

## Treatment of 'twinning' in isopropylcyclohexane

David R. Allan,<sup>a</sup> Pamela A. McGregor,<sup>a</sup> Lorna J. McLachlan,<sup>b</sup> Simon Parsons<sup>b\*</sup> and Colin R. Pulham<sup>b</sup><sup>a</sup>Department of Physics and Astronomy, The University of Edinburgh, King's Buildings, West Mains Road, Edinburgh EH9 3JZ, Scotland, and <sup>b</sup>Department of Chemistry, The University of Edinburgh, King's Buildings, West Mains Road, Edinburgh EH9 3JJ, Scotland

Correspondence e-mail: s.parsons@ed.ac.uk

## Key indicators

Single-crystal X-ray study

T = 150 K

Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$ 

R factor = 0.061

wR factor = 0.237

Data-to-parameter ratio = 13.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Isopropylcyclohexane, C<sub>9</sub>H<sub>18</sub>, which is a liquid under ambient conditions, tends to form a glass on cooling. Laser-assisted zone refinement of the frozen solid yielded a crystalline solid, although the sample was not single. The crystal was not really a twin in the usual sense of the term, but the consequences of the multiplicity of the sample could be modelled with a combination of domains generated by twofold rotations about the reciprocal lattice  $[1k0]$  directions, where  $k = 9-12$ .

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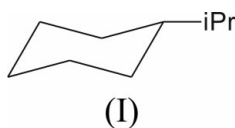
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## Comment

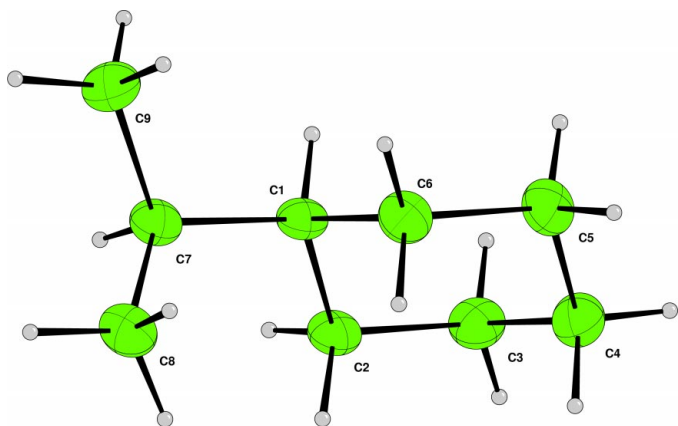
There is active current interest in obtaining crystal structures from compounds which are liquids or gases under ambient conditions (Bond & Davies, 2002*a,b*; Downs *et al.*, 2001; Romano *et al.*, 2001; Tang *et al.*, 2001; Thalladi & Boese, 2000; Thalladi, Nuesse & Boese, 2000; Thalladi, Boese & Weiss, 2000). Such structure determinations can be frustrated if a compound tends to form a glass, a particular problem if the molecules under study are conformationally flexible.

Our interest in isopropylcyclohexane, (I), lay in its possible use as a model for traction fluids (Hentschel, 1985), and we wished to compare its structure after crystallization at low temperature with that obtained on application of high pressure. In the event, crystallization of the compound at high pressure was frustrated by glass formation. However, a crystalline sample was obtained at low temperature by means of Boese's laser-assisted zone-refinement technique (Boese & Nussbaumer, 1994). The X-ray diffraction pattern clearly showed that the sample was not single, but, given the difficulty with which it had been obtained, we were reluctant to attempt to regrow it without collecting a data set.



A suitable indexing of the pattern was achieved by the use of the program *GEMINI* (Sparks, 1999) for 48 out of 132 reflections selected from images taken during data collection. A second matrix indexed a further 29 reflections with a similar unit cell. These two matrices indexed the majority of the strong reflections, and the relationship between them (a possible twin law) could be expressed by the matrix

$$\begin{pmatrix} -0.92 & 1.26 & 0.09 \\ 0.15 & 0.90 & 0.06 \\ 0.09 & 0.06 & -1.01 \end{pmatrix}$$



**Figure 1**  
The molecular structure of (I) in the crystal. Ellipsoids are drawn at the 50% probability level.

The combination of terms in this matrix means that overlap between the reflections from the components that it relates is unlikely to affect refinement.

Of the remaining 55 reflections, 22 could be indexed (using the program *DIRAX*; Duisenberg, 1992) with a third orientation matrix. Attempts made to index the remaining reflections were not successful. The relationship between the first and third matrices can be expressed as

$$\begin{pmatrix} -1.00 & 0.25 & 0.00 \\ 0.03 & 0.98 & 0.01 \\ 0.11 & 0.02 & -0.98 \end{pmatrix}$$

The trace of this matrix is  $-1$  and the determinant approximately  $1$  (0.96), so that it can be considered to be a twofold rotation. The eigenvector of this matrix corresponding to the eigenvalue near  $1$  (actually  $0.98$ ) is  $[0.13, 1.04, 0.01]$ , and the twofold axis can be interpreted as being roughly parallel to the reciprocal lattice  $[180]$  direction (referred to from now on as  $[180]^*$ ) (Sands, 1982). The figures quoted here deviate from ideal values, and their accuracy may be compromised by the relatively small number of rather weak reflections used to determine them, and the difficulty of extracting accurate peak positions for reflections which overlap with reflections from a different domain of the sample.

The data set was integrated using the first orientation matrix derived above. The structure was solved by direct methods (*SIR92*; Altomare *et al.*, 1994), and refined by full-matrix least-squares against  $|F|$  using data with  $I > 2\sigma(I)$  (*CRYSTALS*; Watkin *et al.*, 2002). This strategy was adopted because it is useful to be able to compare weighted and unweighted  $R$  factors directly. This means that the data-to-parameter ratio is *ca* 7.5:1.

Only about half the reflections in the data set had  $I > 2\sigma(I)$ , and it is usual to treat the H atoms with a riding model during refinement under these circumstances. However, H atoms

contribute almost 15% by weight and 25% of  $F(000)$  for this compound and so the H-atom parameters have a significant effect on data-fitting. H-atom positional parameters were therefore refined subject to a similarity restraint on the C–H bond lengths; two common isotropic displacement parameters were refined, one for the methyl groups and the other for the remaining H atoms.

The  $R$  factor for this model converged to 6.93% with unit weights. An attempt was made to model the twinning by incorporating a twofold axis about the  $[180]^*$  direction as a possible twin law. The  $R$  factor dropped only slightly to 6.91%.

At this stage, the *ROTAX* procedure was used to identify possible twin laws using trends in the indices of the poorly agreeing data with  $|F_o| > |F_c|$  (Cooper *et al.*, 2002). The program identified as possible twin laws six twofold axes along the  $[190]^*$ ,  $[1,10,0]^*$ ,  $[1,11,0]^*$ ,  $[1,12,0]^*$ ,  $[12,1,3]$  and  $[\bar{1}04]^*$  directions. An eight-domain twinning model consisting of these domains, plus a domain for a twofold rotation about  $[180]^*$ , was set up using a recently implemented routine in *CRYSTALS* which facilitates this. (Detailed instructions are given under *\_refine\_special\_details* in the CIF.) A reflection from the primary domain was considered to be overlapped with a reflection from another domain if the original and transformed reciprocal lattice points lay within  $0.07 \text{ \AA}^{-1}$  of each other, this value being optimized by trial-and-error. The sum of the domain scale factors was tightly restrained to unity. We have found in the past that refinements of multi-domain twins sometimes need to be stabilized with shift-limiting restraints; these were applied here, although the refinement was quite stable without them. The  $R$  factor dropped to 5.89% on refinement, but four twin scale factors (for the twofold rotations about  $[190]^*$ ,  $[180]^*$ ,  $[1,11,0]^*$  and  $[\bar{1}04]^*$ ) fell to less than 2%. These were fixed at zero in subsequent cycles of refinement, and so the final model was a four domain twin. The  $R$  factor at this stage, with unit weights, was 5.96%. We have previously discussed the use of the Watkin–Carruthers weighting scheme (Carruthers & Watkin, 1979; Cooper *et al.*, 2002) in the analysis of twinned crystal structures. Incorporation of this scheme into the refinement led  $R$  to drop to 5.66%.

The final cycles of least squares were performed against  $|F|^2$  using all data. The differences between the refined structural parameters on making this change were negligibly small, but some effect on the scale factor was anticipated (Hirshfeld & Rabinovich, 1973). The scale factor after the initial stages of  $F$  refinement [ $F > 4\sigma(F)$ ] was 1.282 (15), and 1.224 (15) after  $F^2$  refinement against all data. The correlation between the scale factor and the element scale for the primary domain of the twin meant that this change in scale had a knock-on effect on the twin element scale factors. The largest changes were from 0.631 (14) to 0.721 (14) (domain 1) and from 0.185 (17) to 0.118 (15) ( $[1,12,0]^*$ ). The correlation coefficient between the scale and the primary domain scale factor was  $-0.909$  if weak data were omitted, but  $-0.823$  if they were included. This is a much more compelling argument for including all data in this refinement than, say, the increase in the data-to-parameter ratio. Normal probability plots can be used to assess the

agreement between  $|F_o|$  and  $|F_c|$  (Abrahams & Keve, 1971). After  $F$  refinement with a cut-off of  $4\sigma(F)$ , a normal probability plot using the statistic  $(F_o - F_c)/\sigma(F_o)$  had a gradient of 1.710, an intercept of  $-0.001$  and a correlation coefficient of 0.924. After  $|F|^2$  refinement using all data, the corresponding quantities were 1.343,  $-0.136$  and 0.915, and this shift towards a more ideal gradient is perhaps another reason for using all data in the final stages of this refinement. The  $R$  factor based on  $F$  and  $F > 4\sigma(F)$  was 6.08%.

A full list of twin laws and scale factors is given in the supplementary data. Other refinement parameters are listed in the *Experimental* table. The bond lengths and angles are normal (these have been deposited in the CIF), and the displacement parameters show no unusual features. A view of the molecule is shown in Fig. 1; the isopropyl group is in an equatorial position on the cyclohexane ring, which adopts the expected chair conformation.

A separate integration was performed using the second orientation matrix described above. The diffraction from this domain was rather weaker [mean  $I/\sigma(I) = 1.78$  against 6.62 for the data set obtained with the first matrix]. Although no twin modelling appeared to be necessary, the standard uncertainties on the C—C bond lengths were some three times higher.

The crystal used for the determination of this structure was not really a twin in the usual sense of the term, which is usually taken to be associated with the geometrical properties of the unit cell or a supercell. It is more accurate to describe the sample as a 'multiple crystal'. Nevertheless, the refinement strategy used was rather similar to that employed for a twinned structure. In attempting to model the diffraction pattern from this multiple crystal, it was necessary to use several twin matrices in order to model the contribution of the minor component(s) of the sample. In general, it is preferable to determine a twin law *via* the relationship between the orientation matrices of the different domains. If the orientation matrix so-derived suffers from errors due to poor profile, weak diffraction, overlapped data, *etc.*, this procedure can be subject to systematic errors. In this case, it suggested that a twofold axis about the  $[180]^*$  direction could be used to model twinning, whereas analysis of the poorly fitting data during refinement suggested that it could potentially be described as twofold axes about  $[1k0]^*$ , where  $k$  had values in the range 9–12. The matrices for these operations are not very different, but in a competitive refinement it was found that a combination of these twin laws formed a successful model. An additional twin domain generated by a twofold axis about the  $[12,1,3]$  direct lattice direction was also included in the model, although its refined domain scale factor is small.

## Experimental

The sample of (I) was obtained from Aldrich and used as received. Crystallization of the material at low temperature was achieved with a sample held in a 0.4 mm outside-diameter capillary held at 150 K using the laser-assisted zone-refinement technique of Boese & Nussbaumer (1994).

## Crystal data

$C_9H_{18}$   
 $M_r = 126.24$   
 Monoclinic,  $P2_1/c$   
 $a = 15.689$  (8) Å  
 $b = 5.298$  (3) Å  
 $c = 10.641$  (6) Å  
 $\beta = 101.79$  (1)°  
 $V = 865.9$  (14) Å<sup>3</sup>  
 $Z = 4$

$D_x = 0.968$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 1016 reflections  
 $\theta = 2-27^\circ$   
 $\mu = 0.05$  mm<sup>-1</sup>  
 $T = 150$  K  
 Cylinder, colourless  
 $1.0 \times 0.4 \times 0.4$  mm

## Data collection

Bruker SMART APEX diffractometer equipped with an Oxford Cryosystems low-temperature device and an OHCD laser-assisted crystallization device (Scientific Consulting, Essen, Germany)  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2001)  
 $T_{\min} = 0.554$ ,  $T_{\max} = 1$

5107 measured reflections  
 1950 independent reflections  
 1069 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.04$   
 $\theta_{\text{max}} = 28.3^\circ$   
 $h = -20 \rightarrow 19$   
 $k = 0 \rightarrow 6$   
 $l = 0 \rightarrow 14$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.061$   
 $wR(F^2) = 0.237$   
 $S = 1.04$   
 1950 reflections  
 142 parameters  
 All H-atom parameters refined

Weights: Tukey & Prince method (Carruthers & Watkin, 1979);  
 $w = [\text{weight}]\{1 - [\Delta F/6 * \sigma(F)^2]\}^2$   
 using a four-term Chebychev polynomial, with parameters 69.3, 109, 54.8, 14.3  
 $(\Delta/\sigma)_{\text{max}} = 0.003$   
 $\Delta\rho_{\text{max}} = 0.28$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.16$  e Å<sup>-3</sup>

The refinement strategy is described in the text. A detailed instruction list for building a multi-domain twin model in *CRYSTALS* is given in the CIF under *\_refine\_special\_details*.

Data collection: *SMART* (Siemens, 1993); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2002); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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