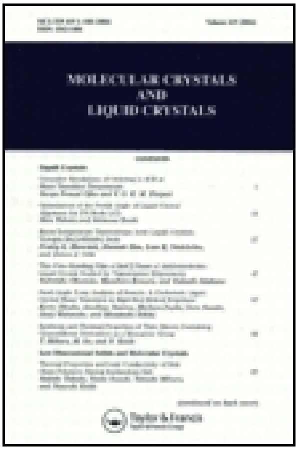

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Solvent-Free Synthesis and Crystal Structure of 9,10-Dihydro-9,10-diphenylanthracene-2,3,6,7-tetraol Inclusion Compounds

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The 9,10-dihydro-9,10-diphenylanthracene-2,3,6,7-tetraol (**1**) *host molecule is synthesized via a solvent-free procedure. Tetraol* **1** *forms a 1:3 hydrogen-bonded cocrystalline adduct with ethanol in space group Fddd and with dimethyl sulfoxide in C2/c. Tetraol* **1** *represents a member of a potential new family of host molecules and could be used as a potential cocrystal former for active pharmaceutical ingredients (API) as well as other industrial applications.*

Keywords: cocrystal former; crystal engineering; inclusion compounds; solvent-free synthesis; X-ray crystal structures

INTRODUCTION

Anthracenes, dihydroanthracenes, and their derivatives have a prominent role to play in the development of organic photochemistry [1]. Because they are easy to modify and have strong fluorescence emission, these compounds have been widely used as luminophores in optically based chemosensors for a wide range of metal ions [2–4], diols [5], glucose [6], and nucleotides [7]. They also have industrial applications

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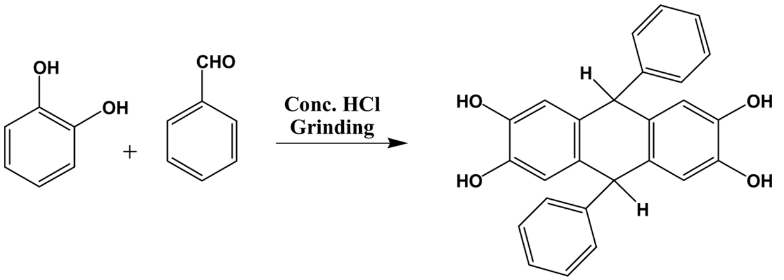
as photoresponsive materials for data storage and optical switching [8,9], light-emitting diodes [10–12], thin-film transistors [13], and novel initiators for anionic and cationic polymerizations [14]. Anthracene–carbohydrate hybrids also function as novel DNA photocleaving and photoselective cytotoxic agents against cancer cells [15]. Crystalline hosts containing anthracene subunits have proven highly efficient in the formation of crystalline inclusion compounds because of their π-stacking and spatial shielding effects [16]. Depending on the positions of substituents attached to the anthracene moiety, they constitute a family of clathrate host molecules with different molecular geometry and supramolecularity [17–19].

Previously, we had been interested in the design and synthesis of V-shaped diquinoline derivatives, which possess flexible structures able to rotate and twist in different modes to adopt the most stable lattice structures [20–27]. Recently, we have focused on linear lattice inclusion hosts. We modified the central alicyclic linker, aromatic wings, and sensor groups, as we did with the diquinolines. For the new system, we can change the R groups using different reacting aldehydes, carrying out benzylic bromination of H and modifying the OH groups to obtain a new family of host anthracene derivatives (Scheme 1).

So far, only one study has been reported on the synthesis of a compound similar to **1** using the classical condensation synthesis route in solution, in which it was proposed as an intermediate [28]. However, the crystal structure and the inclusion properties were not investigated.

In this communication, we report a novel, solvent-free procedure for the synthesis of 9,10-dihydro-9,10-diphenylanthracene-2,3,6,7-tetraol **1**, followed by analysis of the crystal structure and types of interactions present in the inclusion compounds. The X-ray crystal structures of the ethanol and dimethyl sulfoxide inclusion compounds are



SCHEME 1 Synthesis of 9,10-dihydro-9,10-diphenylanthracene-2,3,6,7-tetrol **1**.

TABLE 1 Numerical Details of the Solution and Refinement of the Two Crystal Structures

Compound	(1)·$(C_2H_6O)_3$	(1)·$(C_2H_6OS)_3$
Formula of asymmetric unit	$C_{32}H_{38}O_7$	$C_{32}H_{38}O_7S_3$
Formula weight	534.62	630.80
Temperature (K)	223(2)	223(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	Fddd	C2/*c*
a (Å)	10.6001(4)	27.184(2)
b (Å)	25.7119(10)	10.4456(6)
c (Å)	44.5082(18)	24.8542(14)
α (°)	90	90
β (°)	90	119.1550(10)
γ (°)	90	90
V ($Å^3$)	12130.7(8)	6163.4(7)
Z	16	8
D (calculated) (Mg m^{-3}	1.171	1 360
Absorption coefficient (mm^{-1})	0.082	0.288
F(000)	4560	2672
Crystal size (mm^3)	$0.45 \times 0.26 \times 0.10$	$0.60 \times 0.14 \times 0.10$
Theta range for data collection (°)	1.83 to 24.99	1.72 to 25.00
Index ranges	$-12 \leq h \leq 12$	$-30 \leq h \leq 32$
	$-30 \leq k \leq 25$	$-12 \leq k \leq 12$
	$-52 \leq l \leq 51$	$-29 \leq l \leq 19$
Reflections collected	17028	17657
Independent reflections	2694	5442
R(int)	0.0238	0.0350
Max. and min. transmission	0.9919 and 0.9642	0.9718 and 0.8464
Data/restraints/parameters	2694/21/215	5442/66/431
Goodness of fit on F^2	1.043	1.454
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0506$	$R_1 = 0.1068$
	$wR_2 = 0.1425$	$wR_2 = 0.3315$
R indices (all data)	$R_1 = 0.0604$	$R_1 = 0.1293$
	$wR_2 = 0.1511$	$wR_2 = 0.3566$
Largest diff. peak and hole ($eÅ^{-3}$)	0.215 and -0.217	1.356 and -0.801

discussed. The numerical details of the solution and refinement of these structures are summarized in Table 1.

RESULTS AND DISCUSSION

Preparation of 9,10-Dihydro-9,10-diphenylanthracene-2,3,6,7-tetraol 1

9,10-Dihydro-9,10-diphenylanthracene-2,3,6,7-tetraol **1** was synthesized as shown in Scheme 1. Catechol (2.5 g, 22.7 mmol) was ground with 2.41 g (22.7 mmol) of benzaldehyde in the presence of 1 ml of concentrated hydrochloric acid. The mixture was then kept at room temperature for 10 days. The resulting mixture was then examined using NMR spectroscopy (Bruker 400 MHz) and crystallized from ethanol and water to give the desired tetraol **1** with a yield of 51.90%. There was still some product dissolved in the filtrate. Hence, the filtrate was kept without evaporating the ethanol solvent, and after about 1 week, crystals of diffraction quality were obtained. Single-crystal X-ray diffraction indicated that ethanol molecules were included. ^{1}H NMR (DMSO, 400 MHz) δ 5.06 (2H, s), δ 6.43 (4H, s), δ 7.1–7.3 (10H, m), δ 8.69 (4H, s); ^{13}C NMR (DMSO, 400 MHz): δ 47.08 (CH), δ 115.44 (CH), δ 115.60 (CH), δ 125.74 (CH), δ 128.02 (CH), δ 128.89 (CH), δ 143.83 (C), δ 147.75 (C); one aromatic quaternary C was obscured; *m/z* 395.13 (M^{+}). Anal. calcd. for $C_{26}H_{20}O_4$: C, 78.77; H, 5.09. Found: C, 78.73; H, 5.06. Mp 223–225°C.

Single crystals were also obtained by dissolving 20 mg of **1** in 1 ml of dimethyl sulfoxide. The solvent was allowed to stand and slowly evaporate at room temperature. The data from the single-crystal X-ray diffraction showed that tetraol **1** also acted as a host with dimethyl sulfoxide molecules.

Crystal Structure of (1)·$(C_2H_6O)_3$

Crystallization of **1** from ethanol led to inclusion crystals of (**1**)·$(C_2H_6O)_3$ in an orthorhombic system with Fddd space group. One of the three ethanol molecules included is symmetrically different from the other two. Its CH_3 and OH groups are disordered into two positions. Compound **1** has also two out of its four OH disordered into two positions. There are a number of hydrogen bonds between

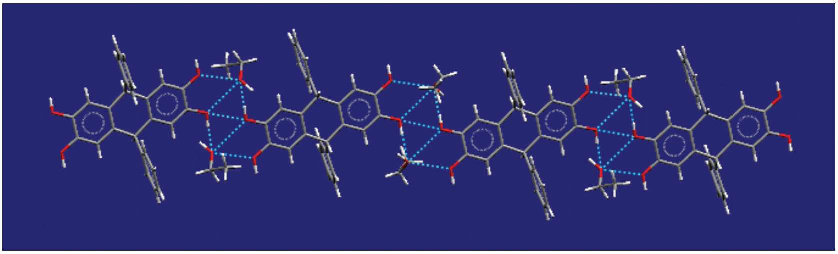


FIGURE 1 Host–guest interactions of (**1**)·$(\text{ethanol})_3$ in which the guest molecules act as bridge to link the host molecules. Color code: C, gray: O, red; H, white.

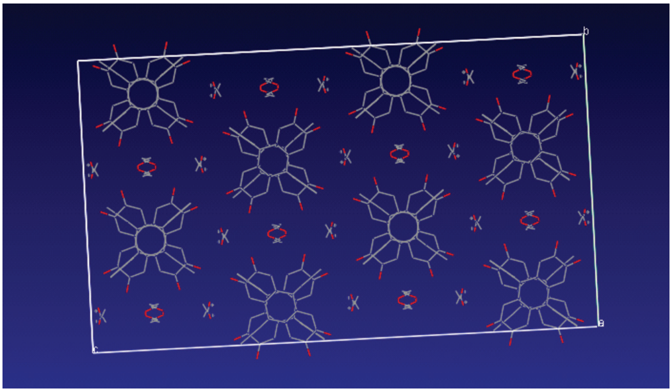


FIGURE 2 Unit cell packing arrangement of (**1**)·(ethanol)$_3$. For clarity, all hydrogen atoms are omitted and the disordered ethanol guest is shown. Color code: C, gray; O, red.

OH of host **1** and the guest molecules. As a result, the guest molecules act as a bridge, linking the host molecules (Fig. 1). The OH of **1** is hydrogen bonded to OH of ethanol (O...O) with varying distances of 2.670(1) to 3.029(1) Å. For (**1**)·(C_2H_6O)$_3$, the host molecules are also linked together by O...O host–host interactions [2.775(3) Å]. There are also guest–guest interactions found in ethanol molecules via O...O with a distance of 2.773(3) Å. Other than hydrogen bonding, many C...H (host–host, host–guest, and guest–guest) interactions of reasonable distances are also present to stabilize the structure. The crystal packing arrangement of (**1**)·(C_2H_6O)$_3$ is shown in Fig. 2.

Crystal Structure of (1)·(C_2H_6OS)$_3$

Crystallization of tetraol **1** from dimethyl sulfoxide yielded crystals of (**1**)·(C_2H_6OS)$_3$ in a monoclinic system with C_2/c space group. The asymmetric unit consists of two halves of tetraol **1** and three dimethyl sulfoxide molecules. The two halves of tetraol **1** are not symmetrically equivalent. Of the three crystallographically independent dimethyl sulfoxide guests, two are disordered. As seen in Fig. 3, the OH of tetraol **1** is hydrogen bonded to either S or O of dimethyl sulfoxide [O...S with distances of 3.210(1), 3.276(11) Å, or O...O with distances of 2.614(8), 2.700(6), 2.873(1), 2.933(1) Å]. Other than hydrogen bonding, many C...H (host–host, host–guest, and guest–guest) interactions of reasonable distances are also

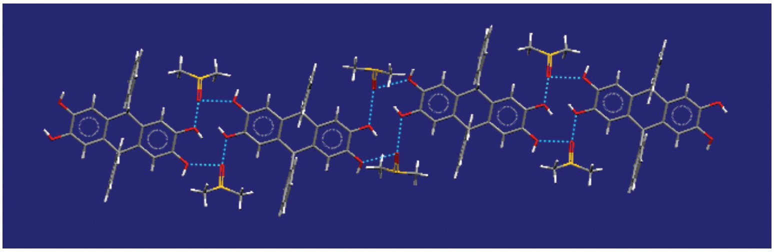


FIGURE 3 Host–guest interactions of (**1**)·(dimethyl sulfoxide)$_3$ where the guest molecules act as bridge to link the host molecules. Color code: C, gray; O, red; H, white; S, yellow.

present in stabilizing the structure. The crystal structure of the dimethyl sulfoxide lattice inclusion compound is illustrated in Fig. 4.

CONCLUSION

Tetraol **1** has been synthesized using solvent-free conditions. It formed inclusion compounds when crystallized from polar solvents such as ethanol and dimethyl sulfoxide; the components of the two adducts were strongly hydrogen bonded. Synthesis of some other derivatives

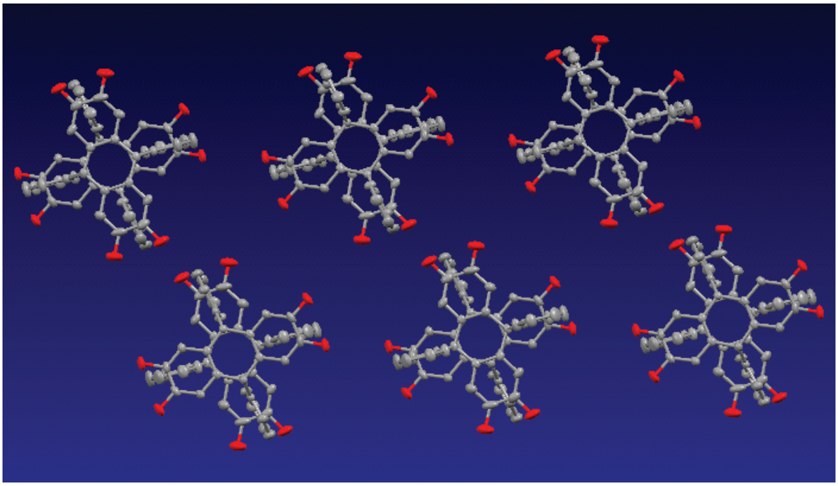


FIGURE 4 Partial structure of (**1**)·(dimethyl sulfoxide)$_3$. For clarity, all guest molecules and hydrogens are omitted. Color code: C, gray; O, red.

and investigation of their abilities to form cocrystals with solid materials possessing hydrogen-bonding functionality is still in progress. In addition, the applications in separation and purification of materials with alcohols and carboxylic acid functionalities are being investigated. The full results will be reported elsewhere.

EXPERIMENTAL

Solution and Refinement of the Crystal Structures

The single-crystal X-ray diffraction experiments were carried out on a Bruker SMART Apex 1000 diffractometer equipped with a charge-coupled device (CCD) detector and Mo-Kα sealed tube at 223(2) K. SMART [29] was used for collecting frames data, indexing reflection, and determination of lattice parameters. SAINT [30] was used for integration of intensity of reflections and scaling. SADABS [30] was used for absorption correction, and SHELXTL [31] was used for space group and structure determination and least-square refinements on F^2. All hydrogen atoms were placed in calculated positions for the purpose of structure factor calculation.

Crystallographic data (cif) have been deposited with the Cambridge Crystallographic Data Centre (deposition numbers CCDC 276915 and 276916). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: + 44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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REFERENCES

[1] Becker, H. D. (1993). *Chem. Rev.*, *93*, 145.
[2] Ghosh, P., Bharadwaj, P. K., Roy, J., & Ghosh, S. (1997). *J. Am. Chem. Soc.*, *119*, 11903.
[3] Hennrich, G., Sonnenschein, H., & Resch-Genger, U. (1999). *J. Am. Chem. Soc.*, *121*, 5073.
[4] Gunnlaugsson, T., Nieuwenhuyzen, M., Richard, L., & Thoss, V. (2002). *J. Chem. Soc., Perkin Trans.*, *2*, 141.
[5] Arimori, S. & James, T. D. (2002). *Tetrahedron Lett.*, *43*, 507.

[6] James, T. D., Sandanayake, K. R. A. S., & Shinkai, S. (1994). *Angew. Chem., Int. Ed. Engl.*, *33*, 2207.

[7] Fabbrizzi, L., Licchelli, M., Mancin, F., Pizzeghello, M., Rabaioli, G., Taglietti, A., Tecilla, P., & Tonellato, U. (2002). *Chem. Eur. J.*, *8*, 94.

[8] Beyeler, A., Belser, P., & De Cola, L. (1997). *Angew. Chem., Int. Ed. Engl.*, *36*, 2779.

[9] Takaguchi, Y., Tajima, T., Ohta, K., Motoyoshiya, J., & Aoyama, H. (2000). *Chem. Lett.*, *29*, 1388.

[10] Zheng, S. & Shi, J. (2001). *Chem. Mater.*, *13*, 4405.

[11] Kan, Y., Wang, L., Gao, Y., Duan, L., Wu, G., & Qiu, Y. (2004). *Synth. Metals*, *141*, 245.

[12] Blouche, C.-M., Berdague, P., Facoetti, H., Robin, P., Le Barny, P., & Schott, M. (1996). *Synth. Metals*, *81*, 191.

[13] Miao, Q., Nguyen, T.-Q., Someya, T., Blanchet, G. B., & Nuckolls, C. (2003). *J. Am. Chem. Soc.*, *125*, 10284.

[14] Bartz, T., Klapper, M., & Mullen, K. (1994). *Macromol. Chem. Phys.*, *195*, 1097.

[15] Toshima, K., Hasegawa, M., Shimizu, J., & Matsumara, S. (2004). *ARKIVOC*, *xiii*, 28.

[16] Weber, E., Ahrendt, J., Czugler, M., & Csoregh, I. (1986). *Angew. Chem., Int. Ed. Engl.*, *25*(8), 746.

[17] Weber, E., Hens, T., Li, Q., & Mak, T. C. W. (1999). *Eur. J. Org. Chem.*, *1999*, 1115.

[18] Weber, E., Hens, T., Brehmer, T., & Csoregh, I. (2000). *J. Chem. Soc., Perkin Trans.*, *2*, 235.

[19] Brehmer, T., Nitsche, S. I., Seichter, W., & Weber, E. (2003). *J. Inclusion Phenom. Macrocyclic Chem.*, *47*, 113.

[20] Alshahateet, S. F., Bishop, R., Craig, D. C., & Scudder, M. L. (2001). *Cryst. Eng. Comm.*, *3*(25), 107.

[21] Alshahateet, S. F., Bishop, R., Craig, D. C., & Scudder, M. L. (2001). *Cryst. Eng. Comm.*, *3*(48), 225.

[22] Alshahateet, S. F., Bishop, R., Craig, D. C., & Scudder, M. L. (2001). *Cryst. Eng. Comm.*, *3*(55), 265.

[23] Alshahateet, S. F., Bishop, R., Craig, D. C., & Scudder, M. L. (2003). *Cryst. Eng. Comm.*, *5*(74), 417.

[24] Alshahateet, S. F., Bishop, R., Craig, D. C., & Scudder, M. L. (2004). *Cryst. Growth Des.*, *4*(4), 837.

[25] Alshahateet, S. F., Bishop, R., Scudder, M. L., Hu, C. Y., Lau, E. H. E., Kooli, F., Judeh, Z. M. A., Chow, P. S., & Tan, R. B. H. (2005). *Cryst. Comm. Eng.*, *7*(21), 139.

[26] Alshahateet, S. F., Ong, T. T., Bishop, R., Kooli, F., & Messali, M. (2006). *Cryst. Growth Des.*, *6*(7), 1676.

[27] Bishop, R., Scudder, M. L., Craig, D. C., Rahman, A. N. M. M., & Alshahateet, S. F. (2005). *Mol. Cryst. Liq. Cryst.*, *440*, 173.

[28] Goossens, R., Smet, M., & Dehaen, W. (2002). *Tetrahedron Lett.*, *43*, 6605.

[29] *SMART and SAINT software reference manuals, version 4.0*, Siemens Energy and Automation, Inc., Analytical Instrumentation: Madison, WI (1996).

[30] Sheldrick, M. (1996): *SADABS. Software for Empirical Absorption Correction*, University of Göttingen: Gottingen, Germany.

[31] *SHELXTL reference manuals, version 5.03*, Siemens Energy and Automation, Inc., Analytical Instrumentation: Madison, WI (1996).