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Identification of a new supramolecular synthon in *o*-anisaldehydes: molecular self-assembly into tapes and staircases

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Abstract

We have shown through a rational design, synthesis and X-ray structural analyses of a set of aldehydes that *o*-methoxybenzaldehydes tend to associate in a centrosymmetric fashion, akin to the carboxylic acids, to give rise to a dimer motif **II**, which derives stabilization from four C–H···O hydrogen bonds in addition to a dipole–dipole interaction. That the synthon **II** is credible to be structure determining is revealed from the crystal structures of aldehydes **1–4** that are devoid of any other competing weak interactions. The aldehydes **1–4** are found to undergo self-assembly into 1-dimensional molecular tapes and staircases. We have shown that the steric factors as in aldehyde **5** and the presence of a functional group such as Br in **6** perturb the expected crystal packing based on synthon **II**.

Keywords: X-ray crystallography; Supramolecular synthon; Molecular tapes and staircases; *o*-Methoxybenzaldehydes; Weak hydrogen bonds

1. Introduction

The control of molecular organization based on specific molecular attributes is a challenge in crystal engineering [1]. Strong and directional properties associated with O/N–H···O/N hydrogen bonds [2] have been reliably exploited in the construction of pre-designed supramolecular architectures [1]. An advantageous approach to the crystal structure prediction and engineering relies on the identification and exploitation of certain patterns of association (i.e. supramolecular synthons [3]) that are robust and recur decisively in the crystal packing. In this direction, a variety of supramolecular synthons based on O/N–H···O/N hydrogen bonds have been identified [3,4]. Although the importance of weak but directional C–H···O/N hydrogen bonds has been amply exemplified [5], the quest for identification of new and novel synthons continues unabated, as it constitutes one of the fundamental objectives of crystal engineering.

The aldehydes represent an important class of functional group of organic compounds. Despite their widespread utility in fragrances and pharmaceuticals as excellent intermediates, the supramolecular interactions associated with the formyl group have been explored only little, if any [6]. Based on a CSD database search analysis, Koppenhoefer showed that the formyl oxygen orients itself away from the *o*-halogen in *o*-haloaromatic aldehydes [7]. In the course of our recent studies on the solid-state photochemistry of aldehydes based on this conformational preference [8a], we uncovered a unique halogen bond-mediated

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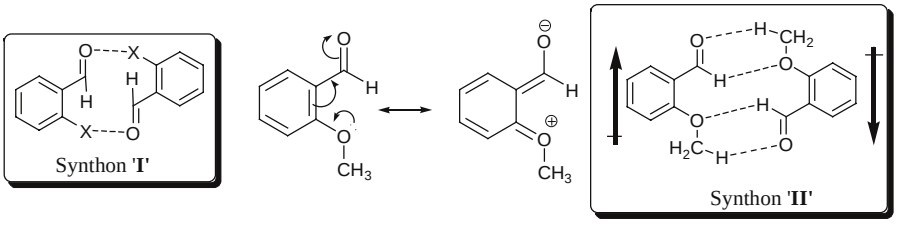
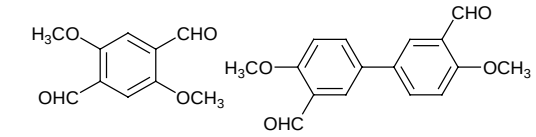
supramolecular dimeric synthon **I** [8b].

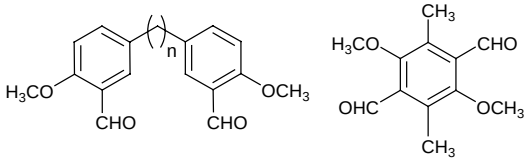


In analogy to *o*-haloaromatic aldehydes, we anticipated a similar conformational preference in the case of *o*-anisaldehydes as well. Indeed, the crystal structure database (CSD) search revealed the conformational preference for formyl oxygen to orient away from the methoxy oxygen [9]. Presumably, the reason for such a preferential orientation is due to subtle interplay of the following factors: (i) minimization of repulsive interaction between the formyl and methoxy oxygen atoms, (ii) intramolecular hydrogen bond between the formyl hydrogen and the methoxy oxygen atoms, and (iii) avoidance of steric hindrance.

Given that the contributing resonance structures lend a strong dipole to such molecular systems and that the *Achiral* polar molecules generally (although not necessarily) tend to pack in a centrosymmetric manner in the solid state, the synthon **II** was readily conceived between centrosymmetrically related molecules to stabilize the crystal packing of *o*-anisaldehydes. In this arrangement, the crystal lattice would energetically benefit from four weak but directional C–H···O hydrogen bonds, in addition to a dipole–dipole interaction arising from the pair of aldehydes. Thus, the combination of a dipole–dipole interaction (worth ca. 5–50 KJ/mol [10]) and the four C–H···O hydrogen bonds, which may contribute as much, may cause the centrosymmetric dimer motif to be decisive in the crystal packing. This premise would be verified if an ensemble of *o*-methoxybenzaldehyde structures reveals the anticipated dimer synthon. Indeed, CSD analysis showed that the synthon **II** is observed in at least one of the crystal structures that contain *o*-methoxybenzaldehyde moiety (code: GOYZAV [9]). However, the absence of synthon **II** in five other molecules containing *o*-methoxy formyl moiety was contrary to our expectation. A careful packing analysis to trace the reasons for the observations against our expectations revealed the strong influence of other functional groups that potentially control the crystal packing. Consequently, we envisaged that *o*-methoxybenzaldehyde derivatives that are *not* endowed with other functional groups would exhibit the dimer Synthon II in their crystal packing. Thus, we designed, synthesized and examined the X-ray crystal structures of aldehydes **1**–**4** that are entirely devoid of other competing interactions to test whether or not the synthon **II** is realizable.

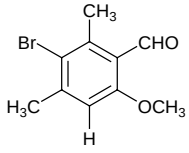


1 **2**



3: n = 1
4: n = 2

5



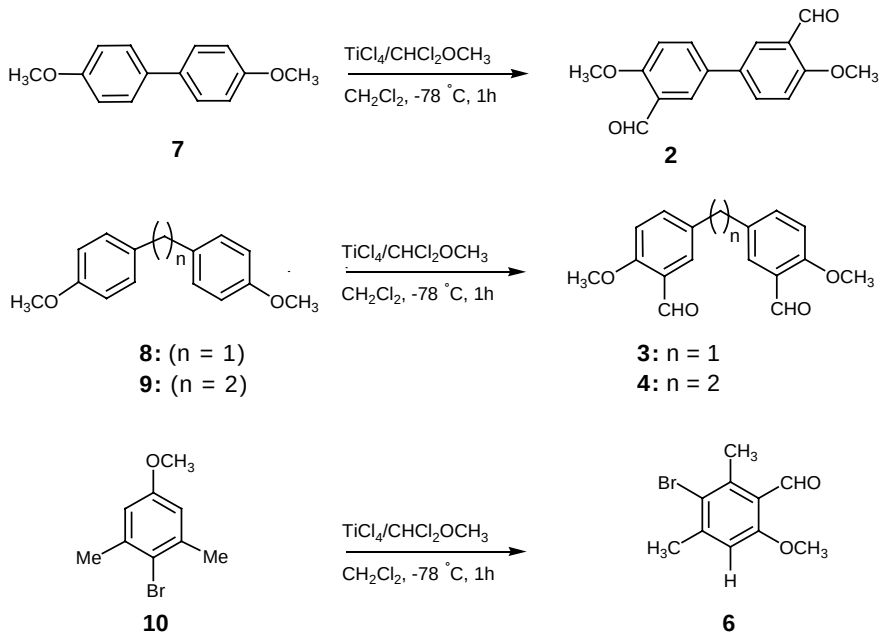
6

We also examined the crystal structures of analogous aldehydes **5** and **6** to probe the credibility of synthon **II** in mediating the crystal packing when steric factors and other interacting groups (such as Br atom) are present. Herein, we report the results of our structural studies.

2. Experimental

2.1. Synthesis of aldehydes

All investigations were carried out using analytical grade chemicals from Lancaster (UK) and S.D. Fine Chemicals (India). Anisaldehydes **1** and **5** were prepared by following the reported procedures [12]. The dimethoxy precursors of aldehydes **2**–**4** and **6**, viz. **7**–**9** and **10**, were prepared according to the literature-reported procedures (Scheme 1) [13]. These dimethoxy-derivatives were subjected to bis-formylation using $TiCl_4/Cl_2CHOCH_3$ in CH_2Cl_2 at −78 °C to obtain the aldehydes **2**–**4** and **6**.



Scheme 1.

Below is described the typical procedure for bis-formylation to obtain the dianisaldehyde **2**. The same procedure was followed for **3** and **4** as well. A similar procedure was employed for the preparation of aldehyde **5**.

*2.1.1. 4,4′-Dimethoxy-3,3′-biphenyldicarboxaldehyde **2***

A 3 mL solution of **7** (0.12 g, 0.714 mmol) in dichloromethane taken in a two-necked round bottom flask under a N_2 gas atmosphere was cooled to −30 °C. Subsequently, $TiCl_4$ (0.37 mL, 3.85 mmol) was added. After stirring for 10 min, the reaction mixture was further cooled to −80 °C over a period of 1 h. At this stage, dichloromethyl methyl ether (0.32 mL, 3.57 mmol) was slowly introduced. The resultant dark-grey solution turned into pink color. The reaction mixture was allowed to attain the room temperature over a period of 1 h and quenched with 10% HCl. The product was extracted with dichloromethane, dried over Na_2SO_4 and concentrated. Filtration of the organic residue over a short-pad silica gel afforded the pure dialdehyde **2** in 81% yield (0.13 g), mp 180 °C; IR (KBr) cm^{-1} 1057, 1255, 1679, 2853, 2922; ^1H NMR (400 MHz) δ 3.97 (s, 6H), 7.07 (d, 2H, $J=8.56$ Hz), 7.80 (dd, 2H, $J_1=8.56$ Hz, $J_2=2.68$ Hz), 8.04 (d, 2H, $J=2.4$ Hz), 10.51 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 112.3, 124.9, 126.3, 132.2, 133.9, 161.3, 189.7.

*2.1.2. Bis(3-formyl-p-anisyl)methane **3***

Yield 81%; mp. 224 °C; IR (KBr) cm^{-1} 1027, 1264, 1682, 2847, 2946; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.90 (s, 6 H), 6.91 (d, 2H, $J=8.0$ Hz), 6.92 (s, 2H), 7.35 (d, 2H, $J=7.08$), 7.63 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 34.9, 55.7, 110.6, 124.7, 128.3, 131.2,136.3, 160.5, 188.9.

*2.1.3. 1,2-Bis(3-formyl-p-anisyl)ethane **4***

Yield 95%; mp 232 °C; IR (KBr) cm^{-1} 1026, 1286, 1676, 2852, 2937; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.85 (s, 4H), 3.90 (s, 6H), 6.89 (d, 2H, $J=8.56$ MHz), 7.28 (m, 2H), 7.62 (s, 2H), 10.44 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.6, 55.7, 111.7, 124.6, 128.1, 133.6, 136.1, 160.4, 189.9.

*2.1.4. 5-Bromo-4,6-dimethyl-o-anisaldehyde **6***

Yield 87%, mp 128–130 °C; IR (KBr) cm^{-1} 2920, 1681; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.47 (s, 3H), 2.69 (s, 3H), 3.88 (s, 3H), 6.77 (s, 1H), 10.51 (s, 1H), 10.51 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.3, 25.6, 55.9, 111.4, 121.3, 122.9, 140.9, 145.4, 161.5, 191.6.

2.2. X-ray crystallography

The compounds were crystallized from appropriate solvents as mentioned in Table 1 by a slow evaporation method over a period of 2–3 days. The X-ray diffraction data for all of the aldehydes **1**–**6** were collected on a Siemens P4 single crystal diffractometer equipped with molybdenum sealed tube ($\lambda=0.71073$ Å) and highly oriented graphite monochromator. A detailed description of the structure solution and refinement are given below for compound **1** as a representative case. The structure determinations of **2**–**6** were performed in similar manner and the details are recorded in Table 1.

Good single crystals of **1** were grown by slow evaporation of the solution of **1** in dichloromethane: ethanol mixture (1.7:1, v/v). A single crystal with dimension $0.30\times0.29\times0.19$ mm^3 was mounted along the largest dimension and used for data collection. The lattice parameters and standard deviations were obtained

Table 1
Crystallographic data for compounds **1–6**

Properties	**1**	**2**	**3**	**4**	**5**	**6**
Chemical formula	$C_{10}H_{10}O_4$	$C_{16}H_{14}O_4$	$C_{17}H_{16}O_4$	$C_{18}H_{18}O_4$	$C_{12}H_{12}O_4$	$C_{10}H_{11}BrO_2$
Formula weight	194.18	270.28	284.30	253.05	222	243.10
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2/n$	$P2_1/n$	$P2_1/n$	$C2/c$
a (Å)	7.289(1)	4.793(1)	17.700(2)	4.801(1)	10.498(1)	14.561(3)
b (Å)	8.063(1)	15.513(2)	4.796(1)	11.031(1)	4.201(1)	10.040(2)
c (Å)	8.520(2)	8.670(1)	18.034(2)	14.425(2)	12.540(1)	13.821(3)
α (°)	99.780(1)	90.0	90.0	90.0	90.0	90.0
β (°)	112.14(1)	94.54(1)	109.82(5)	98.33(1)	96.99(1)	105.74(2)
γ (°)	93.679(1)	90.0	90.0	90.0	90.0	90.0
V (Å)^3	452.55(1)	642.62(3)	1440.20(4)	755.89(2)	548.93(2)	1944.8(7)
Z	2	2	4	2	2	8
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
D_c (Mg m^{-3})	1.425	1.397	1.311	1.311	1.345	1.661
μ (mm^{-1})	0.098	0.100	0.093	0.092	0.101	4.190
F(000)	204	284	600	316	236	976
Reflections collected	1545	1107	2382	1345	897	1580
Unique reflections	1409	983	2263	1190	847	1517
Reflections with $I>2\sigma(I)$	1198	713	1725	1013	680	1196
R_{int}	0.0152	0.0184	0.0163	0.0224	0.0152	0.0377
Final $R_1[I>2\sigma(I)]$	0.0376	0.0851	0.0527	0.0337	0.0525	0.0408
Final wR_2	0.1040	0.1101	0.0681	0.0421	0.1443	0.0569
Solvent of crystallization	CH_2Cl_2/CH_3OH	CH_2Cl_2/hexanes	EtOAc/hexanes	CH_2Cl_2	CH_2Cl_2/hexanes	CH_2Cl_2/hexanes

by least squares fit to 40 reflections ($10.36° < 2\theta < 34.87°$). The data were collected by $2\theta-\theta$ scan mode with a variable scan speed ranging from 2.0° to a maximum of 60.0° min^{-1}. Three reflections were used to monitor the stability and orientation of the crystal and were re-measured after every 97 reflections. Their intensities did not change significantly during 17.85 h X-ray exposure time. The data were corrected for Lorentz and polarization factors. All other relevant information about the data collection is presented in Table 1. The structure was solved by Direct Methods using SHELX-97 package and also refined using the same one [11]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the ideal positions with fixed isotropic U values and were riding. Methyl hydrogen atom coordinates were generated with the SHELXL AFIX 137 command and that they were correctly positioned was verified from difference Fourier maps. A weighting scheme of the form $w=1/[\sigma^2(Fo^2)+(aP)^2+bP]$ with $a=0.0575$ and $b=0.10$ was used. The refinement converged to a final R value of 0.0376 (wR_2 0.1040 for 1198 reflections, $[I>2\sigma(I)]$. The final difference map was featureless. All other information regarding the refinement is also recorded in Table 1.

3. Results and discussion

For X-ray crystallographic analyses, the crystals of all of the aldehydes were grown by a slow evaporation method (Table 1). The details of crystal structure determination

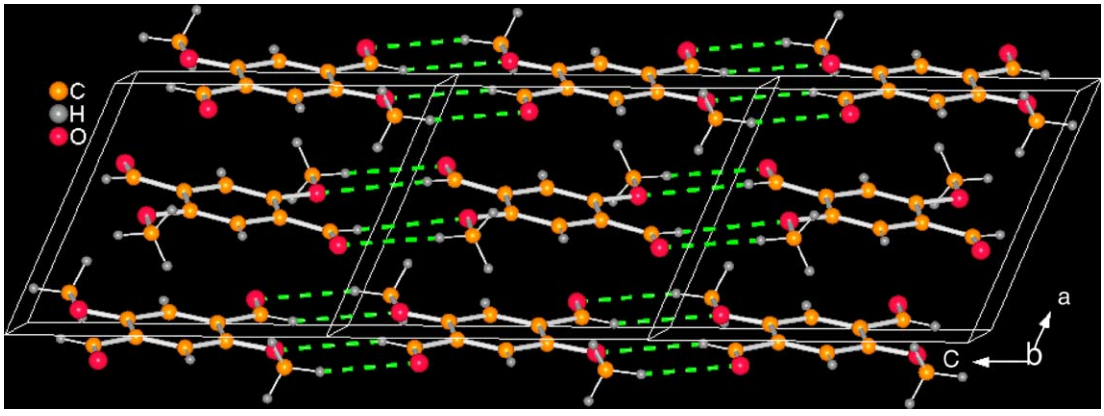


Fig. 1. The crystal packing of aldehyde **1**. Notice that the tapes are constructed by synthon **II**.

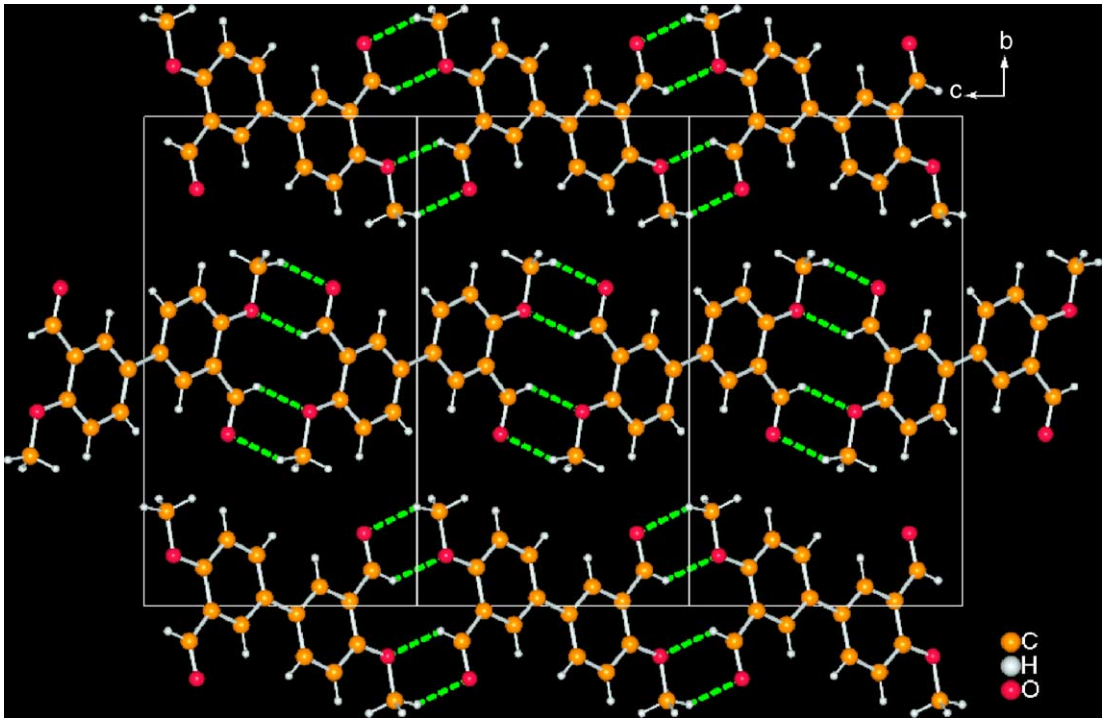


Fig. 2. The crystal packing of biphenyl-dialdehyde **2**. The two phenyl rings are coplanar and the synthon **II** mediates the formation of tapes.

and refinement are given in Table 1. The crystal packing diagrams of all of the aldehydes **1–6** are shown in Figs. 1–6, respectively. A feature that is common to all of the aldehydes **1–6** is that the formyl group orients itself away from the *o*-methoxy group. As mentioned at the outset, this preference may also be due to a subtle interplay of various factors. Be this as it may, the six new structures, in addition to those already reported in the literature [9], clearly demonstrate the fact that the conformation in which the formyl and methoxy oxygen atoms are far apart is the preferred one in *o*-anisaldehydes.

As can be seen, the aldehydes **1–4** exploit the synthon/dimeric motif **II** effectively in the crystal packing. The terephthalaldehyde **1** and the biphenyl derivative **2** yield tapes, which are sustained by the motif **II**. These tapes are stacked in the *bc* plane in **1** (Fig. 1), and a similar stacking with ca. 45° inclination to the *ac* plane is observed in **2** (Fig. 2). This way of building-up the lattice from linear tapes derives the stabilization from attractive $\pi\cdots\pi$ inter-stack interactions (nearest mean aromatic ring separation in **1** and **2** are 3.39 and 3.38 Å, respectively). Due to the intervening methylene/s in **3** and **4**, the molecules assume a twist, which results in an interesting alteration in the molecular packing. Both of the structures preserve the synthon **II**, and propagate in a zigzag manner to make up a supramolecular staircase [14]. There are two additional

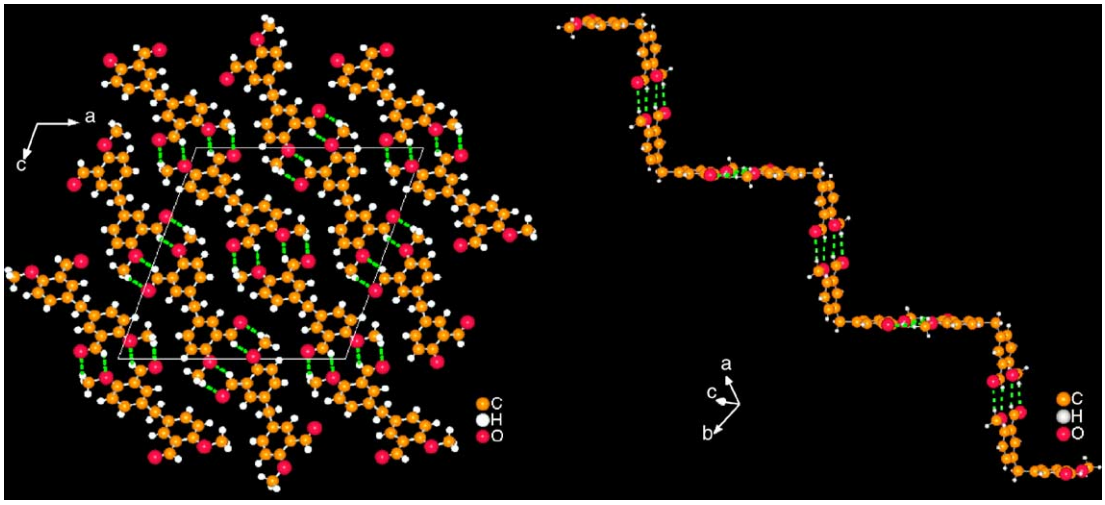


Fig. 3. The crystal packing of diarylmethane **3**. Notice that the tetrahedral angle between the two aryl rings leads to staircase structures mediated by synthon **II**.

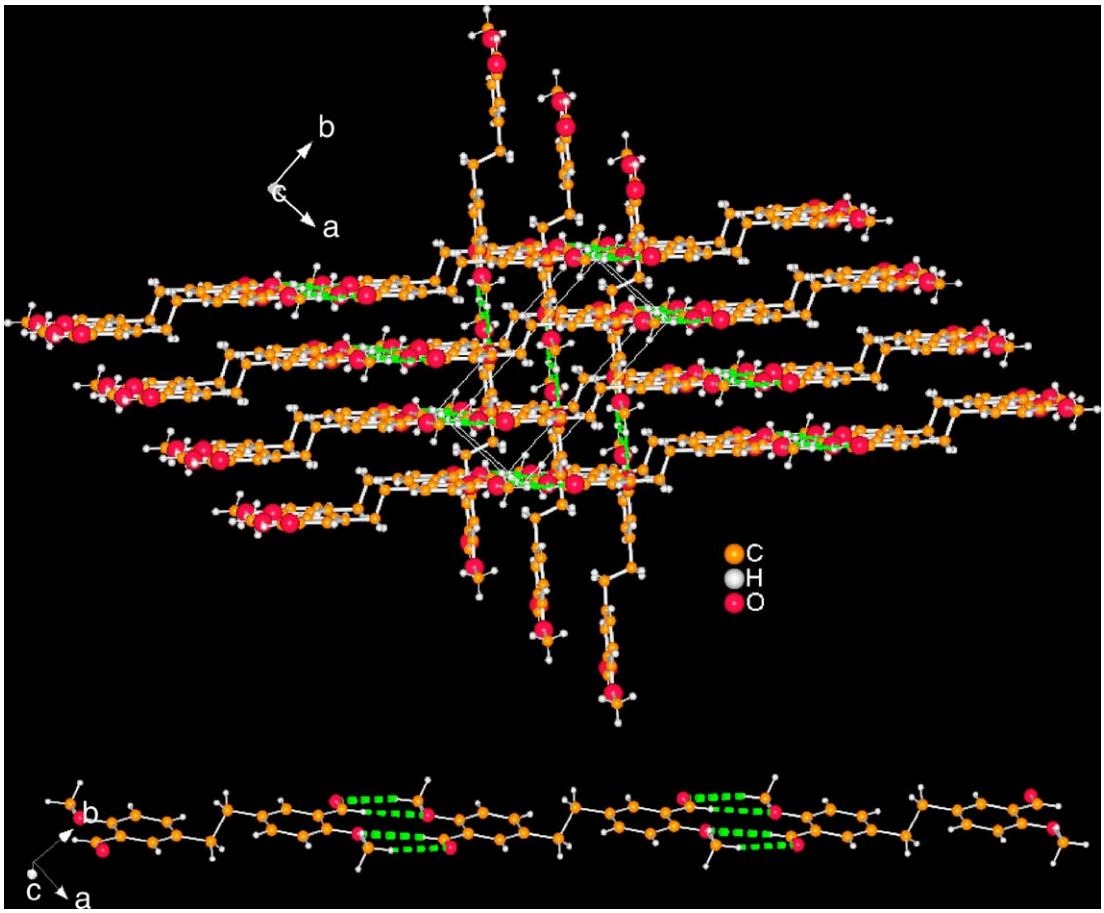


Fig. 4. The crystal packing diagram of diarylethane **4**. The 'steps' are much longer than the 'heights'.

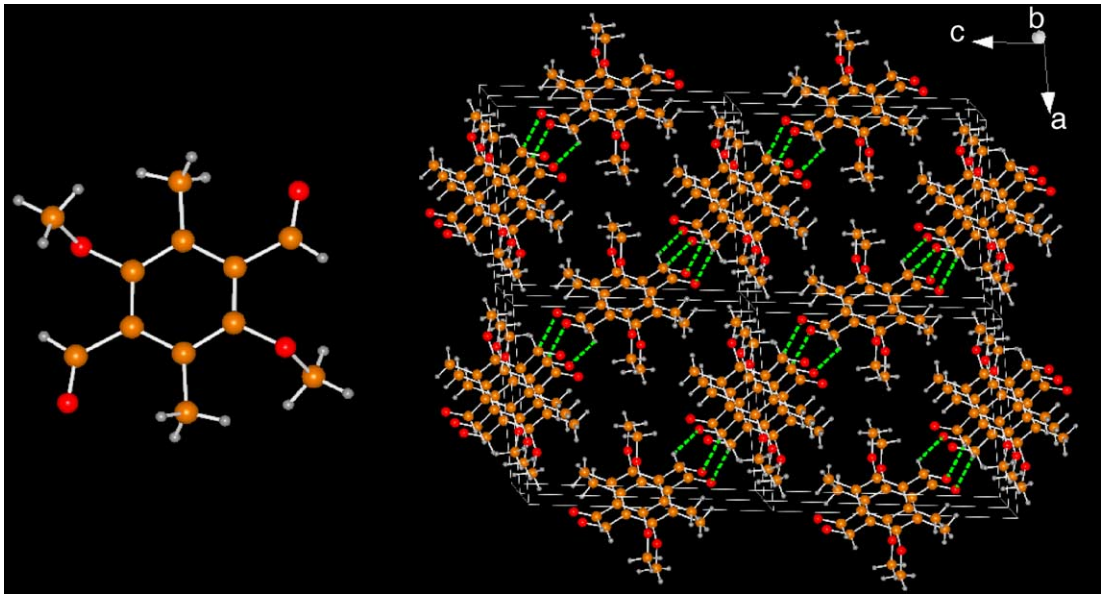


Fig. 5. The molecular structure and crystal packing of dialdehyde **5**. Notice that formyl groups assemble in a helical manner via C–H···O hydrogen bonds involving the formyl groups.

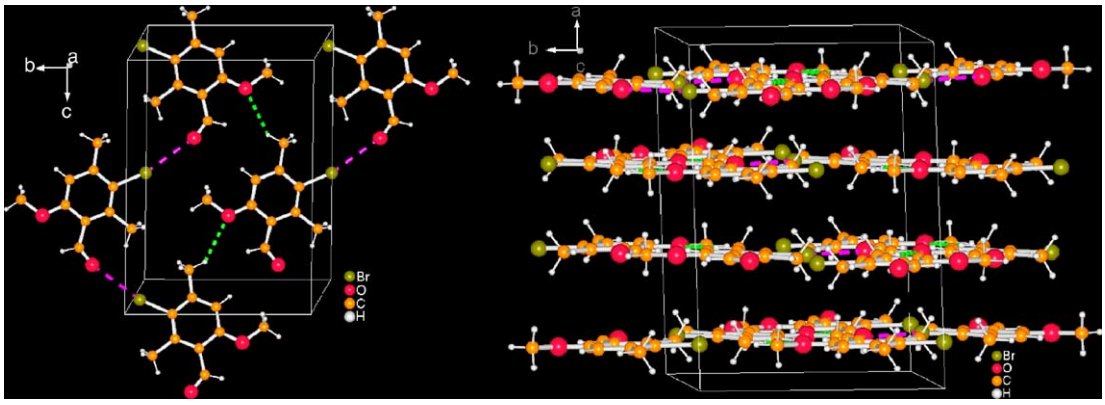


Fig. 6. The crystal packing of aldehyde **6**. Notice that the halogen bonds involving C–Br···O=C mediates the crystal packing into 2-dimensional sheets.

points of interest here. As there is only one $-CH_2$ group that intervenes between the two *o*-anisaldehydes in **3**, the aromatic rings adopt a near orthogonal orientation with respect to each other (angle between the least squares planes of the two rings is 90.7°). When such units assemble through synthon **II** to make up staircase, the 'step' and the 'height' of the staircase are exactly equal; as the methylene group is placed at the meeting points of step and height (see Fig. 3). In **4** however, the two aromatic moieties are placed far apart due to the ethylene group, and are exactly parallel to each other (angle between the least squares planes of the two rings is 0.1°). When these molecules undergo self-assembly, the 'height' is generated from the ethylene part, while the step is generated from the synthon part; expectedly, the height is shorter and the 'step' is longer (Fig. 4).

We shall now analyze the forces that are responsible for the construction of arrays of linear tapes (**1** and **2**) and zigzag staircases (**3** and **4**). Two sets of weak C–H···O hydrogen bonds about the inversion center operate to manifest in the synthon **II**, while an additional dipole–dipole interaction, as mentioned earlier, might also contribute to the stabilization. While the extent of dipolar character due to the resonance structures of *o*-anisaldehydes cannot be easily gauzed, it is certain that a definite dipolar nature of the molecule aids in the centrosymmetric arrangement of the molecules. As two dissimilar C–H···O hydrogen bonds contribute to the synthon **II**, an analysis of their nature and strength is pertinent. In Table 2 are provided the geometrical parameters for C–H···O hydrogen bonds.

A perusal of these parameters shows that the hydrogen bonding interactions between methoxy methyl hydrogen and the carbonyl oxygen are stronger, while those involving the formyl hydrogen and the methoxy oxygen are weaker. This is presumably due to the weaker propensity of the formyl hydrogen atoms to involve in hydrogen bonding. Nonetheless, the reliability of the synthon **II** in decisively controlling the molecular packing in a predetermined manner is amply evident.

The crystal packing based on motifs constituted by weaker intermolecular interactions, unlike the strong O/N–H···O/N hydrogen bonds, are not robust to structural changes. The fact that the synthon **II** does not reproduce itself faithfully is reflected from the crystal structures of **5** and **6**. In aldehyde **5**, the introduction of two methyl groups causes a conformational change about the methoxy group. The molecule sits on the inversion center and the methoxy methyl groups are almost orthogonal to the molecular plane (C1–C2–O2–C5 = 92.8°). However, the molecule does not lose one of its characteristic structural features, i.e. the orientation of the formyl oxygen being away from the methoxy oxygen as observed in all of the aldehydes **1**–**4**. The crystal packing is dominated by O–H···O hydrogen bonds (Fig. 5) involving the formyl oxygen and the formyl hydrogen atoms related by 2_1-screw relationship (symmetry: $1.5-x$, $-0.5+y$, $0.5-z$); the geometrical parameters for this hydrogen bond are: $d_{C-H\cdots O} = 2.61$ Å, $D_{C\cdots O} = 3.29$ Å and $\theta_{C-H\cdots O} = 130.3°$. In a similar manner, the bromo group is also found to preclude the existence of synthon **II** in aldehyde **6**. Indeed, the C–Br···O=C interaction ($d_{C-Br\cdots O} = 3.21$ Å and $\theta_{C-Br\cdots O} = 163.4°$) now controls the crystal packing in aldehyde **6** in spite of the fact that *o*-methoxy formyl moiety is entirely planar with the formyl oxygen oriented away from the methoxy oxygen (Fig. 6). The halogen bond together with one C–H···O hydrogen bond involving the methoxy oxygen and one of the methyl hydrogen atoms ($d_{C-H\cdots O} = 2.81$ Å, $d_{C\cdots O} = 3.62$ Å

Table 2
Geometrical parameters for C–H···O hydrogen bonds of the dimeric motif **II** in aldehydes **1**–**4**

Aldehyde	O–CH_2–H···O=C		O=C–H···OCH_3	
	d (Å)	*θ* (°)	*d* (Å)	*θ* (°)
1[a]	2.63 (2.71)	163.1 (146.7)	2.84 (2.96)	152.1 (133.3)
2	2.59	152.9	2.79	141.9
3[a]	2.56 (2.69)	158.2 (152.4)	2.79 (2.93)	145.6 (139.8)
4	2.72	154.8	2.95	142.0

[a] The values in parentheses refer to second independent molecule in the unit cell.

and $\theta_{C-H\cdots O} = 143.2°$) bring about the molecular ordering in a 2-dimensional sheet form. Thus, it is evident that the formation of synthon **II** based on the dimeric motif is feasible only in the absence of other competitive interactions arising out of strongly interacting functional groups.

4. Summary

In summary, we have shown through a rational design, synthesis and X-ray structural analyses of a set of aldehydes that *o*-methoxybenzaldehydes associate in a centrosymmetric fashion, akin to the carboxylic acids, to give rise to a dimer synthon **II**, which derives stabilization from four C–H···O hydrogen bonds in addition to a dipole–dipole interaction. That the synthon **II** is credible to be structure determining is revealed from the crystal structures of aldehydes **1**–**4**, which undergo self-assembly into 1-dimensional molecular tapes and staircases. We have shown that the steric factors as in aldehyde **5** and the presence of a functional group such Br as in **6** may perturb the expected crystal packing based on synthon **II**. While a variety of ring motifs based on strong O/N–H···O/N interactions have been identified in the realm of supramolecular chemistry for application in crystal engineering [2a,c], the synthons based on weaker interactions are only scant [4]. We believe that this knowledge is important in crystal engineering in spite of the lack of robustness associated with such motifs, for it is weaker interactions that, at times, dictate altogether distinct modes of molecular association even when strong O–H···O hydrogen bonds are involved in the overall crystal packing [15].

5. Supplementary data

Crystallographic data for the structural analysis of **1**–**6** have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK, and are available free of charge from the Director on request quoting the deposition number CCDC 240156-60 and CCDC 225295 (Fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk).

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