

Table 4. Mean-square amplitudes of nuclear displacements ( $\text{\AA}^2 \times 10^3$ ) parallel  $U_{11}$  and transverse  $U_{\perp}$  to C—H and C—D bond directions

	C <sub>2</sub> H <sub>2</sub> (131 K)	C <sub>2</sub> H <sub>2</sub> (141 K)	C <sub>2</sub> D <sub>2</sub> (143 K)	C <sub>2</sub> D <sub>2</sub> (15 K)
C $U_{11}$	55 (2)	60 (2)	47 (2)	15 (1)
C $U_{\perp}$	59 (1)	63 (1)	67 (2)	19 (1), 27 (1)*
H(D) $U_{11}$	65 (4)	65 (4)	60 (2)	23 (2)
H(D) $U_{\perp}$	163 (2)	177 (4)	182 (4)	54 (3), 57 (2)*

\* Normal to layers of molecules ( $= U_{33}$ ).

The neutron diffraction study was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the US Department of Energy and supported by its Office of Basic Energy Sciences. One of us (PP) gratefully acknowledges the financial support of the Belgian National Science Foundation, NFWO.

#### References

- ANDERSON, A. & SMITH, W. H. (1966). *J. Chem. Phys.* **44**, 4216–4219.
- BECKER, P. J. & COPPENS, P. (1974). *Acta Cryst.* **A30**, 129–147.
- BOTTGER, G. L. & EGGERS, D. F. (1964). *J. Chem. Phys.* **40**, 2010–2017.
- BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.
- COLLINS, R. L. (1952). *Acta Cryst.* **5**, 431–432.
- DUNITZ, J. D., GEHRER, H. & BRITTON, D. (1972). *Acta Cryst.* **A28**, 1899–1994.
- FAST, H. & WELSH, H. L. (1972). *J. Mol. Spectrosc.* **41**, 203–221.
- HIRSHFELD, F. L. (1976). *Acta Cryst.* **A32**, 239–244.
- HUANG, Z. S. & MILLER, R. E. (1987). *J. Chem. Phys.* **86**, 6059–6064.
- ITO, M., YOKOYAMA, T. & SUZUKI, M. (1970). *Spectrochim. Acta*, **26A**, 695–705.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- KOESTER, L. (1977). *Springer Tracts in Modern Physics*, Vol. 80, *Neutron Physics*, edited by G. HÖHLER, p. 36. Berlin: Springer.
- KOETZLE, T. F. & MCMULLAN, R. K. (1980). Research Memo C-4. Brookhaven National Laboratory, USA.
- KOSKI, H. K. (1975a). *Z. Naturforsch. Teil A*, **30**, 1028–1031.
- KOSKI, H. K. (1975b). *Acta Cryst.* **B31**, 933–935.
- KOSKI, H. K. (1975c). *Cryst. Struct. Commun.* **4**, 337–341.
- KOSKI, H. K. (1975d). *Cryst. Struct. Commun.* **4**, 343–347.
- KOSKI, H. K. & SÁNDOR, E. (1975a). *Chem. Phys. Lett.* **30**, 501–503.
- KOSKI, H. K. & SÁNDOR, E. (1975b). *Acta Cryst.* **B31**, 350–353.
- KVICK, Å., MCMULLAN, R. K. & NEWTON, M. D. (1982). *J. Chem. Phys.* **76**, 3754–3761.
- LENSTRA, A. T. H., VAN ALSENOY, C., POPELIER, P. & GEISE, H. J. (1992). To be published.
- LUNDGREN, J.-O. (1982). Report UUIC-B13-4-05. Institute of Chemistry, Univ. of Uppsala, Sweden.
- NELSON, D. D., FRASER, G. T. & KLEMPERER, W. (1985). *J. Chem. Phys.* **82**, 4483–4485.
- NES, G. J. H. VAN & VAN BOLHUIS, F. (1979). *Acta Cryst.* **B35**, 2580–2593.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
- READ, W. G. & FLYGARE, W. H. (1982). *J. Chem. Phys.* **76**, 2238–2246.
- SMITH, W. H. (1969). *Chem. Phys. Lett.* **3**, 464–466.
- SUGAWARA, T. & KANDA, E. (1952). *Sci. Rep. Res. Inst. Tôhoku Univ. Ser. A*, **4**, 607–614, as quoted by VAN NES & VAN BOLHUIS (1979).
- WYCKOFF, R. W. G. (1963). *Crystal Structures*, 2nd ed., Vol. 1, p. 368. New York: Interscience.

*Acta Cryst.* (1992). **B48**, 731–737

## meso- and D,L-D<sub>3</sub>-Trishomocubylidene-D<sub>3</sub>-trishomocubane Oxides and D,L-Bi-D<sub>3</sub>-trishomocubyl

BY WILLIAM H. WATSON,\* RAM P. KASHYAP AND MARIUSZ KRAWIEC

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, USA

AND ALAN P. MARCHAND,\* C. MADHUSUDHAN REDDY AND VIJAY R. GADGIL

Department of Chemistry, University of North Texas, PO Box 5068, Denton, Texas 76203, USA

(Received 2 January 1992; accepted 13 April 1992)

#### Abstract

meso-D<sub>3</sub>-Trishomocubylidene-D<sub>3</sub>-trishomocubane oxide, (2a), C<sub>22</sub>H<sub>24</sub>O,  $M_r = 304.44$ , monoclinic,  $P2_1/a$ ,  $a = 12.337$  (2),  $b = 6.361$  (3),  $c = 19.891$  (2) Å,  $\beta = 96.44$  (1)°,  $V = 1551.1$  (9) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.303$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.72$  cm<sup>-1</sup>,  $F(000) = 656$ ,  $T = 296$  K,  $R = 0.049$  for

1321 reflections. D,L-D<sub>3</sub>-Trishomocubylidene-D<sub>3</sub>-trishomocubane oxide, (2b), C<sub>22</sub>H<sub>24</sub>O,  $M_r = 304.44$ , monoclinic,  $C2/c$ ,  $a = 21.471$  (5),  $b = 6.352$  (1),  $c = 12.351$  (3) Å,  $\beta = 117.26$  (1)°,  $V = 1497.4$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.350$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu = 5.77$  cm<sup>-1</sup>,  $F(000) = 656$ ,  $T = 296$  K,  $R = 0.051$  for 1085 reflections. D,L-Bi-D<sub>3</sub>-trishomocubyl, (3), C<sub>22</sub>H<sub>26</sub>,  $M_r = 290.45$ , triclinic,  $P\bar{1}$ ,  $a = 6.324$  (1),  $b = 10.591$  (2),  $c = 11.767$  (3) Å,  $\alpha = 103.14$  (2),  $\beta =$

\* Authors to whom correspondence should be addressed.

99.18 (2),  $\gamma = 95.67$  (1)°,  $V = 750.1$  (3) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.286$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.67$  cm<sup>-1</sup>,  $F(000) = 316$ ,  $T = 298$  K,  $R = 0.063$  for 2387 reflections. The trishomocubane moieties can be considered as formed from three multiply fused norbornane groups. The strained homocubane systems have nine C—C—C angles between 94.1 and 98.8° and 18 between 102.7 and 105.8°. There are three distinct classes of bond lengths which average 1.518 (5), 1.527 (8) and 1.567 (5) Å in the three structures. The X-ray parameters are compared with those from the Cambridge Structural Database and with theoretical calculations of trishomocubane using the programs *MM3*, *AM1* and *GAUSSIAN90*. These parameters are also compared with those from experimental and theoretical studies of norbornane. The density of the D,L-isomer (2b) is significantly larger than that of the *meso*-isomer (2a).

### Introduction

As part of a general investigation of the synthesis and chemistry of novel polycyclic cage systems (Marchand, 1989), we recently reported the synthesis of *meso*- and D,L-*D*<sub>3</sub>-trishomocubylidene-*D*<sub>3</sub>-trishomocubane [(1a) and (1b), respectively] along with the results obtained *via* addition of biparticulate electrophiles (*i.e.*, CF<sub>3</sub>CO<sub>2</sub>H and Br<sub>2</sub>) to the C=C double bond in each of these novel alkenes (Marchand *et al.*, 1990). More recently, we initiated an investigation of the corresponding addition of uniparticulate electrophiles (Paquette, Allen & Broadhurst, 1971) to these systems (see scheme below). In the first study, we investigated the epoxidation of the C=C double bond in (1a) and (1b) by using *m*-chloroperbenzoic acid (MCPBA). Each epoxidation reaction proceeded smoothly, thereby affording the corresponding *meso*-epoxide [(2a), m.p.

Table 1. Crystal data and collection and refinement parameters

	(2a)	(2b)	(3)
Color	Colorless	Colorless	Colorless
Size (mm)	0.43 × 0.45 × 0.28	0.32 × 0.20 × 0.15	0.45 × 0.38 × 0.09
$\lambda$ (Å)	0.71069	1.54178	0.71069
Unit-cell reflections	16	25	25
2 $\theta$ range (°)	20.07–23.39	77.80–79.86	23.74–28.50
Data-collection method	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$
2 $\theta$ range (°)	3–50	3–120	3–50
Scan speed (° min <sup>-1</sup> )	16.0*	8.0*	4–29.3
Reference reflections	3	3	2
<i>hkl</i> range	-2, 14; 0, 7; -21, 21	0, 23; 0, 7; -14, 14	-2, 8; -13, 13; -15, 15
Reflections measured	3752	1414	4962
Unique reflections	3006	1373	3439
$R_{int}$	0.041	0.071	0.007
Reflections > 3 $\sigma(I)$	1321	1085	2387
Systematic absences	<i>h</i> 0 <i>l</i> : <i>h</i> ≠ 2 <i>n</i> 0 <i>k</i> 0: <i>k</i> ≠ 2 <i>n</i>	<i>hkl</i> : <i>h</i> + <i>k</i> ≠ 2 <i>n</i> <i>h</i> 0 <i>l</i> : <i>l</i> ≠ 2 <i>n</i>	None
Transmission factors	0.95–1.00	0.92–1.00	0.92–0.96
<i>R</i>	0.049	0.051	0.063
<i>wR</i>	0.049	0.055	0.056
Number of parameters	305	154	303
<i>S</i>	2.44	5.95	1.39
( $\Delta/\sigma$ ) <sub>max</sub>	0.04	0.01	0.02
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.18, -0.21	0.22, -0.26	0.27, -0.26

\* Weak reflections [ $I < 10.0\sigma(I)$ ] rescanned three times.

463–464 K] and the D,L-epoxide [(2b), m.p. 514 K], respectively. The X-ray structures of compounds (2a) and (2b), as well as the fully saturated reference compound (3), are reported. In addition, the bond lengths and angles in trishomocubane (4) have been investigated theoretically through the use of *MM3* (Allinger, Yuh & Li, 1989), *AMPAC* (Dewar, Zoebisch, Healy & Stewart, 1985) and *GAUSSIAN90* (Frisch *et al.*, 1990). These values are compared with those obtained from the three X-ray structures and from an analysis of literature data. Since trishomocubane can be considered to be composed of three highly fused norbornane moieties, (5), these data are compared with those reported for norbornane.

### Experimental

All compounds were obtained by synthesis. Crystal data and data collection and refinement parameters are given in Table 1. Data for compounds (2a) and (2b) were collected on two Rigaku AFC-6s diffractometers while data for (3) were collected on a Nicolet R3M/ $\mu$  update of a Syntex P2<sub>1</sub> diffractometer. Lorentz and polarization corrections and a  $\psi$ -scan absorption correction were applied. The structures were solved by direct methods and refined by full-matrix least-squares techniques. The function minimized for all structures was  $\sum w(|F_o| - |F_c|)^2$  where  $w = 4F_o^2/\sigma^2(F_o^2)$  with  $\sigma^2(F_o^2)$  from counting statistics with a *p* factor of 0.01 for compounds (2a) and (2b) and  $w = [\sigma^2(F_o) + 0.00043F_o^2]^{-1}$  for compound (3). Neutral-atom scattering factors and

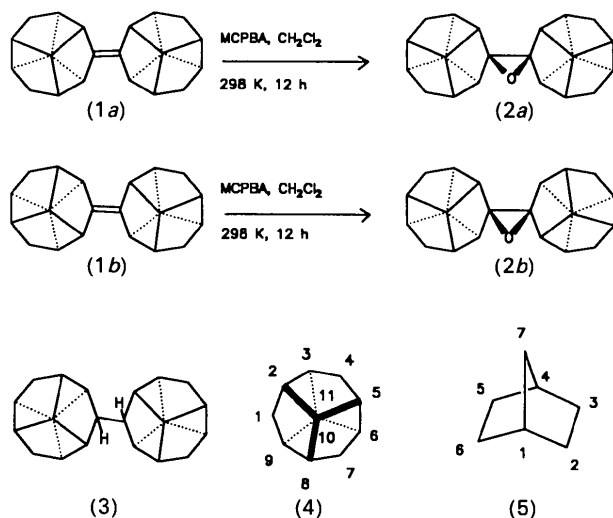


Table 2. Atomic positional parameters for compound (2a)

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq} (\text{\AA}^2)$
O(1)	0.5196 (3)	0.3150 (5)	0.2653 (1)	3.6 (2)
C(1)	0.4778 (4)	0.1305 (7)	0.2265 (2)	2.8 (2)
C(2)	0.5018 (4)	0.1110 (8)	0.1545 (2)	3.0 (2)
C(3)	0.4274 (4)	0.2814 (9)	0.1193 (3)	3.6 (3)
C(4)	0.4104 (5)	0.2084 (10)	0.0465 (3)	4.3 (3)
C(5)	0.3611 (4)	-0.0010 (9)	0.0632 (3)	3.9 (3)
C(6)	0.2631 (4)	0.0611 (10)	0.0973 (3)	4.2 (3)
C(7)	0.2416 (5)	-0.1301 (12)	0.1400 (3)	4.9 (3)
C(8)	0.3538 (4)	-0.1271 (9)	0.1795 (3)	3.8 (3)
C(9)	0.3575 (4)	0.0899 (8)	0.2129 (2)	3.3 (2)
C(10)	0.4364 (4)	-0.0865 (8)	0.1266 (3)	3.6 (3)
C(11)	0.3193 (4)	0.2240 (9)	0.1491 (3)	3.6 (3)
C(12)	0.5506 (4)	0.1030 (7)	0.2896 (2)	2.7 (2)
C(13)	0.5222 (4)	0.0266 (8)	0.3563 (2)	3.1 (2)
C(14)	0.5533 (4)	-0.2053 (8)	0.3544 (2)	3.2 (2)
C(15)	0.5738 (5)	-0.2637 (9)	0.4292 (3)	3.8 (3)
C(16)	0.6637 (4)	-0.1028 (8)	0.4447 (2)	3.4 (2)
C(17)	0.7477 (4)	-0.1607 (9)	0.3971 (3)	3.7 (3)
C(18)	0.8110 (4)	0.0421 (9)	0.3904 (3)	3.8 (3)
C(19)	0.7101 (4)	0.1664 (8)	0.3636 (2)	2.9 (2)
C(20)	0.6677 (4)	0.0441 (7)	0.2998 (2)	2.7 (2)
C(21)	0.6188 (4)	0.1051 (8)	0.4085 (2)	2.9 (2)
C(22)	0.6687 (4)	-0.1829 (8)	0.3299 (2)	3.0 (2)

anomalous scattering factors were taken from *International Tables for X-ray Crystallography* (Cromer & Waber, 1974; Cromer, 1974). Calculations for compounds (2a) and (2b) used the *TEXSAN* (Molecular Structure Corporation, 1985) program package on a MicroVAX 3100/76 cluster. Analysis of compound (3) used a Desktop 30 Microclipse and Nova 4/C configuration and the *SHELXTL* (Nicolet Instrument Corporation, 1986) program package. All theoretical calculations were performed on the MicroVAX cluster using *MM3* (Allinger, Yuh & Li, 1989), *AMPAC* (Dewar, Zoebisch, Healy & Stewart, 1985) and *GAUSSIAN90* (Frisch *et al.*, 1990).

Tables 2–4 contain the atomic positional parameters for compounds (2a), (2b) and (3). Table 5 gives the bond lengths for the three compounds and the average bond lengths for ten fragments extracted

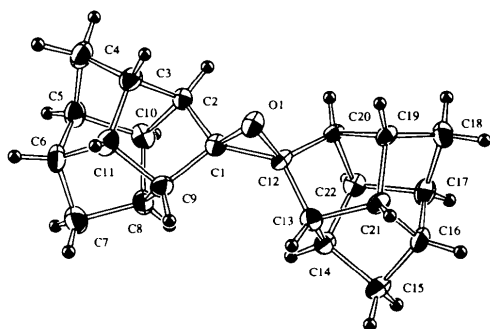


Fig. 1. Thermal-ellipsoid drawing for compound (2a). Ellipsoids are drawn at the 35% probability level. H atoms are represented by spheres of arbitrary size.

Table 3. Atomic positional parameters for compound (2b)

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq} (\text{\AA}^2)$
O(1)	1.000	0.0539 (3)	1/4	4.25 (9)
C(1)	0.9682 (1)	-0.1465 (3)	0.2559 (2)	3.69 (8)
C(2)	0.9585 (1)	-0.1992 (3)	0.3650 (2)	3.84 (9)
C(3)	0.8934 (1)	-0.0728 (4)	0.3454 (2)	4.2 (1)
C(4)	0.8662 (1)	-0.1943 (4)	0.4199 (3)	4.9 (1)
C(5)	0.8566 (1)	-0.3982 (4)	0.3504 (2)	4.6 (1)
C(6)	0.8067 (1)	-0.3372 (4)	0.2186 (2)	4.5 (1)
C(7)	0.8206 (1)	-0.5010 (4)	0.1435 (3)	4.7 (1)
C(8)	0.8979 (1)	-0.4472 (4)	0.1946 (2)	4.1 (1)
C(9)	0.8963 (1)	-0.2151 (4)	0.1617 (2)	3.87 (9)
C(10)	0.9253 (1)	-0.4241 (4)	0.3363 (2)	4.0 (1)
C(11)	0.8446 (1)	-0.1332 (4)	0.2088 (2)	4.1 (1)

from the Cambridge Structural Database (Allen, Kennard & Taylor, 1983; references for the structural fragments are given in Table 5) while Table 6 lists selected valence angles for the three compounds. Figs. 1, 2 and 3 are thermal ellipsoid plots of the three compounds.\*

\* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors for compounds (2a), (2b) and (3) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55148 (57 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0578]

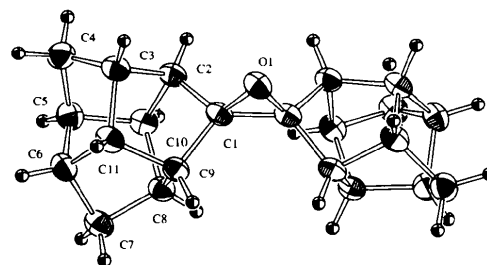


Fig. 2. Thermal-ellipsoid drawing for compound (2b). Ellipsoids are drawn at the 35% probability level. H atoms are represented by spheres of arbitrary size.

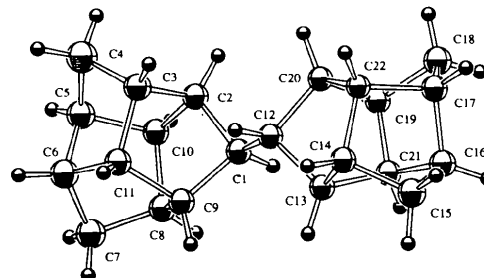


Fig. 3. Thermal-ellipsoid drawing for compound (3). Ellipsoids are drawn at the 35% probability level. H atoms are represented by spheres of arbitrary size.

Table 4. Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\times 10^3$ ) for compound (3)

Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	$x$	$y$	$z$	$U_{eq}(\text{\AA}^2)$
C(1)	2128 (3)	3860 (2)	7681 (2)	33 (1)
C(2)	1216 (4)	2665 (2)	6654 (2)	35 (1)
C(3)	-1220 (4)	2625 (2)	6516 (2)	39 (1)
C(4)	-2091 (4)	1196 (2)	5911 (2)	52 (1)
C(5)	-873 (4)	678 (2)	6889 (2)	43 (1)
C(6)	-1715 (4)	1340 (2)	7983 (2)	44 (1)
C(7)	58 (4)	1300 (2)	9004 (2)	45 (1)
C(8)	1798 (3)	2054 (2)	8575 (2)	38 (1)
C(9)	946 (3)	3344 (2)	8547 (2)	35 (1)
C(10)	1456 (3)	1454 (2)	7204 (2)	36 (1)
C(11)	-1405 (3)	2787 (2)	7852 (2)	38 (1)
C(12)	1662 (3)	5185 (2)	7499 (2)	32 (1)
C(13)	2890 (3)	6363 (2)	8455 (2)	33 (1)
C(14)	2046 (3)	7523 (2)	8056 (2)	35 (1)
C(15)	3825 (4)	8654 (2)	8674 (2)	42 (1)
C(16)	5563 (3)	8013 (2)	8098 (2)	38 (1)
C(17)	4680 (3)	7798 (2)	6775 (2)	37 (1)
C(18)	5837 (4)	6709 (2)	6202 (2)	42 (1)
C(19)	4994 (3)	5745 (2)	6870 (2)	33 (1)
C(20)	2538 (3)	5631 (2)	6501 (2)	32 (1)
C(21)	5230 (3)	6554 (2)	8186 (2)	34 (1)
C(22)	2342 (3)	7131 (2)	6732 (2)	31 (1)

### Discussion

Trishomocubane, (4), can be described as consisting of three highly fused norbornane, (5), units sharing common C—C bonds; *i.e.*, carbons (2, 3, 11, 9, 8, 10, 1), (3, 2, 10, 5, 6, 11, 4) and (8, 9, 11, 6, 5, 10, 7) of (4) each correspond to C(1) through C(7) of (5). Compounds (2a), (2b) and (3) are structures involving two trishomocubanes connected *via* an epoxide ring or a C—C single bond. The bond lengths and

valence angles for these compounds are listed in Tables 5 and 6. If we exclude the bonds and angles centered at C(1) because of the different substituents, the distances and angles from the four independent measurements agree quite well. The errors given in parentheses are the standard deviations calculated from the average of the four independent measurements. These data also show excellent agreement with the equivalent values extracted from the Cambridge Structural Database (Allen, Kennard & Taylor, 1983).

The bond lengths of an isolated norbornane molecule, (5), have been investigated by theoretical calculations and by gas-phase electron diffraction (GED). As a result of starting assumptions and large standard deviations there are a variety of interpretations of the GED (Yokozeki & Kuchitsu, 1971; Morino, Kuchitsu & Yokozeki, 1967; Dallinga & Toneman, 1968; Chiang, Wilcox & Bauer, 1968; Doms, Van den Enden, Geise & Van Alsenoy, 1983); however, a set of  $r_g$  parameters (Doms, Van den Enden, Geise & Van Alsenoy, 1983) has been recommended for (5). These parameters, analysis of data from the Cambridge Structural Database (Doms, Van Hemelrijk, Van de Mierop, Lenstra & Geise, 1985), and distances from a 4-21G basis-set calculation converted to  $R_\alpha$  geometry are given in Table 7. While valence-angle agreement was good, the bond-length variations, skewed distributions found in the X-ray structures from the Cambridge Structural Database, and the large standard deviations in the GED analysis did not permit the unequivocal sequencing of the bond lengths.

Table 5. Observed bond distances ( $\text{\AA}$ ) for compounds (2a), (2b) and (3)

	Compound (2a)		Compound (2b)	Compound (3)		Average X-ray <sup>c</sup>	Literature <sup>c</sup> X-ray
	X-ray	X-ray <sup>b</sup>	X-ray	X-ray	X-ray <sup>b</sup>		
C(1)—C(12)	1.470 (5)	—	1.439 (3)	1.516 (3)	—	—	—
C(1)—O(1)	1.466 (5)	1.469 (5)	1.462 (3)	—	—	—	—
C(1)—C(2)	1.499 (5)	1.491 (6)	1.492 (3)	1.527 (2)	1.523 (2)	1.506 (17)	1.517 (16)
C(1)—C(9)	1.500 (6)	1.484 (6)	1.510 (3)	1.521 (3)	1.523 (3)	1.508 (16)	1.516 (21)
C(2)—C(3)	1.538 (6)	1.526 (7)	1.533 (3)	1.518 (3)	1.525 (3)	1.528 (8)	1.528 (12)
C(2)—C(10)	1.561 (6)	1.571 (6)	1.564 (3)	1.573 (3)	1.565 (3)	1.567 (5)	1.572 (4)
C(3)—C(4)	1.513 (7)	1.526 (6)	1.508 (4)	1.524 (3)	1.518 (3)	1.518 (7)	1.516 (4)
C(3)—C(11)	1.562 (7)	1.563 (6)	1.572 (3)	1.567 (3)	1.565 (3)	1.566 (4)	1.568 (8)
C(4)—C(5)	1.517 (8)	1.515 (7)	1.515 (3)	1.519 (3)	1.518 (3)	1.517 (2)	1.513 (6)
C(5)—C(6)	1.504 (7)	1.526 (7)	1.534 (3)	1.521 (3)	1.525 (3)	1.522 (11)	1.524 (6)
C(5)—C(10)	1.576 (7)	1.576 (6)	1.571 (3)	1.559 (3)	1.568 (3)	1.570 (7)	1.563 (6)
C(6)—C(7)	1.524 (8)	1.521 (7)	1.511 (4)	1.518 (3)	1.513 (3)	1.517 (5)	1.512 (9)
C(6)—C(11)	1.568 (7)	1.570 (6)	1.564 (3)	1.571 (3)	1.563 (3)	1.567 (4)	1.566 (6)
C(7)—C(8)	1.513 (7)	1.520 (7)	1.521 (3)	1.514 (3)	1.528 (3)	1.519 (6)	1.514 (9)
C(8)—C(9)	1.530 (7)	1.530 (6)	1.526 (3)	1.523 (3)	1.529 (3)	1.528 (3)	1.527 (5)
C(8)—C(10)	1.567 (7)	1.564 (6)	1.577 (3)	1.565 (3)	1.566 (3)	1.568 (6)	1.568 (6)
C(9)—C(11)	1.557 (6)	1.562 (6)	1.562 (3)	1.565 (3)	1.571 (3)	1.563 (5)	1.564 (5)

Notes: (a) A search of the Cambridge Database (Allen, Kennard, & Taylor, 1983) yielded ten structural fragments with reported coordinates. The C(1)—C(2) and C(1)—C(9) distances show large standard deviations because of the differing substitution patterns involving C(1). The references are as follows: Marchand, Chou, Ekstrand & van der Helm (1976) (IPCUND); Marchand *et al.* (1990) (KETREG, KETRIK, KETRUIW, KETSAD); Tolstikov, Lerman, Galin, Struchkov & Andrianov (1978) (CUODOCS); Watson, Nagl, Marchand & Deshpande (1989) (JAPBIL, JAPBOR); Watson, Nagl, Marchand & Reddy (1990) (SEJPOM); Watson, Nagl, Marchand & Vidyasagar (1989) (SAZDAY). (b) Numbering for the independent half of the molecule generated by C( $j$ ) = C(11 +  $j$ ), *e.g.* C(2) becomes C(13). (c) Numbers in the parentheses are standard deviations of the five distances from the average value.

Table 6. Selected valence angles ( $^{\circ}$ ) for compounds (2a), (2b) and (3)

	Compound (2a)		Compound (2b)	Compound (3)		Average <sup>a</sup>	Literature average <sup>b</sup>
C(2)—C(1)—C(9)	96.4 (4)	96.8 (4)	96.6 (2)	93.5 (1)	93.7 (1)	95.4 (1.7)	95.9 (8)
C(1)—C(2)—C(3)	101.9 (4)	102.1 (4)	103.6 (2)	104.3 (2)	103.3 (1)	103.0 (1.0)	102.0 (6)
C(1)—C(2)—C(10)	104.9 (4)	104.4 (4)	103.7 (2)	105.0 (2)	106.0 (2)	104.8 (8)	104.6 (6)
C(3)—C(2)—C(10)	98.5 (4)	98.6 (4)	98.9 (2)	98.6 (2)	98.9 (2)	98.7 (2)	98.0 (2)
C(2)—C(3)—C(4)	103.4 (4)	103.1 (4)	102.5 (2)	103.6 (2)	103.1 (2)	103.1 (4)	103.2 (1)
C(2)—C(3)—C(11)	98.8 (4)	99.2 (4)	98.8 (2)	98.4 (2)	98.5 (2)	98.7 (3)	99.3 (3)
C(4)—C(3)—C(11)	105.1 (4)	105.6 (4)	106.0 (2)	105.3 (2)	105.8 (2)	105.6 (4)	105.2 (2)
C(3)—C(4)—C(5)	94.3 (4)	94.1 (4)	94.7 (2)	94.2 (2)	94.1 (1)	94.3 (3)	94.4 (2)
C(4)—C(5)—C(6)	103.3 (5)	104.1 (4)	103.5 (2)	103.0 (2)	103.0 (2)	103.4 (5)	103.3 (2)
C(4)—C(5)—C(10)	105.3 (4)	105.2 (4)	105.2 (2)	105.7 (2)	105.5 (2)	105.4 (2)	105.5 (2)
C(6)—C(5)—C(10)	99.3 (4)	98.4 (4)	98.3 (3)	98.7 (2)	98.8 (1)	98.7 (4)	98.8 (2)
C(5)—C(6)—C(7)	103.9 (5)	103.9 (4)	103.8 (2)	103.3 (2)	103.4 (2)	103.7 (3)	103.0 (4)
C(5)—C(6)—C(11)	98.7 (4)	98.7 (4)	99.0 (2)	98.7 (2)	98.9 (2)	98.8 (1)	98.5 (1)
C(7)—C(6)—C(11)	104.6 (4)	106.1 (4)	105.5 (2)	105.3 (2)	105.3 (2)	105.4 (5)	105.6 (1)
C(6)—C(7)—C(8)	94.2 (5)	93.7 (4)	94.4 (2)	94.1 (2)	94.3 (2)	94.1 (3)	94.7 (2)
C(7)—C(8)—C(9)	102.6 (5)	102.5 (4)	102.7 (2)	103.4 (2)	103.0 (2)	102.8 (4)	102.9 (2)
C(7)—C(8)—C(10)	106.2 (5)	106.5 (4)	105.2 (2)	105.7 (1)	105.6 (2)	105.8 (5)	105.1 (3)
C(9)—C(8)—C(10)	98.4 (4)	98.4 (4)	99.0 (2)	98.4 (2)	98.5 (2)	98.5 (3)	98.2 (2)
C(8)—C(9)—C(1)	102.4 (4)	102.8 (4)	100.6 (2)	103.6 (2)	104.1 (2)	102.7 (1.3)	102.8 (5)
C(1)—C(9)—C(11)	104.8 (4)	104.6 (4)	105.5 (2)	106.0 (2)	105.3 (2)	105.2 (6)	104.5 (3)
C(8)—C(9)—C(11)	98.6 (4)	99.5 (4)	99.0 (2)	98.8 (1)	98.3 (1)	98.8 (5)	98.5 (2)
C(2)—C(10)—C(5)	104.0 (4)	103.7 (4)	103.4 (2)	103.9 (2)	103.6 (2)	103.7 (2)	103.8 (1)
C(2)—C(10)—C(8)	104.0 (4)	104.0 (4)	103.7 (2)	104.0 (1)	104.0 (1)	103.9 (1)	104.3 (2)
C(5)—C(10)—C(8)	103.0 (4)	103.4 (4)	104.0 (2)	103.8 (2)	103.7 (2)	103.6 (4)	104.0 (2)
C(3)—C(11)—C(6)	103.7 (4)	104.0 (4)	103.5 (2)	103.7 (2)	103.6 (1)	103.7 (2)	103.8 (2)
C(3)—C(11)—C(9)	104.1 (4)	103.6 (4)	104.1 (2)	104.0 (2)	103.9 (2)	103.9 (2)	104.1 (2)
C(6)—C(11)—C(9)	104.2 (4)	102.7 (4)	103.7 (2)	103.6 (2)	104.2 (2)	103.7 (6)	104.1 (2)
C(1)—O(1)—C(12)	60.1 (2)	—	59.0 (2)	—	—	—	—
O(1)—C(1)—C(12)	60.0 (3)	—	60.5 (1)	—	—	—	—
O(1)—C(12)—C(1)	59.8 (3)	—	—	—	—	—	—

Notes: (a) Large deviation associated with differing substitution at C(1). (b) See Table 4 for literature references.

Table 7. Bond distances ( $\text{\AA}$ ) and angles ( $^{\circ}$ ) from geometry-averaged X-ray fragments, electron diffraction and *ab initio* calculations for norbornane and trishomocubane averaged data for (2a), (2b) and (3), averaged X-ray fragments, MM3, AM1 and *ab initio* calculations

	Norbornane <sup>a</sup>			Trishomocubane <sup>b</sup>				
	X-ray <sup>c</sup>	GED	<i>Ab initio</i>	X-ray	X-ray <sup>d</sup>	MM3	AM1	<i>Ab initio</i>
C(1)—C(2)	1.544 (23)	1.536 (15)	1.545	1.526 (8)	1.526 (2)	1.532	1.565	1.543
C(1)—C(7)	1.535 (22)	1.544 (24)	1.544	1.518 (5)	1.515 (2)	1.513	1.532	1.534
C(2)—C(3)	1.559 (19)	1.573 (15)	1.576	—	—	—	—	—
C(2)—C(3)/C(1)—C(2)	—	—	—	1.567 (5)	1.567 (3)	1.563	1.578	1.582
C(1)—C(2)—C(3)	103 (2)	102.7	103.1	103.8 (4)	104.1 (2)	103.2	103.7	103.7
C(2)—C(1)—C(6)	108 (5)	109.0	108.0	98.7 (4)	98.6 (3) <sup>e</sup>	99.6	99.4	99.0
C(2)—C(1)—C(7)	102 (3)	102.0 (1)	101.6	103.1 (4)	102.9 (2)	101.9	101.3	102.6
C(1)—C(7)—C(4)	94 (1)	93.4 (1)	94.6	105.4 (4)	105.1 (5) <sup>f</sup>	105.4	105.4	105.3
				94.2 (5)	94.6 (2) <sup>g</sup>	95.1	95.3	94.7

Notes: (a) Taken from the papers of Doms, Van Hemelrijk, Van de Mieroop, Lenstra & Geise (1985) and Doms, Van den Enden, Geise & Van Alsenoy (1983). GED and 4-21G basis-set *ab initio* values converted to  $r_s$  geometries. Norbornane numbering system used in the table. (b) The distances associated with C(1) in the X-ray structures of (2a), (2b) and (3) have been left out of the average value. MM3, AM1 and *ab initio* (3-21G) references in body of paper. (c) Geometry-averaged values from Cambridge Structural Database (Doms, Van Hemelrijk, Van de Mieroop, Lenstra & Geise, 1985). (d) Geometry-averaged values from Cambridge Structural Database. See Table 4 for references. The numbers in parentheses are standard deviations of the average values. (e) Combination of C(2)—C(1)—C(6)/C(1)—C(2)—C(3). (f) Distinction made between C(1)—C(2)—C(3) and C(1)—C(2)—C(10) (trishomocubane numbering) types for compound (4). (g) C(2)—C(1)—C(9) (trishomocubane numbering) in (4) omitted from average because of different substituents at this point.

In the analysis of data from the Cambridge Structural Database (Doms, Van den Enden, Geise & Van Alsenoy, 1983) all compounds in which the norbornane shared a C—C bond with a strained ring were omitted. However, we are interested in the variations in bond lengths, angles and reactivity of such strained ring systems, and in how these values

differ from the isolated component parts. The trishomocubane moiety (4) contains six bonds corresponding to the C(1)—C(7) bond type in norbornane [all bonds involving C(1), C(4) and C(7) are equivalent to the C(1)—C(7) bond in (5)], three bonds which correspond to the C(1)—C(2) bond type in (5) [C(2)—C(3), C(5)—C(6) and C(8)—C(9)], and six

bonds which represent a fusion of C(1)—C(2) and C(2)—C(3) bond types [all bonds involving atoms C(10) and C(11) in (4)].

In Table 5 we have tabulated the bond distances for compounds (2a), (2b) and (3), and X-ray data from the Cambridge Structural Database while Table 7 contains the averaged observed and calculated data for norbornane and trishomocubane. If one excludes the bonds associated with C(1) in the trishomocubane derivatives, there is good internal agreement. Bonds of the norbornane C(1)—C(7) type average 1.518 (5) Å (1.508–1.528 Å), bonds of the C(1)—C(2) type average 1.527 (8) Å (1.504–1.538 Å) while the shared C(1)—C(2) with C(2)—C(3) types average 1.567 (5) Å (1.557–1.576 Å). The averages of the average values from the Cambridge Structural Database are in excellent agreement giving values of 1.515 (2), 1.526 (2) and 1.567 (3) Å for the three bond types. While there is some overlap between the range of values, for every molecule the bond lengths are ordered such that C(1)—C(7) < C(1)—C(2) < C(2)—C(3). This is also true for the X-ray data on the norbornane derivatives. In the more highly strained trishomocubane system the average C(1)—C(7) and C(1)—C(2) bonds are shorter by 0.017 and 0.018 Å than in (5) while the mixed bond is only 0.008 Å longer than the C(2)—C(3) type. *MM3*, *AM1* and *ab initio* calculations provide the same ordering sequence for trishomocubane with *MM3* agreeing more closely with the X-ray data; however, the quantum-mechanical values have not been reduced to  $r_a$  distances. The differences between the C(1)—C(7) and C(1)—C(2) distances and the C(1)—C(7) and C(2)—C(3) distances offer a better comparison. These differences for the trishomocubane X-ray data are 0.008 and 0.049 Å for (2a), (2b) and (3), for the literature structures 0.011 and 0.052 Å, for *MM3* 0.019 and 0.050 Å, and for the STO3-21G calculations 0.009 and 0.048 Å. The C(1)—C(2) distance of 1.565 Å from the *AM1* calculation is inconsistent with all other data. The ordering sequence from these studies differs consistently from that recommended from GED studies for (5); however, the large standard deviations of the GED study would not make an inversion of order unreasonable.

*MM3* calculations give strain energies of 158.9 kJ mol<sup>-1</sup> for norbornane (5) and 392.7 kJ mol<sup>-1</sup> for trishomocubane (4). Compounds (2a), (2b) and (3) have strain energies of 815.3, 807.8 and 793.9 kJ mol<sup>-1</sup> which are slightly more than twice that of trishomocubane (4). From this one might expect the bonds and angles for compounds (2a), (2b) and (3) not to differ significantly from an isolated trishomocubane moiety, (4), except around the C(1) position. Compound (2b) has a slightly lower strain energy than (2a); however, it has a significantly higher density, 1.350 versus

1.304 g cm<sup>-3</sup>, yielding a higher energy per unit volume.

Table 6 lists selected valence angles and averaged values are given in Table 7. The trishomocubane moiety has nine C—C—C angles between 94.1 and 98.8° and 18 between 102.7 and 105.8°. The norbornane units in trishomocubane do not retain the *C<sub>v</sub>* symmetry found in (5), but the molecule is skewed with a pseudo-twofold axis passing through C(7). The C(1)—C(2) and C(3)—C(4) equivalent distances in norbornane are now 1.527 (8) and 1.567 (5) Å in the norbornane units of trishomocubane. The C(2)—C(1)—C(6) angle of 109.0° in norbornane is reduced to 98.7 (4)° and because of fusion is identical to the C(2)—C(3)—C(4) angle. The C(1)—C(2)—C(3) angle of 103.8 (4)° differs significantly from this value. C(2)—C(1)—C(7) and C(6)—C(1)—C(7) which are equivalent in (5) are now 105.4 (4) and 103.2 (4)° in (4).

We thank the Robert A. Welch Foundation (P-074 to WHW, B-963 to APM), the National Science Foundation (CHE-9017654 to WHW), and the Office of Naval Research (APM).

#### References

- ALLEN, F. H., KENNARD, O. & TAYLOR, R. (1983). *Acc. Chem. Res.* **16**, 146–153.
- ALLINGER, N. L., YUH, Y. H. & LI, J.-H. (1989). *J. Am. Chem. Soc.* **111**, 8551–8566.
- CHIANG, J. F., WILCOX, C. F. JR & BAUER, S. H. (1968). *J. Am. Chem. Soc.* **90**, 3149–3157.
- CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- DALLINGA, G. & TCNEMAN, L. H. (1968). *Recl Trav. Chim. Pays-Bas*, **87**, 795–804.
- DEWAR, M. J. S., ZOEBSCH, E. G., HEALY, E. F. & STEWART, J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902–3909.
- DOMS, L., VAN DEN ENDEN, L., GEISE, H. J. & VAN ALSENOY, C. (1983). *J. Am. Chem. Soc.* **105**, 158–162.
- DOMS, L., VAN HEMELRIJK, D., VAN DE MIEROOP, W., LENSTRA, A. T. H. & GEISE, H. J. (1985). *Acta Cryst.* **B41**, 270–274.
- FRISCH, M. J., HEAD-GORDON, M., TRUCKS, G. W., FORESMAN, J. B., SCHLEGEL, H. B., RAGHAVACHARI, K., ROBB, K. A., BINKLEY, J. B., GONZALEZ, C., DEGREES, D. J., FOX, D. J., WHITESIDE, R. A., SEGER, R., MELIUS, C. F., BAKER, J., MARTIN, R. L., KAHN, L. R., STEWART, J. P., TOPPOL, S. & POPLE, J. A. (1990). *GAUSSIAN90*. Gaussian Inc., Pittsburgh, PA, USA.
- MARCHAND, A. P. (1989). *Advances in Theoretically Interesting Molecules*, Vol. 1, edited by R. P. THUMMEL, pp. 357–397. Greenwich, CT: JAI Press.
- MARCHAND, A. P., CHOU, T.-C., EKSTRAND, J. D. & VAN DER HELM, D. (1976). *J. Org. Chem.* **41**, 1438–1444.
- MARCHAND, A. P., REDDY, G. M., DESHPANDE, M. N., WATSON, W. H., NAGL, A., LEE, O. H. & OSAWA, E. (1990). *J. Am. Chem. Soc.* **112**, 3521–3529.

- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.
- MORINO, Y., KUCHITSU, K. & YOKOZEKI, A. (1967). *Bull. Chem. Soc. Jpn.*, **40**, 1552.
- Nicolet Instrument Corporation (1986). *SHELXTL for Desktop 30* (Microclipse), PH-269-1040340, April 1986. Nicolet Instrument Corporation, Madison, Wisconsin, USA.
- PAQUETTE, L. A., ALLEN, G. R. JR & BROADHURST, M. J. (1971). *J. Am. Chem. Soc.* **93**, 4503–4508.
- TOLSTIKOV, G. A., LERMAN, B. M., GALIN, F. Z., STRUCHKOV, YU. T. & ANDRIANOV, V. G. (1978). *Tetrahedron Lett.* pp. 4145–4148.
- WATSON, W. H., NAGL, A., MARCHAND, A. P. & DESHPANDE, M. N. (1989). *Acta Cryst.* **C45**, 1339–1342.
- WATSON, W. H., NAGL, A., MARCHAND, A. P. & REDDY, G. M. (1990). *Acta Cryst.* **C46**, 253–256.
- WATSON, W. H., NAGL, A., MARCHAND, A. P. & VIDYASAGAR, V. (1989). *Acta Cryst.* **C45**, 1770–1773.
- YOKOZEKI, A. & KUCHITSU, K. (1971). *Bull. Chem. Soc. Jpn.*, **44**, 2356–2363.

*Acta Cryst.* (1992). **B48**, 737–741

## A Twinned Structure for *n*-Tetracosane

BY A. R. GERSON AND S. C. NYBURG

*Department of Chemistry, King's College, University of London, Strand, London WC2R 2LS, England*

(Received 4 February 1992; accepted 5 May 1992)

### Abstract

A platy specimen of *n*-C<sub>24</sub>H<sub>50</sub> grown from *n*-dodecane has been found to be a twin. Bragg reflections from the two twins overlap extensively and a cyclic procedure was used to correct the observed intensities for mutual overlapping. The resulting data could only be refined isotropically to *R* = 0.23, but the molecule is not overly distorted. The crystal structure is isostructural with other even triclinic, *P* $\bar{1}$  *n*-alkanes.

### Introduction

The crystal structures of the *n*-alkanes with an even number of C atoms from C<sub>6</sub>H<sub>14</sub> to C<sub>22</sub>H<sub>46</sub> are known with considerable certainty (Nyburg & Gerson, 1992; Heyding, Russell, Varty & St-Cyr, 1990). They are isostructural, triclinic, *P* $\bar{1}$ , with one molecule per unit cell. Their cell dimensions fit well with those predicted from the C<sub>18</sub>H<sub>38</sub> structure (Nyburg & Lüth, 1972) by Nyburg & Potworowski (1973) (N & P). Up to C<sub>22</sub>H<sub>46</sub> no polymorphs have been reported. Above C<sub>22</sub>H<sub>46</sub> the structures become less certain. While lattice parameters consistent with those predicted have been reported for C<sub>24</sub>H<sub>50</sub> and C<sub>26</sub>H<sub>54</sub> (Heyding, Russell, Varty & St-Cyr, 1990) powder patterns have also been reported which yield ambiguous results (Gerson, Roberts & Sherwood, 1991). The cell dimensions predicted for C<sub>28</sub>H<sub>58</sub> (N & P) from the monoclinic C<sub>36</sub>H<sub>74</sub> structure (Shearer & Vand, 1956) have been confirmed (Gerson, Roberts & Sherwood, 1991). An orthorhombic polytypic modification of this structure has also been reported (Boistelle, Simon & Pépe, 1976).

We felt it desirable to attempt the crystal structure analysis of C<sub>24</sub>H<sub>50</sub>. In the event we were frustrated by our inability to grow a single crystal. The best crystals we could grow were twinned. Bragg reflections from the two twins overlap badly and only an approximate crystal structure could be established. However, C<sub>24</sub>H<sub>50</sub> does appear to belong to the isostructural series of triclinic even *n*-alkanes.

### Experimental

A flat plate (1 × 0.6 × 0.3 mm) of C<sub>24</sub>H<sub>50</sub> (Aldrich Chemical Company Ltd) giving well-defined extinctions on rotation in cross-polarized light was cut from an agglomeration grown in *n*-dodecane (C<sub>12</sub>H<sub>26</sub>) by slow cooling from 303 to 298 K.

On a *0kl* precession photograph, the *00l* reflections were clearly resolved. Their spacing  $c^* = 0.033 \text{ \AA}^{-1}$ , agrees well with  $c^* = 0.0331 \text{ \AA}^{-1}$  from the predicted cell (N & P):  $a = 4.285$ ,  $b = 4.82$ ,  $c = 32.50 \text{ \AA}$ ,  $\alpha = 86.43$ ,  $\beta = 68.71$ ,  $\gamma = 72.7^\circ$ .

The *01l* row, by contrast, had less-well resolved reflections and exhibited one striking anomaly: two prominent reflections with a separation of  $1.65c^*$  along  $z^*$  (Fig. 1). This can be explained as due to twinning. First, we assume the *0kl* planes from the two twins, *t*<sub>1</sub> and *t*<sub>2</sub> are coplanar. Second, we assume that the two  $z^*$  axes are collinear or nearly so. If the N & P cell is assumed, the *01l* reflections with anomalous separation can be indexed as *01*,*13* from one twin and  $0\bar{1}$ ,*12* from the other (Fig. 1). Their separation along  $z^*$  calculates as  $1.66c^*$  as required, and allows an unambiguous assignment of the  $x^*$  axes to be made. A consequence of this mutual