

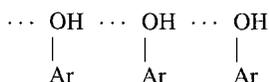
Structure of the Co-Crystalline Solid Formed between 1,4-Dichloronaphthalene-2,3-diol and Dioxane

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Abstract. The 1,4-dichloro-(**1**) and 1,4-dibromo-(**2**) derivatives of naphthalene-2,3-diol crystallise in structures containing acetic acid or dioxane solvent molecules. X-ray crystallographic examination of the compound formed between **1** and dioxane is reported here [$(C_{10}H_6Cl_2O_2)_2 \cdot (C_4H_8O_2)$, $P2_1/c$, $a = 12.358(3)$, $b = 4.9930(7)$, $c = 19.167(4)$ Å, $\beta = 96.09(1)^\circ$, $Z = 2$, $R = 0.035$] and this structure is analysed in crystal engineering terms. The compound is a co-crystalline material involving two types of hydrogen bonding: one phenolic group participates in a



chain, while the second phenolic group hydrogen bonds to a dioxane. Extension of the hydrogen bonding network through the second dioxane oxygen results in heavily corrugated layers. Neighbouring layers interact by a combination of aromatic face–face and edge–face interactions similar to a partial coronene-type γ packing to complete the structure.

Keywords. Phenols, dioxane, hydrogen bonding, co-crystals, aromatic ring interactions, coronene packing.

Supplementary Data relating to this article are deposited with the British Library as supplementary publication No. SUP 82184 (11 pages).

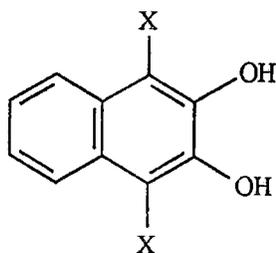
1. Introduction

Many small and/or symmetrical phenols exhibit considerable difficulty in forming efficient crystal packing arrangements. For example, α -hydroquinone (the most stable polymorph at room temperature) contains 54 molecules per unit cell [1]. These packing difficulties are also frequently reflected in the tendency of such compounds to show polymorphic behaviour [2], and their propensity to indulge in co-crystalline behaviour [3].

The latter property results in phenols being a rich source, both as inclusion hosts, and as partners in intimately hydrogen bonded co-crystalline solids. Recently, we

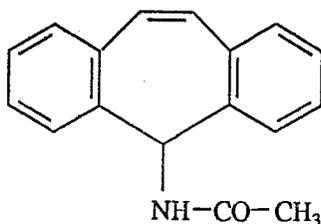
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have reported [4–6] the ability of phenols to form co-crystalline solids with helical tubuland diols whereas, so far as is known, all other organic functional group compounds tend to be included as guests in lattice inclusion compounds [7]. In other words phenols have unique crystal engineering properties with considerable potential in the design of new heteromolecular solids [8]. We are interested in exploring these characteristics with a view to their development in a rational manner.



1 X = Cl

2 X = Br



3

In this contribution we report on the co-crystalline properties of 1,4-dichloronaphthalene-2,3-diol **1**. We first became interested in the behaviour of this particular substance after observing a comment made in 1907 by Willstätter and Parnas [9] that this phenolic derivative formed a 1 : 2 compound with acetic acid.

2. Experimental

2.1. PREPARATIVE WORK

^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded using a Bruker AC300F instrument and are reported as chemical shifts (δ) relative to SiMe_4 . The substitution of carbon atoms was determined by the DEPT procedure. Melting points were determined with a Kofler instrument and are uncorrected. The IR spectra were recorded on a Perkin Elmer 298 spectrophotometer. Combustion analyses were carried out at UNSW by Dr. H. P. Pham.

2.1.1. 1,4-Dichloronaphthalene-2,3-diol **1**

A short burst of chlorine gas was passed through a solution of naphthalene-2,3-diol (2.00 g, 12.5 mmol) in glacial acetic acid (10 mL) until precipitation resulted. The solid was filtered off and recrystallised from chloroform to give the *dichloride* **1** (0.85 g, 30%), m.p. 182 °C; lit. [10] 181 °C. (*Found*: C, 52.57; H, 2.92. $\text{C}_{10}\text{H}_6\text{Cl}_2\text{O}_2$ requires C, 52.44; H, 2.64%). ν_{max} . (paraffin mull) 3460s, 3370s, 1625w, 1600w, 1300s, 1250m, 1200w, 1170w, 1150w, 1100w, 950s, 930w, 745s cm^{-1} . $^1\text{H-NMR}$ δ (d_6 -DMSO) 10.31, br s, 2H, —OH; 8.02–7.96, AA'BB' m, 2H; 7.52–7.46, AA'BB'

m, 2H. $^{13}\text{C-NMR } \delta$ (d_6 -DMSO) 143.8 (C), 125.6 (C), 125.3 (CH), 122.7 (CH), 112.8 (C).

A co-crystalline compound resulted when **1** was crystallised from acetic acid, but crystals of this material proved to be too unstable for X-ray structure determination. A slightly more robust compound was obtained from dioxane: [*Found*: C, 52.88; H, 3.95. $(\text{C}_{10}\text{H}_6\text{Cl}_2\text{O}_2)_2 \cdot (\text{C}_4\text{H}_8\text{O}_2)$ requires C, 52.77; H, 3.69%]. Toluene, benzene, diethyl ether, chloroform, methanol and ethanol were not included.

2.1.2. 1,4-Dibromonaphthalene-2,3-diol **2**

Bromine (2.03 g) in glacial acetic acid (4.1 mL) was added gradually to a stirred solution of naphthalene-2,3-diol (1.0 g, 6.2 mmol) in glacial acetic acid (3.1 mL). The solid produced was filtered and recrystallised from chloroform to yield the *dibromide 2* (1.4 g, 70%), m.p. 178–180 °C; lit. [10] 178 °C. ν_{max} . (paraffin mull) 3440s, 3380s, 1610w, 1595w, 1490w, 1290s, 1235s, 1200m, 1150m, 1100m, 930m, 915m, 740s, 730s cm^{-1} . $^1\text{H-NMR } \delta$ (d_6 -DMSO) 10.24, br s, 2H, —OH; 8.00–7.96, AA'BB' m, 2H; 7.48–7.44, AA'BB' m, 2H. $^{13}\text{C-NMR } \delta$ (d_6 -DMSO) 145.0 (C), 127.3 (C), 125.57 (CH), 125.50 (CH), 105.9 (C).

Co-crystalline solids also resulted when **2** was crystallised from acetic acid and dioxane. It is presumed that these have analogous structures to the corresponding compounds involving **1** but both proved too unstable for structure determination.

2.2. X-RAY DATA COLLECTION, PROCESSING, AND REFINEMENT FOR THE STRUCTURE (**1**)₂·(DIOXANE)

Data were recorded using an Enraf-Nonius CAD4 X-ray diffractometer. Data collection and processing procedures have been described [11]. Corrections were made for absorption [12]. The positions of all 14 non-hydrogen atoms of the phenol were located using direct methods (MULTAN) [13]. A subsequent Fourier synthesis revealed the position of the dioxane molecule, located about a centre of symmetry. Initially all three atoms of the dioxane molecule were included in the structure as carbon atoms. After isotropic refinement, the temperature factors of these three atoms (around the ring) were 2.7, 6.5 and 6.6, making assignment of the oxygen atom unequivocal. This was later supported by the observation of hydrogen bonding between the diol and the dioxane oxygen atoms. Full matrix least squares refinement (BLOCKLS) [14] with anisotropic thermal parameters for the non-hydrogen atoms converged with $R = 0.042$. Hydroxy hydrogen atoms were included in the refinement at positions determined from a difference Fourier map and their positions were refined. All other hydrogens were included at calculated positions. They were assigned isotropic temperature factors equivalent to those of the atoms to which they were bound and were not refined. The dimensions of the dioxane ring at this stage gave the DC(1)—DC(2) bond length as only 1.27 Å, and the angles at the two carbon atoms were approximately 120°. It seemed that this model was a superposition of two possible ring orientations, with the

TABLE I. Numerical details of the solution and refinement of the structure of (1)₂·(dioxane).

Formula, formula mass	(C ₁₀ H ₆ Cl ₂ O ₂) ₂ ·(C ₄ H ₈ O ₂), 546.2
Crystal description	{102}(-100)(-1-11)(012)
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	12.358(3)
<i>b</i> /Å	4.9930(7)
<i>c</i> /Å	19.167(4)
β /°	96.09(1)
<i>V</i> /Å ³	1176.0(4)
Temp./°C	21(1)
<i>Z</i>	2
<i>D</i> _{calc.} /g cm ⁻³	1.54
Radiation, λ /Å	MoK α , 0.7107
μ /cm ⁻¹	5.43
Crystal dimensions/mm	~ 0.2 × 0.15 × 0.2
Scan mode	$\theta/2\theta$
$2\theta_{\max.}$ /°	50
ω scan angle	(0.50 + 0.35 tan θ)
No. of intensity measurements	2383
Criterion for observed reflection	<i>I</i> / σ (<i>I</i>) > 3
No. of independent obsd. reflections	1540
No. of reflections (<i>m</i>) and variables (<i>n</i>) in final refinement	1540, 179
$R = \sum^m \Delta F / \sum^m F_0 $	0.035
$R_w = [\sum^{m_w} \Delta F ^2 / \sum^{m_w} F_0 ^2]^{1/2}$	0.049
$s = [\sum^{m_w} \Delta F ^2 / (m - n)]^{1/2}$	1.83
Crystal decay	1 to 0.97
Max., min. transmission coefficients	0.93, 0.87
Largest peak in final diff. map/ <i>e</i> Å ⁻³	0.29
<i>R</i> for 100 multiple measurements	0.010

oxygen atoms kept fixed, but with the ring puckering either up, or down. The two carbon atoms of the dioxane ring were therefore included in two possible positions, corresponding to the two ring orientations. Refinement was completed using the program RAELS, which is able to incorporate slack constraints [15]. Weak slack constraints kept the DO—C distances equal, the C—C distances at approximately 1.54 Å and the angles all at approximate tetrahedral values. The occupancies of the two components (unprimed and primed atoms in the Tables) were allowed to refine (with their sum fixed at 1.0) and their final values were 0.611(10) and 0.388. *R* converged to 0.035. The largest peak in the final difference Fourier map was 0.29 *e* Å⁻³.

The material deposited comprises atomic coordinates of the hydrogen atoms, thermal parameters, and structure factors.

TABLE II. Atomic coordinates for the non-hydrogen atoms of $(\mathbf{1})_2 \cdot (\text{dioxane})$.

Atom	x	y	z	B_{eq}
Cl(1)	0.2143(1)	1.1947(2)	0.2019(0)	4.96(5)
Cl(2)	0.3098(1)	0.4535(2)	0.4628(0)	4.24(4)
O(1)	0.1073(2)	0.4804(4)	0.3613(1)	4.40(8)
O(2)	0.0692(1)	0.8017(4)	0.2527(1)	4.16(8)
C(1)	0.2447(2)	0.9918(5)	0.2749(1)	3.12(7)
C(2)	0.3484(2)	1.0140(5)	0.3154(1)	3.12(7)
C(3)	0.4291(2)	1.1990(5)	0.2996(1)	3.84(8)
C(4)	0.5274(2)	1.2106(6)	0.3395(2)	4.40(8)
C(5)	0.5494(2)	1.0375(6)	0.3969(2)	4.32(8)
C(6)	0.4733(2)	0.8577(6)	0.4139(1)	3.60(7)
C(7)	0.3702(2)	0.8421(5)	0.3740(1)	2.96(7)
C(8)	0.2881(2)	0.6622(5)	0.3901(1)	3.12(8)
C(9)	0.1899(2)	0.6468(5)	0.3506(1)	3.12(8)
C(10)	0.1682(2)	0.8162(5)	0.2917(1)	3.20(7)
DO	0.0676(2)	0.1317(6)	0.4588(1)	6.96(9)
DC(1)	-0.0328(3)	0.0281(13)	0.4284(1)	5.9(2)
DC(2)	-0.1122(2)	0.0248(12)	0.4839(2)	6.2(2)
DC(1)'	-0.0464(3)	0.1444(20)	0.4421(4)	8.6(5)
DC(2)'	-0.0967(5)	-0.1085(21)	0.4682(2)	7.7(5)

TABLE III. Bond lengths and standard deviations (\AA) for $(\mathbf{1})_2 \cdot (\text{dioxane})$.

Bond, ($\mathbf{1}$)	Length	Bond, (dioxane)	Length
Cl(1)—C(1)	1.735(2)	DO—DC(1)	1.411(3)
Cl(2)—C(8)	1.738(2)	DO—DC(1)'	1.411(3)
O(1)—C(9)	1.349(3)	DO—DC(2) ^a	1.412(3)
O(2)—C(10)	1.367(3)	DO—DC(2)' ^a	1.413(3)
C(1)—C(2)	1.430(3)	DC(1)—DC(2)	1.521(3)
C(2)—C(3)	1.415(4)	DC(1)'—DC(2)'	1.515(4)
C(2)—C(7)	1.417(3)		
C(3)—C(4)	1.367(4)		
C(4)—C(5)	1.403(4)		
C(5)—C(6)	1.364(4)		
C(6)—C(7)	1.416(3)		
C(7)—C(8)	1.414(3)		
C(8)—C(9)	1.362(3)		
C(9)—C(10)	1.414(3)		
O(1)—HO(1)	0.74(4)		
O(2)—HO(2)	0.80(4)		

^a Equivalent position indicator: $-x, -y, 1 - z$.

TABLE IV. Bond angles and standard deviations ($^{\circ}$) for $(1)_2 \cdot (\text{dioxane})$.

Atoms, (1)	Angle	Atoms, (dioxane)	Angle
Cl(1)—C(1)—C(2)	119.8(2)	DC(1)—DO—DC(2) ^a	111.8(1)
Cl(1)—C(1)—C(10)	118.2(2)	DC(1)'—DO—DC(2) ^{'a}	111.7(2)
C(2)—C(1)—C(10)	121.9(2)	DO—DC(1)—DC(2)	108.6(1)
C(1)—C(2)—C(3)	123.1(2)	DO—DC(2) ^a —DC(1) ^a	108.8(1)
C(1)—C(2)—C(7)	117.9(2)	DO—DC(1)'—DC(2)'	108.8(2)
C(3)—C(2)—C(7)	119.0(2)	DO—DC(2) ^{'a} —DC(1) ^{'a}	109.0(1)
C(2)—C(3)—C(4)	120.9(3)		
C(3)—C(4)—C(5)	120.0(3)		
C(4)—C(5)—C(6)	120.7(2)		
C(5)—C(6)—C(7)	120.8(2)		
C(6)—C(7)—C(2)	118.6(2)		
C(6)—C(7)—C(8)	122.9(2)		
C(2)—C(7)—C(8)	118.5(2)		
Cl(2)—C(8)—C(7)	120.2(2)		
Cl(2)—C(8)—C(9)	117.7(2)		
C(7)—C(8)—C(9)	122.1(2)		
O(1)—C(9)—C(8)	126.5(2)		
O(1)—C(9)—C(10)	114.0(2)		
C(8)—C(9)—C(10)	119.5(2)		
O(2)—C(10)—C(1)	120.7(2)		
C(9)—C(10)—C(1)	120.0(2)		
C(1)—C(10)—C(9)	120.0(2)		
C(9)—O(1)—HO(1)	120(3)		
C(10)—O(2)—HO(2)	110(3)		

^a Equivalent position indicator: $-x, -y, 1 - z$.

TABLE V. Dimensions associated with hydrogen bonding in $(1)_2 \cdot (\text{dioxane})$.

O(1)···DO	2.637(3)	C(9)—O(1)···DO	135.6(1)
HO(1)···DO	1.936(38)	DC(1)—DO···O(1)	99.9(2)
		DC(1)'—DO···O(1)	93.8(2)
		O(1)—HO(1)···DO	158(4)
O(2)···O(2) ^b	3.022(2)	C(10)—O(2)···O(2) ^b	122.2(1)
HO(2)···O(2) ^b	2.268(38)	O(2)—HO(2)···O(2) ^b	157.1(36)

^b Equivalent position indicator: $-x, -1/2 + y, 1/2 - z$.

3. Results and Discussion

The contents of the monoclinic unit cell are four molecules of **1** and two of dioxane in space group $P2_1/c$. Figure 1 shows the crystallographic numbering system used.

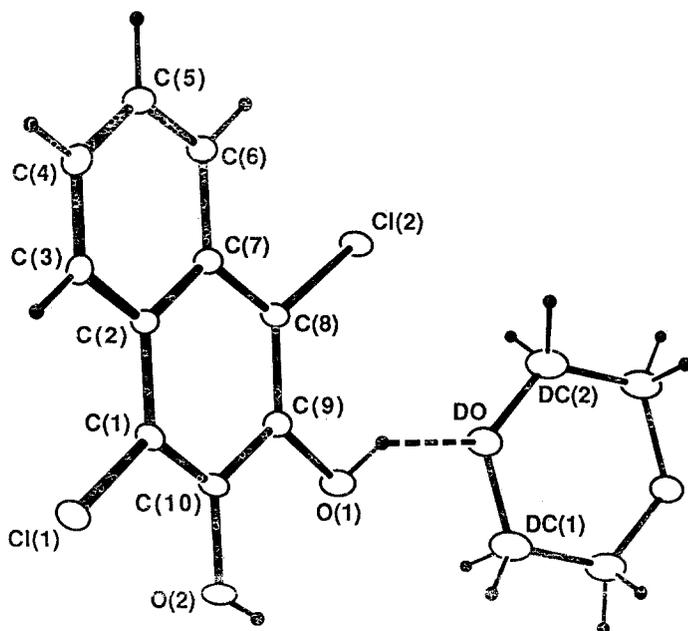


Fig. 1. Crystallographic numbering system used for molecules of 1,4-dichloronaphthalene-2,3-diol **1** and dioxane in the co-crystalline solid $(\mathbf{1})_2 \cdot (\text{dioxane})$. Dioxane atoms are prefixed D, the hydrogen bond is shown as a dashed linkage, and hydrogen atoms drawn as solid spheres.

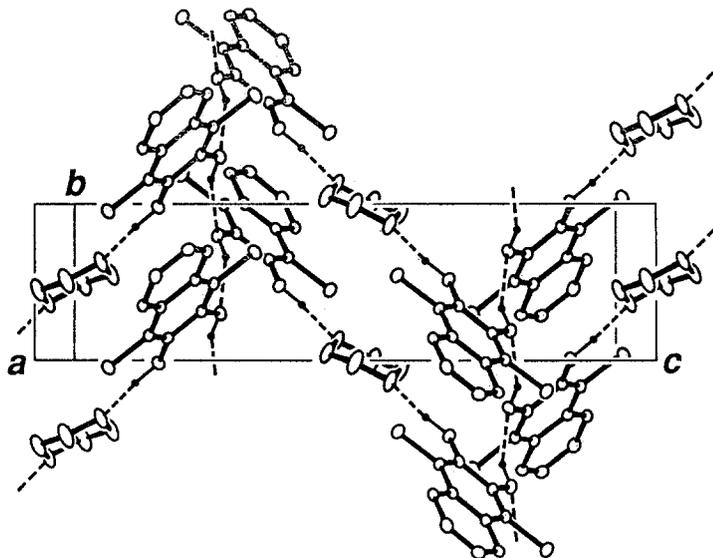
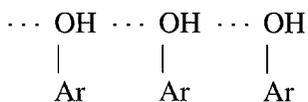


Fig. 2. Unit cell contents viewed down a^* . Hydrogen bonding (shown as dashed lines) links molecules of **1** with each other and with dioxane molecules. Non-hydroxy hydrogens have been omitted for clarity.

The structure incorporates two types of hydrogen bonding (Figure 2). Molecules of **1** are hydrogen bonded together in



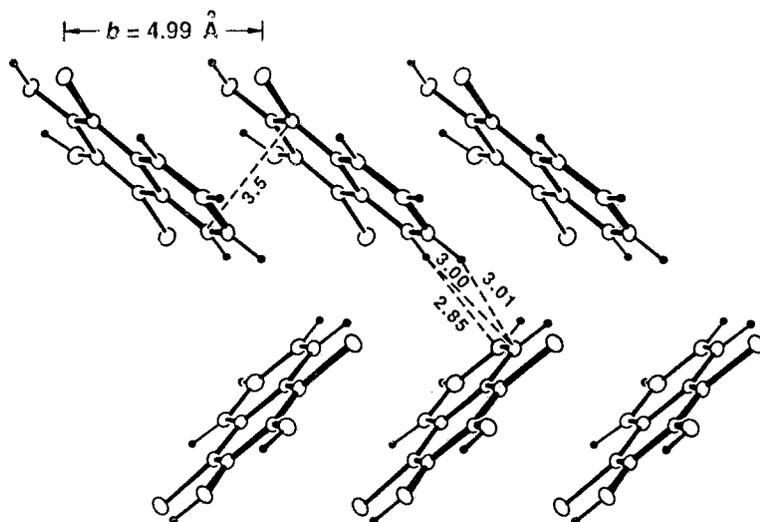


Fig. 3. The partial coronene-type γ arrangement formed where layers of $(\mathbf{1})_2 \cdot (\text{dioxane})$ meet. The shortest contacts $\text{—CH} \cdots \text{C}$ in the edge-face interaction are marked, together with the aromatic ring translational separation, and the perpendicular interplanar spacing (\AA).

chains through one fully hydrogen bonded (one donor and one acceptor) hydroxy group Ar—O(2)—H . Each molecule of $\mathbf{1}$ is hydrogen bonded to two others which are related to it by a 2_1 screw axis parallel to b . The other hydroxy group of $\mathbf{1}$ Ar—O(1)—H forms only one hydrogen bond, as the donor to a dioxane molecule, with each dioxane molecule taking part in two such hydrogen bonds. The dioxane molecule would appear to be a conveniently sized cross-linking spacer between neighbouring molecules of $\mathbf{1}$, thereby overcoming crowding effects that would otherwise result because of the protruding chloro substituents.

The resulting arrangement is a layer perpendicular to a which has heavily corrugated surfaces. Where adjacent layers abut, the molecules of $\mathbf{1}$ come together in a pattern similar to the γ type found in the structure of coronene [8a, 16], with the angles between the normals to the planes being 87.6° (Figure 3). It must be noted, however, that since one end of $\mathbf{1}$ is involved in hydrogen bonding only the other end is free to participate in edge-face aromatic interactions. In contrast, each coronene molecule takes place in edge-face interactions with molecules in two different stacks. For $(\mathbf{1})_2 \cdot (\text{dioxane})$ the shortest $\text{CH} \cdots \text{C}$ distance between the stacks is 2.85 \AA . In addition to this edge-face aromatic interaction, there is also an offset face-face interaction where the molecules of $\mathbf{1}$ in the b direction are separated by translations of only 4.99 \AA (the b cell dimension). The perpendicular distance between these parallel planes is 3.5 \AA .

There are no close contacts between Cl atoms (the shortest contact being 4.79 \AA), unlike other structures where halogen \cdots halogen interactions are one of the prime forces dictating packing [8], and including some of our helical tubuland

diol co-crystalline compounds [4–7]. In addition, there are no $\text{CH}\cdots\text{O}$ interactions (under 3.0 Å) between the molecules of **1** and dioxane, in contrast to those found in the structure of **(3)·(dioxane)₂** where there were $\text{CH}\cdots\text{O}$ contacts as short as 2.42 Å [17]. However, in this latter case there was no hydrogen bonding to the dioxane oxygen atoms. Dioxane is well known as a partner in hydrogen bonded inclusion structures when circumstances are appropriate [18].

Other X-ray structures are reported where hydrogen bonding between phenol and ether groups leads to formation of co-crystalline adducts, for example the compound (hydroquinone)·(cineole)₂ studied by Barnes [19]. The structures of at least two other phenol··dioxane compounds are known. Hydroquinone forms an unstable 1 : 1 substance where the two components alternate along hydrogen bonded chains [20], and pentafluorophenol forms a centrosymmetric 2 : 1 complex [21].

It is noteworthy that any 1 : 1 $\text{Ar—O—H}\cdots\text{O—}$ combination such as these must produce a situation where the phenolic hydroxy group is involved in only one hydrogen bond. However, the steric environment of phenolic groups is such that this does not seem to be an important structural consideration. Whereas these earlier examples of phenol··ether hydrogen bonding result in discrete complexes or linear chains, the presence of the second hydroxy group in **(1)₂·(dioxane)** leads to the formation of two-dimensional hydrogen bonded layers. Aromatic face–face and edge–face interactions facilitate the assembly of these layers into the full structure.

Acknowledgements

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