0, 86.3 and 86.7° for molecule *a*, and 69.8, 72.4 and 73.1° for molecule *b* at the three measurement temperatures. This systematic variation is an indication of anharmonicity in the potential describing the rotation of the ester groups in the respective crystals.

The interatomic distances and angles shown in Fig. 2 are based on the analyses at the lowest temperature for each crystal form. We regard these as the most accurate because the ADP's (and hence the motional corrections as well) are the smallest. Distances and angles for the yellow form with deuterated hydroxyl groups are not shown in Fig. 2; the values at 230 and 289 K are not significantly different from those obtained for the undeuterated crystals at the same temperatures.

Apart from the ester torsion angles, distances and angles obtained at different temperatures are mostly not very different from those shown in Fig. 2. What changes there are correspond, on the whole, to a slight apparent contraction of the entire molecule as the temperature is raised. The atoms most affected are the carboxyl oxygens O(2) and O(3). In the Y-(I) crystal, the apparent C(7)–O(2) distance decreases systematically by 0.017 Å (from 1.219 Å at 105 K to 1.202 Å at 353 K) and the C(7)–O(3) distances by 0.021 Å (from 1.316 to 1.295 Å). Similar, though not

quite so extreme, changes occur for the same atoms in the other two forms. As we shall discuss later, these are the atoms most affected by motional corrections. Systematic errors of this kind raise questions about the meaningfulness of standard bond lengths derived by averaging crystal structure data obtained overwhelmingly from room-temperature analyses.

Fig. 2 shows that there are significant changes in certain bond angles and distances as the molecular conformation changes. For example, the steady decrease from Y to LY to W of the O(3)–C(7)–C(1), C(7)–C(1)–C(3') and C(1')–C(3)–Cl angles, the changes in the external angles at C(2) (up to 7°!), and the increasing Cl...O(1) distance are all consistent with the lessening of the O(3')...Cl and O(2)...O(1) repulsions as the ester groups rotate out of the plane. The steady decrease in the C(1)–C(2) and C(1)–C(3') ring distances (0.028 and 0.013 Å) is consistent with the corresponding lessening of the C(2)...O(2) and C(3')...O(3) repulsions, and finally, the increase in the exocyclic C(1)–C(7) distance (0.015 Å) is ascribable to the diminished conjugation between the ester group and the aromatic system as the overlap between the respective π systems decreases.

Considering the strong overcrowding in the molecules of Y-(I) it is remarkable how closely coplanar the central ring and its substituents are; for the low-temperature structure the central atoms are within 0.002 Å of a common plane and the substituents, Cl, O(1), C(7) deviate from the plane by +0.012, -0.022 and -0.013 Å in that order. In LY-(I) and W-(I) the central ring stays closely planar, but the substituents deviate much more pronouncedly from coplanarity. In LY-(I) (97 K) the deviations (in the same order) are

+0.128, -0.019 and -0.069 Å. In W-(I), the deviations are +0.034, +0.038 and -0.087 Å for molecule *a* and +0.058, +0.064 and -0.073 Å for molecule *b*. Clearly, as the ester groups rotate out of the plane, the atoms attached directly to the central ring experience larger out-of-plane forces.

As discussed by BCP, the main differences between the structures of the yellow and white forms are associated with differences in the hydrogen-bonding patterns. Y-(I) is characterized by intramolecular hydrogen bonding between the hydroxyl groups and the carbonyl O atom of the *ortho* ester groups; for the low-temperature analysis the O(1)···O(2) distance is

2.520 (2) Å and the OH···O angle is 153 (1)°. In W-(I) the hydrogen bonding is intermolecular; the O(H)···O(2) distances are 2.717 (2) Å (from *a* to *b*) and 2.798 (2) Å (from *b* to *a*), while the corresponding OH···O angles are 163 (1) and 149 (1)°. Although the intramolecular O(1)···Cl distances are considerably larger in W-(I) (3.01–3.02 Å) than in Y-(I) (2.75 Å), BCP argue for the existence of an attractive H···Cl interaction in the former, and, indeed, the O–H bonds are oriented towards their respective *ortho* Cl atoms; the C(3)–C(2)–O(1)–H(1) torsion angles are 51° for molecule *a* and 32° for molecule *b*. In the new LY-(I) form the hydrogen bonding is intramolecular, with an

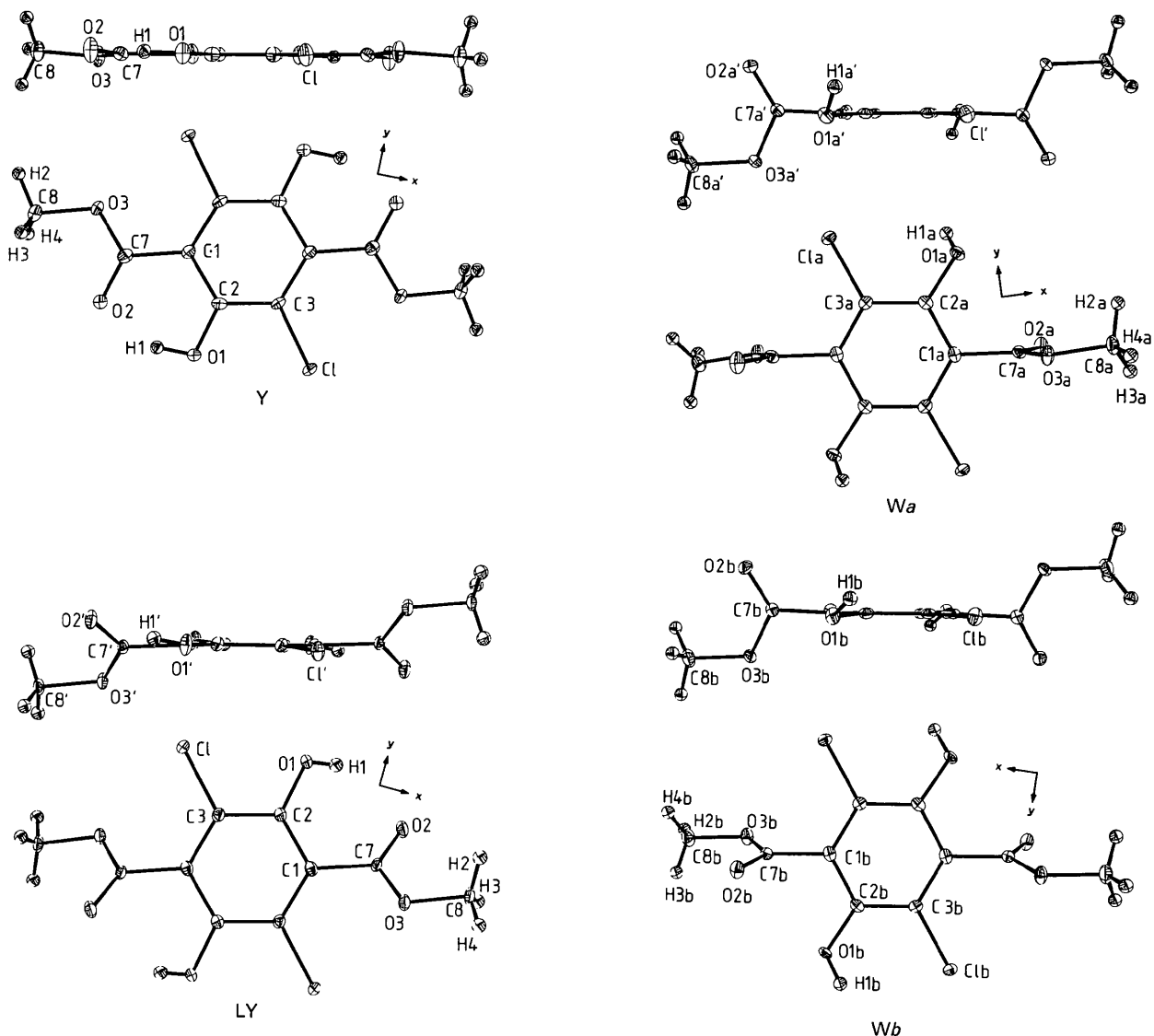


Fig. 1. Dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate, as observed in the Y, LY and W (two independent molecules *Wa* and *Wb*) crystal forms. Each molecule is shown projected onto the mean plane of the benzene ring and perpendicular to this plane. Inertial axes (*x* and *y*) and the atomic numbering used in Tables 3–6 are indicated. Displacement ellipsoids are shown at the 50% probability level for the lowest measurement temperature in each case.

Table 7. Summary of results of motional analysis for Y-(I), DY-(I), LY-(I) and W-(I) (molecules a and b) at various temperatures

Eigenvalues of **T** and **L** are listed together with the direction cosines of the eigenvector $\mathbf{n}(L_i)$ with respect to the inertial axes defined in Fig. 1. The mean-square libration amplitude $\langle \omega^2 \rangle$ refers to the librational motion of the grouping O(2), O(3) and C(8) about the axis C(1)–C(7). The quantity R is defined here as $[\sum w(\Delta U^U)^2 / \sum w(U^U)^2]^{1/2}$ with the weights w taken as inversely proportional to the variance of U^U .

Crystal	Temperature (K)	T ($\text{\AA}^2 \times 10^{-4}$)	L (deg ²)	$\mathbf{n}(L_i)$	$\langle \omega^2 \rangle$ (deg ²)	<i>R</i>
Y-(I)	105	116, 97, 69	6.7, 1.1, 0.7	0.967, 0.240, 0.091	44 (11)	0.078
	180	152, 139, 120	11.5, 2.6, 1.8	0.942, 0.313, 0.120	80 (12)	0.054
	230	184, 179, 146	15.0, 3.7, 2.3	0.929, 0.346, 0.128	105 (13)	0.036
	296	261, 233, 208	21.0, 5.2, 3.3	0.939, 0.326, 0.107	152 (13)	0.032
	353	335, 290, 268	26.0, 7.1, 4.3	0.936, 0.336, 0.107	190 (15)	0.031
DY-(I)	230	192, 178, 145	15.5, 3.7, 2.4	0.937, 0.329, 0.119	108 (12)	0.038
	289	244, 229, 205	20.2, 5.4, 3.3	0.933, 0.342, 0.112	145 (14)	0.036
LY-(I)	97	93, 91, 58	6.4, 1.0, 0.0	1.000, -0.006, -0.022	20 (6)	0.096
	179	137, 132, 99	10.4, 1.6, 0.6	0.999, 0.034, 0.018	32 (7)	0.067
	226	163, 159, 125	13.5, 2.0, 1.4	0.992, 0.032, 0.025	36 (8)	0.063
	296	227, 217, 178	18.3, 3.1, 2.2	0.998, 0.056, 0.032	49 (10)	0.053
	343	293, 259, 204	22.9, 3.8, 2.5	0.999, 0.038, 0.034	60 (12)	0.058
W-(Ia)	98	93, 90, 37	4.2, 1.8, 1.4	0.997, -0.076, 0.167	17 (6)	0.112
	296	245, 239, 183	12.2, 5.9, 3.7	0.980, -0.200, -0.020	62 (12)	0.073
	353	312, 306, 243	15.2, 7.6, 4.4	0.983, -0.185, -0.008	73 (13)	0.058
W-(Ib)	98	94, 85, 34	5.1, 2.0, 1.0	0.997, 0.055, 0.058	12 (5)	0.103
	296	254, 213, 167	15.0, 6.6, 3.5	0.986, 0.160, 0.043	32 (10)	0.051
	353	321, 267, 234	17.3, 8.2, 4.1	0.980, 0.197, 0.037	40 (11)	0.057

having axis 1 parallel to C(1)–C(7), axis 2 in the direction of motion of O(2), and axis 3 normal to these two (Schomaker & Trueblood, 1984). Only the sum of $\langle \omega^2 \rangle$ and $2\langle \omega\lambda_1 \rangle$ can be determined from the ADP's, and it is this sum that we have been calling $\langle \omega^2 \rangle$ up till now. As seen from Table 7, this quantity is in all cases several times larger than the parallel component of **L** and hence it cannot be very different from the true value of $\langle \omega^2 \rangle$. Correlation terms $\langle \omega t_i \rangle$ and $\langle \omega \lambda_i \rangle$ between the internal rotation of the ester groups and the other translational and librational terms were also included in our motional analyses but were found to be not significantly different from zero with one exception. For

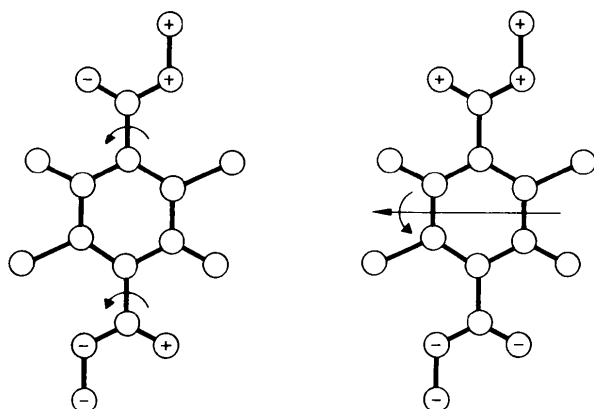


Fig. 3. Torsional rotation of the ester group about the exocyclic C–C bond (left) and libration of the entire molecule about the horizontal axis (right) lead to different relative out-of-plane displacements of the atoms of the ester group.

Y-(I) (deuterated and undeuterated) at temperatures above 230 K we obtained significantly non-zero values of $\langle \omega\lambda_3 \rangle$ amounting to $-17(7)$ and $-23(8)$ deg² at 296 and 353 K respectively. This type of correlation with the perpendicular libration axis adds to the out-of-plane displacement of one of the two ester O atoms and subtracts from the other, leading to unequal out-of-plane r.m.s. displacements (Fig. 3). With a mean-square torsional amplitude of about 150 deg² at room temperature, the r.m.s. displacement of the ester O atoms from the mean molecular plane would amount to about 0.25 Å. The mean-square librational amplitude about the perpendicular axis is about 5 deg², corresponding to r.m.s. displacements of the O atoms of about 0.13 Å. Clearly such large atomic motions must be highly correlated. Introduction of these correlation terms led to a considerable improvement in the agreement factor, from 0.126 to 0.032 for the 296 K data (see Table 7).

Not only are the $\langle \omega^2 \rangle$ values for Y-(I) greater than for the other two forms but so is their temperature dependence (Fig. 4). For Y-(I) and LY-(I) $\langle \omega^2 \rangle$ values at the five measurement temperatures are fitted closely by quadratic regression:

$$\langle \omega^2 \rangle_{Y-(I)} = 7.4 + 0.274T + 6.961 \times 10^{-4}T^2$$

$$\langle \omega^2 \rangle_{LY-(I)} = 13.4 + 0.050T + 2.462 \times 10^{-4}T^2$$

With only three measurement temperatures for W-(I), quadratic curve-fitting is hardly appropriate, but it is evident from Fig. 4 that for both molecules the temperature dependence of $\langle \omega^2 \rangle$ is similar to that of LY-(I) and less than that of Y-(I).

A somewhat more physical interpretation of the observed temperature dependence is possible in terms of a mean-field potential model. Here it is assumed that the motion of an averaged atom (or molecule or rigid grouping) in a crystal is determined by the effective mean force field exerted on the individual atom (or molecule or rigid grouping) by the crystal environment, that is, we ignore all forms of correlation between the motions of atoms belonging to neighbouring molecules or between different rigid groupings within the same molecule. Although the precise physical significance of the effective mean-field force constants and frequencies entering into this kind of model may be open to question, experimental ADP's have been shown to yield mean-field estimates of quadratic force constants (Trueblood & Dunitz, 1983) and rotation barriers (Maverick & Dunitz, 1987) that are at least in the same range as those derived by other physical methods.

The observed $\langle \omega^2 \rangle$ values can be related to vibration frequencies by assuming a Boltzmann distribution over energy levels of a quantized harmonic oscillator. This leads to:

$$\langle \omega^2 \rangle = (h/8\pi^2 I \nu) / \coth(h\nu/2kT)$$

where h is Planck's constant, I the moment of inertia of the librating group, and ν the librational frequency. This is equivalent to:

$$\langle \omega^2 \rangle = 27.973 I \nu / \coth(0.7197 \nu / T)$$

where ω is expressed in radians, I in units of $\text{g cm}^2 \times 10^{-40}$, and ν in cm^{-1} . The moment of inertia of the ester grouping [atoms O(2), O(3), C(8)] about the axis C(1)–C(7) is about $89 \times 10^{-40} \text{ g cm}^2$. Applying the formula to the experimental $\langle \omega^2 \rangle$ values of Y-(I)

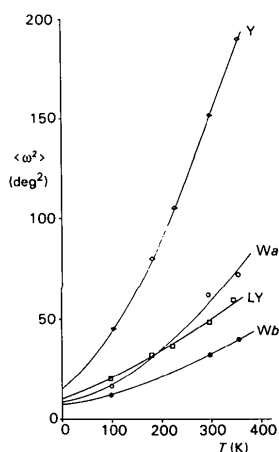


Fig. 4. Mean-square libration amplitudes $\langle \omega^2 \rangle$ of the ester group in the three crystal forms as a function of temperature. The zero-point motions were calculated with the expression $\langle \omega^2 \rangle = (h/8\pi^2 I \nu) \coth(h\nu/2kT)$ from the experimental $\langle \omega^2 \rangle$ values at the lowest measurement temperature (see Table 7).

(Table 7) we obtain frequencies of 60, 57, 56, 53 and 52 cm^{-1} for the internal motion at the five temperatures listed. This is at least in the expected range. The slight frequency decrease as the temperature increases is also reasonable; it corresponds to a general softening of the intermolecular potential as the mean interatomic distances increase. For LY-(I) we obtain somewhat higher frequencies, between 85 and 90 cm^{-1} , similar to those for molecule *a* in W-(I) (80 – 90 cm^{-1}), and for molecule *b* still higher ones, 105 – 110 cm^{-1} . Because of the uncertainty in the true $\langle \omega^2 \rangle$ value, owing to the indeterminate coupling with the overall parallel libration, these estimated frequencies should not be taken too seriously, but they are of the correct order of magnitude.

In a similar way, vibration frequencies can also be estimated for the overall rigid-body librations. As calculated by the *THMA* program, the values (for the room-temperature structures) are 32 , 50 , 68 cm^{-1} for Y-(I), 38 , 56 , 68 cm^{-1} for LY-(I), 39 , 45 , 57 cm^{-1} for molecule *a*, and 38 , 44 , 53 cm^{-1} for molecule *b* in W-(I). Uncertainties in the calculated frequencies resulting from the imprecision of the libration amplitudes amount to 10 – 15% of their values.

The Raman spectra of polycrystalline Y-(I) and W-(I) have been recorded at various temperatures by Swiatkiewicz & Prasad (1982). The Y-(I) spectrum shows fairly sharp peaks at about 31 and 44 cm^{-1} and a broad plateau extending from about 70 to 110 cm^{-1} . The W-(I) spectrum shows a sharp peak at about 60 cm^{-1} with a prominent shoulder at 50 cm^{-1} . These authors offer an interpretation of the spectra in terms of frequencies calculated for the librational modes based on the BCP data. Since they used the rigid-body model, neglecting the internal rotation of the ester groups, their estimated mean-square libration parameters are too large, especially for Y-(I). This means that their estimated frequencies should be too low, compared with ours. However, this does not seem to be the case. While the calculated frequencies lie in the same range as the peaks observed in the Raman spectrum, there seems to be no clear-cut interpretation of the main peaks. A detailed interpretation will probably require a better model than the one we are using. In any case, in our opinion the assignments of Swiatkiewicz & Prasad (1982) should be viewed with reserve.

Instead of relating the $\langle \omega^2 \rangle$ values to frequencies, we can also draw a connection with quadratic force constants of the potential energy in the mean-field model. Also, as mentioned earlier, since the twist angle of the ester group varies slightly with temperature in all three crystal forms, we have evidence for anharmonicity in the respective potentials. We reserve more detailed discussion of these matters to a later paper (Richardson, Yang, Bregger & Dunitz, 1989), where we shall examine the problems associated with the transformations among the three crystal modifications.

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References

- BYRN, S. R., CURTIN, D. Y. & PAUL, I. C. (1972). *J. Am. Chem. Soc.* **94**, 890–898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- CURTIN, D. Y. & BYRN, S. R. (1969a). *J. Am. Chem. Soc.* **91**, 1865–1866.
- CURTIN, D. Y. & BYRN, S. R. (1969b). *J. Am. Chem. Soc.* **91**, 6102–6106.
- DUNITZ, J. D., MAVERICK, E. F. & TRUEBLOOD, K. N. (1988). *Angew. Chem.* **100**, 910–925; *Angew. Chem. Int. Ed. Engl.* **27**, 880–895.
- DUNITZ, J. D., SCHOMAKER, V. & TRUEBLOOD, K. N. (1988). *J. Phys. Chem.* **92**, 856–867.
- DUNITZ, J. D. & WHITE, D. N. J. (1973). *Acta Cryst.* **A29**, 93–94.
- HANTZSCH, A. (1915). *Chem. Ber.* **48**, 797–816.
- MAVERICK, E. F. & DUNITZ, J. D. (1987). *Mol. Phys.* **62**, 451–459.
- RICHARDSON, M. F., YANG, Q.-C., BREGGER, E. & DUNITZ, J. D. (1989). In preparation.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1984). *Acta Cryst.* **A40**, C-339.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- SWIATKIEWICZ, J. & PRASAD, P. N. (1982). *J. Am. Chem. Soc.* **104**, 6913–6918.
- TRUEBLOOD, K. N. & DUNITZ, J. D. (1983). *Acta Cryst.* **B39**, 120–133.
- VENKATESAN, K. (1982). Unpublished results.
- YANG, Q.-C., RICHARDSON, M. F. & DUNITZ, J. D. (1985). *J. Am. Chem. Soc.* **107**, 5535–5537.

Acta Cryst. (1989). **B45**, 323–336

Characterization of an Orientational Disorder in Two Charge-Transfer Complexes: Anthracene–Tetracyanobenzene (A–TCNB) and Naphthalene–Tetracyanobenzene (N–TCNB)

BY JACQUES LEFEBVRE, GÉRARD ODOU AND MICHEL MULLER

Laboratoire de Dynamique des Cristaux Moléculaires, UA 801, Université de Lille I, 59655 Villeneuve d'Ascq CEDEX, France

AND ANDRZEJ MIERZEJEWSKI AND TADEUSZ LUTY

Institute of Organic and Physical Chemistry, Technical University of Wrocław, Wyb. Wyspińskiego 27, 50-370 Wrocław, Poland

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Abstract

A problem of an orientational disorder in mixed-stack charge-transfer crystals has been addressed. New X-ray diffraction data, collected at several temperatures for A–TCNB and N–TCNB complexes, are reported. The data were analysed using conventional structure-refinement procedures and utilizing symmetry-adapted functions. The orientational probability functions allowed the disorder of donor sublattices to be characterized as dynamic in A–TCNB and static in N–TCNB crystals. Conclusions concerning the mechanisms of the orientational phase transitions in both crystals are supported by intensity measurements of some superlattice reflections. The structure of the low-temperature phase of the N–TCNB complex has been determined for the first time, the structure of pure TCNB has been redetermined at 294 K. In addition to observations

concerning characterization and mechanisms of the orientational disorder and instabilities, a general conclusion is drawn that the architecture of the mixed-stack charge-transfer crystals is governed by the close-packing principle. Crystal data at 294 K: A–TCNB, anthracene–1,2,4,5-benzenetetracarbonitrile (1/1), $C_{14}H_{10}C_{10}H_2N_4$, $M_r = 356.4$, $C2/m$, $a = 9.526$ (2), $b = 12.780$ (3), $c = 7.440$ (2) Å, $\beta = 92.36$ (1)°, $V = 905.0$ (7) Å³, $Z = 2$, $D_x = 1.307$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.74$ cm⁻¹, $R = 0.049$ for 916 observed reflections; N–TCNB, naphthalene–1,2,4,5-benzenetetracarbonitrile (1/1), $C_{10}H_8C_{10}H_2N_4$, $M_r = 306.3$, $C2/m$, $a = 9.420$ (2), $b = 12.684$ (2), $c = 6.880$ (1) Å, $\beta = 107.46$ (3)°, $V = 784.2$ (4) Å³, $Z = 2$, $D_x = 1.297$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.75$ cm⁻¹, $R = 0.040$ for 594 observed reflections; TCNB, 1,2,4,5-benzenetetracarbonitrile, $C_{10}H_2N_4$, $M_r = 178.2$, $P2_1/a$, $a = 13.698$ (3), $b = 10.329$ (2), $c = 6.577$ (2) Å,