

## Pseudosymmetry and phase transition in dimethyl 2,3-bis(tricyclo[3.3.1.1<sup>3,7</sup>]dec-2-ylidene)butanedioate

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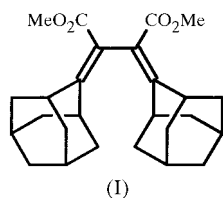
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The crystal structure of the title compound, C<sub>26</sub>H<sub>34</sub>O<sub>4</sub>, shows a reversible phase transition at about 178 K. The structure of the high-temperature phase contains two independent molecules related by pseudosymmetry elements. Cooling through the phase-transition temperature results in a doubling of the *c* axis. The low-temperature structure contains four independent molecules related by pseudosymmetry elements. The phase transition results in a rearrangement of some weak intermolecular C—H···O interactions. The number of very weak C—H···O interactions, with H···O distances between 2.8 and 2.9 Å, is increased in the low-temperature structure.

### Comment

The title compound, (I), shows a reversible phase transition at about 178 K. We present here the results of X-ray crystal structure analyses of both the high- and low-temperature phases, using data collected at 204 and 142 K, respectively.



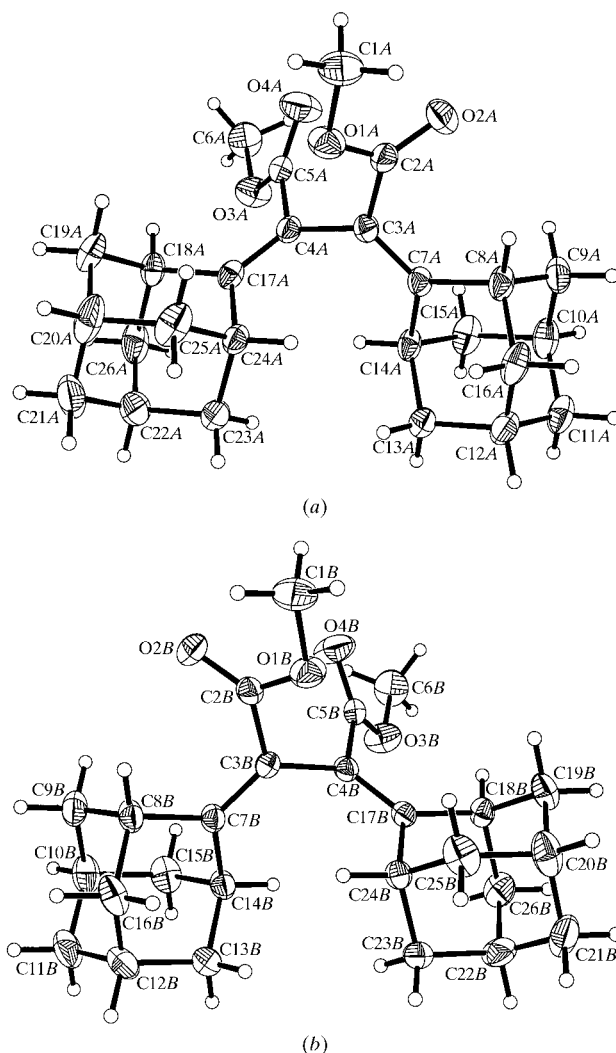
The crystal structure of the high-temperature phase contains two crystallographically independent molecules, *A* and *B*. The dimensions of both molecules are very similar (Fig. 1). A close inspection of the atomic coordinates shows that the coordinates of molecule *B* are related to those of molecule *A* by the approximate relations  $x_B = \frac{1}{2} + x_A$ ,  $y_B = \frac{1}{4} - y_A$  and  $z_B = z_A$ . This corresponds to a localized pseudo-*a*-glide plane about  $y = \frac{1}{8}$ . Molecule *B* is related to symmetry equivalents of molecule *A* by an additional localized pseudo-translation vector of  $(\frac{1}{2}, \frac{3}{4}, \frac{1}{2})$ , a localized pseudo-

inversion centre about  $(\frac{1}{4}, \frac{3}{8}, \frac{1}{4})$  and a localized pseudo-twofold screw axis about  $(\frac{1}{4}, y, 0)$  with a translation vector of  $b/4$ .

The C3—C7 and C4—C17 bonds have lengths of about 1.34 Å and correspond to double bonds. The angle between the best planes through atoms C3 and C4 is 69.83 (5)° for both molecules *A* and *B*. Atoms C4A and C4B show small distortions from planarity: both atoms deviate by about 0.056 Å from the plane through their three neighbours. Atoms C3A and C3B are almost planar.

Each molecule shows two intramolecular C—H···O contacts, with H···O distances between 2.32 and 2.36 Å (C8—H8···O2 and C18—H18···O3; Table 1). The crystal packing shows a considerable number of weak intermolecular electrostatic C—H···O interactions. The intermolecular H···O distances are about 2.65–2.70 Å and thus are rather long.

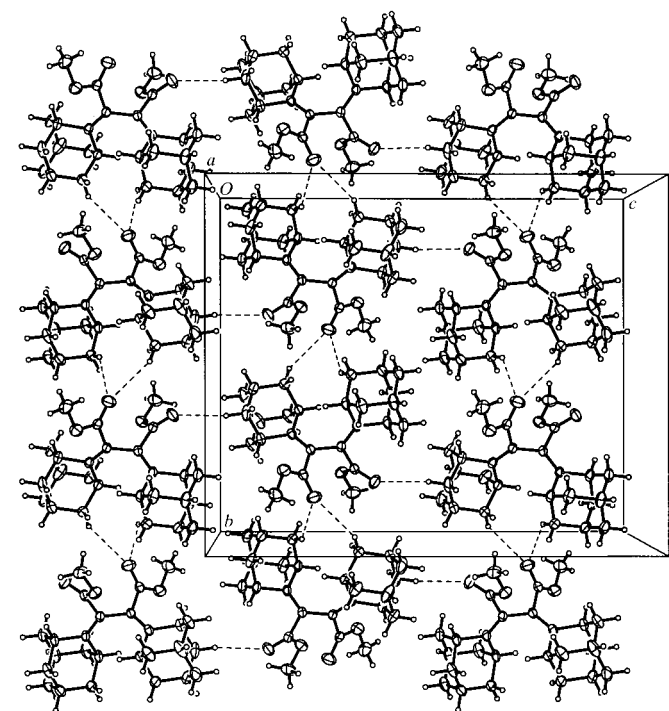
The pseudosymmetry between molecules *A* and *B* is a result of the very similar packing arrangements of both molecules. Both molecules are arranged into almost identical chains about a twofold screw axis; molecule *A* about  $(0, y, \frac{1}{4})$  and molecule *B* about  $(\frac{1}{2}, y, \frac{1}{4})$ . Molecules within these chains are



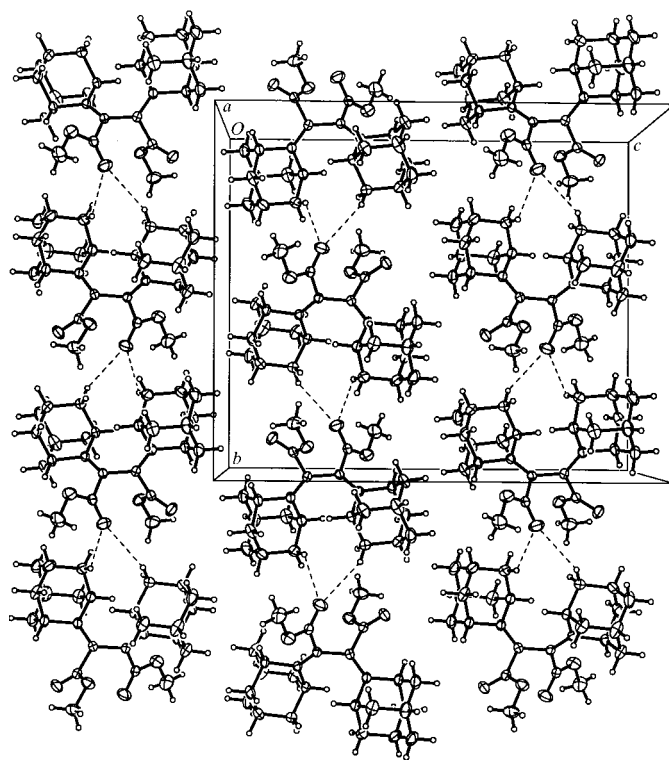
**Figure 1**

The structures of the two independent molecules of (I) at 204 K with 50% probability displacement ellipsoids, showing (a) molecule *A* and (b) molecule *B*.

connected by two intermolecular C—H···O interactions. Adjacent chains displaced in the *c* direction form  $2_1/c$  layers. The  $2_1/c$  layer at  $-\frac{1}{4} < x < \frac{1}{4}$  consists of molecules *A* only



(a)



(b)

**Figure 2**

The crystal packing of (I) at 204 K viewed down *a*, showing (a) a section with  $-\frac{1}{4} < x < \frac{1}{4}$  containing only molecules of type *A*, and (b) a section with  $\frac{1}{4} < x < \frac{3}{4}$  containing only molecules of type *B*.

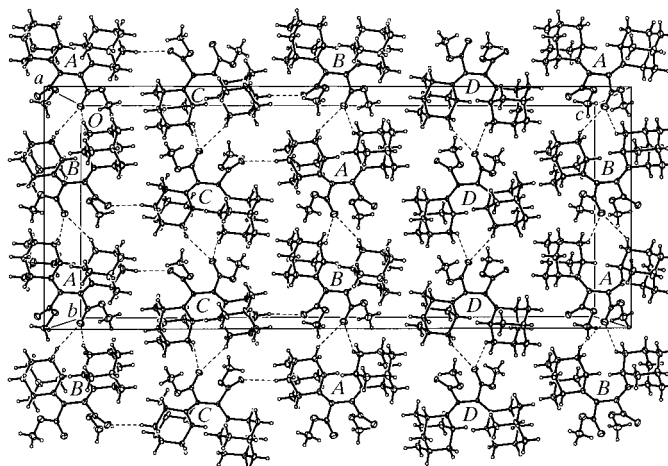
(Fig. 2a). A C26A—H26A···O2A interaction connects adjacent chains in this layer. The  $2_1/c$  layer at  $\frac{1}{4} < x < \frac{3}{4}$  consists of molecules *B* only (Fig. 2b). Adjacent chains in this layer show a displacement of  $b/2$  compared with the layer consisting of molecules *A*. As a result, no C26—H26···O2 interactions are found in this layer. Two intermolecular C6—H6···O4 interactions connect the layers made up of molecules *A* and *B*.

A doubling of the cell volume is observed on cooling through the phase-transition temperature. Measurement of the cell constants just above and below the transition temperature showed no significant changes in the cell parameters *a*, *b* and  $\beta$ , while an almost exact doubling was observed for the length of the *c* axis.

The structure of the low-temperature phase contains four independent molecules, *A*, *B*, *C* and *D*. The dimensions of the four molecules are very similar. Again, short intramolecular C8—H8···O2 and C18—H18···O3 contacts are found (Table 2).

The crystal packing in the low-temperature phase is rather similar to that observed in the high-temperature structure. The molecules are again arranged into chains about screw axes in the *b* direction (Fig. 3). Molecules *A* and *B* alternate in a chain about a pseudo-twofold screw axis about  $(\frac{1}{4}, y, 0)$ , molecule *C* forms a chain about a screw axis along  $(\frac{1}{4}, y, \frac{1}{4})$  and molecule *D* forms a chain about a screw axis along  $(\frac{1}{4}, y, \frac{3}{4})$ . Intermolecular C—H···O interactions within these chains and intermolecular C6—H6···O4 interactions between layers displaced by  $a/2$  are similar to those observed in the high-temperature structure.

There is, however, a striking difference between the high- and low-temperature structures: each fourth chain in the low-temperature structure is translated by  $b/2$  compared with the high-temperature structure. This results in a rearrangement of the C26—H26···O2 interactions between neighbouring chains. The number of such interactions, however, is the same as in the high-temperature structure. Thus, there would be no overall stabilization of the structure upon cooling through the phase-transition temperature. A stabilization of the low-temperature structure, however, may result from an increased



**Figure 3**

The crystal packing of (I) at 142 K viewed down *a* showing a section with  $0 < x < \frac{1}{2}$ .

number of very long intermolecular C—H···O interactions, with H···O distances in the range 2.8–2.9 Å. Five such interactions are found in the high-temperature structure. Due to the cell doubling, there should be ten in the low-temperature structure. In fact, the low-temperature structure shows 14 such weak interactions, 11 of which have C—H—O angles in the range 150–170°. Desiraju & Steiner (1999) have shown that such long C—H···O interactions may play a significant role in crystal packing.

## Experimental

Compound (I) was obtained by a procedure similar to that described by Jefferson & Warkentin (1992) for other compounds. 1-Acetyl-2-adamantenyldenehydrazone was prepared by refluxing a solution of acetylhydrazine (2.47 g, 33.3 mmol) and adamantone (5.00 g, 33.3 mmol) in ethanol (20 ml), with the addition of Na<sub>2</sub>SO<sub>4</sub> (4.00 g, 28.2 mmol) and catalytic amounts of acetic acid (0.1 ml, 1.75 mmol), for 24 h. The solution was then removed under vacuum and the residue was recrystallized from ethanol to afford the acetylhydrazone (4.77 g, 23.1 mmol) in 69% yield as a mixture of its *E* and *Z* isomers. Reaction of the latter acetylhydrazone (4.47 g, 21.7 mmol) and lead tetraacetate (10.0 g, 22.6 mmol) in absolute methanol (94 ml) afforded 5-methoxy-5-methylspiro( $\Delta^3$ -1,3,4-oxadiazolin-2,2'-tricyclo[3.3.1.1<sup>3,7</sup>]decane) (1.43 g, 6.05 mmol, 28%) as a racemic mixture. A solution of the latter oxadiazoline (1.00 g, 4.23 mmol) and dimethyl acetylenedicarboxylate (1.50 g, 10.6 mmol) in diethyl ether (200 ml) was irradiated with a medium pressure mercury lamp at room temperature for 11 h. After the volatiles had been removed *in vacuo*, column chromatography (silica gel, hexane/ethyl acetate 30:1) provided 296 mg (34%) of (I). Single crystals of (I) were obtained by slow evaporation of a solution in pentane/dichloromethane at 273 K.

### Compound (I) at 204 K

#### Crystal data

C<sub>26</sub>H<sub>34</sub>O<sub>4</sub>  
*M<sub>r</sub>* = 410.53  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 13.5686 (9) Å  
*b* = 16.0982 (18) Å  
*c* = 19.615 (3) Å  
 $\beta$  = 91.086 (12)°  
*V* = 4283.7 (8) Å<sup>3</sup>  
*Z* = 8

#### Data collection

Siemens SMART diffractometer  
 $\omega$  scans  
 Absorption correction: numerical  
 using six faces (*SHELXTL*;  
 Sheldrick, 1996)  
*T*<sub>min</sub> = 0.959, *T*<sub>max</sub> = 0.971  
 74 545 measured reflections  
 12 064 independent reflections  
 7584 reflections with *I* > 2 $\sigma$ (*I*)

#### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.059  
*wR*(*F*<sup>2</sup>) = 0.159  
*S* = 1.14  
 12 064 reflections  
 545 parameters  
 H-atom parameters constrained

*D<sub>x</sub>* = 1.273 Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation  
 Cell parameters from 318  
 reflections  
 $\theta$  = 3–23°  
 $\mu$  = 0.08 mm<sup>-1</sup>  
*T* = 204 (2) K  
 Block, colourless  
 0.52 × 0.44 × 0.40 mm

*R*<sub>int</sub> = 0.052  
 $\theta$ <sub>max</sub> = 30°  
*h* = -18 → 18  
*k* = -20 → 22  
*l* = -27 → 26  
 708 standard reflections  
 frequency: 600 min  
 intensity decay: none

$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 1.3P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.55 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$

**Table 1**

Hydrogen-bonding geometry (Å, °) for (I) at 204 K.

| <i>D</i> —H··· <i>A</i>        | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|--------------------------------|-------------|---------------|-----------------------|-------------------------|
| C8A—H8A···O2A                  | 0.99        | 2.35          | 3.014 (2)             | 123                     |
| C8B—H8B···O2B                  | 0.99        | 2.36          | 3.009 (2)             | 123                     |
| C18A—H18A···O3A                | 0.99        | 2.33          | 3.005 (2)             | 124                     |
| C18B—H18B···O3B                | 0.99        | 2.32          | 3.002 (2)             | 125                     |
| C6A—H6B···O4B <sup>i</sup>     | 0.97        | 2.64          | 3.472 (2)             | 143                     |
| C6B—H6E···O4A <sup>ii</sup>    | 0.97        | 2.62          | 3.481 (2)             | 149                     |
| C13A—H13A···O4A <sup>ii</sup>  | 0.98        | 2.65          | 3.379 (2)             | 131                     |
| C13B—H13C···O4B <sup>iii</sup> | 0.98        | 2.69          | 3.424 (2)             | 132                     |
| C23A—H23B···O4A <sup>ii</sup>  | 0.98        | 2.73          | 3.499 (2)             | 136                     |
| C23B—H23D···O4B <sup>iii</sup> | 0.98        | 2.66          | 3.405 (2)             | 133                     |
| C26A—H26A···O2A <sup>iv</sup>  | 0.98        | 2.63          | 3.591 (2)             | 167                     |

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

### Compound (I) at 142 K

#### Crystal data

C<sub>26</sub>H<sub>34</sub>O<sub>4</sub>  
*M<sub>r</sub>* = 410.53  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 13.5304 (15) Å  
*b* = 16.005 (2) Å  
*c* = 39.089 (7) Å  
 $\beta$  = 91.147 (12)°  
*V* = 8463 (2) Å<sup>3</sup>  
*Z* = 16

*D<sub>x</sub>* = 1.289 Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation  
 Cell parameters from 211  
 reflections  
 $\theta$  = 3–23°  
 $\mu$  = 0.09 mm<sup>-1</sup>  
*T* = 142 (2) K  
 Block, colourless  
 0.52 × 0.44 × 0.40 mm

#### Data collection

Siemens SMART diffractometer  
 $\omega$  scans  
 Absorption correction: numerical  
 using six faces (*SHELXTL*;  
 Sheldrick, 1996)  
*T*<sub>min</sub> = 0.960, *T*<sub>max</sub> = 0.971  
 94 848 measured reflections  
 26 202 independent reflections  
 14 015 reflections with *I* > 2 $\sigma$ (*I*)

*R*<sub>int</sub> = 0.082  
 $\theta$ <sub>max</sub> = 31.5°  
*h* = -17 → 18  
*k* = -24 → 21  
*l* = -58 → 50  
 599 standard reflections  
 frequency: 600 min  
 intensity decay: none

**Table 2**

Hydrogen-bonding geometry (Å, °) for (I) at 142 K.

| <i>D</i> —H··· <i>A</i>         | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|---------------------------------|-------------|---------------|-----------------------|-------------------------|
| C8A—H8A···O2A                   | 1.00        | 2.35          | 3.003 (4)             | 122                     |
| C8B—H8B···O2B                   | 1.00        | 2.34          | 3.019 (4)             | 125                     |
| C8C—H8C···O2C                   | 1.00        | 2.34          | 3.012 (3)             | 124                     |
| C8D—H8D···O2D                   | 1.00        | 2.35          | 3.008 (3)             | 123                     |
| C18A—H18A···O3A                 | 1.00        | 2.34          | 2.999 (4)             | 123                     |
| C18B—H18B···O3B                 | 1.00        | 2.31          | 3.002 (3)             | 126                     |
| C18C—H18C···O3C                 | 1.00        | 2.33          | 3.006 (3)             | 124                     |
| C18D—H18D···O3D                 | 1.00        | 2.32          | 3.005 (3)             | 125                     |
| C6A—H6C···O4A <sup>i</sup>      | 0.98        | 2.58          | 3.463 (4)             | 149                     |
| C6B—H6F···O4B <sup>ii</sup>     | 0.98        | 2.51          | 3.440 (4)             | 159                     |
| C6C—H6I···O4D <sup>iii</sup>    | 0.98        | 2.66          | 3.454 (4)             | 138                     |
| C6D—H6K···O4C <sup>iv</sup>     | 0.98        | 2.64          | 3.460 (4)             | 141                     |
| C13A—H13B···O4B <sup>v</sup>    | 0.99        | 2.69          | 3.437 (4)             | 133                     |
| C13B—H13D···O4A <sup>v</sup>    | 0.99        | 2.62          | 3.334 (4)             | 129                     |
| C13C—H13E···O4C <sup>vi</sup>   | 0.99        | 2.61          | 3.353 (4)             | 132                     |
| C13D—H13G···O4D <sup>vii</sup>  | 0.99        | 2.65          | 3.391 (4)             | 132                     |
| C23A—H23B···O4B <sup>v</sup>    | 0.99        | 2.70          | 3.499 (4)             | 138                     |
| C23B—H23C···O4A <sup>v</sup>    | 0.99        | 2.63          | 3.364 (4)             | 131                     |
| C23C—H23F···O4C <sup>vi</sup>   | 0.99        | 2.69          | 3.469 (4)             | 135                     |
| C23D—H23H···O4D <sup>vii</sup>  | 0.99        | 2.62          | 3.391 (3)             | 134                     |
| C26A—H26B···O2C                 | 0.99        | 2.62          | 3.590 (3)             | 166                     |
| C26C—H26E···O2B <sup>viii</sup> | 0.99        | 2.58          | 3.556 (3)             | 167                     |

Symmetry codes: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $1 - x, 1 - y, 2 - z$ ; (iii)  $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$ ; (iv)  $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$ ; (v)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$ ; (vi)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (vii)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (viii)  $x, y, z - 1$ .

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.100$   
 $wR(F^2) = 0.246$   
 $S = 1.16$   
 26 202 reflections  
 1089 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 13P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.007$   
 $\Delta\rho_{\max} = 0.73 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.35 \text{ e } \text{Å}^{-3}$

The  $h0l$  reflections at 204 K were absent for  $l$  odd and were extremely weak, but were not absent for  $h$  odd. As  $0k0$  reflections were absent for  $k$  odd, the space group could be determined as  $P2_1/c$ . The  $h0l$  reflections with  $h$  odd or  $l$  odd at 142 K showed no significant net intensity. Thus, the space group could not be derived from the systematically absent reflections alone. The structure determination at 142 K was attempted with *SHELXS97* (Sheldrick, 1997) using the *TREF* 100000 option in space groups  $P2_1/a$ ,  $P2_1/c$  and  $P2_1/n$ . No meaningful solution was obtained in  $P2_1/c$ , a solution corresponding to a partly disordered structure was obtained in  $P2_1/a$  and a promising solution with four independent ordered molecules was obtained in  $P2_1/n$ . Thus,  $P2_1/n$  was taken as the correct space group. The H atoms were taken from a difference Fourier synthesis and were refined with fixed individual displacement parameters [ $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  and  $U(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$ ], using a riding model with fixed distances: methyl, secondary and primary H—C distances of 0.97, 0.98 and

0.99 Å at 204 K, and 0.98, 0.99 and 1.00 Å at 142 K, respectively. The torsion angles about the C—O bonds of the methoxy groups were refined.

For (I) at both temperatures, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1459). Services for accessing these data are described at the back of the journal.

## References

- Desiraju, G. R. & Steiner, T. (1999). Editors. *The Weak Hydrogen Bond*, ch. 2. Oxford University Press.
- Jefferson, E. A. & Warkentin, J. (1992). *J. Am. Chem. Soc.* **114**, 6318–6325.
- Sheldrick, G. M. (1996). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.