This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Supramolecular Chemistry

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

Complexation with diol host compounds. Part 18. Structures and thermal analysis of *trans*-9,10-dihydroxy-9,10-di-p-tolyl-9,10-dihydroanthracene and its inclusion compounds with acetone, diethyl ether and pyridine

Leonard J. Barbour[a]; Mino R. Caira[a]; Luigi R. Nassimbeni[a]
[a] Department of Chemistry, University of Cape Town, Rondebosch, South Africa

To cite this Article Barbour, Leonard J. , Caira, Mino R. and Nassimbeni, Luigi R.(1995) 'Complexation with diol host compounds. Part 18. Structures and thermal analysis of *trans*-9,10-dihydroxy-9,10-di-p-tolyl-9,10-dihydroanthracene and its inclusion compounds with acetone, diethyl ether and pyridine', Supramolecular Chemistry, 5: 2, 167 — 171

To link to this Article: DOI: 10.1080/10610279508029490

URL: http://dx.doi.org/10.1080/10610279508029490

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SUPRAMOLECULAR CHEMISTRY, Vol. 5, pp. 167–171
Reprints available directly from the publisher
Photocopying permitted by license only

Complexation with diol host compounds. Part 18. Structures and thermal analysis of *trans*-9,10-dihydroxy-9,10-di-p-tolyl-9,10-dihydroanthracene and its inclusion compounds with acetone, diethyl ether and pyridine

LEONARD J. BARBOUR, MINO R. CAIRA and LUIGI R. NASSIMBENI*

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

(Received July 14, 1994)

The structure of the host compound *trans*-9,10-dihydroxy-9,10-di-p-tolyl-9,10-dihydroanthracene and those of its inclusion compounds with acetone, diethyl ether and pyridine have been elucidated. The non-porous α-phase of the host has a structure in which the molecules are packed in layers parallel to the (100) plane, but exhibit no intermolecular hydrogen bonding. The host:guest stoichiometry of each inclusion compound is 1:2, and the structures are each stabilised by O-H···O or O-H···N hydrogen bonds between host and guest. The thermal decompositions of the acetone and diethyl ether compounds are characterised by single endotherms of the guest-release reaction, but the pyridine inclusion compound has a more complex decomposition, characteristic of similar pyridine inclusion compounds.

INTRODUCTION

Most of the classical compounds which act as hosts in clathrate structures were discovered by chance.[1,2] However, in the last twenty years considerable effort has gone into the synthesis of host molecules with specific properties, and Weber has recently reviewed the principles of directed host design.[3,4] He has shown that a successful host molecule should be bulky and rigid in order to provide suitable cavities which can accommodate a guest. In addition, it may be helpful to have a high-affinity functional group in the host molecule, which can engage in specific host-guest interactions. Our laboratory has studied a number of inclusion compounds where the host molecules contain the hydroxyl moiety as a hydrogen bonding donor, giving rise to "coordinatoclathrates".

Some of the most successful host molecules are of the "wheel-and-axle" type which were first synthesised by Toda,[5] and we have studied the dynamics of enclathration of 1,1,6,6-tetraphenyl-hexa-2,4-diyne-1,6-diol with acetone, as well as its solid-solid reaction with benzophenone.[6] We have also elucidated the structures of this host compound with the xylenes[7] and with selected ketones.[8] The current study follows from the study of the related host compound *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene, whose inclusion compounds with a variety of guests have been studied extensively.[9–12] We have noted that, by substituting the phenyl ring at the 4-position, the clathrating ability of the host compound may be enhanced dramatically and have demonstrated this with the host *trans*-9,10-dihydroxy-9,10-di(4-*tert*-butylphenyl)-9,10-dihydroanthracene. This compound enclathrates diethyl ether from the vapour, forming a stable inclusion compound whose structure we have elucidated.[13] Differential scanning calorimetry (DSC) showed that the onset temperature for the guest release occurred at 64.2 °C, which is 29.8 °C above its normal boiling point. We now present the structures of the tolyl derivative, (**1**), those of its 1:2 inclusion compounds with acetone (**2**), diethyl ether (**3**) and pyridine (**4**) and discuss their thermal stabilities.

EXPERIMENTAL SECTION

The host compound (Figure 1) was synthesised by reacting the Grignard derivative of 4-bromotoluene with an-

---

*To whom correspondence should be addressed.

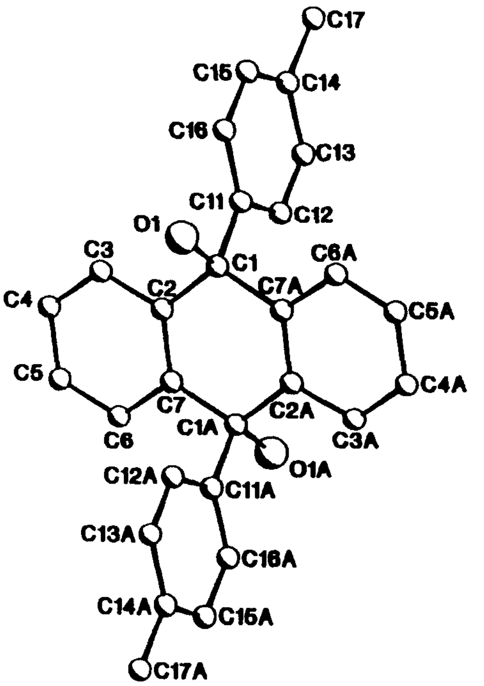

Figure 1 Atom numbering scheme for *trans*-9,10-dihydroxy-9,10-di-p-tolyl-9,10-dihydroanthracene.

thraquinone. Crystals of the non-porous α-phase of the host were obtained by slow evaporation of the compound from benzene, and the inclusion compounds by dissolving the host in a minimum volume of the liquid guest and subsequent slow evaporation of the solution at room temperature.

For all four compounds preliminary cell dimensions and space-group symmetry were determined photographically. X-ray diffraction data were then measured on a Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) and the $\omega - 2\theta$ technique. Measurements were carried out at room temperature and crystal stabilities were checked by monitoring three reference reflections periodically. The structures were solved by direct methods using SHELXS-86[20] and refined by least squares using SHELX-76[21].

For **1**, only very small lath-shaped crystals could be obtained despite many attempts at crystal growth, and these yielded a relatively small number of observed reflections. The structure was therefore refined with only the methyl carbon C(17) and the hydroxyl oxygen O(1) as anisotropic, but with the remaining heavy atoms isotropic. The aromatic and methyl hydrogen atoms were subjected to constrained refinement with common temperature factors. The hydroxyl hydrogen atom could not be located in the final difference electron density map and was omitted from the final model. For compounds **2**, **3** and **4**, the final refinement employed anisotropic temperature factors on the heavy atoms of the host and guest molecules and constrained refinement for all the hydrogen atoms. In particular, the hydroxyl hydrogens were unequivocally located in all cases, and refined with appropriate O-H bond length constraints according to a function of the O···O or O···N versus O-H distance.[14]

Differential Scanning Calorimetry and Thermogravimetry (TG) were performed using a Perkin

Table 1 Crystal data and refinement parameters

	1	*2*	*3*	*4*
Formula unit	$C_{28}H_{24}O_2$	$C_{28}H_{24}O_2\bullet 2(C_3H_6O)$	$C_{28}H_{24}O_2\bullet 2(C_4H_{10}O)$	$C_{28}H_{24}O_2\bullet 2(C_5H_5N)$
Formula weight	392.5	508.66	540.74	550.70
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a / Å	5.876(2)	9.494(4)	8.706(2)	9.661(1)
b / Å	21.349(9)	11.961(4)	10.911(2)	9.724(2)
c / Å	8.971(2)	12.771(8)	16.614(6)	16.398(4)
α / °	90	95.69(4)	90	90
β / °	108.70(3)	101.75(4)	94.90(3)	95.61(2)
γ / °	90	99.80(3)	90	90
V / Å^3	1066(1)	1413(1)	1572(1)	1533(1)
Refinement of the unit cell				
No of reflections used	24	24	24	24
θ range / °	16–17	16–17	16–17	16–17
Z	2	2	2	2
Dc / g cm^{-3}	1.223	1.195	1.142	1.193
F(000)	416	544	584	584
μ / cm^{-1} (Mo Kα radiation)	0.70	0.72	0.68	0.68
Crystal size / mm	0.06 × 0.19 × 0.25	0.50 × 0.50 × 0.50	0.31 × 0.31 × 0.34	0.22 × 0.22 × 0.25
Range of θ collected / °	1–20	1–25	1–25	1–25
No. of collected reflns	836	4219	2165	1954
No. of reflns with I > 2σI	621	3150	1411	1240
Intensity instability (%)	0.5	0.6	2.5	6.4
No. of refined parameters	142	372	197	200
$R = [\Sigma\lvert\Delta F\rvert/\Sigma\lvert Fo\rvert]$	0.047	0.052	0.057	0.058
$wR = [(\Sigma w\lvert\Delta F\rvert^2/\Sigma w\lvert Fo\rvert^2)^{1/2}]$	0.061	0.065	0.064	0.062
Weighting : $w = [\sigma^2F + gF^2]^{-1}$ g =	0.11	0.012	0.0026	0.00084
Final $\Delta\rho_{max}/\Delta\rho_{min}$ [e Å^{-3}]	0.18/−0.18	0.26/−0.22	0.22/−0.26	0.23/−0.17

Elmer PC7 system. In order to carry out the analyses, crystals were removed from their mother liquor, blotted dry on filter paper and crushed. The sample weight in each case was ca 5 mg. The temperature range was 30 to 300 °C at a heating rate of 10 °C min^{-1}. A constant stream of nitrogen (flow rate 40 cm^3 min^{-1}) was passed over the samples.

RESULTS AND DISCUSSION

Crystal data and salient refinement parameters are given in Table 1. The tricyclic moiety of the host molecule is essentially planar, with the hydroxyl and tolyl groups located perpendicular to this. The packing of compound **1**, the non-porous α-phase, is shown in Figure 2. The molecules lie in sheets parallel to the (100) planes, and interestingly, there are no hydrogen bonds between the layers.

For the acetone inclusion compound, **2**, the space group is P$\bar{1}$ with $Z = 2$. Thus the asymmetric unit comprises one host molecule and two crystallographically independent acetone guests. This is unusual in that many structures based on this host compound and its modifications have the host molecule located on a centre of inversion, requiring the central ring to be either planar or in the conformation of a shallow chair.[15,16,17] However, in this structure the central ring has a shallow boat conformation as shown in Figure 3. The guest acetone molecules are hydrogen bonded to the host via the hydroxyl moieties, with O···O distances of 2.819(3) Å and 2.898(4) Å, as shown in Figure 4. The molecular structure of **3** is shown in Figure 5. This compound crystallises in space group P2$_1$/n with $Z = 2$, requiring the host molecule to be located at a centre of symmetry. There is only one guest in the asymmetric unit and the diethyl ether molecule is hydrogen bonded to the host with an O···O distance of 2.840(4) Å. The packing of the structure is shown in Figure 6, which was drawn using the program MOLMAP[18], and gives a representation of the guest ether molecules situated in undulating channels running along [010]. Compound **4** has a similar structure to that of **3**. The host:guest stoichiometry is identical and the space group is P2$_1$/n with the host molecule again situated on a centre of inversion. The pyridine guest molecules are hydrogen bonded to the host hydroxyl groups with an O···N distance of 2.826(5) Å. The packing is shown in Figure 7, in which the channels again run parallel to [010], but the undulations are more pronounced in order to accommodate the pyridine guests.

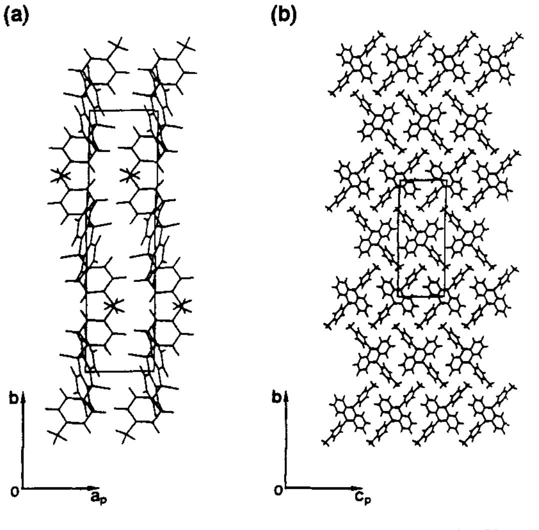

Figure 2 Projections of **1** along (a) [001] and (b) [100].

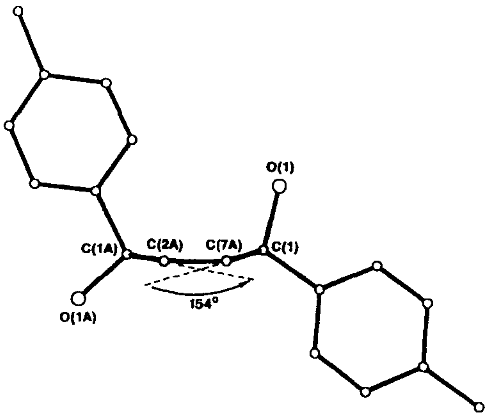

Figure 3 Perspective view of the host molecule of **2** viewed parallel to the plane through C(2), C(7), C(2A) and C(7A) showing the puckering of the central ring of the tricyclic moiety (the peripheral rings are omitted).

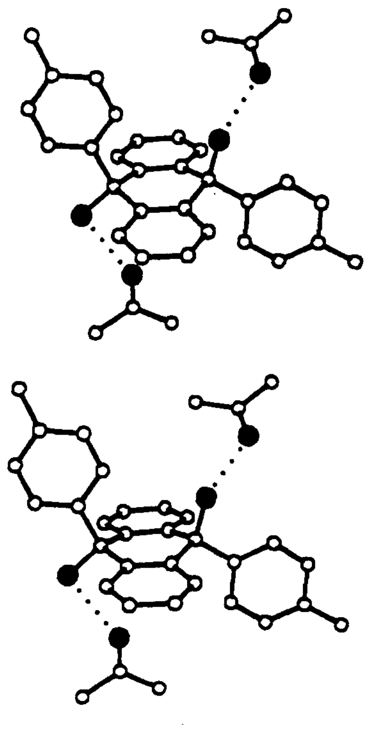

Figure 4 The molecular structure of **2**.

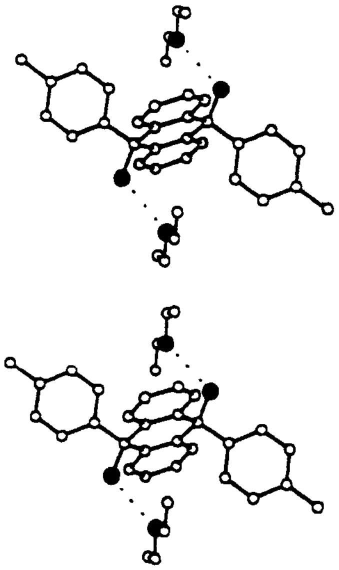

Figure 5 The molecular structure of **3**.

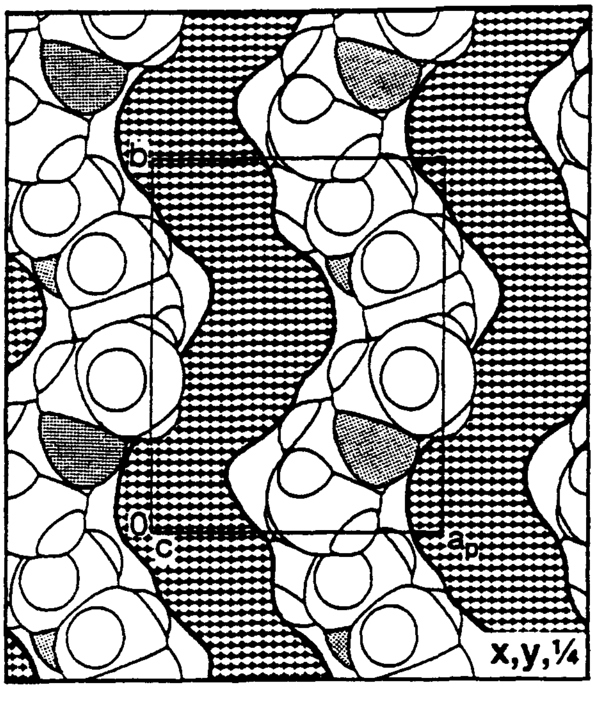

Figure 6 Cross section of the host molecules of **3** on (004) viewed along [001]. The guest molecules are shown in channels at ³/₄,y,¹/₄.

Details of the hydrogen bonding are given in Table 2, final atomic coordinates and lists of bond lengths, bond angles and structure factors have been deposited.

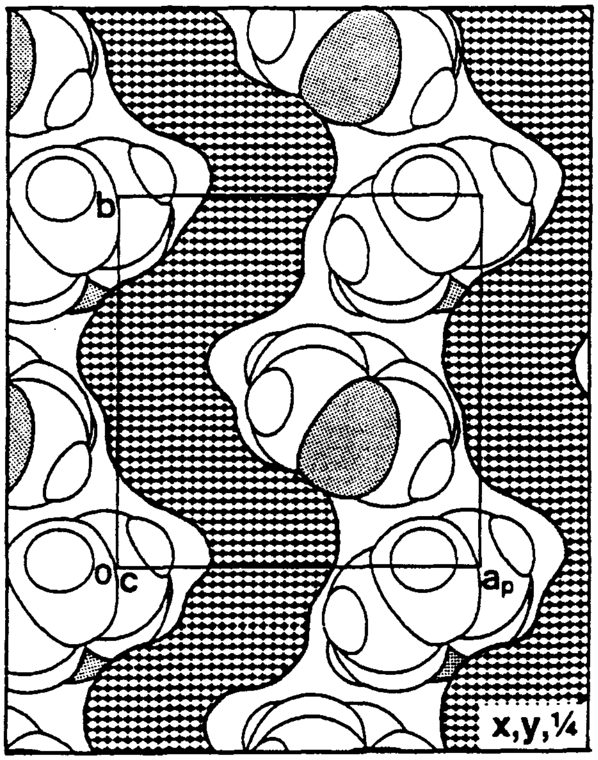

Figure 7 Cross section of the host molecules of **4** on (004) viewed along [001]. The guest molecules are shown in channels at ³/₄,y,¹/₄.

Table 2 Hydrogen bond details for structures with Host 1

Compd.	*(D)onor*	*(A)cceptor*	*D-H(Å)*	*D···A(Å)*	*H···A(Å)*	*D-H···A(°)*
2	O(1)	O(1G1)	0.96(2)	2.819(3)	1.89(3)	162(2)
	O(1A)	O(1G2)	0.97(3)	2.898(4)	1.94(3)	169(2)
3	O(1)	O(1G)	0.96(2)	2.840(4)	1.93(2)	158(3)
4	O(1)	N(1G)	1.00(2)	2.826(5)	1.84(3)	168(4)

The thermal analysis results of **2**, **3** and **4** are given in Figure 8, and the relevant thermal data are tabulated in Table 3. The weight loss measured in each case is in close agreement with the calculated value. This confirms the host:guest ratios which were subsequently employed in the crystal structure analysis of each compound.

The DSC curves of **2** and **3** are characterised by the two distinct endotherms: A, corresponding to the guest release reaction, and B, due to the melting of the host compound. Interestingly, for **4**, the pyridine guest is released in two distinct steps, giving rise to two separate endotherms, A and B, followed by the host melting endotherm C. We have noted this phenomenon with other inclusion compounds of pyridine. In particular, we have studied the thermal decomposition of the pyridine clathrate of 1,1'-binaphthyl-2,2'-bis(diphenylhydroxymethyl).[19] However, this compound has a host:guest ratio of 1:3, with one of the pyridine guests hydrogen bonded to the host, but the other two only held by weak non-bonded interactions. This is not the case with **4**,

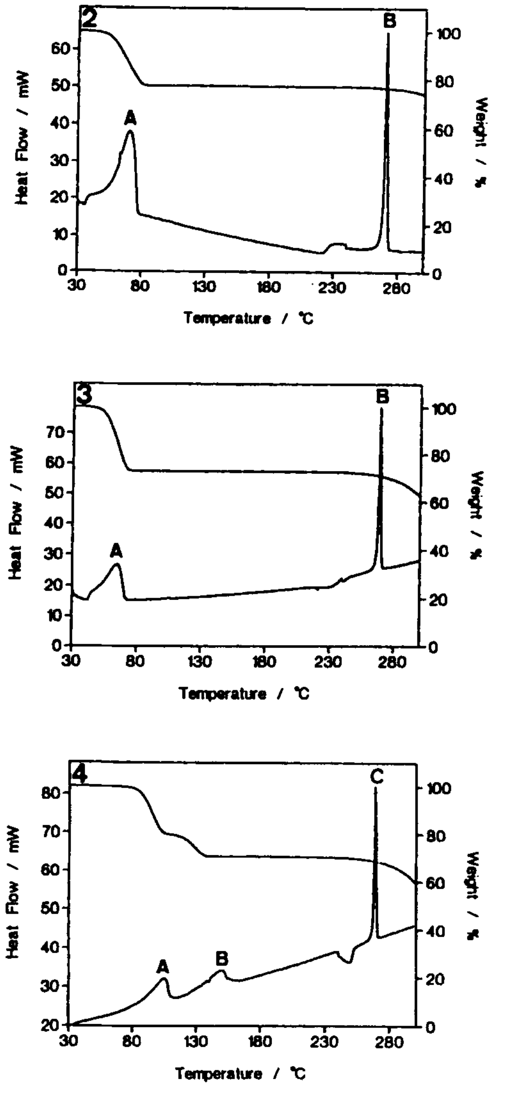

Figure 8 DSC and TG traces of compounds 2 to 4.

however, in which the pyridine guests are crystallographically equivalent. The thermal analysis of this compound therefore suggests a phase change after partial loss of the pyridine guest, followed by the second endotherm due to the final loss of guest.

Table 3 Thermal analysis

Compound	*2*	*3*	*4*
Host:guest ratio	1:2	1:2	1:2
Boiling point of guest (°C)	56.2	34.6	115.4
TG			
Weight loss expected (%)	22.8	27.4	28.7
Weight loss obtained (%)	22.8	27.1	29.1
DSC			
Endotherm A onset temperature (°C)	46.7	44.2	88.9
Endotherm B onset temperature (°C)	262.2	263.7	138.0
Endotherm C onset temperature (°C)	–	–	263.2

* see Figure 8 for labeling of endotherms A to C

REFERENCES

1 Hagan, M.; *Clathrate Inclusion Compounds*; Reinhold Publ. Corp.: New York, 1962.
2 Mandelcorn, L.; *Non-stoichiometric Compounds*: Academic Press: New York, 1964.
3 Weber, E.; *Molecular Inclusion and Molecular Recognition—Clathrates I*; Topics in Current Chemistry, Vol. 140; Springer Verlag: Berlin, 1987.
4 Weber, E.; *Inclusion Compounds*, Vol. 4, Eds. Atwood, J.L., Davies, J.E.D. and MacNicol, D.D.; Oxford University Press, 1991.
5 Toda, F.; Akagi, K.; *Tetrahedon Lett.* **1968**, *33*, 3695.
6 Bond, D.R.; Johnson, L.; Nassimbeni, L.R.; Toda, F.; *J. Solid State Chem.* **1991**, *92*, 68.
7 Nassimbeni, L.R.; Johnson, L.; Toda, F.; *Supramolecular Chem.* **1993**, *2*, 233.
8 Johnson, L.; Nassimbeni, L.R.; Toda, F.; *Acta Cryst.* **1992**, *B48*, 827.
9 Bond, D.R.; Nassimbeni, L.R.; Toda, F.; *J. Inclusion Phenomen. Mol. Recog. Chem.* **1989**, *7*, 623.
10 Bond, D.R.; Nassimbeni, L.R.; Toda, F.; *J. Crystall. Spectrosc. Res.* **1989**, *5*, 847.
11 Bond, D.R.; Caira, M.R.; Harvey, G.A.; Nassimbeni, L.R.; Toda, F.; *Acta Cryst.* **1990**, *B46*, 771.
12 Caira, M.R.; Nassimbeni, L.R.; Schubert, W.-D.; Toda, F.; *Thermochim. Acta.* **1992**, *206*, 265.
13 Barbour, L.J.; Caira, M.R.; Nassimbeni, L.R.; *J. Chem. Soc., Perkin Trans. 2*, **1993**, 1413.
14 Schuster, P.; Zundel, G; Sanderfly, C; *The Hydrogen Bond II. Structure and Spectroscopy*; North-Holland: Amsterdam, 1976.
15 Bond, D.R.; Nassimbeni, L.R.; Toda, F.; *J. Crystallogr. Spectrosc. Res.* **1989**, *19*, 847.
16 Bond, D.R.; Nassimbeni, L.R.; Toda, F.; *J. Incl. Phenom.* **1989**, *7*, 623.
17 Bond, D.R.; Caira, M.R.; Harvey, G.A.; Nassimbeni, L.R.; Toda, F.; *Acta Cryst.* **1990**, *B46*, 771.
18 MOLMAP, Barbour, L.J.; unpublished computer program, 1993.
19 Weber, E.; Skobridis, K.; Wierig, A.; Barbour, L.J.; Caira, M.R.; Nassimbeni, L.R.; *Chem. Ber.* **1993**, *126*, 1141.
20 Sheldrick, G.M.; SHELXS-86, in Crystallographic Computing 3. Eds. Sheldrick, G.M.; Kruger, C.; Goddard, G.; Oxford University Press, Oxford, **1985**, p175.
21 Sheldrick, G.M.; SHELX-76, "A program for Crystal Structure Determination", University of Cambridge, **1976**.