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Contact Twinning of Embedded Polymorphs: The Crystal and Molecular Structures of Two of the Polymorphs of Tri-*tert*-butylmethyl *p*-Nitrobenzoate

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Clusters of twins of the title compound are deposited from acetone solution. Any one such twin, separated from the cluster, can be cleaved. The two fragments thus obtained are not homogeneous individual crystals for they all show two superimposed reciprocal lattices. They consist of two embedded closely-related polymorphic structures of which one is present (in the sample examined) to about 90% extent. Both components belong to space group $P2_1/c$ with their y and their z axes antiparallel. Major component data are: a = 11·541 (9), b = 8·161 (7), c = 21·289 (7) Å, β = 107·39 (1)°, Z = four molecules per cell; minor component: $\mathbf{a}' = \mathbf{a} + \frac{1}{2}\mathbf{c}$, $\mathbf{b}' = -\mathbf{b}$, $\mathbf{c}' = -\mathbf{c}$, $\sin\beta'/\sin(\beta+\beta') = -2|\mathbf{a}|/|\mathbf{c}|$, $Z = 4$. The structure of the major component was refined to a conventional R of 0·104. Embedding causes reflections with l even from both components to overlap. Approximate atomic coordinates were found for the minor component but its low contribution to the intensities of the overlapped reflections made refinement impracticable.

Introduction

We report here X-ray structural analyses of two closely-related polymorphic forms of the title compound. These polymorphic forms are embedded in fragments which have been cleaved from twins. A brief report on the molecular structure of the molecule in the major component has been published elsewhere (Cheng, Nyburg, Thankachan & Tidwell, 1977).

Experimental

Crystals of the title compound were kindly supplied by Professor T. T. Tidwell and had been prepared according to the method of Bartlett & Stiles (1955). The first crystals obtained from acetone–water solutions are single colorless needles; crystals from the mother liquor appear as pale-yellow clusters. The structure of the latter crystals is reported here; the structure of the colorless needles (yet a third polymorph) will be reported later.

All crystals broken from the clusters were suspected to be twinned because they had re-entrant angles at their broken ends. X-ray photographs showed, in fact, that either of two types of contact twinning were involved: block (I) + block (II), twinned on (001), or block (I) + block (III), twinned on $(\bar{1}02)$, shown schematically in Fig. 1. Such twins can be separated by

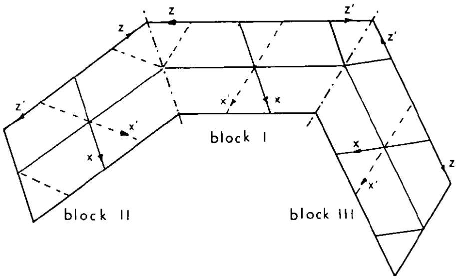

Fig. 1. Twinning and polymorphic embedding in the y projection. Three twinned blocks are shown (minor component axes are in broken lines).

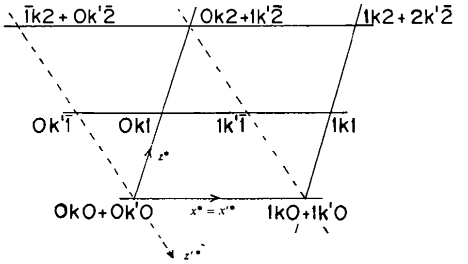

Fig. 2. The kth (= $-k'$th) level of reciprocal space showing the two lattices. (Primed indices and broken lines refer to the minor component.)

cleaving but in every case the resultant fragments were found, from X-ray photographs, to be composed of two lattices, one from a major, the other from a minor component. Both belong to $P2_1/c$ and have their y and their z axes antiparallel. The components are polymorphs and the orientation of the lattice rows within the blocks is shown in Fig. 1 (primed axes correspond to the minor component). Structure analysis was carried out on one block.

The relation between the reciprocal lattices of the polymorphic components is shown in Fig. 2: the complete overlapping of reflections with l even should be noted. The relation between real-cell parameters (Fig. 1) is $\mathbf{a}' = \mathbf{a} + \frac{1}{2}\mathbf{c}$, $\mathbf{b}' = -\mathbf{b}$, $\mathbf{c}' = -\mathbf{c}$, $\sin\beta'/\sin(\beta + \beta') = -2|\mathbf{a}|/|\mathbf{c}|$ [*i.e.* $a' = 13{\cdot}156$ (9), $b' = 8{\cdot}161$ (7), $c' = 21{\cdot}289$ (7) Å, $\beta' = 123{\cdot}16$ (1)°].

The fragment used for data collection was approximately parallelepipedal of dimensions *ca* 0·3 × 0·2 × 0·1 mm. It was mounted about x^*, parallel to the longest dimension. Cell dimensions of the major component were obtained from diffractometer settings of twelve well centered reflections.

Crystal data

$C_{20}H_{31}NO_4$, $M_r = 349$, monoclinic, $P2_1/c$, $a = 11{\cdot}541$ (9), $b = 8{\cdot}161$ (7), $c = 21{\cdot}289$ (7) Å, $\beta = 107{\cdot}39$ (1)°, $V = 1913{\cdot}5$ Å^3, $D_m = 1{\cdot}20$, $D_c = 1{\cdot}21$ g cm^{-3} for $Z = 4$, μ(Cu $K\alpha$) = 5·61 cm^{-1}.

Intensities from the two reciprocal lattices were collected as separate, consecutive sets on a computer-controlled Picker diffractometer equipped with a pulse-height analyzer using Ni-filtered Cu $K\alpha$ radiation. Scanning was in the θ–2θ mode at 2° min^{-1}. Background was determined for 30 s at each end of the scan range. The take-off angle was 3°. During the course of data collection there was a gradual loss in intensity, presumably due to crystal deterioration, to a maximum of *ca* 20%. Absorption corrections were not applied. Intensities were placed on a common scale by measurement of a standard every 50 reflections.

As noted above, half of all hkl reflections of the major component, namely those with l even, overlap with reflections $h + \frac{1}{2}l, \bar{k}, \bar{l}$ of the minor component (Fig. 2). Initially no correction to the major component intensity data was made for this overlap. Counting statistics and an Abrahams factor (Abrahams & Bernstein, 1965) of 0·01 were used to estimate $\sigma(I)$. Of the 3191 independent reflections measured from the major twin 2160 were considered significant on the criterion $|F_o| > \sigma(F_o)$. Despite l-even intensity overlap the structure of the major twin could be determined using the 462 reflections having $|E| > 1{\cdot}42$ by the use of *MULTAN* (Germain, Main & Woolfson, 1971). A unique solution was obtained, the E map revealing all 25 non-hydrogen atoms. Refinement was by *ORXFLS*3 (Busing, Martin & Levy, 1971) using $[\sigma(F_o)]^{-2}$ as weights and Hartree–Fock scattering factors (Cromer & Mann, 1968). Only the 1060 reflections having l odd were used for this stage of (isotropic) refinement.

Solution of the minor component structure could not proceed until corrections for overlap from the major twin component had been made. After a number of trials, the following procedure proved successful. Those F_c with l even were calculated for the major component with structural parameters refined thus far. Those $|F'_o|$ with l even for the minor component were taken as $(F_o^2 - F_c^2)^{1/2}$. This latter set of $|F'|$'s was normalized as was the set of l-odd non-overlapping reflections. These were used to generate two sets of E values which were combined for phasing by *MULTAN*. The best E map based on the 474 reflections having $|E| > 1{\cdot}52$ revealed the positions of all 25 non-hydrogen atoms of the minor component crystal structure.

The structures of the two components prove to be closely related, there being a simple transformation of atomic coordinates: $x' = x$, $y' = -y$, $z' = \frac{1}{2}x - z + \frac{1}{4}$ (0 or $\frac{1}{2}$ can be added to x', y' and z' depending on which center is chosen as origin).

The minor component structure could not be refined on the basis of the l-odd reflections alone, the residual remaining high (0·35). Because of the large estimated errors in intensity of the l-even reflections, it was felt that these could not be used. Accordingly, the minor component structure was not refined.

To refine the major component structure further it was necessary to estimate the fraction m of scattering volume contributed by the minor component to the overlapping reflections: $I_{\text{tot}} = (1 - m)I + mI'$. Ideally one might use a procedure such as that used by Wei, Wilkes & Dahl (1967). Unfortunately, this is not possible because, given the relation between Miller indices and fractional coordinates above, one finds $|F(hkl)| = |F'(h + \frac{1}{2}l, \bar{k}, \bar{l})|$ for all hkl with l even. Thus any value of m will satisfy the observations. Accordingly, refinement was based on two separate scale factors for F_c: k_e for l even and k_o for l odd. It was uneventful. At $R = 0{\cdot}16$ a difference map revealed all the H atom positions which were then included in further refinement cycles. A final refinement cycle with anisotropic thermal factors for non-hydrogen atoms (the B factors for some H atoms were fixed at 10·0 Å^2) had a conventional unweighted R of 0·104* with 1·328 for the e.s.d. of a unit observation. The final difference map showed no peaks greater than 0·32 e Å^{-3}.

The fraction m which is minor component is given by $(k_e^2/k_o^2) - 1$ and was 0·102. Thus the minor component has a scattering volume only 10% that of the major component.

Final atomic coordinates of the major component structure are listed in Table 1.

Discussion

The molecule (based on major component atomic coordinates) is illustrated in Fig. 3. Bond lengths and angles are given in Fig. 4.

Table 1. *Final atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *of the major twin structure*

	x	y	z
O(1)	7521 (3)	3105 (3)	3647 (1)
O(2)	7505 (4)	1238 (4)	2850 (2)
O(3)	9355 (4)	7323 (6)	1142 (2)
O(4)	8817 (4)	9151 (5)	1730 (2)
N	8968 (4)	7722 (7)	1593 (2)
C(1)	8054 (4)	3980 (6)	2719 (2)
C(2)	8383 (5)	3579 (6)	2163 (2)
C(3)	8715 (5)	4823 (7)	1803 (2)
C(4)	8695 (4)	6416 (6)	2001 (2)
C(5)	8384 (4)	6846 (6)	2549 (2)
C(6)	8070 (4)	5599 (5)	2918 (2)
C(7)	7647 (4)	2607 (6)	3075 (2)
C(8)	6871 (3)	2399 (5)	4096 (2)
C(9)	5499 (4)	3034 (5)	3772 (2)
C(10)	7601 (4)	3364 (5)	4771 (2)
C(11)	7028 (4)	447 (5)	4172 (2)
C(12)	5007 (5)	2636 (7)	3016 (2)
C(13)	4571 (5)	2289 (6)	4089 (3)
C(14)	5355 (5)	4908 (6)	3785 (3)
C(15)	6884 (5)	3523 (6)	5275 (2)
C(16)	7988 (5)	5135 (5)	4642 (2)
C(17)	8850 (4)	2618 (7)	5131 (2)
C(18)	6145 (6)	−577 (6)	3612 (2)
C(19)	6754 (5)	−185 (5)	4804 (2)
C(20)	8336 (5)	−144 (6)	4206 (3)
H(2)	840 (3)	239 (5)	203 (2)
H(3)	895 (3)	450 (5)	147 (2)
H(5)	836 (4)	808 (6)	266 (2)
H(6)	785 (3)	583 (4)	333 (2)
H(12*A*)	509 (3)	150 (5)	291 (2)
H(12*B*)	553 (5)	326 (6)	278 (2)
H(12*C*)	420 (8)	308 (10)	292 (4)
H(13*A*)	453 (3)	108 (5)	402 (2)
H(13*B*)	482 (6)	261 (7)	457 (3)
H(13*C*)	375 (6)	279 (7)	388 (3)
H(14*A*)	548 (3)	529 (4)	424 (2)
H(14*B*)	589 (3)	540 (4)	355 (2)
H(14*C*)	451 (4)	503 (5)	354 (2)
H(15*A*)	661 (4)	241 (5)	545 (2)
H(15*B*)	613 (5)	424 (7)	514 (2)
H(15*C*)	752 (5)	392 (7)	569 (3)
H(16*A*)	848 (4)	505 (5)	436 (2)
H(16*B*)	734 (5)	578 (6)	439 (2)
H(16*C*)	827 (3)	559 (5)	510 (2)
H(17*A*)	936 (4)	238 (5)	481 (2)
H(17*B*)	874 (4)	138 (5)	529 (2)
H(17*C*)	924 (5)	325 (7)	554 (3)
H(18*A*)	633 (4)	−164 (5)	373 (2)
H(18*B*)	634 (4)	−34 (5)	318 (2)
H(18*C*)	539 (4)	−51 (6)	370 (2)
H(19*A*)	692 (4)	−131 (6)	481 (2)
H(19*B*)	577 (5)	11 (7)	480 (3)
H(19*C*)	739 (4)	30 (6)	525 (2)
H(20*A*)	830 (4)	−84 (7)	387 (3)
H(20*B*)	885 (10)	83 (14)	418 (6)
H(20*C*)	870 (5)	−72 (8)	463 (3)

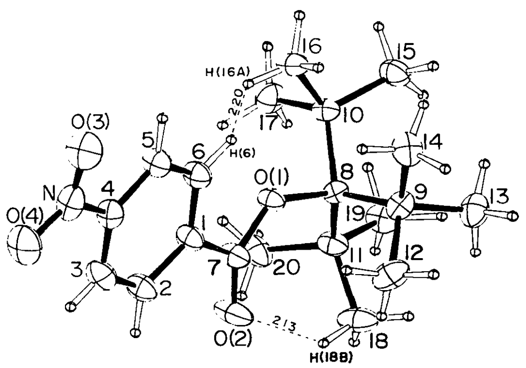

Fig. 3. A view of the molecule with 20% probability ellipsoids (hydrogen atoms are shown as arbitrary spheres).

The three *tert*-butyl groups are crowded, resulting in lengthening of the three C(8)—C bonds to an average of 1·618 (6) Å and an opening up of C—C(8)—C angles to an average of 113·8 (3)°. The source of this overcrowding can be traced to short methyl H···H contacts of 2·0 Å in each case: H(13*A*)···H(19*B*), H(14*A*)···H(15*B*) and H(12*A*)···H(18*B*). The C—Me bonds are normal [average 1·555 (7) Å] but the angles Me—C—Me are somewhat compressed [average 105·1 (4)°]. There is a noticeably short intramolecular

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33614 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

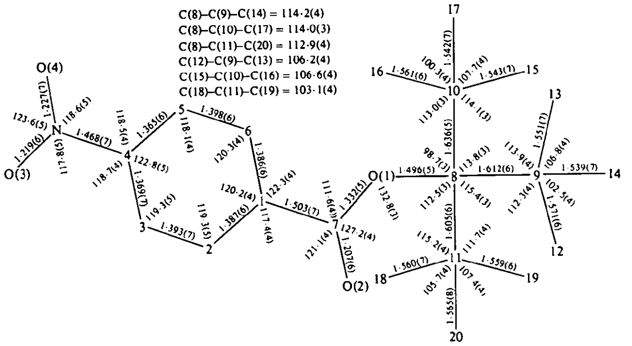

Fig. 4. Molecular bond lengths (Å) and angles (°).

Table 2. *Best least-squares planes*

(*a*) Coefficients of planes $AX + BY + CZ = D$ where X, Y, Z are real orthogonal coordinates (in Å); X is along x, Z along z^* and Y furnishes a right-handed system.

Plane	A	B	C	D
1 (phenyl)	−0·827	0·089	−0·556	−9·041
2	−0·655	0·738	−0·162	−4·674

(*b*) Deviations from planes (10^{-3} Å). Atoms marked by an asterisk were not included in the calculations of the best least-squares planes.

Plane				
1	C(1)	8	C(2)	1
	C(3)	−9	C(4)	6
	C(5)	4	C(6)	−10
	O(1)*	−107	O(2)*	253
	O(3)*	−39	O(4)*	252
	N*	87	C(7)*	81
2	C(11)	−0	C(18)	1
	O(2)	0	H(18*B*)	−40

(*c*) Angle between normals to planes (°)

45·8

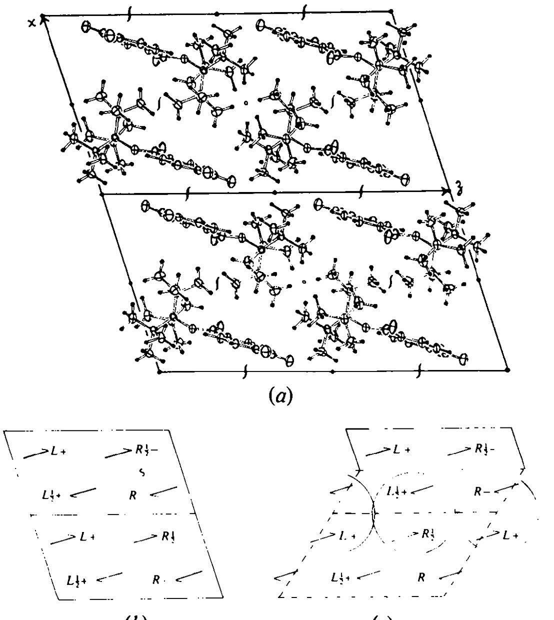

Fig. 5. (*a*), (*b*) Packing diagrams of the major component. (*c*) One possible mode of embedding showing minor component packing in lower half. Circles indicate conflicting molecules.

contact O(2)···H(18*B*) of 2·13 Å and yet, surprisingly, C(11), C(18), H(18*B*) and O(2) are virtually coplanar (Table 2). It seems that H(18*B*) has turned into this plane to satisfy some attractive force to O(2) and, in so doing, has actually opened up O(1)–C(8)–C(11) to 112·5 (3)°, C(8)–C(11)–C(18) to 115·2 (4)° and C(7)–O(1)–C(8) to 132·8 (3)°. H(18*B*) nestles between H(12*B*) and H(12*C*) but, at distances of 3·1 and 3·7 Å respectively, there seems no reason why it should lie exactly in the C(11), C(18), O(2) plane unless, as we have said, some attractive force to O(2) is at play.

The *p*-nitrobenzoyl moiety is entirely planar with normal bond lengths and angles.

The crystal structure of the major component is shown for two adjacent unit cells in Fig. 5(*a*) and schematically in Fig. 5(*b*) where molecules of opposite chirality have been labelled arbitrarily L and R. This structure has no short intermolecular contacts. We have not explored all the possible ways in which embedding might occur but one is that depicted in Fig. 5(*c*). It suffers from somewhat short phenyl ring intermolecular C···C contacts of 3·31 (1) Å between molecules $R(-)$, $L(+)$ and $L(\frac{1}{2}+)$, $R(\frac{1}{2}-)$. [These short contacts do not occur in the major component structure, the molecules in question then being $R(-)$, $R(\frac{1}{2}-)$ and $L(\frac{1}{2}+)$, $L(+)$.] The fact that the minor component structure suffers from short intermolecular contacts may explain why it is present to only a minor extent. An examination of its E map did not reveal any tendency for the conflicting phenyl groups to move apart but this map is not an accurate representation of the electron density.

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