*Acta Cryst.* (1996). **B52**, 697–706

# Structural, Kinetic and Thermodynamic Aspects of the Conformational Dimorphism of Diethyl 3,6-Dibromo-2,5-dihydroxyterephthalate

Christian Näther,[a] Norbert Nagel,[a] Hans Bock,[a]* Wolfgang Seitz[a] and Zdenek Havlas[b]

[a]*Institute of Inorganic Chemistry, Johann Wolfgang Goethe University, Marie-Curie-Strasse 11, D-60439 Frankfurt/Main, Germany, and* [b]*Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Flemingovo Nam 2, CR-1160 Prague 6, Czech Republic*

(*Received 18 October 1995; accepted 4 March 1996*)

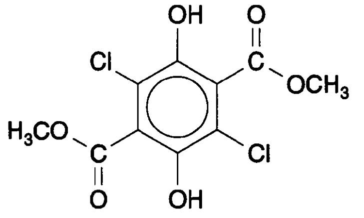
## Abstract

The crystal structures of the title compound and of its ethanol solvate have been determined by X-ray diffraction. The compound crystallizes in two different crystal forms (I: $P2_1/n$, high-temperature stable modification, II: $P2_1/c$, room-temperature stable modification), which differ in molecular conformation and hydrogen bonding. *Ab initio* calculations show that both observed conformations correspond to local energy minima and predict the conformation in polymorph (II) to be energetically more favourable. Packing energy calculations confirm that form (II) should be more stable than form (I). Crystals of both modifications and a solvate, containing 2 equiv. of ethanol, can be obtained by slow crystallization from ethanolic solution. Modification (II) transforms to (I) at 391 K, as shown by optical microscopy, powder diffraction and differential thermal analysis (DTA), whereas (I) melts at 429 K without previous transformation.

## 1. Introduction

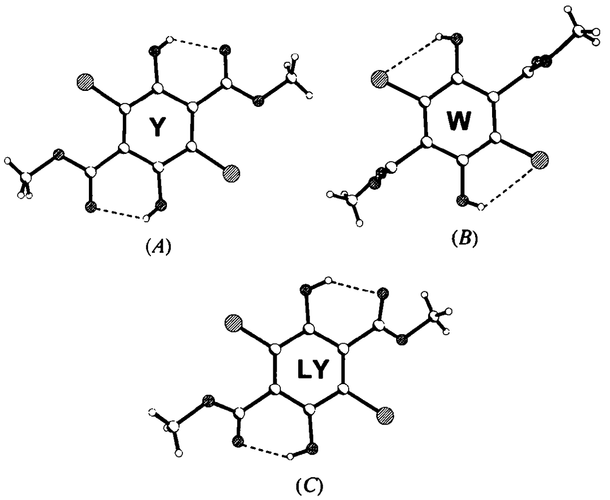
Polymorphism, defined as the ability of a compound to exist in more than one crystalline modification, is a widespread phenomenon. Polymorphic modifications often show different physical properties, such as solubility, density, optical behaviour and conductivity. Therefore, this phenomenon is important in a number of areas, such as pharmaceutical development (Haleblian & McCrone, 1969) and material science (Miyazaki, Watanabe & Miyata, 1988). Crystal structures of polymorphs provide information on intermolecular interactions in crystals and the influence of crystal environment on molecular conformation (Bernstein, 1987, 1993; Bernstein & Hagler, 1978; Hagler & Bernstein, 1978; Bar & Bernstein, 1984, 1987).

The conformational trimorphism of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate (1), for example, has been the subject of several studies.



(1)

At present, three modifications are known and structurally characterized: In the yellow form Y (2*A*) both ester groups are coplanar with the six-membered ring, forming two intramolecular hydrogen bonds to the hydroxy oxygen, whereas in the white form W (2*B*) both ester groups are twisted by ~90°, leading to intermolecular O—H···O plus weaker intramolecular O—H···Cl interactions (Hantzsch, 1915; Byrn, Curtin & Paul, 1972). In the third light yellow form LY (2*C*) both ester groups are twisted by ~40° out of the benzene plane, leading to intra- and intermolecular O—H···O hydrogen bonds (Yang, Richardson & Dunitz, 1985, 1989).



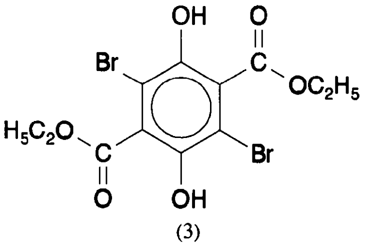
(*A*) (*B*)

(*C*)

(2)

Investigations of the phase transitions between these three forms (Byrn, Curtin & Paul, 1972; Richardson, Yang, Novotny-Bregger & Dunitz, 1990) established the order of thermodynamic stability at room temperature as Y > LY > W and at temperatures above 360 K as W > Y > LY. A topological description of thermodynamic aspects of this trimorphism as well as general rules for the corresponding phase-transition diagram have been discussed (Ceolin, Toscani, Agafonov & Dugue, 1992) and the mechanism of the phase transition Y → W has been investigated (Swiatkiewicz & Prasad, 1982). Crystal structure analysis of the three modifications shows that the transformations Y → W as well as LY → W are accompanied by extreme structural changes, which lead to the destruction of the crystals. Although the crystal structures of Y and LY are similar, it remains to be clarified whether the transformation Y → LY is a single-crystal to single-crystal transformation or not. The vibrational amplitudes of the ester groups in Y, which were estimated from the anisotropic displacement parameters as a function of temperature, are large enough to transform these groups into the LY conformation (Yang, Richardson & Dunitz, 1985, 1989).

In the present paper we report on the room-temperature crystal structures of two modifications of diethyl 3,6-dibromo-2,5-dihydroxyterephthalate (3), an intermediate product in the synthesis of tetracyano-*p*-benzoquinone (Seitz, 1995) as well as *ab initio* and packing energy calculations. The phase transition has been investigated by optical microscopy, differential thermal analysis (DTA) and powder diffraction. An ethanol solvate of the bromo ester has also been isolated and its crystal structure determined at 150 K.



(3)

## 2. Experimental

### 2.1. *Synthesis of diethyl 3,6-dibromo-2,5-dihydroxyterephthalate*

The bromo ester was synthesized as described by Seitz (1995). Recrystallization from ethanol yielded crystals with m.p. 429 K; elemental analysis: calc. H 2.94, C 34.98; obs. H 2.90, C 35.01; IR (KBr): 3200 s, 2950 m, 1670 s, 1410 s, 1350 s, 1190 s, 1140 s, 1090 m, 1000 s, 910 w, 850 m, 830 m, 780 w, 730 w, 660 w cm$^{-1}$; $^1$H NMR (250 MHz, $CDCl_3$): 8.94 (s, 2H; OH), 4,50 (q, 4H; $CH_2$), 1.45 (t, 6H; $CH_3$); $^{13}$C NMR (270 MHz, $CDCl_3$): C1/4: 121.5, C2/5: 148.6, C3/6: 109.6, C7/10: 166.6, C8/11: 63.0, C9/12: 14.0.

### 2.2. *Crystal structure analysis*

All crystal structure analyses were performed with a Stoe AED-II four-circle diffractometer (Mo $K\alpha$; 0.71073 Å; graphite monochromator) equipped with a low-temperature device from Oxford Instruments. Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Absorption was corrected by $\psi$ scans: *XEMP/SHELXTL/PC* (Sheldrick, 1990). Molecular graphics: *SHELXTL/PC/XP* (Sheldrick, 1990). Tables for publication: *SHELXL*93, *CIFTAB* (Sheldrick, 1993).

All structures were solved by direct methods using *SHELXS*86 (Sheldrick, 1985). Refinement was carried out against $F^2$ using *SHELXL*93 (Sheldrick, 1993). All, C, O and Br atoms were refined anisotropically. All hydrogens bound to carbon were placed in ideal positions and refined with a riding model and fixed isotropic displacement parameters. The hydroxy hydrogens were located from a difference map and refined with individual isotropic displacement parameters. The ester group (O12/O13/C18/C19) in (I) seems to be slightly disordered, but refinement using a split model was not successful.*

### 2.3. *Powder diffraction*

The powder diffraction measurements were carried out with a Stoe Stadi P diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.540561$ Å; scan range: $5 \leq 2\theta \leq 40^\circ$; step width 0.01°).

### 2.4. *Ab initio and packing energy calculations*

All *ab initio* calculations were performed at the HF-SCF level with *GAMESS* (Schmidt, Baldridge, Boatz, Elbert, Gordon, Jensen, Koseki, Matsunaga, Nguyen, Su, Windus, Dupuis & Montgomery, 1993) program package on an IBM RISC 6000. A MIDI split-valence double-zeta basis set was used. The geometries of both conformers have been totally optimized starting from the crystal structure data with hydrogen–carbon bond distances normalized to 1.09 Å. The fictitious structure with two intramolecular O—H···O hydrogen bonds was calculated from the optimized molecular structure in (II) by twisting the ester groups in the benzene ring plane.

The packing coefficients $C_K$ (Kitaigorodski, 1961) were calculated using the program *OPEC* (Gavezzotti, 1983, 1985). The packing energies were calculated using a 6-exp-potential (Gavezzotti & Filippini, 1994; Filippini & Gavezzotti, 1993; Gavezzotti, 1975) according to the atom–atom potential method (Pertsin & Kitaigorodski, 1986) with *OPEC*. The hydrogen-bond distances were normalized to 1.08 Å for C—H and to 1.00 Å for O—H.

---

* Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SE0188). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental details*

| | (I) | (II) | Ethanol solvate |
|---|---|---|---|
| Crystal data | | | |
| Chemical formula | $C_{12}H_{12}Br_2O_6$ | $C_{12}H_{12}Br_2O_6$ | $C_{12}H_{12}Br_2O_6.2C_2H_6O$ |
| Chemical formula weight | 412.04 | 412.04 | 504.17 |
| Cell setting | Monoclinic | Monoclinic | Triclinic |
| Space group | $P2_1/n$ | $P2_1/c$ | $P\bar{1}$ |
| $a$ (Å) | 9.622 (1) | 8.267 (1) | 8.002 (2) |
| $b$ (Å) | 7.853 (1) | 25.037 (4) | 8.232 (2) |
| $c$ (Å) | 19.103 (3) | 7.526 (1) | 8.966 (2) |
| $\alpha$ (°) | | | 116.82 (3) |
| $\beta$ (°) | 93.11 (1) | 113.44 (1) | 96.10 (3) |
| $\gamma$ (°) | | | 102.29 (3) |
| $V$ (Å$^3$) | 1441.3 (3) | 1429.2 (3) | 500.9 (2) |
| $Z$ | 4 | 4 | 1 |
| $D_x$ (Mg m$^{-3}$) | 1.899 | 1.915 | 1.671 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 |
| No. of reflections for cell parameters | 78 | 112 | 68 |
| $\theta$ range (°) | 14–17 | 15–19 | 19–22.5 |
| $\mu$ (mm$^{-1}$) | 5.645 | 5.693 | 4.084 |
| Temperature (K) | 293 (2) | 293 (2) | 150 (2) |
| Crystal form | Block | Prism | Prism |
| Crystal size (mm) | 0.4 × 0.3 × 0.3 | 0.5 × 0.4 × 0.3 | 0.5 × 0.4 × 0.3 |
| Crystal colour | Colourless | Colourless/light violet | Colourless |
| Data collection | | | |
| Diffractometer | Stoe AED–II | Stoe AED–II | Stoe AED–II |
| Data collection method | $\theta/2\theta$ | $\theta/2\theta$ | $\theta/2\theta$ |
| Absorption correction | $\psi$ scans (Sheldrick, 1990) | $\psi$ scans (Sheldrick, 1990) | $\psi$ scans (Sheldrick, 1990) |
| $T_{min}$ | 0.169 | 0.475 | 0.383 |
| $T_{max}$ | 0.244 | 0.660 | 0.522 |
| No. of measured reflections | 2876 | 7088 | 3556 |
| No. of independent reflections | 2546 | 4126 | 3328 |
| No. of observed reflections | 1892 | 2850 | 3001 |
| Criterion for observed reflections | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ |
| $R_{int}$ | 0.0140 | 0.0197 | 0.0527 |
| $\theta_{max}$ (°) | 25.01 | 30.03 | 32.52 |
| Range of $h$, $k$, $l$ | $-11 \rightarrow h \rightarrow 11$<br>$-5 \rightarrow k \rightarrow 9$<br>$0 \rightarrow l \rightarrow 22$ | $0 \rightarrow h \rightarrow 11$<br>$-33 \rightarrow k \rightarrow 29$<br>$-10 \rightarrow l \rightarrow 9$ | $0 \rightarrow h \rightarrow 11$<br>$-12 \rightarrow k \rightarrow 12$<br>$-13 \rightarrow l \rightarrow 13$ |
| No. of standard reflections | 4 | 4 | 4 |
| Frequency of standard reflections (min) | 120 | 120 | 120 |
| Intensity decay (%) | <1 | <1 | <1 |
| Refinement | | | |
| Refinement on | $F^2$ | $F^2$ | $F^2$ |
| $R[F^2 > 2\sigma(F^2)]$ | 0.0490 | 0.0393 | 0.0429 |
| $wR(F^2)$ | 0.1391 | 0.1176 | 0.1257 |
| $S$ | 1.144 | 1.106 | 1.126 |
| No. of reflections used in refinement | 2546 | 4124 | 3327 |
| No. of parameters used | 186 | 189 | 120 |
| H-atom treatment | H atoms treated using a riding model | H atoms treated using a riding model | H atoms treated using a riding model |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0804P)^2 + 3.0422P]$, where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0792P)^2 + 0.8769P]$, where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0834P)^2 + 0.7709P]$, where $P = (F_o^2 + 2F_c^2)/3$ |
| $(\Delta/\sigma)_{max}$ | −0.001 | −0.001 | −0.001 |
| $\Delta\rho_{max}$ (e Å$^{-3}$) | 1.023 | 0.553 | 1.042 |
| $\Delta\rho_{min}$ (e Å$^{-3}$) | −0.904 | −0.926 | −2.603 |
| Extinction method | *SHELXL*93 (Sheldrick, 1993) | None | None |
| Extinction coefficient | 0.0017 (6) | – | – |
| 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) |

### 2.5. *Thermochemical measurements and optical microscopy*

The thermochemical measurements were carried out with a Mettler thermoanalytical System TA3000 with TC10A processor. Optical microscopy was performed with a Kofler heating unit from Wagner and Munz.

## 3. Results

### 3.1. *Crystallization and morphology*

Single crystals of (I) were obtained from several solvents such as ethanol, ethyl acetate, dimethoxyethane and an acetone–water mixture. The crystallization of

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$) *for (I)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| Br1 | 0.80829 (7) | −0.64140 (9) | 0.46781 (4) | 0.0668 (3) |
| O1 | 0.5528 (5) | −0.5923 (5) | 0.3642 (2) | 0.0503 (10) |
| O2 | 0.2292 (5) | −0.5949 (5) | 0.3626 (2) | 0.0645 (13) |
| O3 | 0.2786 (4) | −0.3167 (5) | 0.3625 (2) | 0.0567 (11) |
| C1 | 0.4004 (6) | −0.4850 (6) | 0.4455 (3) | 0.0393 (12) |
| C2 | 0.5289 (6) | −0.5509 (6) | 0.4318 (3) | 0.0404 (12) |
| C3 | 0.6290 (5) | −0.5640 (6) | 0.4869 (3) | 0.0399 (11) |
| C7 | 0.2920 (6) | −0.4745 (7) | 0.3856 (3) | 0.0466 (13) |
| C8 | 0.1760 (8) | −0.2833 (10) | 0.3046 (4) | 0.068 (2) |
| C9 | 0.0434 (8) | −0.2450 (13) | 0.3334 (5) | 0.100 (3) |
| Br11 | 0.18413 (7) | 0.14013 (9) | 0.51466 (4) | 0.0688 (3) |
| O11 | 0.3404 (4) | 0.0793 (5) | 0.3795 (2) | 0.0518 (10) |
| O12 | 0.6417 (5) | 0.0847 (5) | 0.3293 (2) | 0.0597 (12) |
| O13 | 0.6042 (5) | −0.1941 (5) | 0.3416 (2) | 0.0675 (13) |
| C11 | 0.5498 (6) | −0.0204 (6) | 0.4342 (3) | 0.0399 (12) |
| C12 | 0.4174 (5) | 0.0453 (6) | 0.4396 (3) | 0.0391 (11) |
| C13 | 0.3675 (5) | 0.0639 (6) | 0.5068 (3) | 0.0410 (12) |
| C17 | 0.6036 (6) | −0.0352 (7) | 0.3617 (3) | 0.0448 (13) |
| C18 | 0.6559 (9) | −0.2316 (10) | 0.2724 (4) | 0.082 (2) |
| C19 | 0.5421 (9) | −0.2802 (16) | 0.2247 (4) | 0.110 (4) |

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$) *for (II)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| Br1 | −0.21176 (5) | −0.055462 (14) | −0.10064 (6) | 0.05055 (14) |
| Br2 | 0.06988 (5) | −0.30089 (2) | −0.04748 (6) | 0.05305 (14) |
| O1 | −0.4172 (3) | −0.15299 (10) | −0.1047 (4) | 0.0457 (6) |
| O2 | −0.4689 (4) | −0.25235 (11) | −0.0697 (5) | 0.0582 (8) |
| O3 | −0.2925 (3) | −0.31227 (10) | −0.1148 (4) | 0.0462 (6) |
| O4 | 0.2539 (3) | −0.19808 (10) | −0.0435 (4) | 0.0434 (5) |
| O5 | 0.2469 (4) | −0.07049 (12) | 0.0617 (4) | 0.0524 (6) |
| O6 | 0.1416 (4) | −0.08794 (11) | −0.2568 (4) | 0.0468 (6) |
| C1 | −0.2016 (4) | −0.22187 (12) | −0.0816 (4) | 0.0331 (6) |
| C2 | −0.2555 (4) | −0.16802 (13) | −0.0893 (5) | 0.0347 (6) |
| C3 | −0.1392 (4) | −0.12712 (12) | −0.0870 (5) | 0.0342 (6) |
| C4 | 0.0279 (4) | −0.13818 (12) | −0.0762 (5) | 0.0340 (6) |
| C5 | 0.0848 (4) | −0.19098 (13) | −0.0623 (5) | 0.0343 (6) |
| C6 | −0.0292 (4) | −0.23232 (12) | −0.0679 (4) | 0.0319 (6) |
| C7 | −0.3331 (4) | −0.26337 (13) | −0.0889 (5) | 0.0363 (6) |
| C8 | −0.4160 (5) | −0.35488 (14) | −0.1202 (6) | 0.0443 (8) |
| C9 | −0.3355 (6) | −0.40589 (15) | −0.1421 (7) | 0.0545 (9) |
| C10 | 0.1528 (4) | −0.09444 (13) | −0.0773 (5) | 0.0370 (6) |
| C11 | 0.2599 (6) | −0.0487 (2) | −0.2846 (7) | 0.0578 (11) |
| C12 | 0.2452 (10) | −0.0540 (2) | −0.4864 (10) | 0.083 (2) |

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$) *for ethanol solvate*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| Br1 | −0.16378 (3) | −0.06760 (4) | −0.37913 (3) | 0.02093 (11) |
| O1 | −0.3406 (2) | −0.2367 (3) | −0.1631 (2) | 0.0155 (3) |
| O2 | −0.2975 (3) | −0.1279 (3) | 0.2497 (3) | 0.0171 (3) |
| O3 | −0.1928 (2) | −0.3674 (2) | 0.0887 (3) | 0.0149 (3) |
| C1 | −0.0998 (3) | −0.0886 (3) | 0.0740 (3) | 0.0093 (3) |
| C2 | −0.1740 (3) | −0.1190 (3) | −0.0879 (3) | 0.0096 (3) |
| C3 | −0.0708 (3) | −0.0293 (3) | −0.1611 (3) | 0.0099 (4) |
| C7 | −0.2084 (3) | −0.1938 (3) | 0.1488 (3) | 0.0103 (4) |
| C8 | −0.2927 (3) | −0.4910 (3) | 0.1459 (3) | 0.0160 (4) |
| C9 | −0.2729 (4) | −0.6853 (4) | 0.0389 (4) | 0.0235 (5) |
| O4 | −0.4105 (3) | 0.2023 (3) | 0.3530 (3) | 0.0227 (4) |
| C11 | −0.3702 (4) | 0.2946 (5) | 0.5366 (4) | 0.0238 (5) |
| C12 | −0.1765 (4) | 0.3963 (5) | 0.6124 (5) | 0.0310 (7) |

(II) is more difficult to reproduce: recrystallization from a concentrated ethanolic solution always yields first crystals of (I), which transform over 1 week to crystals of (II). Most of these crystals contain adhered small crystals of (I). When single crystals of both forms were placed simultaneously in a saturated ethanolic solution, first crystals of form (I) were replaced by crystals of form (II), but before complete transformation crystals of a new form appear, containing 2 molar equiv. of ethanol. The crystals of both modifications can be separated by hand according to their colour and morphology. Crystals of (I) mostly form colourless plates or blocks, whereas those of (II) crystallize as prisms, which are colourless on (010) and light violet on (100), (011) and (01$\bar{1}$).

### 3.2. *Crystal structure of (I)*

Modification (I) crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. The asymmetric unit contains two independent molecular halves, each located around a centre of inversion. The ester groups of the two molecules are twisted out of the ring plane by 77.2 (3) and 75.4 (4)° (Figs. 1*a* and *b*) and represent the antiperiplanar arrangement normally found for such esters [$\omega$(C1—C7—O3—C8) 179.3 (5), $\omega$(C11—C17—O13—C18) −179.0 (6)° (Schweizer & Dunitz, 1982)]. The orientations of the ethyl groups differ distinctly: in one molecule they point towards the bromine substituent [$\omega$(C7—O3—C8—C9) 89.2 (8)°], in the other towards the hydroxyl group [$\omega$(C17—O13—C18—C19) 108.7 (8)°]. Thus, the ethyl groups do not adopt an antiperiplanar conformation, which represents the global energy minimum for such esters, but a conformation corresponding to a second local energy minimum (Wilson, 1972). The hydroxyl substituents exhibit torsion angles of $\omega$(C3—C2—O1—HO1) 42 (4) and $\omega$(C13—C12—O11—HO11) 48 (4)° and are oriented towards the bromine substituents. The intramolecular distances Br1···O1 are 3.096 (4) and Br11···O11 3.095 (4) Å, and the distances Br1···HO1 are 2.78 (4) and Br11···HO11 2.83 (4) Å. Due to steric interactions between the bromine substituents and the hydroxyl groups, the angles C3—C2—O1 and C13—C12—O11 are widened to 123.6 (5) and 123.7 (5)° (Table 5).

In the crystal structure of (I), the molecules are stacked nearly perpendicular to (010) (Figs. 1*c* and *d*) with interplanar angles of 13.8 (3)° between the six-membered rings of adjacent molecules within a stack and are connected by intermolecular O—H···O hydrogen bonds between the O—H substituents and the carbonyl O centres. Within these stacks, each hydrogen of the hydroxyl substituents coordinates to one molecule below or above. The intermolecular O···O distances of 2.770 (6) and 2.785 (6) Å, as well as the O···H

Table 5. *Selected geometric parameters (Å, °) for (I)*

| | | | |
|---|---|---|---|
| Br1—C3 | 1.883 (5) | Br11—C13 | 1.877 (5) |
| O1—C2 | 1.363 (6) | O11—C12 | 1.359 (7) |
| O2—C7 | 1.193 (7) | O12—C17 | 1.196 (6) |
| O3—C7 | 1.319 (7) | O13—C17 | 1.306 (7) |
| O3—C8 | 1.465 (8) | O13—C18 | 1.468 (7) |
| C1—C2 | 1.378 (8) | C11—C12 | 1.384 (7) |
| C1—C3$^{i}$ | 1.392 (7) | C11—C13$^{ii}$ | 1.386 (8) |
| C1—C7 | 1.508 (7) | C11—C17 | 1.509 (7) |
| C2—C3 | 1.392 (7) | C12—C13 | 1.402 (7) |
| C3—C1$^{i}$ | 1.392 (7) | C13—C11$^{ii}$ | 1.386 (8) |
| C8—C9 | 1.447 (11) | C18—C19 | 1.437 (11) |
| C7—O3—C8 | 118.0 (5) | C17—O13—C18 | 117.7 (5) |
| C2—C1—C3$^{i}$ | 120.6 (5) | C12—C11—C13$^{ii}$ | 121.4 (5) |
| C2—C1—C7 | 117.8 (5) | C12—C11—C17 | 117.4 (5) |
| C3$^{i}$—C1—C7 | 121.5 (5) | C13$^{ii}$—C11—C17 | 121.1 (5) |
| O1—C2—C1 | 117.9 (5) | O11—C12—C11 | 118.2 (5) |
| O1—C2—C3 | 123.6 (5) | O11—C12—C13 | 123.7 (5) |
| C1—C2—C3 | 118.4 (5) | C11—C12—C13 | 117.9 (5) |
| C2—C3—C1$^{i}$ | 120.9 (5) | C11$^{ii}$—C13—C12 | 120.6 (5) |
| C2—C3—Br1 | 118.8 (4) | C11$^{ii}$—C13—Br11 | 120.9 (4) |
| C1$^{i}$—C3—Br1 | 120.2 (4) | C12—C13—Br11 | 118.5 (4) |
| O2—C7—O3 | 125.7 (5) | O12—C17—O13 | 126.4 (5) |
| O2—C7—C1 | 123.5 (5) | O12—C17—C11 | 123.0 (5) |
| O3—C7—C1 | 110.9 (5) | O13—C17—C11 | 110.6 (5) |
| C9—C8—O3 | 108.8 (6) | C19—C18—O13 | 109.9 (6) |

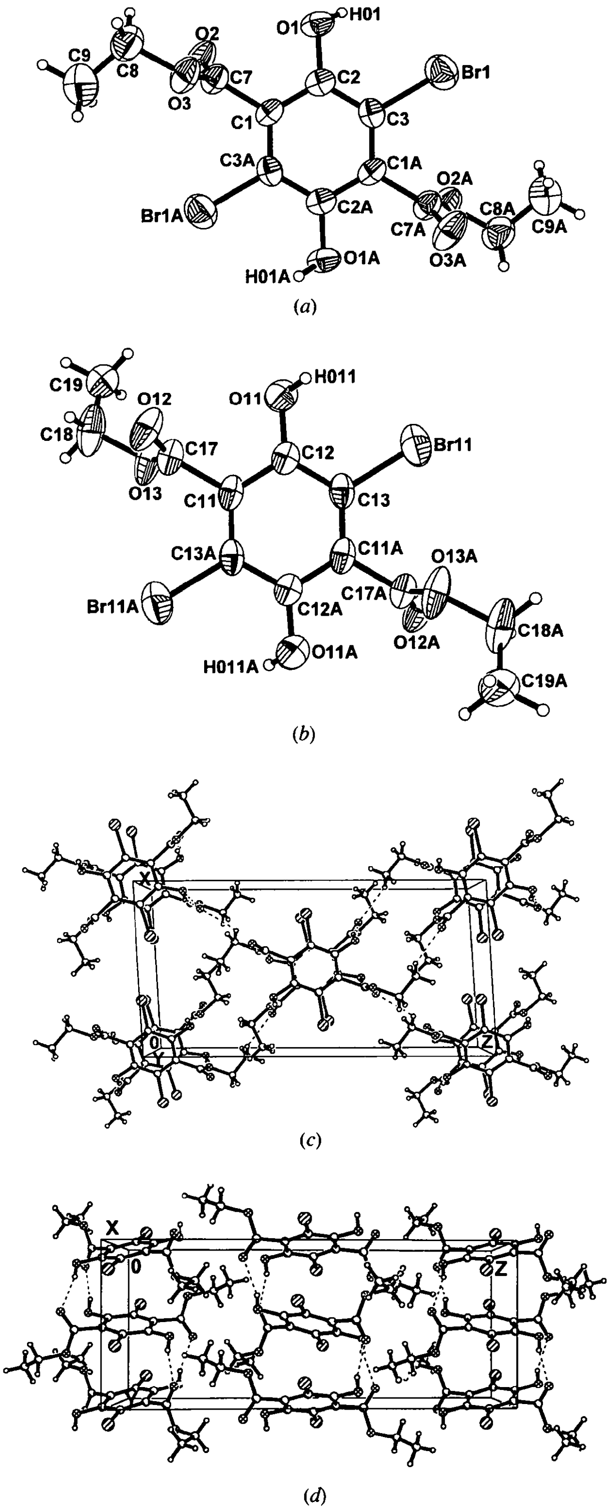
Symmetry codes: (i) $1 - x, -1 - y, 1 - z$; (ii) $1 - x, -y, 1 - z$.

distances of 2.01 (2) and 1.99 (1) Å, suggest a rather weak interaction (Ichikawa, 1978). The O—H···O angles are 154 (4) and 163 (4)°. The C=O···H angles are 118 (1) and 119 (1)° and it is the anti lone pair of the carbonyl O that is involved.

### 3.3. *Crystal structure of (II)*

Modification (II) crystallizes in the monoclinic space group $P2_1/c$ ($Z = 4$) with one molecule in the asymmetric unit. The conformations of both ester groups differ: one is twisted out of the benzene plane by 84.3 (2)°, the other by only 11.9 (3)° (Fig. 2*a*). This conformation corresponds to the mixed conformational species of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate proposed to occur in solution, with one intramolecular O—H···Hal and one O—H···O hydrogen bond (Curtin & Byrn, 1969*a*,*b*) and differs significantly from those found in the three modifications of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate (Yang, Richardson & Dunitz, 1985, 1989).

Both ester groups exhibit an s-*cis* conformation. The six-membered ring is planar to within 0.014 (2) Å. One hydroxy group is engaged in hydrogen bonding to the carbonyl oxygen of the coplanar ester group [O1···O2 2.556 (4), O2···H01 1.94 (4) Å]. Steric demands enforce an O1—H01···O2 angle of only 131 (4)°. The hydrogen involved lies close to the plane of the benzene ring [$\omega$(C1—C2—O1—H01) 20 (5)°]. The widening of the C1—C2—O1 angle to 123.7 (3)° is due to steric interaction with the carbonyl oxygen (Table 6). Due to the twist of the second ester group, an intramolecular O—H···O hydrogen bond can no longer be formed and the hydroxy hydrogen is therefore oriented towards the



(*a*)

(*b*)

(*c*)

(*d*)

Fig. 1. Diethyl 3,6-dibromo-2,5-dihydroxyterephthalate (I): (*a*) and (*b*) crystallographically independent molecules projected onto the mean plane of the six-membered ring with labelling and displacement ellipsoids shown at the 50% probability level (room temperature); (*c*) crystal structure viewed along the *b* axis; (*d*) along the *a* axis (C: ; Br: ; O: ).

bromine substituent with a C6—C5—O4—H04 torsional angle of 3 (4)°. The O4· · ·Br2 distance of 2.984 (3) Å is shorter than the sum of the corresponding van der Waals radii by *ca* 0.058 Å (Bondi, 1964) and the H04· · ·Br2 distance of 2.441 (4) Å indicates an O—H· · ·Br hydrogen bond. Steric interactions also expand the C6—C5—O4 angle to 124.2 (3)°.

In the crystal structure of (II) the molecules are arranged in displaced stacks almost parallel to [001].

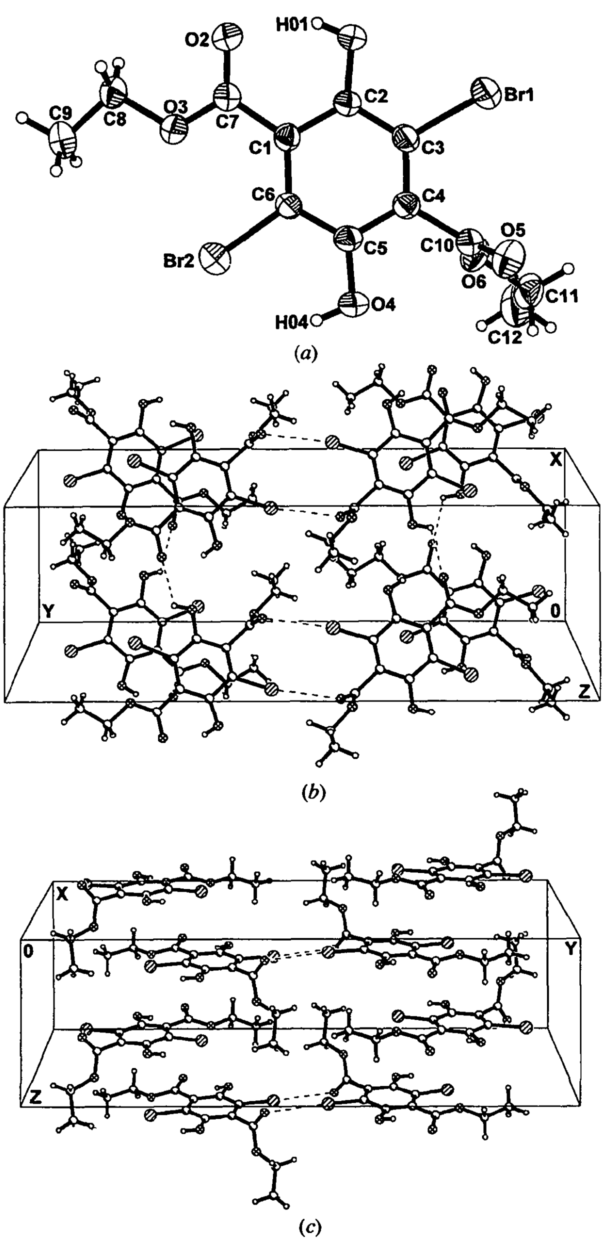


Fig. 2. Diethyl 3,6-dibromo-2,5-dihydroxyterephthalate (II): (*a*) projection onto the mean plane of the six-membered ring with labelling and displacement ellipsoids shown at the 50% probability level (room temperature); (*b*) crystal structure with view on (001); (*c*) on (100) (C: ○ ; Br: ◌ ; O: ▨ ).

Table 6. *Selected geometric parameters (Å, °) for (II)*

| | | | |
|---|---|---|---|
| Br1—C3 | 1.881 (3) | C1—C6 | 1.412 (4) |
| Br2—C6 | 1.882 (3) | C1—C2 | 1.414 (4) |
| O1—C2 | 1.348 (4) | C1—C7 | 1.489 (4) |
| O2—C7 | 1.220 (4) | C2—C3 | 1.400 (4) |
| O3—C7 | 1.304 (4) | C3—C4 | 1.379 (4) |
| O3—C8 | 1.466 (4) | C4—C5 | 1.393 (4) |
| O4—C5 | 1.360 (4) | C4—C10 | 1.508 (4) |
| O5—C10 | 1.188 (4) | C5—C6 | 1.389 (4) |
| O6—C10 | 1.327 (4) | C8—C9 | 1.480 (5) |
| O6—C11 | 1.460 (4) | C11—C12 | 1.481 (7) |
| C7—O3—C8 | 118.0 (3) | O4—C5—C6 | 124.2 (3) |
| C10—O6—C11 | 116.7 (3) | O4—C5—C4 | 115.7 (3) |
| C6—C1—C2 | 118.2 (3) | C6—C5—C4 | 120.0 (3) |
| C6—C1—C7 | 125.0 (3) | C5—C6—C1 | 121.1 (3) |
| C2—C1—C7 | 116.8 (3) | C5—C6—Br2 | 114.2 (2) |
| O1—C2—C3 | 116.7 (3) | C1—C6—Br2 | 124.7 (2) |
| O1—C2—C1 | 123.7 (3) | O2—C7—O3 | 122.2 (3) |
| C3—C2—C1 | 119.5 (3) | O2—C7—C1 | 122.1 (3) |
| C4—C3—C2 | 121.4 (3) | O3—C7—C1 | 115.7 (3) |
| C4—C3—Br1 | 119.0 (2) | O3—C8—C9 | 107.0 (3) |
| C2—C3—Br1 | 119.6 (2) | O5—C10—O6 | 126.2 (3) |
| C3—C4—C5 | 119.7 (3) | O5—C10—C4 | 124.9 (3) |
| C3—C4—C10 | 121.7 (3) | O6—C10—C4 | 108.9 (3) |
| C5—C4—C10 | 118.6 (3) | O6—C11—C12 | 107.5 (4) |

There is a short intermolecular Br· · ·O distance to the carbonyl oxygen of 3.191 (3) Å (Figs. 2*b* and *c*). The corresponding angles C—Br· · ·O and Br· · ·O—C of 167.4 (1) and 121.9 (2)° are compatible with an electrophile-nucleophile interaction (Hassel & Romming, 1967; Leser & Rabinovich, 1978; Ramasubbu, Parthasarathy & Murray-Rust, 1986) with the bromine acting as the acceptor and the oxygen as the donor. There are additional intermolecular O—H· · ·O contacts with distances of 2.61 (3) and 2.28 (1) Å between the hydroxyl hydrogen and the carbonyl oxygen of the ester group. The O· · ·O distances of 3.142 (3) and 2.737 (3) Å, as well as the O—H· · ·O angles of 124 (3) and 116 (1)°, indicate a rather weak interaction (Ichikawa, 1978).

### 3.4. *Crystal structure of diethyl 3,6-dibromo-2,5-dihydroxyterephthalate bis(ethanol)*

Diethyl 3,6-dibromo-2,5-dihydroxyterephthalate bis(ethanol) crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit contains a half molecule around a centre of inversion and one ethanol molecule in a general position. Both ester groups are twisted out of the benzene plane by $\omega$(C2—C1—C7=O3) 83.4 (3)° (Fig. 3*a*) and the hydroxy hydrogen by $\omega$(H10—O1—C2—C3) 29 (3)°. The hydroxy hydrogen points approximately towards the bromine substituent. The intramolecular O1· · ·Br1 distance of 3.142 (2) Å as well as the H01· · ·Br1 distance of 273 (2) Å indicate an intramolecular O—H· · ·Br hydrogen bond. Steric interactions enlarge the C3—C2—O1 angle to 125.2 (2)° (Table 7).

In this crystal structure the molecules are arranged in parallel chains along the *c* axis (Fig. 3*b*). Within these chains there are short intermolecular Br· · ·O distances of 3.161 (2) Å between the bromine substituents and the

Table 7. *Selected geometric parameters (Å, °) for ethanol solvate*

| | | | |
|---|---|---|---|
| Br1—C3 | 1.874 (2) | C1—C2 | 1.396 (3) |
| O1—C2 | 1.356 (3) | C1—C7 | 1.511 (3) |
| O2—C7 | 1.216 (3) | C2—C3 | 1.397 (3) |
| O3—C7 | 1.321 (3) | C3—C1$^{i}$ | 1.393 (3) |
| O3—C8 | 1.465 (3) | C8—C9 | 1.503 (4) |
| C1—C3$^{i}$ | 1.393 (3) | O4—C11 | 1.430 (4) |
| C7—O3—C8 | 117.5 (2) | C1$^{i}$—C3—C2 | 121.0 (2) |
| C3$^{i}$—C1—C2 | 121.2 (2) | C1$^{i}$—C3—Br1 | 119.6 (2) |
| C3$^{i}$—C1—C7 | 121.0 (2) | C2—C3—Br1 | 119.4 (2) |
| C2—C1—C7 | 117.7 (2) | O2—C7—O3 | 125.0 (2) |
| O1—C2—C1 | 117.0 (2) | O2—C7—C1 | 124.8 (2) |
| O1—C2—C3 | 125.2 (2) | O3—C7—C1 | 110.3 (2) |
| C1—C2—C3 | 117.8 (2) | O3—C8—C9 | 106.1 (2) |

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

carbonyl oxygens of neighbouring molecules. The C—Br···O and Br···O—C angles are 176.56 (8) and 114.6 (2)°, and the intermolecular Br···Br distance and C—Br···Br angle are 3.866 (1) Å and 117.40 (7)°. This structural motif is similar to that in the crystal structure of (II) and is also compatible with an electrophile–nucleophile interaction (Hassel & Romming, 1967; Leser & Rabinovich, 1978; Ramasubbu, Parthasarathy & Murray-Rust, 1986). One fundamental difference to the crystal structure of (II) derives from the fact that in the solvated compound (Fig. 3*b*) both ester groups are twisted out of the benzene plane and, therefore, an infinite chain of molecules connected by Br···O contacts is formed. In the crystal structure of (II) (Fig. 2*c*) only one ester group is twisted out of the ring plane and, therefore, only dimers occur.

The hydroxy hydrogen of the ethanol molecule forms a hydrogen bond to the carbonyl oxygen of the ester group [O2···H04 1.995 (3), O2···O4 2.832 (3) Å]. The O4—H4···O2 angle is 174 (1)°, with hydrogen oriented towards the carbonyl oxygen lone pair [C7—O2···H04 130 (1)°]. In addition, the oxygen of the ethanol molecule acts as a hydrogen-bond acceptor for the hydroxy hydrogen of another bromo ester [O4···H01 1.854 (7), O4···O1 2.628 (3) Å, O1—H01···O4 152 (4)°].

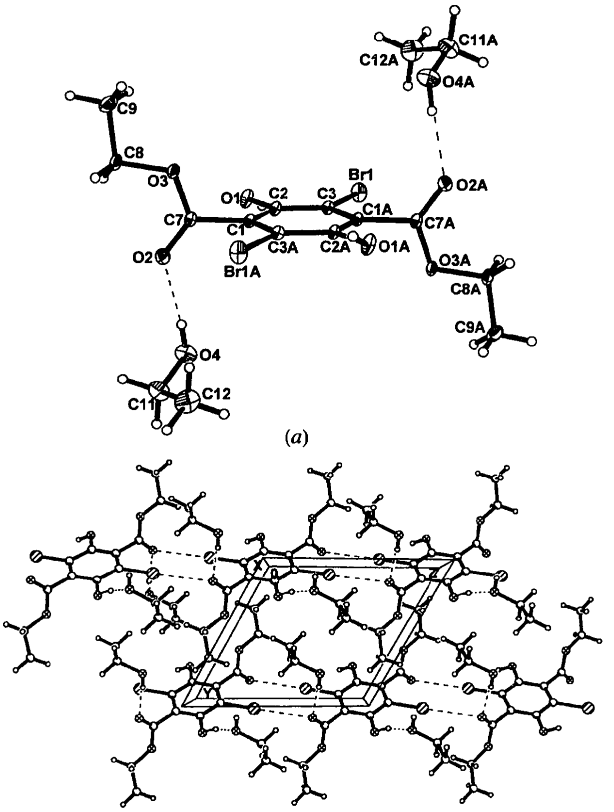
### 3.5. *Ab initio and packing energy calculations*

*Ab initio* calculations for the three observed conformers demonstrate that they all represent local energy minima with the optimized structures very close to the experimental ones. The calculations predict the molecular structure in (II) to be energetically more favourable than in (I) by 15 kJ mol$^{-1}$. The difference between the two conformations in form (I) is only *ca* 0.5 kJ mol$^{-1}$. An additional calculation for the non-observed structure with two intramolecular O—H···O hydrogen bonds predicts this to be more favourable by ~30 kJ mol$^{-1}$ than the conformation in form (I).

The packing energy is calculated to be ~−61 kJ mol$^{-1}$ for (II) and ~−54 kJ mol$^{-1}$ for (I). This small difference of 7 kJ mol$^{-1}$ is in the normal range for polymorphic modifications of organic compounds (Kuhnert-Brandstatter, 1971; Gavezzotti & Filippini, 1995). In agreement with these results, the calculated density $\rho$ and packing coefficient $C_K$ of form (II) ($\rho = 1.915$ g cm$^{-3}$, $C_K = 0.725$) are larger than of form (I) ($\rho = 1.899$ g cm$^{-3}$, $C_K = 0.717$).

### 3.6. *Phase transformations*

Heating single crystals of (II) to ~391 K usually causes a two-step phase transformation. Originating at crystal defects, a wave moves through the crystal, which does not change its transparency. Attempts to stop the process at this stage remained unsuccessful. In the second step, the crystal becomes full of cracks. Optical microscopy with polarized light as well as X-ray methods indicate that the transformed material no longer consists of single crystals. The way in which the transformation proceeds depends predominantly on the crystal quality. In some crystals a uniform wavefront moves from one end of the crystal to the other. If the crystal contains optical defects, various



(*a*)

(*b*)

Fig. 3. Diethyl 3,6-dibromo-2,5-dihydroxyterephthalate bis(ethanol): (*a*) molecular structure with labelling and displacement ellipsoids shown at the 50% probability level (150 K); (*b*) crystal structure with view along the *a* axis (C: ○; Br: ◌; O: ▨).

wavefronts starting at the defects pass through the crystal in different directions. The powder diffraction pattern of transformed single crystals of form (II) (Fig. 4*a*) corresponds to the pattern calculated for form (I) (Fig. 4*b*).

In agreement with this result, DTA measurements show an endothermic peak at ~391 K, corresponding to the transformation (II)→(I) and a second endothermic peak at ~428 K, which corresponds to the melting point of (I). The peak width and shape as well as the transformation temperature depends on the crystal quality and the heating rate. DTA measurements at different heating rates provide no hints for two different successive transformations.

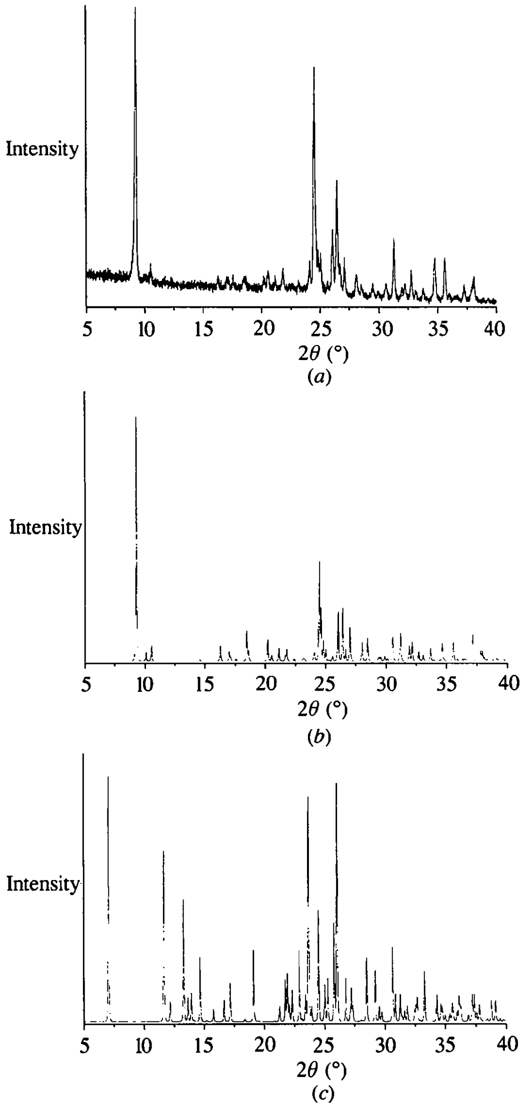


Fig. 4. (*a*) Measured powder diffraction patterns for transformed single crystals of (II), (*b*) calculated powder diffraction pattern from single crystal data for (I) and (*c*) for (II).

After the transformation (II)→(I) was completed (Fig. 5i) and the sample cooled to room temperature, the transformation was not observed again on repeated heating (Fig. 5ii). Slow cooling of the melt always leads to form (I) accompanied by supercooling (Fig. 5iii). Form (I) is also obtained by rapid freezing of the melt. These results are substantiated by the powder diffraction patterns of such samples, which correspond to the pattern calculated for form (I). On heating the solidified melt again, no transformation was observed (Fig. 5iv). The melting point of (II) could not be determined, because this modification always transforms to modification (I).

In agreement with these results, DTA measurements on single crystals of form (I) obtained by crystallization from solution show no phase transition in the range between room temperature and the melting point of 429 K (Fig. 6).

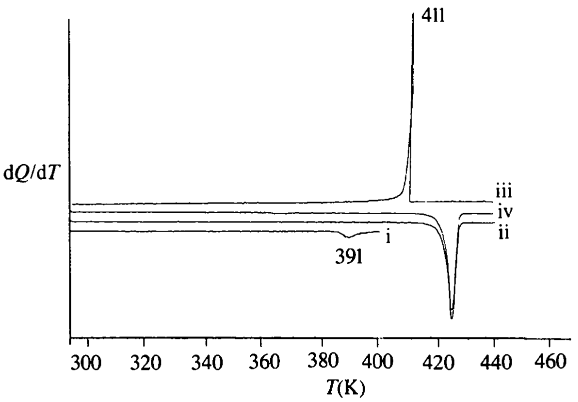


Fig. 5. Typical DTA curves measured for single crystals of (II) between 293 and 443 K (2 K $\mathrm{min}^{-1}$, 13.41 mg): (i) heating to 403 K, (ii) heating after cooling to 293 K, (iii) cooling curve and (iv) repeated heating curve.

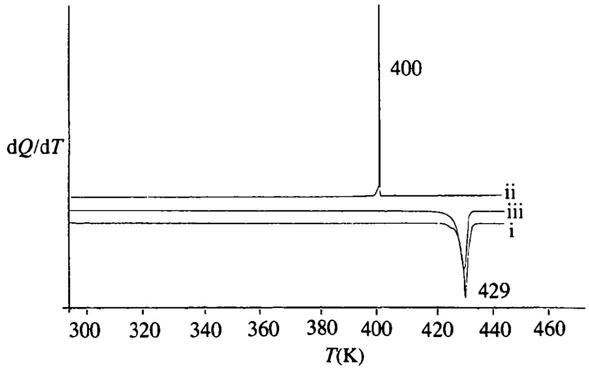


Fig. 6. Typical DTA curves measured for (I) between 293 and 443 K (2 K $\mathrm{min}^{-1}$, 15.59 mg): (i) heating curve, (ii) cooling curve and (iii) repeated heating curve.

## 4. Discussion

The conformational polymorphism of the dialkyl 3,6-dihalogenated 2,5-dihydroxytherephthalates seems to originate from their ability to form different intra- and intermolecular hydrogen-bond patterns as well as halogen–oxygen and halogen–halogen interactions.

The conformation in form (I) (Figs. 1*a* and *b*) corresponds to the conformation in W (2*B*) of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate with two intramolecular O—H···halogen interactions as well as intermolecular O—H···O hydrogen bonds. Both crystal structures contain two independent molecules in the asymmetric unit, each located around a centre of inversion. In addition, their crystal packing is similar: In both structures the molecules are stacked in columns and connected by intermolecular hydrogen bonds O—H···O to adjacent molecules within the stacks.

In contrast, the conformation in (II) with one ester group almost perpendicular to the benzene plane and the other in-plane leads to a completely different crystal packing (Fig. 2*a*) than in Y with both ester groups in-plane (2*A*) and in LY with both slightly out-of-plane (2*C*). In Y and LY intermolecular O—H···O hydrogen bonding between the hydroxy hydrogen and the carbonyl oxygen leads to infinite chains and in Y adjacent chains are linked by additional Cl···Cl interactions. On the contrary, the crystal structure of (II) is built up by dimers of molecules, which are connected by intermolecular O···Br interactions (Fig. 2*b* and *c*). In addition, weak intermolecular O—H···O bonds are formed.

The conformation of the ester groups in the ethanol solvate (Fig. 3*a*) is similar to those found in (I) and W, but the ethanol molecules prevent a stacking of the ester molecules perpendicular to their ring planes. Here, both ester groups are involved in intermolecular O···Br interactions, which lead to infinite chains instead of dimers (Fig. 3*b*).

A conformation with two intramolecular O—H···O hydrogen bonds and both ester groups in-plane of the benzene ring, which is predicted by *ab initio* calculations to be the energetically most favourable, is not observed in the crystal structures of the bromo ester. Possibly, a third modification exists at lower temperatures.

Concerning the thermodynamic aspects of the dimorphism in the bromo esters, the crystallization experiments as well as the DTA measurements show that form (II) is the thermodynamically stable modification at room temperature, form (I) the metastable one and that the system is enantiotropic. This order of stability is in agreement with the calculated densities and packing coefficients for both modifications. According to Ostwalds' law of stages (Ostwald, 1897), the less stable modification should crystallize first from a supersaturated solution. As the crystallization proceeds, this modification transforms *via* dissolution and repeated crystallization to the thermodynamically stable form. At temperatures above 391 K form (I) becomes the thermodynamically stable one. Due to hysteresis of the transformation, the real thermodynamic transition point may be below the transformation temperature observed in the DTA experiment. It is remarkable that the modification W of the chloro ester and (I) of the bromo ester with almost identical packing motifs and conformations each represents the thermodynamically least stable modification at room temperature.

In contrast to the results for the chloro ester, the reverse transformation from the room-temperature metastable modification to the stable one (I→II) has not been observed in our DTA experiments; the only way to transform them is *via* solution.

The optical microscopy experiments carried out on single crystals of diethyl 3,6-dibromo-2,5-dihydroxyterephthalate yield results similar to the observations for dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate (Byrn, Curtin & Paul, 1972; Richardson, Yang Novotny-Bregger & Dunitz, 1990). Analogously, the transformation starts at optical defects and leads to the disruption of the crystals. The distinctly different crystal structures of both modifications and all experimental results suggest that no smooth microscopic pathway can be expected for the transformation (II)→(I) and that the transformation presumably proceeds by nucleation and growth of a new phase.

This work has been supported by the Deutsche Forschungsgemeinschaft, the State of Hesse, the Fonds der Chemischen Industrie and the A. Messer Foundation.

### References

Bar, I. & Bernstein, J. (1984). *J. Phys. Chem.* **88**, 243–250.

Bar, I. & Bernstein, J. (1987). *Tetrahedron*, **43**, 1299–1305.

Bernstein, J. (1987). *Organic Solid State Chemistry; Conformational Polymorphism*, edited by G. R. Desiraju, pp. 471–518. Amsterdam: Elsevier Science Publishers B.V.

Bernstein, J. (1993). *J. Phys. D*, **26**, B66–76.

Bernstein, J. & Hagler, A. T. (1978). *J. Am. Chem. Soc.* **100**, 673–681.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Byrn, S. R., Curtin, D. Y. & Paul, I. C. (1972). *J. Am. Chem. Soc.* **94**, 890–898.

Ceolin, R., Toscani, S., Agafonov, V. & Dugue, J. (1992). *J. Solid State Chem.* **98**, 366–378.

Curtin, D. Y. & Byrn, S. R. (1969*a*). *J. Am. Chem. Soc.* **91**, 1865–1866.

Curtin, D. Y. & Byrn, S. R. (1969*b*). *J. Am. Chem. Soc.* **91**, 6102–6106.

Filippini, G. & Gavezzotti, A. (1993). *Acta Cryst.* B**49**, 868–880.

Gavezzotti, A. (1975). *Acta Cryst.* A**31**, 645–654.

Gavezzotti, A. (1983). *J. Am. Chem. Soc.* **105**, 5220–5225.

Gavezzotti, A. (1985). *J. Am. Chem. Soc.* **107**, 962–967.

Gavezzotti, A. & Filippini, G. (1994). *J. Phys. Chem.* **98**, 4831–4837.

Gavezzotti, A. & Filippini, G. (1995). *J. Am. Chem. Soc.* **117**, 12299–12305.

Hagler, A. T. & Bernstein, J. (1978). *J. Am. Chem. Soc.* **100**, 6349–6354.

Haleblian, J. & McCrone, W. (1969). *J. Pharm. Sci.* **58**, 8911–8929.

Hantzsch, A. (1915). *Chem. Ber.* **48**, 797–816.

Hassel, O. & Romming, C. (1967). *Acta Chem. Scand.* **21**, 2659–2662.

Ichikawa, M. (1978). *Acta Cryst.* B**34**, 2074–2080.

Kitaigorodski, A. I. (1961). *Organic Chemical Crystallography*. New York: Consultans Bureau.

Kuhnert-Brandstatter, M. (1971). *Thermomicroscopy in the Analysis of Pharmaceuticals*. New York: Pergamon Press.

Leser, J. & Rabinovich, D. (1978). *Acta Cryst.* B**34**, 2250–2252.

Miyazaki, T., Watanabe, T. & Miyata, S. (1988). *Jpn. J. Appl. Phys.* **27**, L1724–1725.

Ostwald, W. (1897). *Z. Phys. Chem.* **22**, 289–330.

Pertsin, A. J. & Kitaigorodski, A. I. (1986). *The Atom–Atom Potential Method*. Berlin: Springer.

Ramasubbu, N., Parthasarathy, R. & Murray-Rust, P. (1986). *J. Am. Chem. Soc.* **108**, 4308–4314.

Richardson, M. R., Yang, Q., Novotny-Bregger, E. & Dunitz, J. D. (1990). *Acta Cryst.* B**46**, 653–660.

Schmidt, M. W., Baldridge, K. K., Boatz, J. A., Elbert, S. T., Gordon, M. S., Jensen, J. J., Koseki, S., Matsunaga, N., Nguyen, K. A., Su, S., Windus, T. L., Dupuis, M. & Montgomery, J. A. (1993). *J. Comput. Chem.* **14**, 1347–1363.

Schweizer, B. & Dunitz, J. D. (1982). *Helv. Chim. Acta*, **65**, 1547–1554.

Seitz, W. (1995). Ph.D. Thesis. University of Frankfurt.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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

Stoe & Cie (1988*a*). *DIF4. Diffractometer Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1988*b*). *REDU4. Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

Swiatkiewicz, J. & Prasad, P. N. (1982). *J. Am. Chem. Soc.* **104**, 6913–6918.

Wilson Jr, E. B. (1972). *Chem. Soc. Rev.* **1**, 293–318.

Yang, Q., Richardson, M. R. & Dunitz, J. D. (1985). *J. Am. Chem. Soc.* **107**, 5535–5537.

Yang, Q., Richardson, M. R. & Dunitz, J. D. (1989). *Acta Cryst.* B**45**, 312–323.