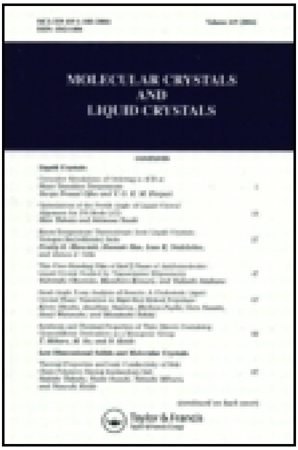


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Building Supramolecular Tapes

Elaine Batchelor [a], Jacek Klinowski [a] & William Jones [a]

[a] University of Cambridge, Department of Chemistry, Lensfield Road, CB2 1EW

To cite this article: Elaine Batchelor, Jacek Klinowski & William Jones (2001): Building Supramolecular Tapes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 356:1, 263-272

To link to this article: http://dx.doi.org/10.1080/10587250108023706

Mol. Cryst. and Liq. Cryst., 2001, Vol. 356, pp. 263-272
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Building Supramolecular Tapes

ELAINE BATCHELOR, JACEK KLINOWSKI and WILLIAM JONES

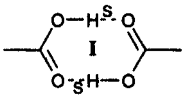
University of Cambridge, Department of Chemistry, Lensfield Road, CB2 1EW

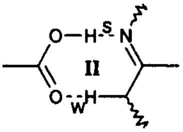
The crystal structures of six complexes containing phenazine and a dicarboxylic acid are discussed. In each structure extended tapes are formed. The packing of these tapes is discussed with respect to the influence of the aromatic rings.

Keywords: couplings; synthons; crystal engineering; pi-pi stacking

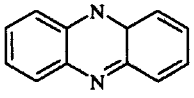
INTRODUCTION

The physical and chemical properties of molecular crystals are not only dependent on the component molecular species but also on the way in which these molecules are arranged relative to one another within the solid.[1] A key strategy to emerge within crystal engineering has been the identification and utilisation of "couplings/synthons" to direct the self-assembly of molecules into predesigned motifs.[2, 3] In particular, couplings based on traditional hydrogen bonds have been successfully used to engineer supramolecular motifs. More recently, couplings involving weaker interactions have been identified and utilised. While most crystal engineering research has focussed on couplings in which the component interactions were of comparable strength (e.g. **I** below), Pedireddi et al. showed that coupling **II** which consists of both a "strong" and a "weak" interaction could be used to direct the self-assembly of molecules.[2]

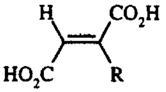




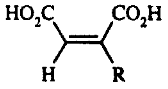
In order to test further the robustness of coupling **II** in the design of supramolecular motifs, phenazine (**Ph**) was co-crystallised with each of the dicarboxylic acids shown below:



Ph



R=H, FA
R=CH$_3$, MeA



R=H, MaA
R=CH$_3$, CA

HO$_2$C—(CH$_2$)n—CO$_2$H

n=2, SA
n=3, GA

RESULTS

Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation from solution. Details are given in Table 1.

Complex	Solvent	Sp.gr.	a/Å	b/Å	c/Å	α°	β°	γ°
Ph.FA	MeOH	$P2_1/c$	5.336	8.765	14.95	90	98.871	90
Ph.MeA	E.A.	C2/c	26.83	7.095	19.61	90	127.46	90
Ph.SA	E.A. + MeOH	$P2_1/n$	5.279	9.057	15.05	90	99.141	90
Ph.2MaA	E.A.	P-1	5.513	6.733	13.03	95.32	99.39	100.24
Ph.2CA	E.A.	$P2_1/n$	6.679	18.66	8.933	90	105.13	90
Ph.2GA	E.A.	P-1	5.676	9.997	10.89	116.6	95.12	90.04

TABLE 1. Space group and lattice parameters. (MeOH= methanol; E.A.= ethyl acetate)

<u>Description of tapes.</u>

Acids **FA**, **MeA** and **SA** each form 1:1 co-crystals with **Ph** in which molecules are assembled via coupling **II** to give supramolecular tapes, Figure 1. The left hand view is normal to the least squares plane through the tape; the right hand view is parallel to the plane and approximately along the tape axis. Tapes may be described as near-linear and are relatively flat (within 10°).

Acids **MaA**, **CA** and **GA** each form 1:2 co-crystals with **Ph**. Once again supramolecular tapes are observed, Figure 2. In each structure, acid molecules are coupled via centrosymmetric coupling **I**

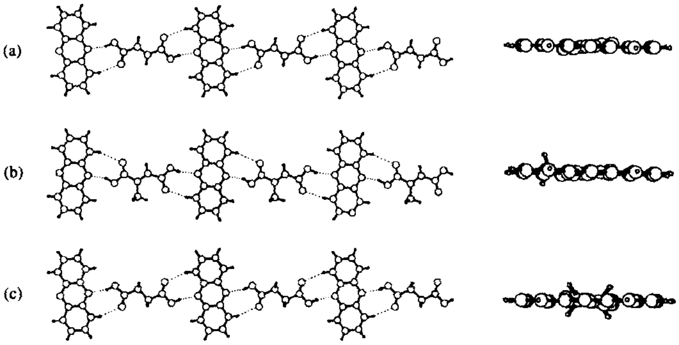


FIGURE 1 1:1 molecular tapes (LHS view normal to tape, RHS view along tape), (a) **Ph.FA**, (b) **Ph.MeA** and (c) **Ph.SA**.

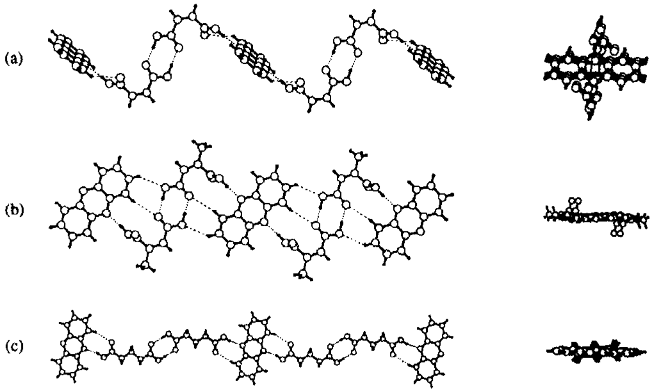


FIGURE 2 1:2 molecular tapes (LHS view normal to tape, RHS view along tape) (a) **Ph.2MaA** (b) **Ph.2CA** and (c) **Ph.2GA**.

giving rise to dimers which in turn interact with base molecules to produce the overall tape topography. Coupling **II** is observed in complexes **Ph.2MaA** and **Ph.2GA.** In complex **Ph.2CA**, acid and base molecules are coupled solely by the O—H···N hydrogen bond, coupling **II** not being present. The overall tape topography for **Ph.2CA** and **Ph.2GA** is approximately flat, with the exception of one carbonyl oxygen in **Ph.2CA**. The molecules in tapes of **Ph.2MaA** are not co-planar, the angle between coupling **I** and molecules of **Ph** being approximately perpendicular.

Packing of Tapes

1:1 tapes.

Each of the 1:1 tapes pack by forming stacks in which the long axes and planes of the tapes are parallel, Figure 3(a). In complexes **Ph.FA** and **Ph.SA**, tapes within a stack are related by translation along the a-axis. In **Ph.MeA**, tapes are related by inversion. Perpendicular (d_z) and lateral displacement (d_{xy}) parameters were calculated for the parallel stacked **Ph** molecules (see Table 2). No C—H···O contacts are observed between tapes within a stack.

Tapes in adjacent stacks are aligned with their long axes twisted by some angle, θ, as shown in Figure 3(b). This angle is ca. 80° for complexes **Ph.FA** and **Ph.SA** and ca. 30° for **Ph.MeA**. In each of the structures, a number of C—H···O interactions are observed between stacks. Unlike in the twisted tape structures described by Schwiebert et al.,[4] no C—H···C(aromatic) contacts less than the sum of the van der Waal's radii are present.

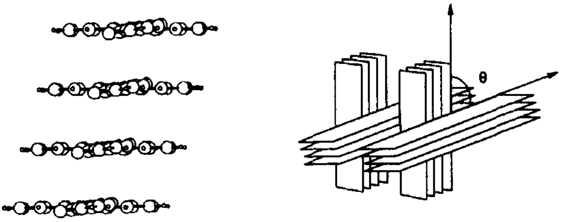


FIGURE 3. (a) Stacking of **Ph.FA** tapes (b) three-dimensional packing of 1:1 tapes

Co-crystal	d_{xyz}	d_z	d_{xy}
Ph.FA	5.336	3.246	4.236
Ph.MeA	4.996	3.241	3.802
Ph.MeA	3.780	3.417	1.617
Ph.SA	5.279	3.217	4.185
Ph.2MaA	5.513	3.051	4.592
Ph.2CA	6.679	3.743	5.531
Ph.2GA	5.675	3.255	4.649
PHENAZ02	5.050	3.483	3.656
PHENAZ04	5.072	3.493	3.677

TABLE 2. Displacement parameters of stacked **Ph** molecules. (d_z, d_{xy} see text; d_{xyz} corresponds to the atom-atom distance). **PHENAZ02** and **PHENAZ04** are the refcodes of the crystal structures of pure **Ph** as obtained from the Cambridge Structural Database.

1:2 tapes.

The overall three-dimensional arrangement of the 1:2 tapes differ. Tapes of **Ph.2MaA** (the only complex in which the tapes are significantly distorted from planarity) form stacks via translation along the a-axis as shown in Figure 4. The interplanar separation and lateral offset between stacked **Ph** molecules was calculated (Table 2). A C—H···O interaction occurs between the carbonyl oxygen of coupling **I** and an olefinic hydrogen on an adjacent molecule within the same stack.

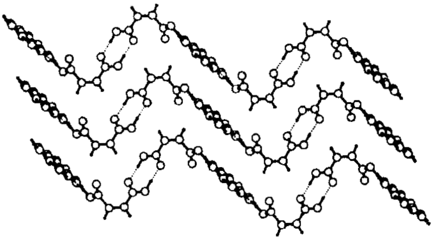


FIGURE 4. Stacking of **Ph.2MaA** tapes.

Figure 5 shows the packing diagram for **Ph.2CA**. Tapes stack via translation along the a-axis. A C—H···O interaction is observed between molecules within a stack. Displacement parameters for the stacked **Ph** molecules are given in Table 2. When viewed along the tape length, the stacks are arranged in a herringbone manner. No C—H···O or edge-to-face aromatic-aromatic interactions are observed between stacks.

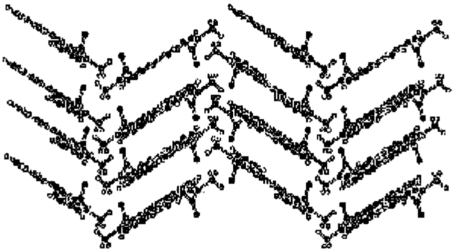


FIGURE 5. Packing diagram for **Ph.2CA**.

Ph.2GA tapes pack to give a planar sheet structure (Figure 6). C—H···O interactions are observed between adjacent tapes within the sheet. Sheets stack via translation along the a-axis with a C—H···O interaction taking place between an aliphatic hydrogen of one sheet and a carbonyl oxygen in an adjacent sheet. The interplanar separation and lateral offset of nearest neighbour **Ph** molecules in adjacent sheets were calculated (see Table 2).

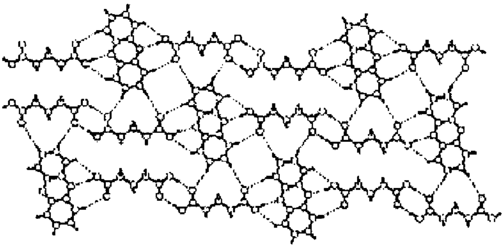


FIGURE 6. Two-dimensional sheet structure of **Ph.2GA**.

DISCUSSION

Coupling **II** was successfully used to design new supramolecular tapes, being present in five of the six complexes. Its robustness is limited by the weakness of the C—H···O interaction which may undergo distortion or be completely lost.

Table 2 gives the interplanar separation and lateral offset of stacked **Ph** molecules in each of the six complexes and in the two polymorphs of **Ph**. The structures of pure **Ph** are dominated by pi···pi stacking interactions.[5] Upon co-crystallisation, it can be seen that the interplanar separation decreases (except for **Ph.2CA**) and the lateral offset increases (except for **Ph.MeA**). The offsets for **Ph.FA** and **Ph.SA** are similar, although it is interesting that the values are slightly smaller in **Ph.SA** despite aliphatic hydrogens protruding above and below the tape backbone. In both complexes, **Ph** molecules are overlaid by carboxyl groups from adjacent tapes. **Ph.MeA** tapes stack in pairs as indicated by the two sets of parameters. The interdigitisation of tapes in adjacent stacks may influence the stacking observed for the 1:1 complexes.

Within each of the 1:1 complexes, C—H···O contacts do not occur between tapes within a stack. In the 1:2 complexes, however, C—H···O contacts are observed within a stack. The lateral offsets for the 1:2 co-crystals are significantly longer than the 1:1 complexes. It is possible that the irregular shape of **Ph.2MaA** tapes and the presence of the bulky methyl groups in **Ph.2CA** are significant in the offsets observed for these two complexes. In Figure 5, it can be seen that methyl groups in adjacent stacks are interdigitised. The displacement of stacked tapes in **Ph.2GA** is of interest, since the flat nature of the sheets and the lack of bulky substituents means that packing effects are likely to be less significant in this co-crystal. The interplanar separation is similar to the values observed for the 1:1 complexes, although the lateral offset is significantly longer. Unlike the 1:1 complexes, an inter-sheet C—H···O interaction is observed.

Acknowledgements

We gratefully acknowledge financial support from the EPSRC and help from Dr. Neil Feeder in the X-ray diffraction work.

References

[1] W. Jones, *Organic Molecular Solids: Properties and Applications*, Boca Raton: CRC Press, Inc., (1997).
[2] V. R. Pedireddi, W. Jones, A. P. Chorlton, and R. Docherty, *J. Chem. Soc. Chem. Commun.*, (1996).
[3] G. R. Desiraju, *Angew. Chem. Int. Ed. Engl.*, **34** (1995).
[4] K. E. Schwiebert, D. N. Chin, J. C. Macdonald, and G. M. Whitesides, *J. Am. Chem. Soc.*, **118**, (1996).
[5] G. R. Desiraju and A. Gavezzotti, *Acta Crystallogr. Sect. B*, **B45**, (1989).