Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Coetzee, Anita(1998) 'Crystal Structure and Desolvation Kinetics of a Methanol Inclusion Compound of *trans*-9,10-dihydroxy-9,10-di-*p*-*tert*-butylphenyl-9,10-dihydroanthracene', Supramolecular Chemistry, 9: 2, 109 — 114
To link to this Article: DOI: 10.1080/10610279808034974
URL: http://dx.doi.org/10.1080/10610279808034974

SUPRAMOLECULAR CHEMISTRY, Vol. 9, pp. 109–114
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Crystal Structure and Desolvation Kinetics of a Methanol Inclusion Compound of *trans*-9,10-dihydroxy-9,10-di-*p*-*tert*-butylphenyl-9,10-dihydroanthracene

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(Received 27 June 1997)

The host *trans*-9,10-dihydroxy-9,10-di-*p*-*tert*-butylphenyl-9,10-dihydroanthracene (DDTBDA) forms a 1:1 inclusion compound with methanol. The crystal structure, thermal analysis and kinetics of desolvation, using isothermal thermogravimetry is described. Space group: $P\bar{1}$, a = 10.036 (3)Å, b = 12.174 (2), c = 13.294 (4) Å, α = 69.86 (2)°, β = 70.20 (2)°, γ = 79.09 (2)°, Z = 2, V = 1430.0 (6)^3, $D_c = 1.181\ g cm^{-3}$, number of reflections observed with $I_{rel} > 2\sigma I_{rel} = 2850$, $R1(I_{rel} > 2\sigma I_{rel}) = 0.0482$. The extent of reaction, α *vs.* time curves were deceleratory and were best described by the F1 reaction mechanism. An activation energy of 81(8) kJ · mol^{-1} was obtained.

Keywords: Inclusion compound, desolvation, kinetics, structure, activation energy

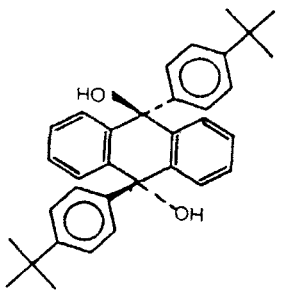
INTRODUCTION

Diol host compounds based on substituted *trans*-9,10-dihydroxy-9,10-dihydroanthracenes (see Scheme 1) form a variety of inclusion compounds with both aromatic and aliphatic guest molecules [1, 2, 3]. The compound with *R* = phenyl (DDDA) was first synthesised by Toda [4]. The structure of the inclusion compound of DDDA with acetonitrile was elucidated and its decomposition kinetics has been investigated [5], using the method of Flynn and Wall [6]. The enclathration and desolvation kinetics of the host has also been studied with acetone [7] and 1,3-dioxolane [8]. The host compound *trans*-9,10-dihydroxy-9,10-di-*p*-*tert*-butylphenyl-9,10-dihydroanthracene (DDTBDA) is directly related to the parent host. The crystal structure and the kinetics of desolvation of its inclusion compound with benzene has been studied using isothermal TG [9].

We are now reporting the crystal structure, thermal decomposition and desolvation kinetics of the 1:1 methanol inclusion compound of DDTBDA.

RESULTS AND DISCUSSION

The thermal analysis results are shown in Figure 1. A single mass loss step observed in the TG experiment established a host:guest



SCHEME 1

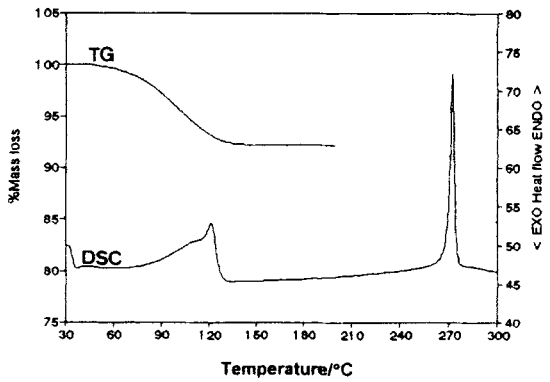


FIGURE 1 Thermal analysis results for the desolvation of DDTBDA.methanol, carried out at 20°Cmin.

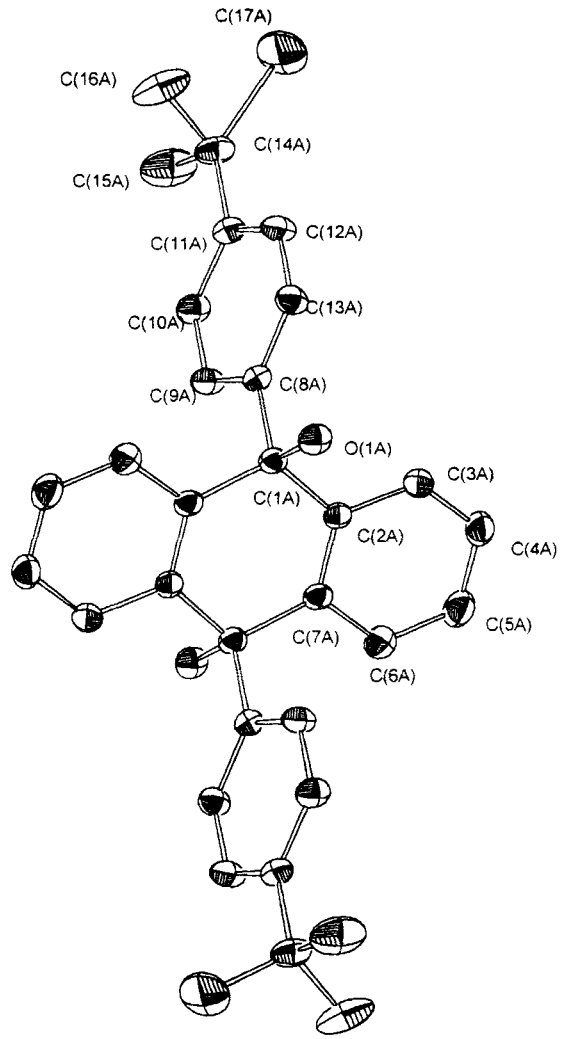


FIGURE 2 X-ray structure of the crystallographically independent host molecule A, showing the numbering scheme used. Ellipsoids are drawn at 30% probability level.

ratio of 1:1 (calc. 6.3%; obs. 7.3%). This corresponds to an endotherm in the DSC trace with an onset temperature of 60°C. A sharp endotherm at 270°C corresponds to the melt of the host, which is accompanied by sublimation.

Two crystallographically independent half host molecules were placed in the unit cell ($Z = 2$). Both molecules were located at centres of inversion. The host compound is rather rigid and conformational changes can be ascribed to rotation of the *p-tert*-butylphenyl group. The conformation of host molecule A, with atomic numbering scheme, is shown in Figure 2. The conformations of the two independent host molecules were similar, except for the relative orientations of the *p-tert*-butylphenyl groups to the central 9,10-dihydroxyanthracene. This can be described by the torsion angles C(2A)-C(1A)-C(8A)-C(9A) = −74.4(3)° and C(2B)-C(1B)-C(8B)-C(9B) = −57.6(3)°. All bond lengths and angles are comparable with known values [10].

An intermolecular hydrogen bond exists between the two host molecules with O(1A)···O(1B) = 2.823(2)Å. The host : guest ratio of 1:1 requires that one guest molecule is situated in a general position, in the asymmetric unit. The methanol guest is hydrogen bonded to host molecule A with O(1A)···O(1G) = 2.821(3)Å.

Typically diol host compounds, which possess two potential H-donor groups form inclusion compounds with host:guest ratios of 1:2, where one host molecule is hydrogen bonded to two guests via its two hydroxy moieties [1,2,3]. In this case a 1:1 inclusion compound was formed. Host molecule B is involved in host to host hydrogen bonding only. Each host molecule A, on the other hand, is involved in host to host hydrogen bonding with host molecule B and host to guest hydrogen bonding with two methanol molecules. Hence host molecule A forms the characteristic host–guest pairs similar to those observed in the 1:2 inclusion compounds.

A projection of the crystal packing viewed along [001] is shown in Figure 3. The hydrogen bonding scheme is indicated with dotted lines. The host molecules are linked by an infinite chain of hydrogen bonds connecting alternating layers of crystallographically independent host molecules, stacked along [010]. Hydrogen bonds from O(1A) link the host framework with the methanol guest molecules. The guests are situated in channels running parallel to [010] as shown in Figure 4, where the hatched area represents the host and the guest molecules are represented with van der Waals radii. The channels vary in width between 4.7 at the widest part to constricted areas of 1.8 Å.

Upon guest loss the inclusion compound undergoes a phase change to form the non-porous α-phase of the host alone. In Figure 5 the calculated X-ray powder diffraction pattern for the inclusion compounds is compared with that obtained experimentally after desolvation. It is clear that the XRD patterns are very different

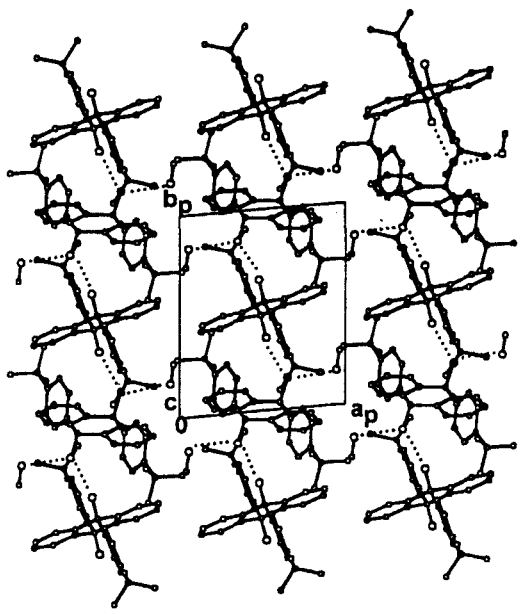


FIGURE 3 Crystal packing in DDTBDA.methanol as viewed down [001]. Hydrogen bonds are indicated with dotted lines.

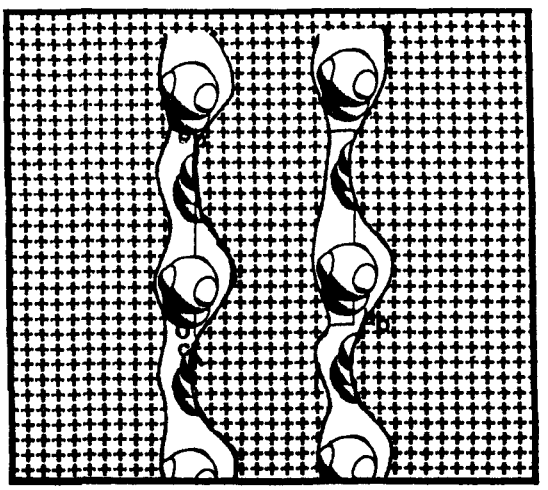


FIGURE 4 A projection of the crystal structure of DDTBDA.methanol, viewed down [001]. The hatched area represents a cross-section of the host molecules cut at $z = 0$. The guest molecules are show with van der Waals radii.

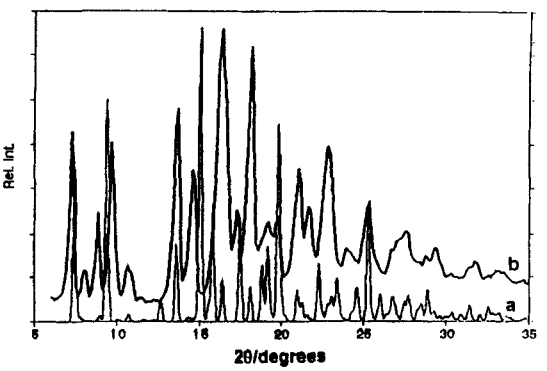


FIGURE 5 X-ray powder diffraction patterns for a) DDTBDA.methanol and b) the desolvated α-phase of DDTBDA.

and that a rearrangement of the host structure occurs upon desolvation. The crystal structure of the α-phase is not known, since it has not yet been possible to grow single crystals which did not include the solvent from which it has been grown.

A series of isothermal TG experiments were carried out on the inclusion compound at 5°C intervals over a temperature range of 40–65°C. The resultant mass loss *vs* time curves were converted to fractional reaction, α, *vs* time curves and were found to be deceleratory. A variety of deceleratory kinetic models were tested for linearity. The F1 reaction mechanism: $kt = \ln[1-(1-\alpha)]$ was found to fit the data best over an α range of 0.05–0.95. The Arrhenius plot, shown in Figure 6, yielded an activation energy of 81(8) kJ · mol^{-1}.

CONCLUSION

The crystal structure of the inclusion compound is such that the guest molecules are located in channels, with no physical barriers to the escape of the gaseous desolvation products. The guests are hydrogen bonded to the host. The guest loss reaction takes place in a single deceleratory step and the F1 reaction mechanism fits the data best. The activation energy of 81(8) kJ · mol^{-1} is comparable to that previously published for the benzene inclusion compound of the same host [9], in which the guest molecules were also located in channels. The desolvation is accompanied by the collapse of the host crystalline phase to the non-porous α-phase. The proposed kinetic mechanism deals only with the guest loss as rate determining step, since TG measures only the mass loss and does not account for concomitant thermal events.

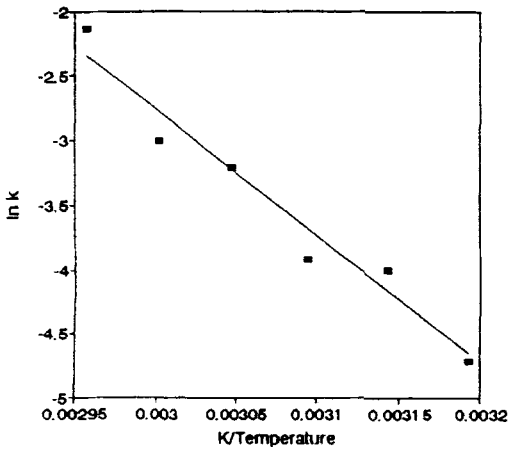


FIGURE 6 Arrhenius plot for the desolvation of DDTBDA.-methanol.

EXPERIMENTAL

The inclusion compound was obtained by slow evaporation of a solution of host compound in methanol. The crystals obtained were transparent, colourless parallelepipeds. A single crystal of diffraction quality was flame sealed in a Lindemann capillary tube together with mother liquor in order to prevent desorption of the guest during data collection. X-ray diffraction data were measured on an Enraf-Nonius CAD4 diffractometer, using graphite-monochromated MoK_α radiation, ($\lambda = 0.710$). Accurate cell parameters were determined from 24 reflections at θ 10–12°. The unit cell was refined by least-squares analysis of the setting angles of 24 reflections collected in the θ range 16–17° and centred on the diffractometer. Data were collected in the ω–2θ scan mode with a final acceptance limit of 2σ at 20° min^{-1} and a maximum scan time of 40 s. The vertical aperture length was fixed at 4 mm, the aperture width at $(1.12 + 1.05 \tan\theta)$ mm and the scan width at $\omega = (0.80 + 0.35 \tan\theta)$. During data collection three reference reflections were monitored periodically to check crystal stability. The data reduction included correction for Lorentz

and polarisation effects. Crystal data and other experimental detail are given in Table I.

Structure Solution and Refinement

The structure was solved by direct methods, using the program SHELX-86 [11] and refined by full matrix least squares refinement, using the program, SHELX-93 [12]. The data were refined on F^2 with the weighting scheme

$$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$$

where $P = [\max(0, F_o^2) + 2F_c^2]/3$ and a and b were allowed to refine.

TABLE I Crystal data and structure refinement parameters for DDTBDA.methanol

Molecular formula	$C_{34}H_{38}O_2 \cdot (CH_3OH)$
M_rg mol^{-1}	508.67
TemperatureK	294(2)
Crystal data	
Crystal system	Triclinic
Space group	$P\bar{1}$
a	10.036(3)
b	12.174(2)
c	13.294(4)
α°	69.86(2)
β°	70.20(2)
γ°	79.09(2)
Z	2
V^3	1430.0(6)
D_cg cm^{-3}	1.181
(MoK$_\alpha$)cm^{-1}	0.73
F (000)	548
Data collection	
Crystal dimensionsmm	0.37 × 0.25 × 0.25
Range scanned θ°	1.71 to 25.01
Range of indices *h*, *k*, *l*,	−11, 11; −13, 14; 0, 15
No. of reflections collected	5270
No. of unique reflections	5029
No. of reflections observed with $I_{rel}>2\sigma I_{rel}$	2850
Final refinement	
No. of restraints	4
No. of parameters	376
$R1(I_{rel}>2\sigma I_{rel})$	0.048
$wR2(I_{rel}>2\sigma I_{rel})$	0.118
Max. height in electron density map/e Å^{-3}	0.22
Min. height in electron density map/e Å^{-3}	−0.23

Direct methods yielded the positions of all the host non-hydrogen atoms in the asymmetric unit. The non-hydrogen atoms in the guest molecule were located upon subsequent refinement in the difference electron density maps. All non-hydrogen atoms were refined anisotropically. The host hydroxyl hydrogen atoms were located in the difference electron density map and refined with bond length constraints [13] and individual temperature factors. The rest of the host hydrogen atoms were placed with geometric constraints and refined with a common isotropic temperature factor for similar groups. The methyl hydrogen atoms on the guest were placed in idealised positions and allowed to refine, with a common temperature factor. The guest hydroxyl hydrogen atom was not located and was omitted from the final model. Final fractional coordinates are presented in Table II and all data has been deposited at the Cambridge Crystallographic Data Centre.

Thermal Analysis

Differential Scanning Calorimetry (DSC) and ThermoGravimetry (TG) were performed on a Perkin Elmer PC7 series system. Programmed temperature runs were done at 20°C min^{-1} over a temperature range 30–300°C. Powdered specimens were blotted dry on filter paper and placed in open platinum pans for TG experiments and in crimped, but vented aluminium sample pans for DSC experiments. Sample weight in each case was 2 to 5 mg. The samples were purged by a stream of nitrogen flowing at 40 mL min^{-1}. Data for the kinetics of desolvation were obtained from isothermal TG experiments done at selected temperatures in the range 40–65°C.

X-Ray Powder Diffraction

X-ray Powder Diffraction (XRD) patterns were obtained using Ni-filtered CuK$_\alpha$ radiation

TABLE II Atomic coordinates and equivalent displacement parameters (Å^2) for DDTBDA.methanol. U (eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U (eq)
O (1A)	0.3477(2)	0.8492(1)	−0.0042(1)	0.043(1)
C(1A)	0.3943(2)	0.9655(2)	−0.0413(2)	0.035(1)
C(2A)	0.5539(2)	0.9509(2)	−0.0923(2)	0.035(1)
C(3A)	0.6053(3)	0.9006(2)	−0.1798(2)	0.044(1)
C(4A)	0.7479(3)	0.8850(2)	−0.2311(2)	0.051(1)
C(5A)	0.1575(3)	1.0781(2)	0.1967(2)	0.055(1)
C(6A)	0.2059(3)	1.0299(2)	0.1110(2)	0.049(1)
C(7A)	0.3504(2)	1.0148(2)	0.0567(2)	0.035(1)
C(8A)	0.3283(2)	1.0472(2)	−0.1326(2)	0.033(1)
C(9A)	0.3413(3)	1.1670(2)	−0.1698(2)	0.041(1)
C(10A)	0.2850(3)	1.2412(2)	−0.2533(2)	0.045(1)
C(11A)	0.2132(2)	1.2001(2)	−0.3039(2)	0.040(1)
C(12A)	0.2002(3)	1.0803(2)	−0.2656(2)	0.045(1)
C(13A)	0.2557(3)	1.0055(2)	−0.1817(2)	0.041(1)
C(14A)	0.1492(3)	1.2798(2)	−0.3964(2)	0.054(1)
C(15A)	0.1893(4)	1.4049(3)	−0.4365(3)	0.091(1)
C(16A)	−0.0121(3)	1.2817(3)	−0.3509(3)	0.096(1)
C(17A)	0.2019(5)	1.2344(3)	−0.4982(3)	0.002(1)
O(1B)	0.5220(2)	1.3550(2)	−0.1182(2)	0.057(1)
C(1B)	0.4897(3)	1.4670(2)	−0.0981(2)	0.046(1)
C(2B)	0.3687(3)	1.4598(2)	0.0095(2)	0.046(1)
C(3B)	0.2419(3)	1.4203(2)	0.0185(3)	0.060(1)
C(4B)	0.1276(3)	1.4118(3)	0.1116(3)	0.068(1)
C(5B)	0.1366(3)	1.4430(3)	0.1993(3)	0.066(1)
C(6B)	0.7405(3)	1.5177(3)	−0.1922(2)	0.060(1)
C(7B)	0.6230(3)	1.5088(2)	−0.0981(2)	0.046(1)
C(8B)	0.4418(3)	1.5511(2)	−0.1976(2)	0.044(1)
C(9B)	0.3936(3)	1.6665(2)	−0.2014(2)	0.057(1)
C(10B)	0.3518(3)	1.7430(2)	−0.2909(2)	0.057(1)
C(11B)	0.3546(3)	1.7098(2)	−0.3815(2)	0.042(1)
C(12B)	0.4035(3)	1.5953(2)	0.3776(2)	0.051(1)
C(13B)	0.4472(3)	1.5174(2)	−0.2878(2)	0.052(1)
C(14B)	0.3072(3)	1.7985(2)	−0.4795(2)	0.047(1)
C(15B)	0.3937(4)	1.9055(3)	−0.5265(3)	0.074(1)
C(16B)	0.1500(3)	1.8371(3)	−0.4373(3)	0.086(1)
C(17B)	0.3291(3)	1.7482(3)	−0.5746(2)	0.069(1)
O(1G)	0.0534(2)	1.8309(2)	0.0538(2)	0.080(1)
C(1G)	0.0362(4)	0.7359(3)	0.0236(3)	0.086(1)

($\lambda = 1.5418$ Å). The patterns were recorded on a Philips PW105080 vertical goniometer with a PW 1394 motor control unit and a PW11390 channel control unit, linked to a personal computer. The powder patterns were collected over a 2θ range of 6–40°. The powdered samples were packed in an aluminium holder and step scans were recorded at 0.1° 2θ intervals and 1 s counts. Automatic receiving and divergence slits were used. Calculated XRD patterns were obtained using a modified version of the computer program LAZY-PULVERIX [14]. The input includes cell parameters, space group symmetry, atomic coordinates and Debye-Waller factors.

Acknowledgments

The author would like to thank Profs. M. R. Caira and L. R. Nassimbeni for discussion, and the FRD and UCT for financial assistance.

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