

Low-temperature (110 K) single-crystal neutron diffraction study of ( $\pm$ )-camphoric anhydrideDitebogo B. Kgomo,<sup>a</sup>  
Demetrius C. Levendis,<sup>b</sup> Arsen  
Gukasov,<sup>c</sup> Alain Cousson,<sup>c\*</sup>  
Ludwig F. R. Schöning<sup>b</sup> and  
Andrew M. Venter<sup>a</sup><sup>a</sup>Radiation Utilisation, Nuclear Technology, South African Nuclear Energy Corporation, Church Street West Ext Pelindaba, Pretoria 0001, South Africa, <sup>b</sup>Molecular Sciences Institute, Jan Boeyens Structural Chemistry Laboratory, School of Chemistry, University of the Witwatersrand, Private Bag 3, Wits 2050, Johannesburg, South Africa, and <sup>c</sup>Laboratoire Léon Brillouin, CEA, Saclay, 91191 Gif-sur-Yvette CEDEX, FranceCorrespondence e-mail:  
cousson@dsm-mail.saclay.cea.fr

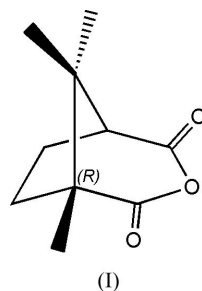
## Key indicators

Single-crystal neutron study  
 $T = 110\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$   
 $R$  factor = 0.059  
 $wR$  factor = 0.057  
Data-to-parameter ratio = 6.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

This single-crystal neutron diffraction study of ( $\pm$ )-camphoric anhydride [systematic name: (*RS*)-1,8,8-trimethyl-3-oxabicyclo[3.2.1]octane-2,4-dione],  $\text{C}_{10}\text{H}_{14}\text{O}_3$ , at 110 K was undertaken to determine accurately the positions of the H atoms. The crystal packing of these molecules depends on intermolecular hydrogen bonding. The (+) and (−) molecules are held together by weak  $\text{C}-\text{H}\cdots\text{O}$  interactions to form chains in the crystal structure.

## Comment

Camphoric anhydride, (I), is a chiral polar near-spherical molecule, the enantiomers of which are miscible in a wide range of proportions in the solid state (Mjojo & Welsh, 1992). It has been used in organic syntheses, such as in the synthesis of  $\alpha$ -necrodols (Dmowski & Piasecka-Maciejewska, 2000) and chiral carboxylic acid ligands (Moloney *et al.*, 1996).



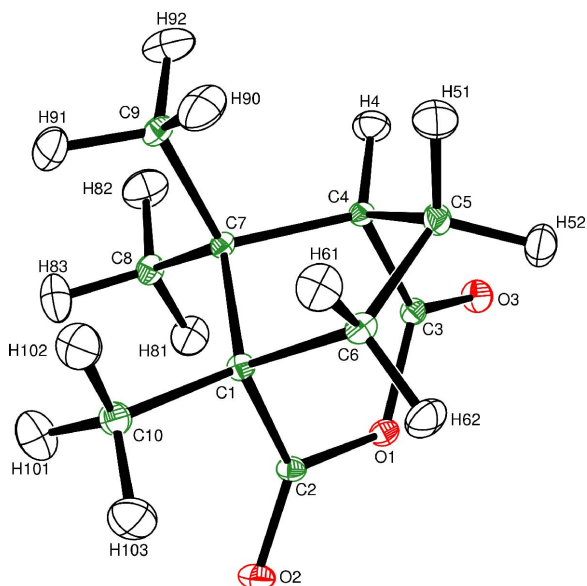
In previous studies, it was found that, for all compositions of mixtures of (+)- and (−)-camphoric anhydride, the only transition occurring is a first-order relaxation process involving orientational disorder (Mjojo & Welsh, 1992). The transition in the racemate occurs at a lower temperature compared with the pure isomer, due to the presence of strong chirodiastaltic interactions in the pure isomer. The crystal structure was first studied with X-rays by Wichmann & Bradaczek (1987). The interaction between neighbouring (+)-(+) or (+)-(−) enantiomers has also been of interest in related near-spherical molecules, such as camphor, which shows three solid phases (Mjojo, 1979; Schäffer & Wagner, 1958). The racemic and (+)-camphor structures have been studied recently using high-resolution powder X-ray diffraction data (Mora & Fitch, 1997; Brunelli *et al.* 2002). Weak  $\text{C}-\text{H}\cdots\text{O}$  interactions, which have long been recognized as significant in determining the structure of organic solids (Desiraju, 1996; Desiraju, 2002), play an important role in stabilizing both the camphor and the camphoric anhydride structures (Kumaradhas *et al.* 2000).

The structure of (I) at 110 K was studied with X-rays by Kumaradhas *et al.* (2000). In the present work, the single-crystal neutron diffraction study at 110 K was carried out to

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**Figure 1**

A view of the molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level for all atoms.

determine accurately the positions of the H atoms and to compare the results with the X-ray studies at the same temperature. It is known that bond lengths determined by neutron diffraction are usually longer than those obtained from X-ray diffraction. The bond lengths found in the present neutron diffraction study are also longer than those obtained in earlier X-ray studies. In our case, the C–H bond length varies between 1.094 (6) and 1.115 (7) Å, compared with 0.91 (2) and 1.02 (2) Å from X-ray studies (Kumaradhas *et al.*, 2000). Note that the average C–H distance for neutron diffraction studies is given as 1.083 Å (Rowland & Taylor, 1996). On the other hand, the bond angles are found to be in good agreement with those from X-ray diffraction.

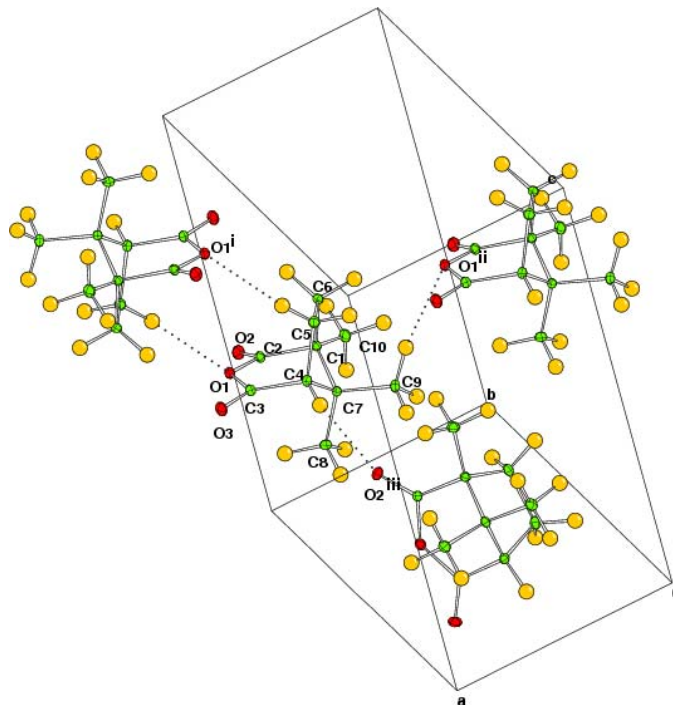
The three most significant C–H···O interactions in (I) are reported in Table 1, with H···O distances ranging from 2.51 (1) to 2.58 (1) Å. In the (+)-camphor structure, the reported H···O distances range between 2.36 and 2.90 Å (Brunelli *et al.* 2002). The network of C–H···O interactions in (I) is shown in Fig. 2.

## Experimental

Commercial grade (±)-camphoric anhydride was recrystallized from toluene by slow evaporation at room temperature.

### Crystal data

$C_{10}H_{14}O_3$	Neutron radiation
$M_r = 182.22$	$\lambda = 0.833 \text{ \AA}$
Monoclinic, $P2_1/n$	Cell parameters from 15 reflections
$a = 6.5001 (8) \text{ \AA}$	$\theta = 16\text{--}22^\circ$
$b = 11.5624 (14) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 12.7093 (15) \text{ \AA}$	$T = 110 \text{ K}$
$\beta = 92.179 (2)^\circ$	Prism, colourless
$V = 954.5 (2) \text{ \AA}^3$	$5.0 \times 4.0 \times 3.0 \text{ mm}$
$Z = 4$	
$D_x = 1.268 \text{ Mg m}^{-3}$	


**Figure 2**

A packing diagram for (I), showing the C–H···O interactions. [Symmetry codes: (i)  $2 - x, 2 - y, 1 - z$ ; (ii)  $x - 1, y, z$ ; (iii)  $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$ ]

### Data collection

5C2 four-circle diffractometer	1594 reflections with $I > 3\sigma(I)$
(Orphée reactor, Saclay, France)	$R_{\text{int}} = 0.047$
$\omega$ scans	$\theta_{\text{max}} = 39.5^\circ$
Absorption correction: none	$h = -9 \rightarrow 9$
4137 measured reflections	$k = -17 \rightarrow 1$
3553 independent reflections	$l = 0 \rightarrow 19$

### Refinement

Refinement on $F$	$= F_o/F_{\text{max}}$ and $T_i$ are Chebyshev
$R[F^2 > 2\sigma(F^2)] = 0.059$	polynomials (Watkin, 1994;
$wR(F^2) = 0.057$	Prince, 1982)
$S = 1.10$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1594 reflections	$\Delta\rho_{\text{max}} = 0.12 \text{ e \AA}^{-3}$
245 parameters	$\Delta\rho_{\text{min}} = -0.14 \text{ e \AA}^{-3}$
All H-atom parameters refined	Extinction correction: Larson
$w = [1 - (F_o - F_c)^2 / (0.703T_0(x) - 0.458T_1(x) + 0.556T_2(x) - 0.177T_3(x) + 0.0795T_4(x))] \text{ where } x$	(1970), eq. 22
	Extinction coefficient: 3.4 (8)

**Table 1**

Hydrogen-bond geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$C4\text{--}H4\cdots O2^i$	1.11 (1)	2.51 (1)	3.514 (3)	149 (1)
$C5\text{--}H52\cdots O1^{iii}$	1.10 (1)	2.58 (1)	3.655 (3)	165 (1)
$C9\text{--}H90\cdots O1^{iii}$	1.10 (1)	2.54 (1)	3.633 (3)	171 (1)

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

The H atoms were located in the Fourier map and refined anisotropically.

Data collection: *DIF4N* (modified Linux version of *DIF4*; Stoe & Cie, 1991); cell refinement: *DIF4N*; data reduction: *PRON98*

(modified version of *REDU4*; Stoe & Cie, 1990); program(s) used to solve structure: a previous X-ray study gave position parameters for heavy atoms (Kumaradhas *et al.*, 2000); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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