

This study was supported by the Bundesministerium für Forschung und Technologie, FKZ 03 SA1 FUB 6.

References

- ALLEN, F. H., BELLARD, S., BRICE, M. D., CARTWRIGHT, B. A., DOUBLEDAY, A., HIGGS, H., HUMMELINK, T., HUMMELINK-PETERS, B. G., KENNARD, O., MOTHERWELL, W. D. S., RODGERS, J. R. & WATSON, D. G. (1979). *Acta Cryst.* **B35**, 2331–2339.
- Cambridge Structural Database (1990). Univ. Chemical Laboratory, Lensfield Road, Cambridge, England.
- CECCARELLI, C., JEFFREY, G. A. & TAYLOR, R. (1981). *J. Mol. Struct.* **70**, 255–271.
- CHENG, X. & SCHOENBORN, B. P. (1990). *Acta Cryst.* **B46**, 195–208.
- CHENG, X. & SCHOENBORN, B. P. (1991). *Acta Cryst.* **A47**, 314–317.
- CHIARI, G. & FERRARIS, G. (1982). *Acta Cryst.* **B38**, 2331–2341.
- JEFFREY, G. A. & MALUSZYNSKA, H. (1990). *Acta Cryst.* **B46**, 546–549.
- JEFFREY, G. A. & SAENGER, W. (1991). *Hydrogen Bonding in Biological Structures*. Berlin: Springer.
- NAKAMOTO, K., MARGOSHES, M. & RUNDLE, R. E. (1955). *J. Am. Chem. Soc.* **77**, 6480–6486.
- OLOVSSON, I. & JÖNSSON, P.-G. (1976). *The Hydrogen Bond, Recent Developments in Theory and Experiments*, edited by P. SCHUSTER, G. ZUNDEL & C. SANDORFY, pp. 393–455. Amsterdam: North-Holland.
- SAVAGE, H. (1986). *Water Science Reviews*, Vol. 2, edited by F. FRANKS, pp. 67–147. Cambridge Univ. Press.
- SAVAGE, H. F. J. & FINNEY, J. L. (1986). *Nature (London)*, **322**, 717–720.
- STEINER, TH., MASON, S. A. & SAENGER, W. (1990). *J. Am. Chem. Soc.* **112**, 6184–6190.
- STEINER, TH., MASON, S. A. & SAENGER, W. (1991). *J. Am. Chem. Soc.* **113**, 5676–5687.
- STEINER, TH. & SAENGER, W. (1991). *Acta Cryst.* **B47**, 1022–1023.
- STEINER, TH. & SAENGER, W. (1992). *J. Am. Chem. Soc.* **114**. In the press.
- TAYLOR, R. & KENNARD, O. (1984). *Acc. Chem. Res.* **17**, 320–326.
- ZABEL, V., SAENGER, W. & MASON, S. A. (1986). *J. Am. Chem. Soc.* **108**, 3664–3673.

Acta Cryst. (1992). **B48**, 827–832

Complexation with Diol Host Compounds. 8. Structures and Thermal Analysis of 1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol with Selected Ketones

BY LOUISE JOHNSON AND LUIGI R. NASSIMBENI

Department of Chemistry, University of Cape Town, Rondebosch 7700, South Africa

AND FUMIO TODA

Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790, Japan

(Received 5 March 1991; accepted 29 April 1992)

Abstract

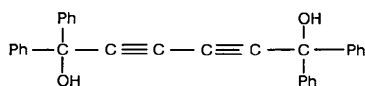
The structures of three inclusion compounds of 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol with methyl ethyl ketone (1), diethyl ketone (2) and acetophenone (3) have been determined and their thermal decomposition investigated by thermogravimetry and differential scanning calorimetry. Crystal data are: (1), $C_{30}H_{22}O_2 \cdot 2C_4H_8O$, $M_r = 558.72$, monoclinic, $P2_1/n$, $a = 8.321$ (3), $b = 11.845$ (3), $c = 17.153$ (4) Å, $\beta = 100.35$ (2)°, $V = 1663$ (1) Å³, $Z = 2$, $D_m = 1.09$ (3), $D_x = 1.12$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.39$ cm⁻¹, $F(000) = 596$, $T = 294$ K, final $R = 0.073$ ($wR = 0.084$) for 1494 independent reflections. (2), $C_{30}H_{22}O_2 \cdot 2C_5H_{10}O$, $M_r = 586.77$, monoclinic, $P2_1/n$, $a = 10.108$ (2), $b = 8.579$ (1), $c = 20.536$ (2) Å, $\beta = 102.45$ (1)°, $V = 1738.9$ (4) Å³, $Z = 2$, $D_m = 1.10$ (2), $D_x = 1.12$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.33$ cm⁻¹, $F(000) = 628$, $T = 294$ K, final $R = 0.081$ ($wR = 0.090$) for 1818 independent reflections. (3), $C_{30}H_{22}O_2 \cdot 2C_8H_8O$, $M_r = 654.80$, triclinic, $P\bar{1}$,

$a = 11.204$ (4), $b = 11.856$ (6), $c = 16.236$ (6) Å, $\alpha = 69.50$ (4), $\beta = 79.32$ (3), $\gamma = 62.98$ (4), $V = 1799$ (2) Å³, $Z = 2$, $D_m = 1.20$ (1), $D_x = 1.21$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.41$ cm⁻¹, $F(000) = 692$, $T = 294$ K, final $R = 0.096$ ($wR = 0.102$) for 2106 independent reflections.

Introduction

A large number of organic compounds can act as hosts in the formation of inclusion compounds. Some can be classified as clathrates because the host-guest aggregate is stabilized by steric factors alone. However, when there is hydrogen bonding between host and guest, the compounds are better classified as coordinato clathrates (Weber & Josel, 1983). Diol host compounds are particularly versatile hosts and their uses with respect to the isolation and optical resolution of racemates, as well as their role in controlling guest reactions in clathrates have been

reviewed recently (Toda, 1987, 1988). We have studied the clathrating properties of the tetraphenyl diol host shown in the scheme below.



Thus we have described the structure of the host 1,1,2,2-tetraphenylethane-1,2-diol and that of its molecular complex with dimethyl sulfoxide (Bond, Bourne, Nassimbeni & Toda, 1989). We have also used the latter host to form inclusion complexes with selected lutidines, have measured their thermal stabilities and related them to their structures (Bourne, Nassimbeni & Toda, 1991).

The structure of the title host compound has been reported in its non-porous α -form, and we have investigated the kinetics of acetone vapour absorption as well as the kinetics of the solid–solid reaction with benzophenone (Bond, Johnson, Nassimbeni & Toda, 1991). In this study we extend the structural work to the guests methyl ethyl ketone, diethyl ketone and acetophenone. The compounds were characterized by X-ray analysis, thermal gravimetry (TG) and differential scanning calorimetry (DSC).

Experimental

Suitable crystals of the molecular complexes were obtained by slow evaporation of dilute solutions of the host in the various guest liquids. The time required ranged from 3 to 20 days. Thermal analyses were performed using a Perkin–Elmer PC7 system. For thermal gravimetry, crystals were removed from their mother liquor, blotted dry on filter paper and crushed. The sample weight, in each case, was approximately 4 mg. The thermograms were recorded under a stream of nitrogen with a flow rate of 40 ml min⁻¹. The temperature range was typically 298 to 473 K at various heating rates. Differential scanning calorimetry was performed over the same temperature range also under a stream of nitrogen flowing at 40 ml min⁻¹. The heating rate was 10 K min⁻¹ for each sample.

Preliminary cell dimensions and space-group assignments were carried out photographically for the structure determinations. For all three compounds the intensity data were collected with crystals mounted in Lindemann capillary tubes in order to minimize crystal deterioration. Accurate cell parameters were then obtained by least-squares analyses of 24 reflections measured in the range $16 < \theta < 17^\circ$ or $12 < \theta < 14^\circ$ on a Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). Crystal data and experimental details of the data collections are listed in Table 1. A decay

Table 1. *Crystal data and experimental details*

	Compound (1)	Compound (2)	Compound (3)
Data collection (294 K)			
Crystal dimensions (mm)	0.31 × 0.47 × 0.50	0.44 × 0.47 × 0.47	0.47 × 0.25 × 0.31
Range scanned θ ($^\circ$)	1–25	1–25	1–22
Range of indices h,k,l	$\pm 9, +14, +20$	$\pm 12, +10, +24$	$\pm 11, \pm 12, +17$
No. of reflections for lattice parameters, θ range ($^\circ$)	24, 16–17	24, 16–17	24, 12–14
Instability of standard reflections (%)	–6.0	–22.4	6.0
Scan mode	ω -2 θ	ω -2 θ	ω -2 θ
Scan width ($^\circ$)	0.85 + 0.35tan θ	0.85 + 0.35tan θ	0.85 + 0.35tan θ
Vertical aperture length (mm)	4	4	4
Aperture width (mm)	(1.12 + 1.05tan θ)	(1.12 + 1.05tan θ)	(1.12 + 1.05tan θ)
No. of reflections collected (unique)	2266	2507	3251
No. of reflections observed [with $I_{rel} > 2\sigma(I_{rel})$]	1494	1818	2106
Final refinement			
No. of parameters	181	216	353
R	0.073	0.081	0.096
wR	0.084	0.090	0.102
w	$(\sigma^2F + 0.001F^2)^{-1}$	$(\sigma^2F + 0.003F^2)^{-1}$	$(\sigma^2F + 0.005F^2)^{-1}$
Max. shift/e.s.d.	0.24	0.20	0.003
Max. height in difference Fourier map (e \AA^{-3})	0.23	0.19	0.39
Min. height in difference Fourier map (e \AA^{-3})	–0.24	–0.31	–0.37

correction was applied to structure (2) (B. A. Frenz & Associates Inc., 1982).

The structures of all three compounds were solved by direct methods and refined by full-matrix least-squares routines using the *SHELXS86* and *SHELXL76* program systems (Sheldrick, 1976, 1985). The non-H atoms were treated anisotropically in all cases and the aromatic hydrogens were constrained to 1.0 \AA from their parent carbons, with a common temperature factor. The hydroxyl hydrogens possessed individual temperature factors and were located by difference electron density maps and refined with a simple bond-length constraint to their parent oxygens. The final refinement parameters are shown in Table 1. The fractional atomic coordinates and temperature factors of compounds (1), (2) and (3) are shown in Table 2.* Inclusion compounds of this type often have high R values because they are intrinsically unstable with relatively high vapour-pressure guests yielding poor quality crystals.

Results and discussion

The molecular structure of the host, shown in Fig. 1 is similar in all three compounds and the salient bond lengths, reported in Table 3, are similar to those found in the non-porous α -form of the host compound (Bond, Johnson, Nassimbeni & Toda, 1991). The long molecular axis of the host appears to

* Lists of structure factors, anisotropic thermal parameters, bond lengths, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55238 (53 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

Compound (1)	x	y	z	U_{iso}/U_{eq}
O(1)	1116 (3)	8264 (2)	572 (2)	74 (1)
H(1)	1471 (55)	7997 (37)	1127 (11)	115 (16)
C(1)	1800 (4)	7541 (3)	53 (2)	60 (1)
C(2)	1058 (4)	6406 (3)	52 (2)	64 (1)
C(3)	387 (4)	5516 (3)	22 (2)	64 (1)
C(12)	705 (4)	9105 (2)	-903 (2)	89 (2)
C(13)	326 (4)	9541 (2)	-1670 (2)	10 (2)
C(14)	617 (4)	8899 (2)	-2312 (2)	12 (3)
C(15)	1287 (4)	7820 (2)	-2187 (2)	15 (3)
C(16)	1667 (4)	7384 (2)	-1421 (2)	15 (2)
C(11)	1376 (4)	8027 (2)	-779 (2)	53 (2)
C(22)	4534 (3)	6480 (2)	400 (2)	59 (2)
C(23)	6233 (3)	6496 (2)	615 (2)	606 (3)
C(24)	7059 (3)	7523 (2)	741 (2)	114 (3)
C(25)	6186 (3)	8534 (2)	656 (2)	118 (3)
C(26)	4488 (3)	8519 (2)	441 (2)	92 (2)
C(21)	3662 (3)	7492 (2)	313 (2)	64 (1)
O(1G)	11190 (6)	7474 (5)	2098 (3)	169 (3)
C(1G)	11701 (11)	8191 (9)	3493 (5)	184 (5)
C(2G)	11162 (8)	7095 (10)	2727 (6)	188 (5)
C(3G)	10925 (15)	6421 (17)	3204 (8)	305 (12)
C(4G)	10385 (14)	5443 (9)	2402 (8)	224 (6)
Compound (2)				
O(1)	7431 (2)	1608 (3)	8807 (1)	72 (1)
H(1)	7882 (45)	1993 (56)	9240 (12)	111 (16)
C(1)	6009 (3)	1785 (4)	8731 (2)	54 (1)
C(2)	5568 (4)	1020 (4)	9295 (2)	61 (1)
C(3)	5210 (4)	365 (4)	9744 (2)	59 (1)
C(11)	5625 (3)	3512 (4)	8687 (2)	57 (1)
C(12)	4902 (5)	4222 (5)	9106 (2)	76 (2)
C(13)	4616 (6)	5815 (5)	9030 (2)	97 (2)
C(14)	5062 (5)	6657 (5)	8547 (3)	94 (2)
C(15)	5741 (5)	5954 (5)	8128 (3)	91 (2)
C(16)	6028 (4)	4388 (5)	8194 (2)	77 (2)
C(21)	5306 (3)	960 (4)	8088 (2)	56 (1)
C(22)	3921 (4)	900 (5)	7919 (2)	70 (2)
C(23)	3262 (5)	117 (5)	7346 (2)	89 (2)
C(24)	4008 (5)	-578 (6)	6940 (2)	89 (2)
C(25)	5376 (6)	-513 (5)	7098 (2)	88 (2)
C(26)	6068 (4)	244 (4)	7677 (2)	70 (1)
O(1G)	9089 (5)	2162 (8)	10059 (3)	192 (3)
C(1G)	11658 (11)	3278 (15)	9932 (5)	231 (7)
C(2G)	11312 (7)	2588 (12)	10519 (4)	163 (4)
C(3G)	10002 (6)	2054 (7)	10525 (3)	107 (2)
C(4G)	9906 (9)	1369 (10)	11217 (4)	167 (7)
C(5G)	8583 (10)	828 (17)	11251 (6)	226 (7)
Compound (3)				
O(1A)	1767 (5)	4200 (5)	5919 (3)	49 (3)
H(1A)	1823 (102)	4114 (104)	6516 (21)	109 (7)
C(1A)	3072 (7)	3335 (8)	5683 (5)	38 (2)
C(2A)	3925 (8)	4057 (8)	5403 (5)	38 (2)
C(3A)	4592 (7)	4659 (7)	5149 (5)	37 (2)
C(12A)	2902 (5)	1364 (6)	6832 (4)	54 (5)
C(13A)	3371 (5)	223 (6)	7552 (4)	68 (6)
C(14A)	4607 (5)	-196 (6)	7898 (4)	69 (6)
C(15A)	5371 (5)	526 (6)	7524 (4)	66 (6)
C(16A)	4902 (5)	1667 (6)	6804 (4)	51 (5)
C(11A)	3667 (5)	2085 (6)	6458 (4)	36 (5)
C(22A)	4066 (4)	2022 (5)	4618 (3)	49 (5)
C(23A)	3986 (4)	1666 (5)	3904 (3)	55 (6)
C(24A)	2773 (4)	2250 (5)	3485 (3)	56 (6)
C(25A)	1641 (4)	3190 (5)	3781 (3)	56 (5)
C(26A)	1722 (4)	3546 (5)	4495 (3)	42 (5)
C(21A)	2935 (4)	2962 (5)	4913 (3)	33 (4)
O(1B)	1856 (6)	9073 (6)	1100 (4)	64 (4)
H(1B)	2023 (105)	9187 (105)	1611 (40)	109 (7)
C(1B)	3141 (8)	8256 (8)	772 (5)	44 (2)
C(2B)	3957 (8)	9036 (8)	431 (5)	45 (2)
C(3B)	4614 (8)	9657 (8)	156 (5)	49 (2)
C(12B)	3933 (4)	6973 (5)	-320 (4)	53 (5)
C(13B)	3721 (4)	6659 (5)	-1015 (4)	67 (6)
C(14B)	2465 (4)	7321 (5)	-1390 (4)	71 (6)
C(15B)	1421 (4)	8298 (5)	-1070 (4)	75 (7)
C(16B)	1632 (4)	8612 (5)	-374 (4)	66 (6)
C(11B)	2889 (4)	7950 (5)	1 (4)	38 (4)
C(22B)	3200 (5)	6144 (6)	1887 (4)	63 (5)
C(23B)	3779 (5)	4987 (6)	2578 (4)	72 (6)
C(24B)	5008 (5)	4663 (6)	2891 (4)	61 (5)

Table 2 (cont.)

	x	y	z	U_{iso}/U_{eq}
C(25B)	5659 (5)	5496 (6)	2513 (4)	60 (6)
C(26B)	5080 (5)	6653 (6)	1821 (4)	54 (6)
C(21B)	3850 (5)	6977 (6)	1508 (4)	42 (4)
O(1G)	1218 (7)	15399 (9)	2389 (5)	195 (6)
C(1G)	-636 (12)	15793 (12)	1716 (8)	77 (3)
C(1MG)	-884 (14)	17178 (13)	1344 (9)	121 (10)
C(12G)	1195 (7)	15171 (6)	603 (4)	69 (6)
C(13G)	2137 (7)	14227 (6)	211 (4)	88 (8)
C(14G)	2276 (7)	12919 (6)	530 (4)	99 (9)
C(15G)	1474 (7)	12553 (6)	1240 (4)	95 (8)
C(16G)	532 (7)	13498 (6)	1632 (4)	78 (8)
C(11G)	392 (7)	14806 (6)	1313 (4)	57 (6)
O(2G)	1643 (8)	9108 (8)	2890 (5)	101 (6)
C(2G)	1438 (11)	8400 (11)	3596 (8)	80 (3)
C(2MG)	1036 (13)	7323 (13)	3639 (9)	109 (9)
C(22G)	1881 (6)	9546 (6)	4414 (4)	75 (6)
C(23G)	2032 (6)	9702 (6)	5195 (4)	70 (7)
C(24G)	1935 (6)	8796 (6)	6001 (4)	106 (9)
C(25G)	1685 (6)	7734 (6)	6025 (4)	87 (7)
C(26G)	1535 (6)	7578 (6)	5243 (4)	81 (7)
C(21G)	1632 (6)	8484 (6)	4438 (4)	61 (5)

Table 3. Salient bond lengths (\AA)

	α -form	(1)	(2)	(3a)*	(3b)*
C1—C2	1.466 (6)	1.479 (5)	1.482 (6)	1.472 (14)	1.491 (15)
C2—C3	1.195 (6)	1.189 (5)	1.201 (6)	1.184 (14)	1.194 (15)
C3—C4	1.360 (6)	1.377 (5)	1.373 (6)	1.398 (14)	1.361 (15)
C1—C11	1.533 (7)	1.520 (5)	1.529 (5)	1.525 (8)	1.523 (13)
C1—C21	1.533 (5)	1.534 (4)	1.530 (5)	1.516 (12)	1.532 (8)
C1—O1	1.436 (5)	1.425 (5)	1.420 (4)	1.431 (8)	1.453 (9)
Average phenyl					
C—C length	1.375 (8)	1.395 (4)	1.381 (6)	1.395 (8)	1.395 (8)

* a and b correspond to the two half host molecules that are obtained in the asymmetric unit in (3).

dictate the packing in many of these structures as there is a definite trend for the molecules to align these axes parallel to one another. The guest can act as a template and yield a structure in which shape and symmetry are dependent on the ability of the guest molecule to hydrogen bond. In all three crystal systems the host hydroxy groups lie *trans* to one another. In each case there is hydrogen bonding between these hydroxy groups and the carbonyl groups of the ketonic guests to yield the ratio of two guests per one host molecule.

In compound (1) the centrosymmetric host molecule lies at Wyckhoff position *c* and each hydroxyl moiety is hydrogen bonded to one methyl ethyl

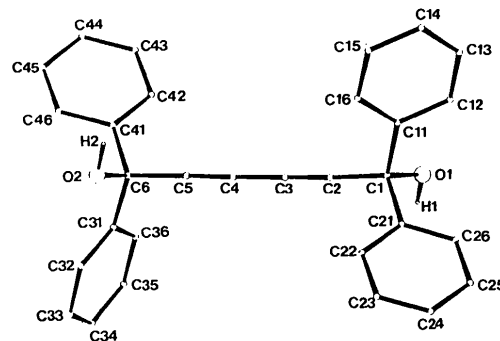


Fig. 1. A molecule of 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol.

ketone with $O-O = 2.770(6) \text{ \AA}$. The packing is shown in Fig. 2 (Motherwell, 1974). A similar packing situation obtains for compound (2) where the diethyl ketone is hydrogen bonded to the host with $O-O = 2.788(6) \text{ \AA}$. This is shown in Fig. 3. In compound (3) (Fig. 4), the stoichiometry requires two crystallographically distinct $O-H \cdots O=C$ interactions, and the hydrogen bonds between the host hydroxyls and the acetophenone oxygens are $2.885(11)$ and $2.859(11) \text{ \AA}$, significantly longer than those in compounds (1) and (2).

Thermal analysis

Thermal gravimetry and differential scanning calorimetry were carried out on all three compounds. The results are shown in Figs. 5(a), 5(b) and 5(c). The TG curves show that the weight loss, reported in Table 4, is in good agreement with the theoretical value, thus confirming the declared host-guest ratios. For compound (1), the DSC (Fig. 5a), shows two distinct endotherms, the first with onset temperature T_{on} at 323 K followed by the endotherm at 416 K corresponding to the melting point of the host compound.

Fig. 5(b) shows that compound (2) behaves similarly, with T_{on} at 345 K for the loss of diethyl ketone, followed by the melting of the host compound. Compound (3), however, shows a different decompositional behaviour in that the single endotherm, $T_{on} = 346 \text{ K}$, corresponds to the loss of acetophenone with concomitant dissolution of the host compound. The thermal gravimetry experiments were carried out at various heating rates in order to study the activation energy of the reaction (Flynn & Wall, 1966). In this method the temperatures of decomposition at a fixed percentage weight loss are measured at the various heating rates. A plot of the logarithm of the heating rate *versus* the reciprocal of the absolute temperature is then examined. If parallel straight lines are obtained, these indicate a single-step decomposition for the reaction. This method, originally developed for the thermal decomposition of polymers, has also been applied to the decomposition of inorganic coordination compounds (Herman, Hofmans & Dessey, 1985).

We did not analyse the decomposition of compound (1) because the TG curve obtained at the heating rate of 2 K min^{-1} (Fig. 5a) had a point of inflection indicating a multi-step decomposition at this heating rate, but not at the higher heating rates. The semilogarithmic plot for compound (2) was not linear, but distinctly curved, indicating that the mechanism of decomposition was temperature dependent. The results for the decomposition of compound (3) are shown in Fig. 6, where the semilogarithmic plots yield reasonably straight lines with activation energies varying from 42 to 51 kJ mol^{-1} .

These values are lower than those obtained from the decomposition of the inclusion compounds formed between *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene and acetonitrile, 2,4-dimethylpyridine and 2,6-dimethylpyridine, which all

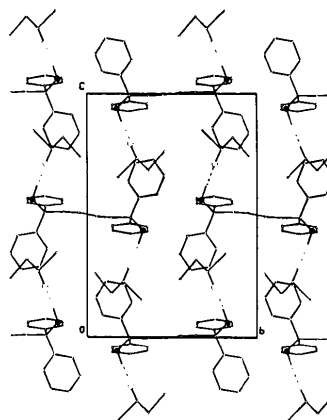


Fig. 2. The packing and hydrogen bonding of compound (1).

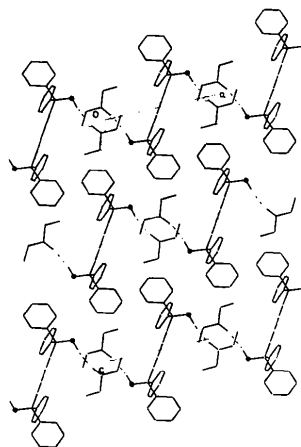


Fig. 3. The packing and hydrogen bonding of compound (2).

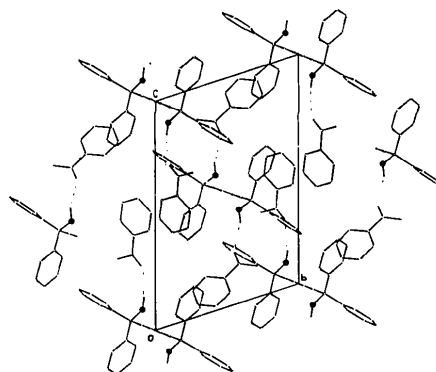


Fig. 4. The packing and hydrogen bonding of compound (3).

Table 4. Experimental thermal gravimetry weight loss values compared with the theoretical values

MEK = methyl ethyl ketone. DEK = diethyl ketone. ACEPH = acetophenone. ACET = acetone.

Reaction	Calc. weight loss (%)	Measured weight loss (%)	Onset temp. (K)	ΔH (kJ mol ⁻¹)	$T_{on} - T_b$ (K)	O—O (Å)
H.(MEK) ₂ → H + 2MEK	25.8	23.8	323	36.0	-29.9	2.77
H.(DEK) ₂ → H + 2DEK	29.4	28.9	345	50.4	-29.9	2.79
H.(ACEPH) ₂ → H + 2ACEPH	36.7	37.5	346	52.3	-129.4	2.86
H.(ACET) ₂ → H.ACET + ACET → H + 2ACET	21.9	21.9	333	56	+4	2.73

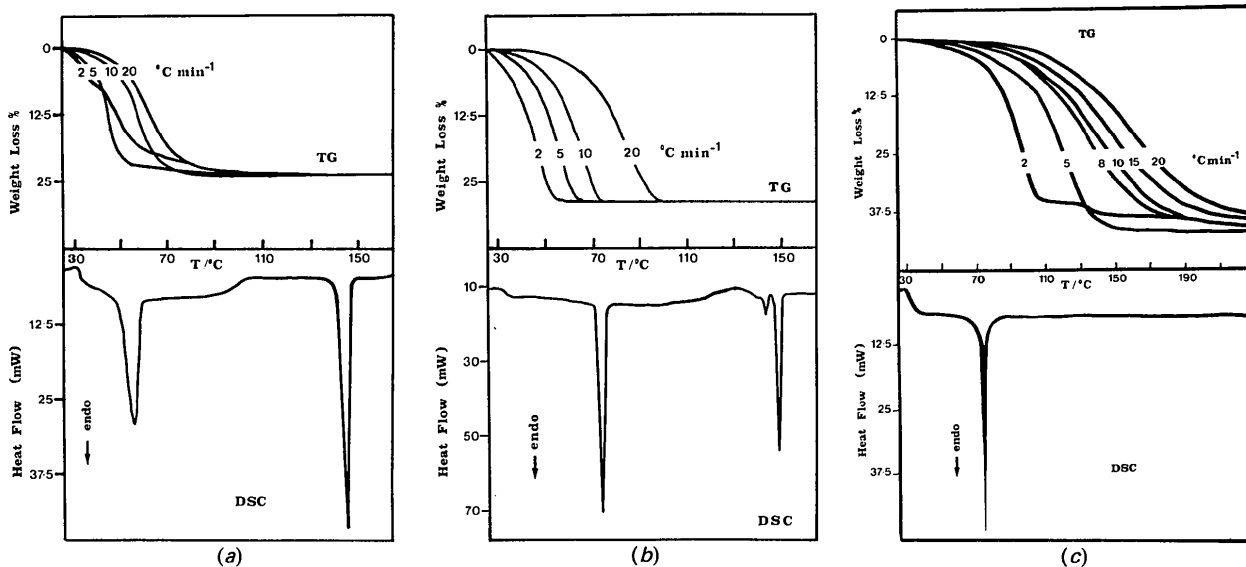


Fig. 5. Thermograms showing the DSC and TG curves of (a) compound (1), (b) compound (2), and (c) compound (3).

yield activation energies which range from 75 to 115 kJ mol⁻¹ (Caira, Nassimbeni & Schubert, 1991).

The objective of carrying out thermal analysis on these compounds is to reconcile thermodynamics with structure. Thus it should be possible to relate certain thermal parameters of the guest-release reactions and the host-guest interactions as revealed by the crystal structure. For inclusion compounds of a

given host with various guests, the onset temperatures T_{on} are a function of both the host-guest interactions and of the normal boiling point of the guest compound, T_b . We suggest that a useful measure of the relative stabilities of these compounds is the difference $T_{on} - T_b$. Thus $T_{on} > T_b$ would indicate a stable inclusion compound and *vice versa*.

The thermal results are summarized in Table 4, to which we have added the results of the decomposition of the H.(acetone)₂ compound (Bond, Johnson, Nassimbeni & Toda, 1991). In the present study one might expect correlation between the O—O hydrogen-bond distance and $T_{on} - T_b$. However we suffer from a paucity of data, and while there is a trend that the compounds with the shorter O—O distances are the more stable, more compounds of this nature will have to be characterized before a possible correlation can be established. We are therefore undertaking the structural analyses of other compounds which have similar structural features.

We thank the University of Cape Town and the Foundation for Research Development, Pretoria, for research grants. L. Johnson thanks AECI Ltd for a scholarship.

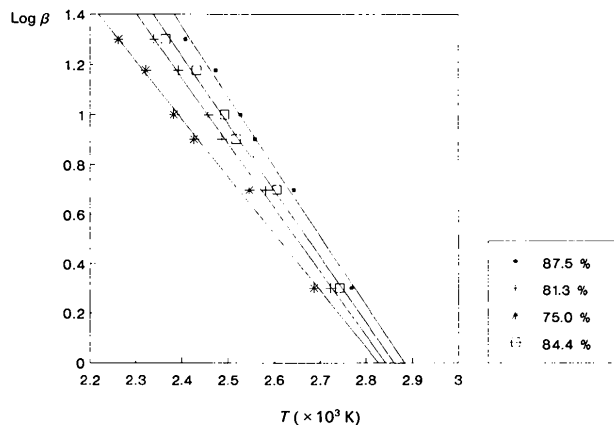


Fig. 6. Activation-energy determination for compound (3).

References

- B. A. FRENZ & ASSOCIATES INC. (1982). *DECAY. Structure Determination Package*. College Station, Texas 77840, USA.
- BOND, D. R., BOURNE, S. A., NASSIMBENI, L. R. & TODA, F. (1989). *J. Crystallogr. Spectrosc. Res.* **19**, 809–822.
- BOND, D. R., JOHNSON, L., NASSIMBENI, L. R. & TODA, F. (1991). *J. Solid State Chem.* **92**, 68–79.
- BOURNE, S. A., NASSIMBENI, L. R. & TODA, F. (1991). *J. Chem. Soc. Perkin Trans. 2*, pp. 1335–1341.
- CAIRA, M. R., NASSIMBENI, L. R. & SCHUBERT, W. D. (1991). Unpublished work.
- FLYNN, J. H. & WALL, L. A. (1966). *Polymer Lett.* **4**, 323–328.
- HERMAN, M. A., HOFMANS, H. & DESSEYN, H. O. (1985). *Thermochim. Acta*, **85**, 63–66.
- MOTHERWELL, W. D. S. (1974). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1985). *SHELX86. Crystallographic Computing 3*, edited by G. M. SHELDRIK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
- TODA, F. (1987). *Topics in Current Chemistry*, Vol. 140, edited by E. WEBER, pp. 43–69. Heidelberg: Springer-Verlag.
- TODA, F. (1988). *Topics in Current Chemistry*, Vol. 149, edited by E. WEBER, pp. 211–238. Heidelberg: Springer-Verlag.
- WEBER, E. & JOSEL, H. P. (1983). *J. Incl. Phenom.* **1**, 79–85.

Acta Cryst. (1992). **B48**, 832–837

Structures of Secocubane and Nortwistbrendane Derivatives

BY HERMAN L. AMMON

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, USA

AND A. BASHIR-HASHEMI

Geo-Centers Inc., 762 Route 15 South, Lake Hopatcong, New Jersey 07849, USA

(Received 6 December 1991; accepted 7 May 1992)

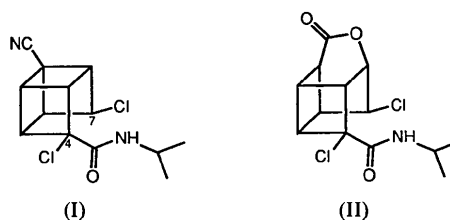
Abstract

(I): 4,7-Dichloro-1-cyano-*N*-isopropyltetracyclo[4.2.0.0^{2.5}.0^{3.8}]octane-4-carboxamide, $C_{13}H_{14}Cl_2N_2O$, $M_r = 285.17$, orthorhombic, *Fdd2*, $a = 34.012$ (1), $b = 15.791$ (2), $c = 10.899$ (1) Å, $Z = 16$, $D_x = 1.29$ g cm⁻³, $Cu K\alpha$ ($\lambda = 1.5418$ Å), $\mu = 39.2$ cm⁻¹, $F(000) = 2368$, $T = 293$ K, 1504 reflections with $I > 3\sigma(I)$, $R = 0.042$. (II): 4,7-Dichloro-*N*-isopropyl-10-oxo-9-oxatetracyclo[4.4.0.0^{2.5}.0^{3.8}]decane-4-carboxamide, $C_{13}H_{15}Cl_2NO_3$, $M_r = 304.17$, monoclinic, *P2₁/a*, $a = 9.902$ (2), $b = 9.381$ (2), $c = 15.174$ (2) Å, $\beta = 103.25$ (1)°, $Z = 4$, $D_x = 1.47$ g cm⁻³, $Cu K\alpha$ ($\lambda = 1.5418$ Å), $\mu = 43.1$ cm⁻¹, $F(000) = 632$, 2107 reflections with $I > 3\sigma(I)$, $R = 0.036$. (I) represents the first crystallographic example of a secocubane. The nonbonded distances (C4...C7) are 2.742 (5) and 2.717 (3) Å in (I) and (II). C—C distances in the cage portions of the molecules are typical of cubanes.

Introduction

Cage compounds are of interest as potential high-density energetic materials and pharmaceutical intermediates. Selective carbon-carbon bond cleavage of substituted cubanes has led to the synthesis of polycyclic compounds such as the secocubanes and nortwistbrendanes. The detailed structures of a seco-

cubane derivative (I)* [a preliminary report is given by Bashir-Hashemi, Dave, Ammon & Axenrod (1990)] and a nortwistbrendane derivative (II)* are reported here.



Experimental

(I) was prepared according to Bashir-Hashemi, Dave, Ammon & Axenrod (1990). (II) was prepared from the reaction of 1-(*N,N*-diisopropylcarboxamido)-4-cubanecarboxylic acid and HBr/acetic acid according to Eaton, Millikan & Engel (1990), followed by reaction of the lactone intermediate with thionyl chloride. Crystallographic parameters and data are given in Table 1. Enraf-Nonius CAD-4

* The IUPAC names of (I) and (II) are 4,7-dichloro-1-cyano-*N*-isopropyltetracyclo[4.2.0.0^{2.5}.0^{3.8}]octane-4-carboxamide and 4,7-dichloro-*N*-isopropyl-10-oxo-9-oxatetracyclo[4.4.0.0^{2.5}.0^{3.8}]decane-4-carboxamide.