organic compounds

Pseudomerohedrally twinned crystal structure of 2,3-diphenylbuta-1,3-diene

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The title compound, $C_{16}H_{14}$, is twinned by reticular pseudo-merohedry of twin index 2. The primitive monoclinic cell of the single crystal can be transformed into a B-centred pseudo-orthorhombic supercell with a fourfold volume. The two-fold twin operation about the reciprocal a^* axis of the primitive monoclinic cell is co-directional with the approximate C_2 axis of the molecule and a symmetry element of the orthorhombic supercell. A tentative twin domain model is proposed.

Comment

In the course of our studies of electronic interactions in branched π-conjugated systems (van der Wiel *et al.*, 2004), the crystal structure of 2,3-diphenylbuta-1,3-diene, (I), was determined in order to obtain more insight into the electronic spectra.

(I)
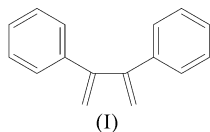
In the crystal structure, (I) has an approximate non-crystallographic C_2 symmetry (Fig. 1). The maximum deviation of an atom from an exact C_2 symmetry is 0.0245 Å (Pilati & Forni, 1998). This approximate molecular C_2 axis is perpendicular to the monoclinic b axis. The two perpendicular twofold rotations imply a third C_2 axis. In fact, this third C_2 axis is here parallel to the crystallographic c axis. In other words, the approximate molecular C_2 axis is parallel to the a^* axis. It appears that the molecular C_2 symmetry and the orientation of the C_2 axis in the unit cell result in a twinned crystal with this rotation as the twin operation. The twin relationship was taken into account during the intensity evaluation with *EVALCCD* (Duisenberg *et al.*, 2003) and the

HKLF5 refinement with *SHELXL97* (Herbst-Irmer & Sheldrick, 1998). The twin fraction refined to a value of 0.319 (2).

Because this light-atom structure does not reveal sufficient anomalous dispersion, a distinction between proper and improper rotations as twin operations is not possible here. We chose the proper rotation based on the approximate molecular symmetry in the discussion below.
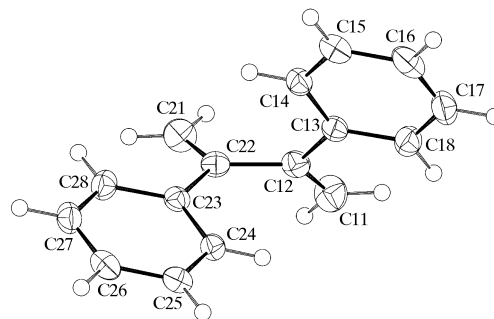

Figure 1
A plot of (I), showing the *gauche* conformation. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown with arbitrary radii. The view is along the approximate molecular C_2 axis.
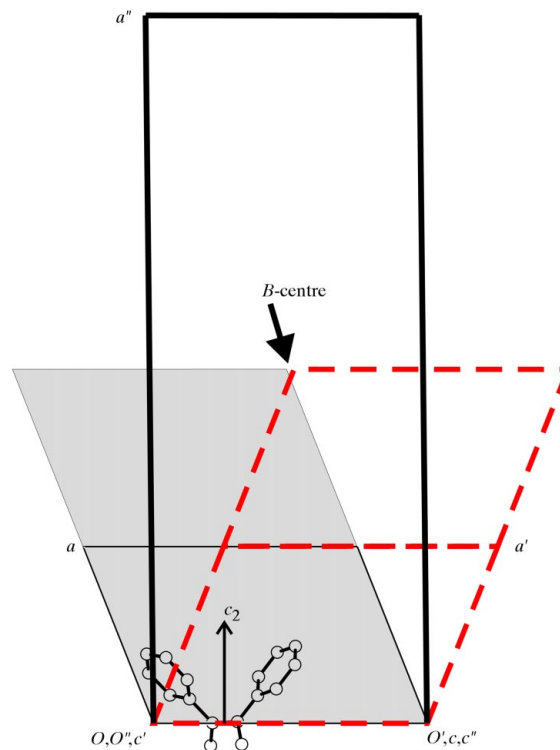

Figure 2
A view of the unit cell along the crystallographic b axis. The approximate molecular C_2 axis is oriented perpendicular to the direct b and c axes and parallel to the reciprocal a^* axis. The twin cell, marked in dashed lines and labeled with primes, is generated by a twofold rotation about a^*. A primitive supercell containing both unit cells (shaded in grey) is obtained by a doubling of the a axis. This primitive supercell is monoclinic and can be transformed into a B-centred pseudo-orthorhombic cell (drawn in thick lines and labeled with double primes), where the original twin axes along a^* and c are now part of the lattice.

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The twofold twin axis about *c* is a symmetry element of a pseudo-orthorhombic *B*-centred supercell (Fig. 2) with a fourfold volume and *a* = 31.8982 Å, *b* = 5.7966 Å, *c* = 12.3414 Å and β = 90.568°. The corresponding transformation
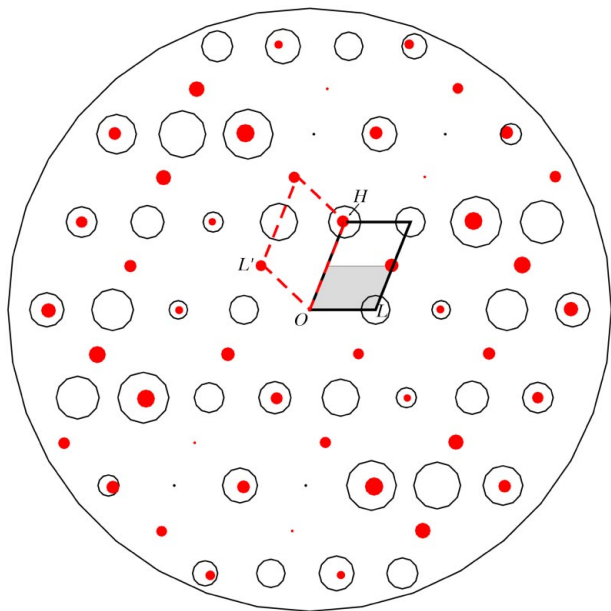

Figure 3
A simulated precession photo of the *h0l* plane showing the twin relationship in reciprocal space as a twofold rotation about *a**. The radii of the circles indicate the intensities of the reflections. The main twin domain is drawn in open circles; the minor twin domain, with a twin fraction of 0.319 (2), is drawn in filled circles. The approximate primitive subcell in reciprocal space, covering both twin domains, is obtained by halving *a** and is shaded in grey in the drawing.
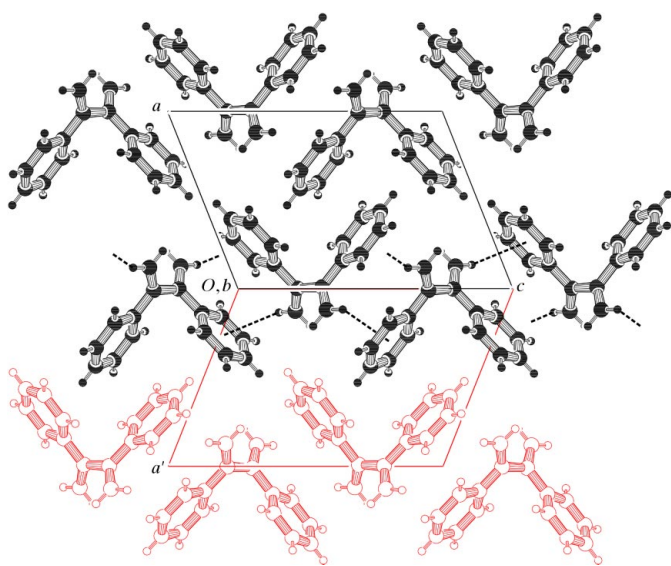

Figure 4
The proposed stacking fault at the domain interfaces of the two-dimensional layers in the *bc* plane leading to a twinned structure as a result of the local twofold axial symmetry. In one of the layers, the C—H···π interactions are shown as dashed lines.

matrix from subcell to supercell is (401/010/001). The twin index, derived from the primitive lattices, is consequently 2, and we can describe the twinning as reticular pseudomerohedral. The primitive supercell in direct space is obtained by a doubling of the *a* axis or, correspondingly, the primitive subcell in reciprocal space by halving of the *a** axis (Fig. 3). We were able to find the supercell with the indexing program *DIRAX* (Duisenberg, 1992) or, independently, by applying the Le Page algorithm for finding twin laws (Le Page, 2002) as implemented in *PLATON* (Spek, 2003). With an exact orthorhombic cell, we would expect a perfect overlap of the two twin domains for all reflections with *hkl*, *l* = 2*n*. In an exact orthorhombic cell we also would expect additional (non-space-group) extinctions due to the twinning; all reflections with both *l* = 2*n* and *h* + *l* = 4*n* + 2 are absent. However, because of the non-zero obliquity of 0.568°, the overlap is not perfect and the supercell is not really suitable for the intensity evaluation. An exact description of the diffraction experiment for the prediction of reflection size, shape and position on the CCD detector was used instead, as implemented in *EVALCCD* (Duisenberg *et al.*, 2003).

The intermolecular interactions are determined by weak C—H···π interactions (Table 2 and Fig. 4), leading to a two-dimensional arrangement in the crystallographic *bc* plane. Stacking faults of these two-dimensional layers due to local twofold axial symmetry are a plausible structural explanation for the twinned crystallization (Fig. 4). The changes in the local environments of the molecules are very minor and the energetic differences at the interface between the twin domains are small. Similar effects on boundary layers of twinned crystals have been described before (see *e.g.* Cannas *et al.*, 1972).

The butadiene subsystem is in a *gauche* conformation, with a C11—C12—C22—C21 torsion angle of −55.6 (2)°. There is only one comparable crystal structure of a diene in the literature, 2,3-di-*tert*-butyl-1,3-butadiene, which has a torsion angle of 96.62 (14)° (Roth *et al.*, 1991). Interestingly enough, a similar torsion angle for this compound is found by electron diffraction in the gas phase [reference given by Roth *et al.* (1991)], so that crystal packing effects can be excluded. In fact, quantum chemical calculations indicate that 2,3-diphenylbuta-1,3-diene also has the same conformation in the crystal and in the free molecule (van Walree *et al.*, 2005). Thus, in both cases, the central torsion angle is a molecular rather than a crystal property.

The C11—C12—C13—C18 and C21—C22—C23—C28 torsion angles are −17.0 (3) and −19.3 (3)°, respectively. This picture supports the idea of two relatively planar styrene units linked at their α atoms. The C12—C22 bond length (Table 1) supports this assumption because it is rather long for a Csp^2—Csp^2 bond, even in a *gauche* conformation. On the other hand, the C12—C13 and C22—C23 bond lengths (Table 1) are quite long for Csp^2—C$_{ar}$ bonds in styrene-type systems. We assume that this slight bond elongation is caused by steric effects.

Atoms H11*A*/H18 and H21*A*/H28 are in close proximity, with intramolecular distances of 2.08 and 2.13 Å, respectively, thus prohibiting perfect planarity of the styrene entities.

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Experimental

2,3-Diphenylbuta-1,3-diene was synthesized by a double Wittig reaction of benzil with methyltriphenylphosphonium bromide. Details of the synthesis will be published elsewhere (van Walree *et al.*, 2005). Crystals were grown by sublimation at 20 mm Hg pressure with gentle heating. During sublimation, the cold finger was cooled with an ice–salt mixture.

Crystal data

$C_{16}H_{14}$	$D_x = 1.201$ Mg m^{-3}
$M_r = 206.27$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 290
$a = 8.5791$ (12) Å	reflections
$b = 5.7966$ (3) Å	$\theta = 4.0–27.1°$
$c = 12.3414$ (17) Å	$\mu = 0.07$ mm^{-1}
$\beta = 111.645$ (10)°	$T = 150$ (2) K
$V = 570.46$ (12) Å^3	Needle, colourless
$Z = 2$	$0.48 \times 0.24 \times 0.24$ mm

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.041$
φ and ω scans	$\theta_{max} = 27.7°$
14 083 measured reflections	$h = -11 \rightarrow 11$
1444 independent reflections	$k = -7 \rightarrow 7$
1355 reflections with $I > 2\sigma(I)$	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.042P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$+ 0.0638P]$
$wR(F^2) = 0.080$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
1444 reflections	$\Delta\rho_{max} = 0.17$ e Å^{-3}
146 parameters	$\Delta\rho_{min} = -0.16$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C11—C12	1.329 (3)	C21—C22	1.335 (3)
C12—C13	1.491 (2)	C22—C23	1.486 (2)
C12—C22	1.492 (2)		
C11—C12—C13—C18	−17.0 (3)	C21—C22—C23—C28	−19.3 (3)
C11—C12—C22—C21	−55.6 (2)		

Table 2
Hydrogen-bond geometry (Å, °).

$Cg1$ and $Cg2$ are the centroids of rings C13–C18 and C23–C28, respectively.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C11—H11$A\cdots Cg1^i$	0.95	3.05	3.96	161
C21—H21$A\cdots Cg2^{ii}$	0.95	2.90	3.75	149

Symmetry codes: (i) $-x, y - \frac{1}{2}, -z$; (ii) $-x, y + \frac{1}{2}, -z + 1$.

728 frames were collected with a φ scan and 893 frames with ω scans. The crystal-to-detector distance was 40 mm, the rotation angle was 0.5° per frame and the exposure time was 20 s per frame. The refinement was performed in a non-reduced setting of space group $P2_1$ in order to align the twin axis parallel to the crystallographic a^* axis. In the reduced setting, the twin axis would be parallel to a face diagonal. The cell parameters of the reduced setting are $a = 8.5791$ (12) Å, $b = 5.7966$ (3) Å, $c = 12.1575$ (14) Å and $\beta = 109.344$ (9)°, and the transformation matrix from the present setting to the reduced setting is $(100/0\bar{1}0/\bar{1}0\bar{1})$. The absolute structure could not be determined reliably. Therefore, an arbitrary absolute structure was chosen and Friedel pairs were merged prior to the refinement using the program *MERGEHKLF5* (Schreurs, 2003), which also merged the redundant data taking the twin relationship into account. All H atoms were located in a difference Fourier map and were constrained to ride on their parent atoms, with U_{iso}(H) values of $1.2U_{eq}$(C) and C—H distances of 0.95 Å.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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