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A small library of C–H···O hydrogen bonds based on supramolecular architectures of 1,5-diketone malonates in the solid state

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Hirshfeld surface analysis

Abstract Structural supramolecular architectures in the solid state of 1,5-diketone malonates **1a-g** are proposed to construct a small library of hydrogen bonds by C–H···O interactions by crystal structure analysis. A possible route of crystallization mechanism at different levels of hierarchy considers the next strategic steps: a) Intramolecular interactions provide a kite-like molecular conformation. b) Intermolecular interactions provide molecular recognition between the structural unit, synthon, and macrocycles. c) The supramolecular architectures obtained from the conjunction of the multiple functions performed by the C–H···O interactions. X-ray studies and Hirshfeld Surface Analysis are described.

1. Introduction

1,5-diketones are typical precursors in intramolecular aldol condensation (Nielsen et al., 1968) and pinacol coupling reactions. (Harrowven et al., 1998) Their synthesis can be achieved by the addition of activated methylene compound to α,β-unsaturated ketones, (March 1992) condensation of ketone enolates and the Mannich base derived from methyl ketones, (Rao et al., 2002) or with the reported methods: The ruthenium-catalyzed coupling between α,β -unsaturated ketones, alkynes and water, (Trost et al., 1997) the aryllithium addition to 3,4-dihydropyranones and TMSCl in THF, (Harrowven et al., 1998, 1999), or more specifically, the addition of difluoroenoxysilane to α,β -unsaturated ketones to produce 2,2-difluoro-1,5-diketones. (Lefebvre et al., 1998) In addition, other reported syntheses are the ferrocenyl substituted 1,5-diketone synthesis under ultrasound irradiation, (Ji et al., 2004) a tandem cross-coupling reaction of ketones with aldehydes promoted by barium hydride or barium alkoxides, (Takahashi et al., 2006) the asymmetric direct Michael addition of α,β-unsaturated aldehydes with acetophenone catalyzed by a Jørgensen-Hayashi- catalyst in methanol, (Li et al., 2011) a catalyzed reaction by aqueous KOH between aryl methyl ketones and aldehydes and the subsequent dimerizations. (Liu et al., 2015).

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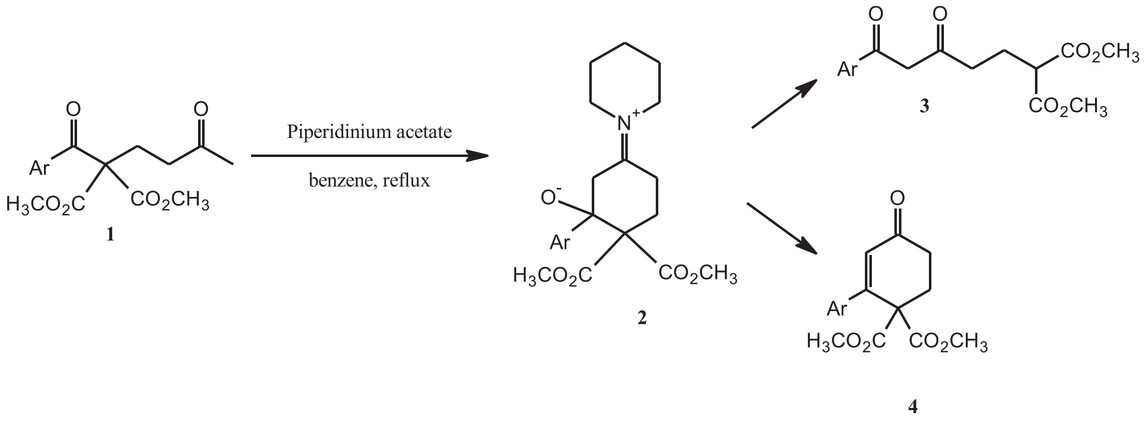


Fig. 1 The reaction of 1,5 diketone malonate **1** to 1,3-diketone rearrangement **3** versus aldol-dehydration products **4**.

Likewise, regarding structural studies, the 1,5-diketone moiety is present in benzamarone (1,2,3,4,5-pentaphenylpentan-1,5-dione), which presents two and three stereocenters in their structure evidenced by X-ray and NMR spectroscopy. (Mufato et al., 2011) In this context, we reported that 1,5-diketone malonate **1** performed a rearrangement to 1,3-diketone **3** via an aldol intermediate **2**. (Jiménez-Cruz et al., 1998, 2000). In these cases, the aldol-dehydration product **4** is undetected, Fig. 1. The presence of the 2,2-bis-methoxycarbonyl adjacent to the aroyl moiety is the key to the C–C bond cleavage in compound **2**.

It should be noted that 1,5-diketones with one methoxycarbonyl and even with two electron-withdrawing fluorine atoms produced the expected cyclohexenone. (Walker, 1955, Hernández-Ortega, 2001).

On the other hand, the study of spatial arrangements of intermolecular and intramolecular interactions marks a milestone in crystal engineering to recognize 1D, 2D and 3D spatial configurations in crystalline molecular structures. Supramolecular synthons in crystals are structural units formed with intermolecular interactions to analyze the complex interplay between close packing, hydrogen bonding and other interactions in crystal structures. (Desiraju, 2013) A significant role of C–H···O hydrogen bonds are associated with intramolecular and intermolecular interactions constituting supramolecular synthons and supramolecular architectures. (Dunitz et al., 2005) In particular, C–H···O interactions are of interest in molecular recognition (Sutor, 1962, 1963, Taylor et al., 1982, Desiraju, 1996) and crystal engineering. (Desiraju, 1996).

This work describes supramolecular architectures in various crystals of 1,5-diketone malonates **1a-g**, Fig. 2.

Considering the adjacent quaternary carbon to the carbonyl in the of the titled 1,5-diketone malonates **1a-g** (Fig. 2) and the particular crystals architecture for the aryl, naphthyl and adamantyl moieties in the molecular structure, we are motivated to show a small library of hydrogen bonds exclusively by C–H···O interactions. From the results obtained on the crystalline structure of these compounds, a structural hierarchy is proposed that allows exploring and tracing a possible route of the elements that constituted their crystallization mechanism: a) Intramolecular interactions provide an unexpected kite-like molecular conformation through the complementary association between hydrogen bond interactions and electronic delocalization. b) Intermolecular interactions provide molecular recognition between the structural units, synthons, and macrocycles, through C–H···O hydrogen bond interactions, and c) The supramolecular architectures obtained from the conjunction of the C–H···O cooperative hydrogen bonds at different levels of hierarchy, supported by experimental and Hirshfeld surface analysis.

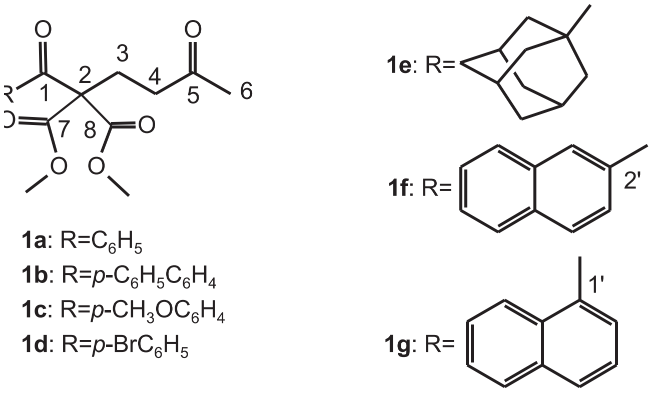


Fig. 2 1,5 diketone malonates **1 a-g** of this study.

2. Experimental

2.1. Preparation, isolation, and crystallization

1,5-diketone malonates **1a-g** were synthesized according to the procedure previously described. (Jiménez-Cruz et al., 1998, 2000) It consists of the C-aroylation of the dimethyl malonate anion (NaH in THF) with the corresponding aroyl chlorides to produce an aroylmalonate. Chemical reagents and solvents were provided by Sigma Aldrich and were used as received. Then, the Michael type addition of the aroylmalonates to methyl vinyl ketone using Triton B or Et_3N in THF affording the 1,5-diketones malonates. ^1H and ^{13}C NMR for the unreported 1,5 diketones **1e-g** are described here, which were recorded in a Varian Unity Spectrometer at 300 MHz for proton and 75.4 MHz for carbon. The ^1H NMR chemical shifts are expressed in ppm relatives to tetramethylsilane (TMS), and the ^{13}C NMR chemical shifts were referenced with the triplet of $CDCl_3$ ($\delta = 77$ ppm). NMR results and the corresponding spectra are shown in the supplementary section (Figures S1-S6). The characterization for **1a–d** was reported elsewhere. (Jiménez-Cruz et al., 1998, 2000) Crystals were grown from 2:1 ethanol–water solutions by slow evaporation for all 1,5-diketone malonates **1a-g**.

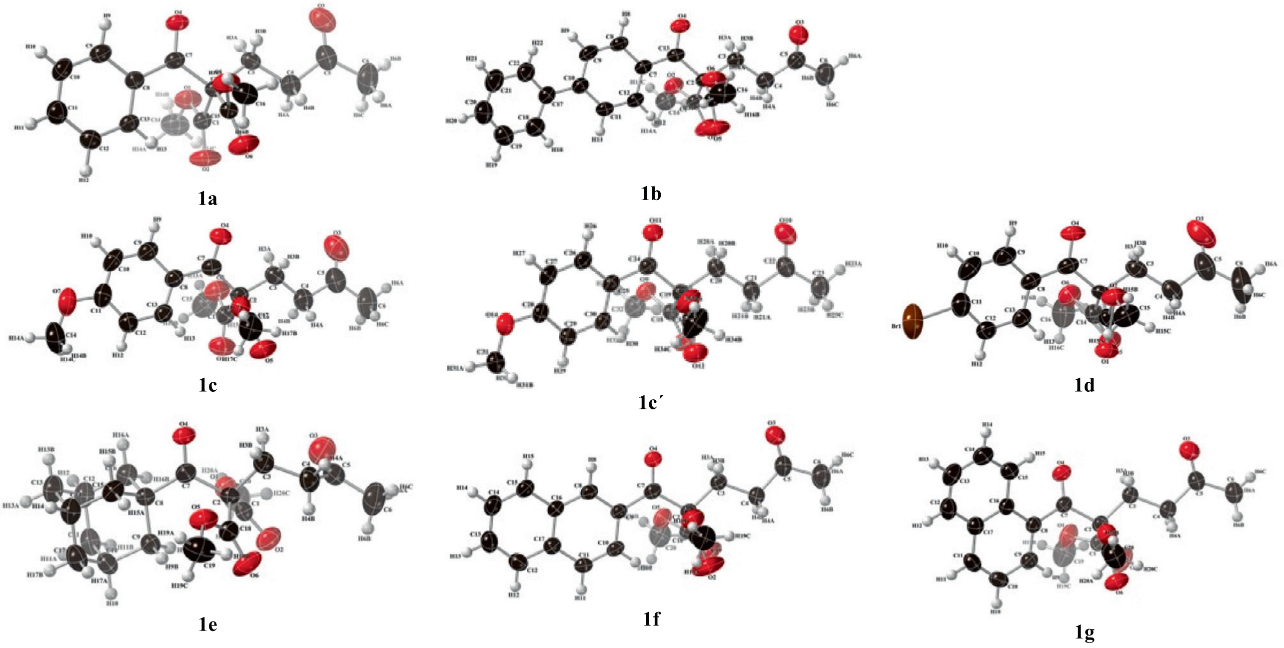
2.2. X-ray structural determination

The X-ray data for the single crystal of 1,5-diketone dimethyl malonates **1a** and **1c-g** were collected at 293 K using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on a

Table 1 Crystal and collection data for 1,5-diketone malonates **1a-g**.

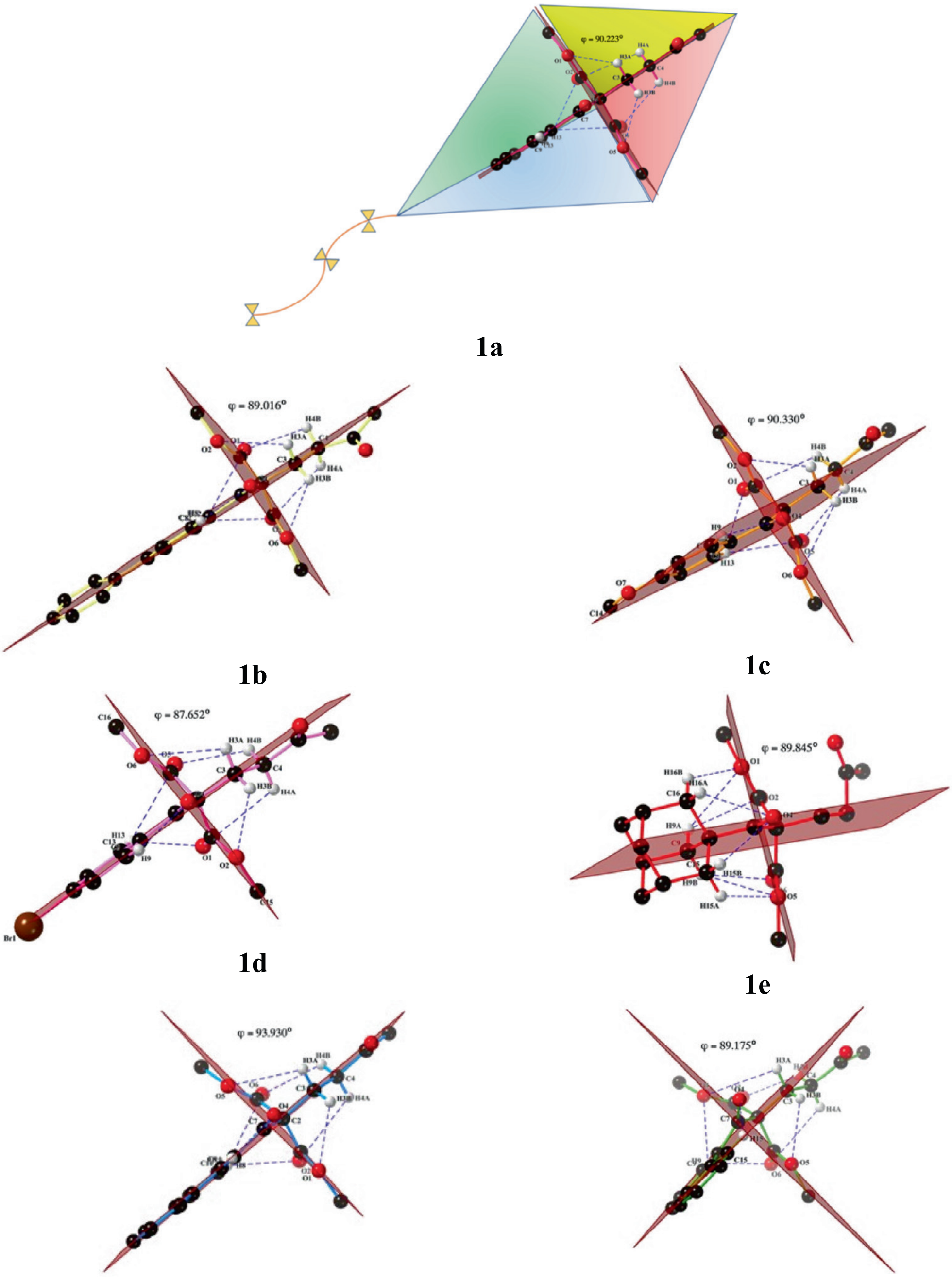
Compound (temp, K)							
Crystal data	1a (293)	1b (293)	1c (293)	1d (291)	1e (293)	1f (293)	1 g (293)
Cryst. Syst.	Monoclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	*P2₁/n*	*P1*	*P1*	*P2₁/c*	*Pbca*	*P1*	*P2₁/c*
Formula	$C_{16}H_{18}O_6$	$C_{22}H_{22}O_6$	$C_{17}H_{20}O_7$	C_{16} H_{17} BrO	$C_{20}H_{28}O_6$	$C_{20}H_{20}O_6$	$C_{20}H_{20}O_6$
M, gmol^{-1}	306.30	382.40	336.33	385.21	364.42	356.36	356.36
a, Å	8.134 (1)	8.8501 (3)	8.259 (2)	8.1988(11)	9.391 (3)	8.7366 (11)	8.4703 (5)
b, Å	16.618 (1)	8.9253 (3)	9.905(2)	19.9380(16)	19.261 (3)	10.0008 (12)	13.7770 (12)
c, Å	11.436 (1)	13.5517 (5)	21.203 (2)	10.6674(14)	21.290 (3)	10.5306 (11)	15.7530 (15)
β, deg	98.67 (1)	b	a	96.531(14)	90	c	102.003 (6)
d, g/cm^3	1.331	1.288	1.302	1.477	1.257	1.320	1.316
Crystal form	Colorless block	Colorless prism	Colorless prism	Colorless prism	Colorless prism	Colorless block	Colorless block
Crystal size, mm	0.68x0.60x 0.40	0.40x0.20x 0.20	0.60x0.40x 0.24	0.38 × 0.20 × 0.12	0.44x0.24x 0.12	0.40x0.16x 0.10	0.40x0.16x 0.04
Z	4	2	4	4	8	2	4
Diffractometer			Siemens P4/PC				
Radiation	Mo Kα	Cu Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ, mm^{-1}	0.102	0.774	0.101	0.2399	0.092	0.098	0.097
Scan mode	θ-2θ	θ-2θ	ω	ω	ω	ω	ω
Measured Reflections	3051	2839	6490	3274	3382	5527	5048
Independent Reflections	2845 (R_{int} = 0.0528)	2632 (R_{int} = 0.0171)	6032 (R_{int} = 0.0635)	3051 (R_{int} = 0.0441)	3382 (R_{int} = 0.000)	5210 (R_{int} = 0.0422)	4779 (R_{int} = 0.0375)
Refinement on F^2							
R	0.0525	0.0505	0.0476	0.0461	0.0561	0.0510	0.0485
Rw	0.1128	0.1304	0.1025	0.0612	0.0885	0.0760	0.0827
GOF	1.011	1.043	0.899	0.835	0.875	0.890	0.869

[a] α = 97.05 (1), β = 92.83 (2), γ = 93.06 (2). [b] α = 72.973 (3), β = 75.842 (3), γ = 79.745 (3). [c] α = 81.420 (11), β = 85.153 (9), γ = 80.846 (11).



1a **1b** **1c** **1c´** **1d** **1e** **1f** **1g**

Fig. 3 View of compounds **1a-g**, the displacement ellipsoids are drawn at the 50 % probability level.



1a

1b

1c

1d

1e

1f

1g

Fig. 4 Intramolecular hydrogen bonds in molecular structures of compounds **1a-g** (blue dashed lines) and inspired kite conformation morphology.

Table 2 Distances (Å) and angles (°) of intramolecular hydrogen bonds in the structure of compounds 1a-g, calculated with PLATON (Spek, 2020).

Compound **1a**

D—H---A	H---A	D---A	∠D—H---A
C3—H3A---O1	2.52(3)	2.851(3)	99.4(17)
C3—H3B---O5	2.64(3)	2.967(4)	100(2)
C4—H4A---O2	3.09(3)	3.556(4)	113(2)
C4—H4B---O6	2.72(3)	3.277(4)	118(2)
C9—H9---O4	2.42(3)	2.771(4)	102(2)
C13—H13---O2	2.57(3)	3.325(4)	138(3)
C13—H13---O6	2.98(3)	3.708(4)	135(2)

Compound **1b**

D—H---A	H---A	D---A	∠D—H---A
C3—H3A---O2	2.92	3.137(3)	94
C3—H3B---O6	2.58	2.904(3)	100
C4—H4A---O5	2.84	3.500(4)	126
C4—H4B---O1	2.71	3.126(5)	107
C8—H8---O4	2.44	2.758(4)	100
C12—H12---O1	3.25	3.966(3)	135
C12—H12---O5	2.74	3.495(4)	138

Compound **1c**

D—H---A	H---A	D---A	∠D—H---A
C3—H3A---O2	2.56	2.838(4)	97
C3—H3B---O6	2.99	3.213(4)	94
C4—H4A---O5	2.52	3.089(3)	118
C4—H4B---O1	2.94	3.525(3)	120
C9—H9---O4	2.51	2.790(4)	98
C13—H13---O1	2.72	3.362(4)	127
C13—H13---O5	3.18	3.968(4)	144

Compound **1d**

D—H---A	H---A	D---A	∠D—H---A
C3—H3A---O6	2.92	3.181(6)	96
C3—H3B---O2	2.56	2.795(6)	94
C4—H4A---O1	3.09	3.554(6)	111
C4—H4B---O5	2.56	3.187(6)	123
C9—H9---O4	2.45	2.744(7)	99
C13—H13---O1	2.66	3.346(7)	131
C13—H13---O5	3.19	3.957(7)	141

Compound **1e**

D—H---A	H---A	D---A	∠D—H---A
C9—H9A---O2	3.13	3.825(5)	130
C9—H9B---O6	2.87	3.584(5)	131
C9—H9A---O1	2.71	3.347(5)	123
C9—H9B---O5	2.71	3.364(5)	125
C15—H15A---O5	2.61	3.287(5)	127
C15—H15B---O4	2.57	2.878(5)	98
C16—H16A---O4	2.63	2.926(5)	98

Compound **1f**

D—H---A	H---A	D---A	∠D—H---A
C3—H3A---O5	3.01	3.218(3)	93
C3—H3B---O1	2.64	2.927(3)	97
C4—H4A---O2	2.97	3.492(3)	115
C4—H4B---O6	2.52	3.111(3)	119
C8—H8---O4	2.42	2.740(3)	100
C10—H10---O2	2.90	3.609(3)	134
C10—H10---O6	3.25	3.999(3)	139

Compound **1g**

D—H---A	H---A	D---A	∠D—H---A
C3—H3A---O1	3.25	3.383(3)	90
C3—H3B---O5	2.63	2.887(2)	96
C4—H4A---O6	2.95	3.513(3)	118
C4—H4B---O2	2.41	3.016(3)	120
C9—H9---O1	2.67	3.138(3)	112
C9—H9---O6	2.74	3.378(3)	126
C15—H15---O4	2.31	2.868(3)	118
C3—H3A---O1	3.25	3.383(3)	90

Siemens P4/PC diffractometer. The data collection, (Siemens, 1994) cell refinement and data reduction were carried out using XSCANS. The structure was solved with direct methods and refined by full-matrix least-square methods based on F^2 using SHELXS97 and SHELXL97 packages. (Sheldrick, 1997, 2008) In addition, 1,5-diketone dimethyl malonate **1b** was performed with Cu Kα radiation (λ = 1.54178 Å) at 293 K on a Nicolet P3/F diffractometer; and cell refinement and data reduction were performed with Nicolet P3 Software 1980.

3. Results and discussion

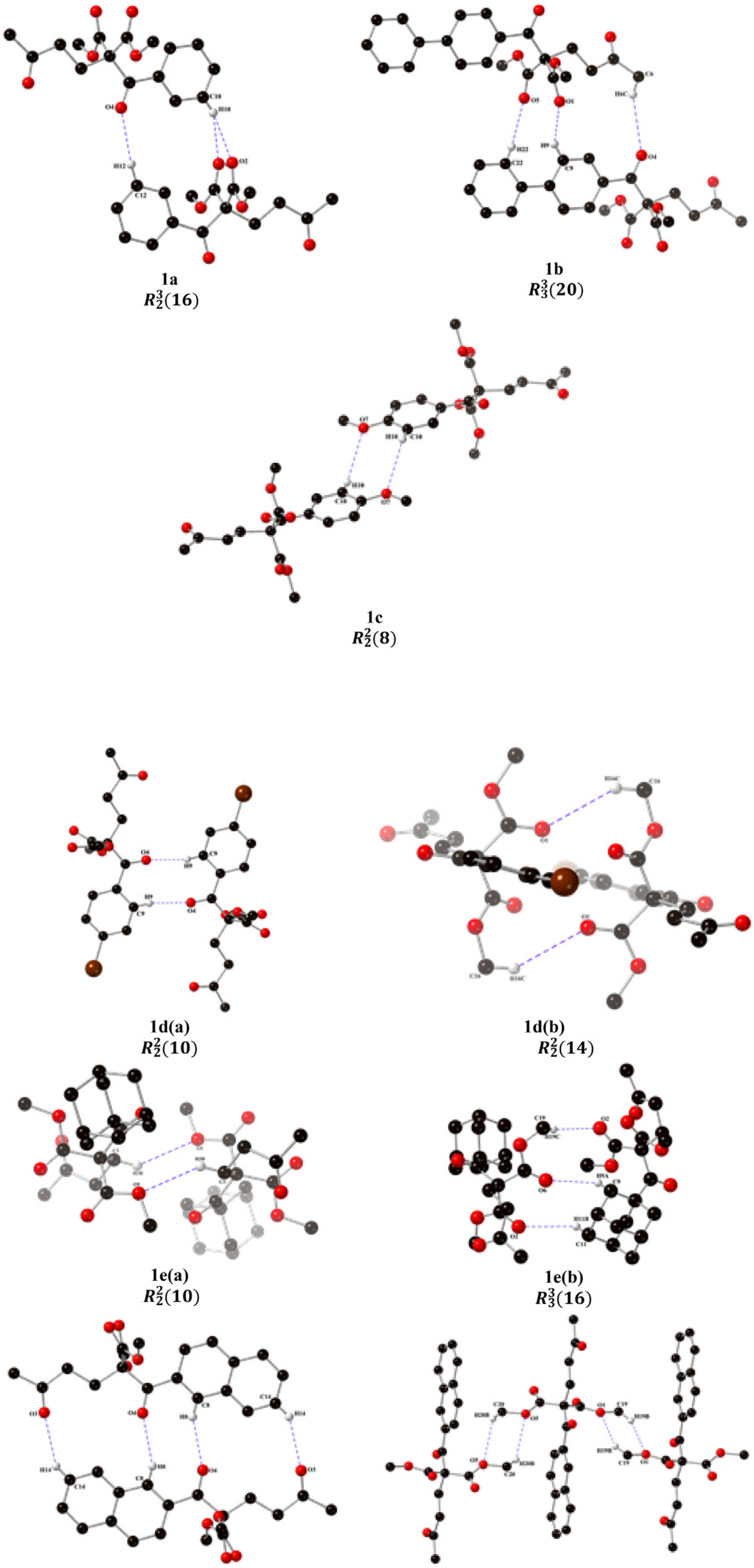
3.1. X-ray crystallographic data for 1,5-diketone malonates 1 a-g

Data for 1,5-diketone malonates **1a-g** are shown in Table 1, and geometry parameters such as bond lengths and angles are depicted in Table S1 (Supplementary information).

Crystals suitable for X-ray diffraction were obtained from 1,5-diketone malonates **1a-g**; their structural parameters are shown in Table 1. The structure of the compounds **1a-g**; is formed by 1,5-diketone and dimethyl malonate, also with substituent groups linked at C1: phenyl, 1,1′-biphenyl, 4-methoxyphenyl, 4-bromophenyl, 1-adamantyl, l-naphthyl and 2-naphthyl, for **1a**, **1b**, **1c**, **1d**, **1e**, **1f** and **1 g**, respectively. Fig. 3 shows a drawing displacement ellipsoids of 1,5-diketone malonates **1a-g**.

3.2. Structural hierarchy of the small library of hydrogen bonds based on supramolecular architectures of 1,5-diketone malonates 1a-g

From the results obtained on the crystalline structure of these compounds, a structural hierarchy is proposed that allows exploring and tracing a possible route of the elements that constituted their crystallization mechanism leading to the construction of a small library of hydrogen bonds exclusively by C–H···O interactions. The crystal structure of the 1,5-diketone malonates **1a-g** was analyzed according to the strategy steps: a) Intramolecular hydrogen bonds, b)



1a
$R_2^3(16)$

1b
$R_3^3(20)$

1c
$R_2^2(8)$

1d(a)
$R_2^2(10)$

1d(b)
$R_2^2(14)$

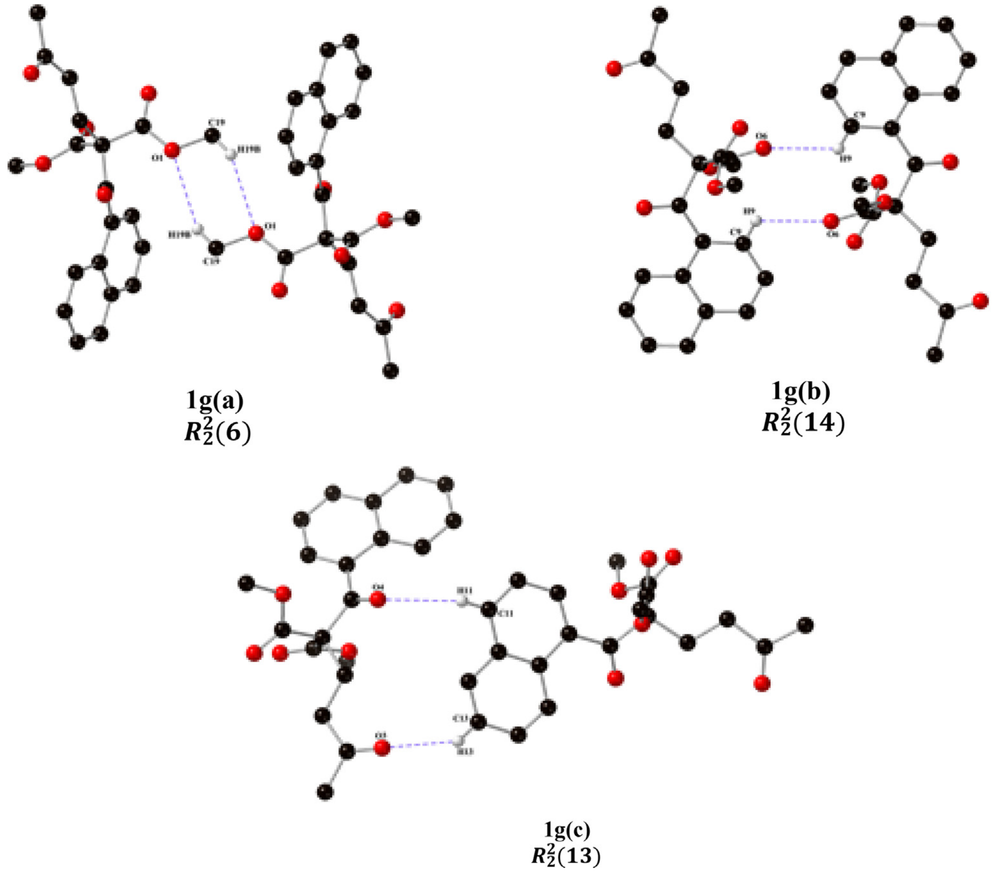
1e(a)
$R_2^2(10)$

1e(b)
$R_3^3(16)$

1f(a)
$R_2^2(10)R_2^2(24)$

1f(b)
$2R_2^2(6)$

Fig. 5 Crystal structure of dimers formed by two supramolecular synthons through the two hydrogen bonds in diketone malonates **1a-g**.



1g(a)
$R_2^2(6)$

1g(b)
$R_2^2(14)$

1g(c)
$R_2^2(13)$

Fig. 5 (*continued*)

Intermolecular hydrogen bonds in synthons and macrocycles, and c) Supramolecular architectures.

The strategic sequence of steps for the hierarchy that helps assess the supramolecular architecture in the titled 1,5-diketones is described below.

3.2.1. Intramolecular hydrogen bonds in monomer molecular structure of 1,5-diketones 1a-g

The first approach is to analyze the presence of intramolecular hydrogen bonds observed in the monomer molecular structure of 1,5-diketones **1a-g**. Regarding Fig. 4, these bonds generate the kite conformation of each compound and the quasi-perpendicular conformation between the two molecular fragments that constitute the molecule. Thus, the 1,5-diketones and dimethyl malonate moieties resemble two perpendicular molecular axes with a total angle between planes near φ = 90° for the seven molecular structures: the angle between planes(φ) is 90.223, 89.016,90.330, 87.652, 89.845, 93.930 and 89.175° for **1a**, **1b**, **1c**, **1d**, **1e**, **1f** and **1 g**, respectively.

The compounds **1a-g** have an average of seven intramolecular hydrogen bonds formed from the carbonyl group of the 1,5-diketones and the functional group –COO in the malonate with the -C–H of the molecule. As a result of this interaction, compounds **1a-g** have a kite-like topology given the two perpendicular molecular axes, which are constituted on average by the seven intramolecular hydrogen bonds indicated by blue dashed lines between molecular planes, Fig. 4. Remarkably, C–H···O hydrogen bond interactions are key to supporting the kite conformation. Tables 2 show the intramolecular hydrogen bonds in the molecular structure of **1a-g** compounds.

3.2.2. Dimers based on synthons and macrocycles by intermolecular hydrogen bonds of 1,5-diketones 1a-g

Hierarchical analysis of the supramolecular structure of 1,5-diketone dimers **1a-g** was performed from a synthon and macrocycle approach. A synthon is defined as a representative structural unit that links molecules and crystals and is implicated in all the stages through which molecules progress as they form crystals. (Desiraju, 2013, 1995, 2003) On another side, the motifs generated from intermolecular hydrogen bonds are defined as a type of graph set, such as C (chain), R (ring), D (dimer), and S denotes an intramolecular hydrogen bond. Additionally, the number of donors (d) and acceptors (a) used in motifs are assigned as subscripts and superscripts. In contrast, the size of the motif corresponding to the number of atoms in the repeat unit is indicated in parentheses. (Etter, 1990).

By applying the former concepts, the dimeric structure of compound **1a** is formed by the C12-H12---O4 interaction (Fig. 5), which is a simple hydrogen bond due to the donor interacting with an acceptor. However, because of the long-range hydrogen bonding, a donor may interact with more than one acceptor simultaneously. Also, the **1a** dimeric structure presents a bifurcated arrangement of hydrogen bonds

(Steiner, 2002) constituted by the C10-H10 donor and the O2 and O6 acceptors. The dimer formed a 16-atom ring with three acceptors and two donors: $R_2^3(16)$. Table 3 shows the distance (Å) and the angle (°) of the intermolecular hydrogen bonds in the structure of dimeric structure **1a**.

For structure **1b,** the supramolecular dimer is formed by three simple intermolecular hydrogen bonds: C6—H6C---O4, C9—H9---O1 and C22—H22---O5. The dimer formed a 20-atom ring with three acceptors and three donors: $R_3^3(20)$**,** Fig. 5. Table 3 presents the distance (Å) and angle (°) of the intermolecular hydrogen bonds in structure **1b**; the values of distances and bond angles are like those described in the literature. (Sutor,1962, 1963, Steiner, 2002).

The dimeric compound **1c** is formed by the interaction C10—H10---O7. This compound is an example of the role of hydrogen bonds in molecular recognition patterns by structural units called supramolecular synthons, Fig. 5. The synthon constitutes a dimer, an 8-atom ring, with two acceptors and two donors: $R_2^2(8)$**.** Table 3 presents the distance (Å) and angle (°) of intermolecular hydrogen bonds in the structure of compound **1c**. The compound **1d** has two dimers formed by two supramolecular synthons through C9—H9---O4 and

Table 3 Distances (Å) and angles (°) of intermolecular hydrogen bonds in the structure of compounds 1a-g, calculated with PLATON, (Spek, 2020).

Compound **1a**

D—H---A	H---A	D---A	∠D—H---A
C10—H10---O2	2.69(3)	3.347(4)	131.6(18)
C10—H10---O6	2.77(3)	3.586(4)	152.2(19)
C12—H12---O4	2.63(3)	3.634(4)	174.9(16)

Compound **1b**

D—H---A	H---A	D---A	∠D—H---A
C22—H22---O5	2.77	3.690(5)	170
C9—H9---O1	2.41	3.221(4)	145
C6—H6C---O4	3.01	3.802(8)	140

Compound **1c**

D—H---A	H---A	D---A	∠D—H---A
C10—H10---O7	2.94	3.480(4)	118

Compound **1d**

D—H---A	H---A	D---A	∠D—H---A
C9—H9---O4	2.38	3.280(6)	164
C16—H16C---O1	2.96	3.754(6)	140

Compound **1e**

D—H---A	H---A	D---A	∠D—H---A
C3—H3B---O5	2.71	3.513(5)	140
C11—H11B---O2	2.99	3.779(5)	139
C9—H9A---O6	2.69	3.464(5)	137
C19—H19C---O2	2.47	3.260(5)	140

Compound **1f**

D—H---A	H---A	D---A	∠D—H---A
C8—H8---O4	2.59	3.449(3)	154
C14—H14---O3	2.62	3.431(3)	146
C20—H20B---O5	2.81	3.485(3)	128
C19—H19B---O1	2.75	3.598(4)	148

Compound **1g**

D—H---A	H---A	D---A	∠D—H---A
C19—H19B---O1	2.77	3.601(3)	145
C9—H9---O6	2.94	3.561(3)	125
C13—H13---O3	2.61	3.285(3)	130
C11—H11---O4	2.86	3.678(3)	148

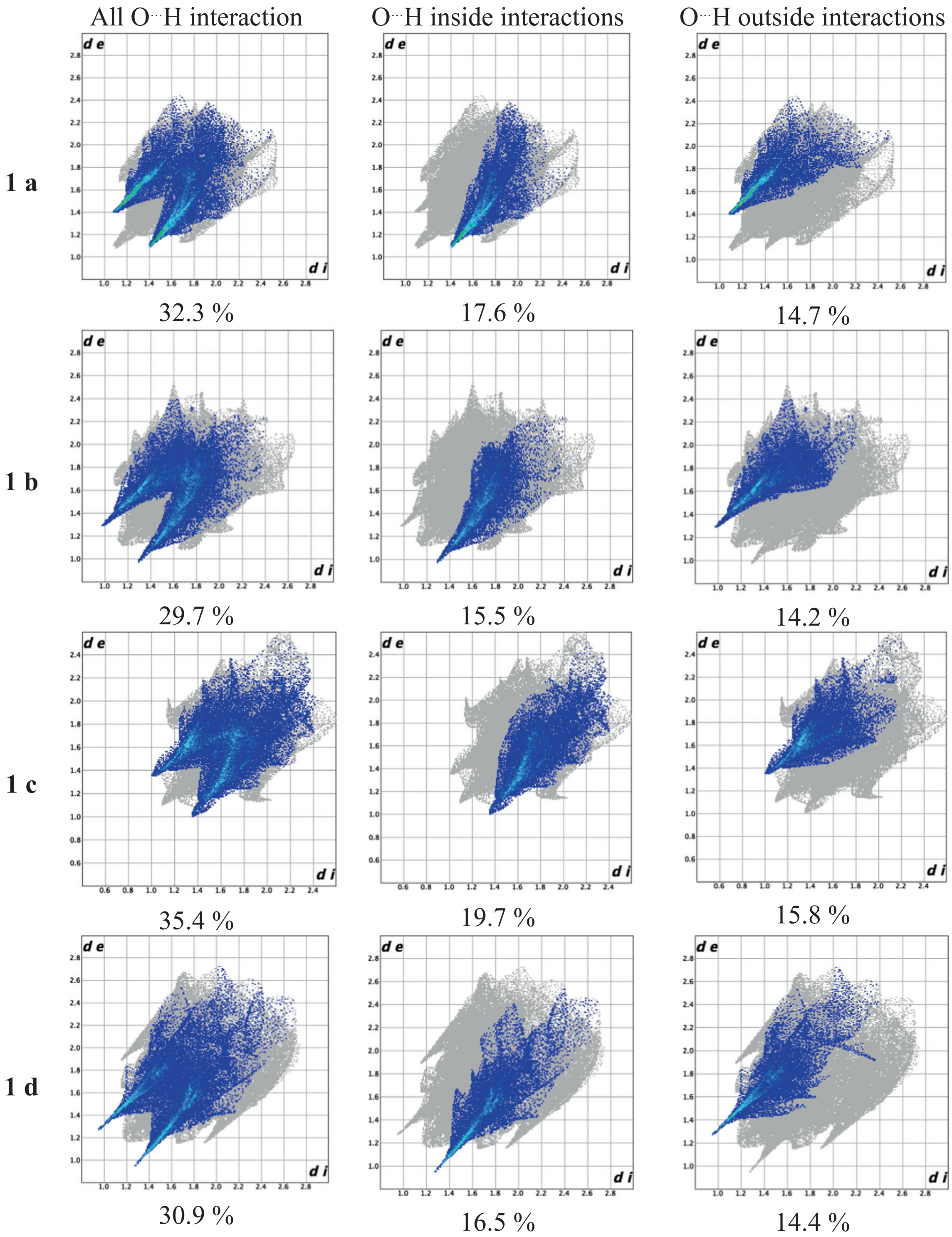


Fig. 6 O–H Atom-atom interactions and their contribution to the Hirshfeld fingerprint plot for 1,5-diketones **1a** – **g**.

C16—H16C---O1 interactions, Fig. 5. Each of the dimers **1d(a)** and **1d(b)** formed a 10-atom ring with two acceptors and two donors, $R_2^2(10)$ and $R_2^2(14)$, respectively. Table 3 presents the distance (Å) and angle (°) of the intermolecular hydrogen bonds in compound **1d**.

The molecular structure of dimer **1e(a)** is formed by the structural unit C3—H3B---O5, a 10-atom ring with two acceptors and two donors: $R_2^2(10)$. A supramolecular dimer is present in the crystal structure of **1e(b),** constituted by three acceptors and three donors: $R_3^3(16)$, a ring with sixteen members. Table 3 presents the distance (Å) and angle (°) of intermolecular hydrogen bonds in the structure of compound **1e**.

The molecular structure of **1f(a)** has a particular dimer formed by two supramolecular synthons through

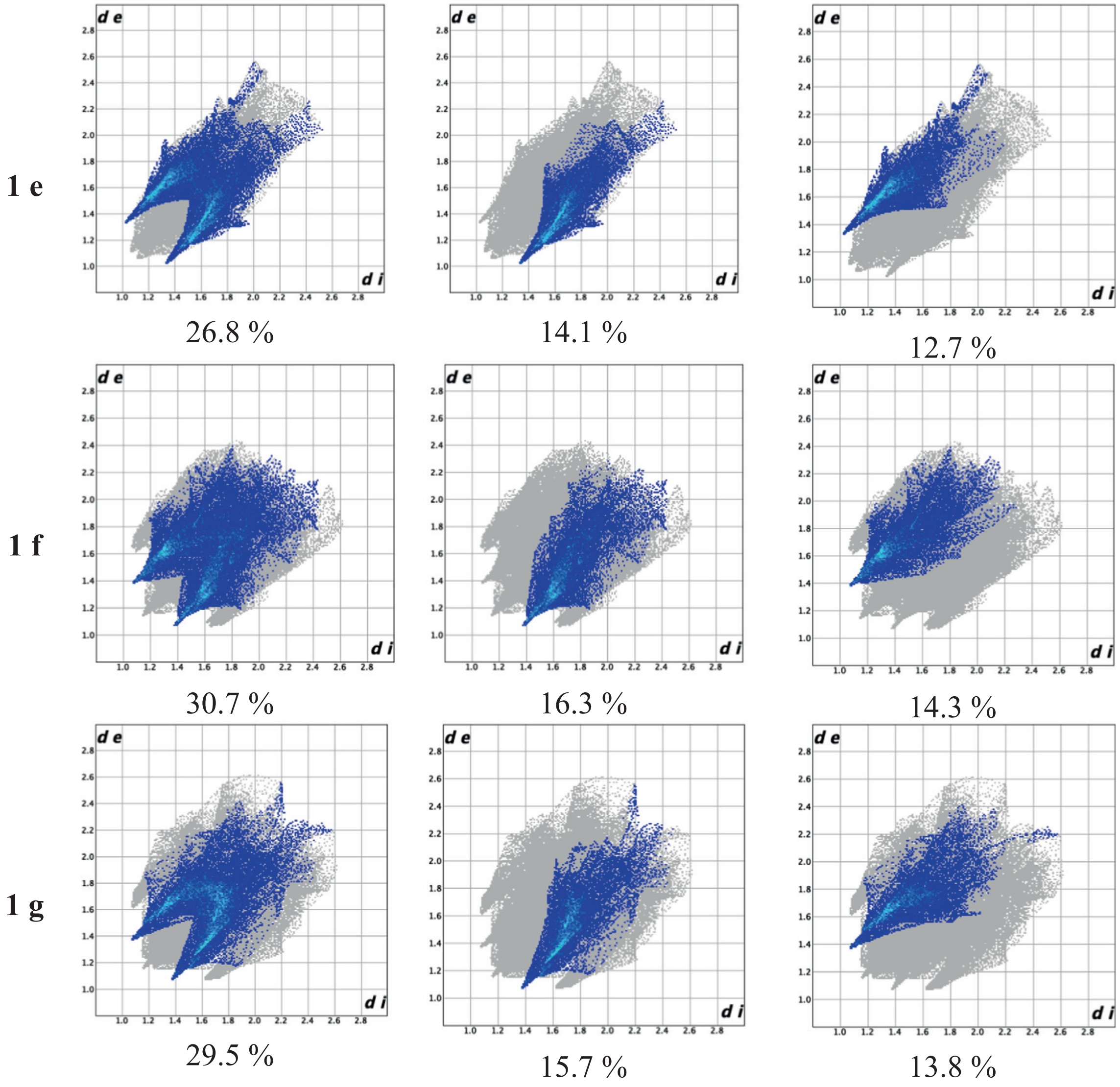


Fig. 6 (*continued*)

C8—H8---O4 and C14—H14---O3 interactions, with a synthon inside the other. This dimer is formed of two rings, one with 10 atoms and the other with 24 atoms, with two acceptors and two donors in each ring: $\boldsymbol{R}_2^2(10)$and$\boldsymbol{R}_2^2(24)$, respectively; furthermore, two small **1f(b)** synthons, each which with a 6-atoms ring ($2\boldsymbol{R}_2^2(6)$) by C19—H19B---O1 and C20—H20B---O5 interactions are observed. The dimeric compound **1 g(a)** with a supramolecular synthon shows the C19—H19B---O1 interaction, forming a 6-membered ring with two acceptors and two donors: $\boldsymbol{R}_2^2(6)$, Fig. 5.

The second supramolecular structural unit **1 g(b)** is formed by the C9—H9---O6 interaction that assembles two molecules, the synthon formed by a 14-atom ring with two acceptors and two donors: $\boldsymbol{R}_2^2(14)$.Finally, t he third supramolecular structure, **1 g(c)**, corresponds to a macrocycle with C13—H13---O3 and C11—H11---O4 interactions. These interactions comprise a 13-membered ring with two acceptors and two donors: $\boldsymbol{R}_2^2(13)$. Table 3 presents the distance (Å) and angle (°) of intermolecular hydrogen bonds in the structure **1 g**.

3.3. *Hirshfeld surface analysis of 1,5-diketones*

Hirshfeld surface analysis (Wolff et al., 2012) was performed to quantify and visualize the close intermolecular atomic contacts in the crystal structure and the associated fingerprint plots of the molecule showing the significant contributions of the different intermolecular interactions on the Hirshfeld surface. (Spackman & Jayatilaka, 2009) These results show the importance of the intramolecular and the intermolecular C–H···O hydrogen-bonds non-covalent interaction in the primary kite-like conformation and the dimer motifs for the 1,5-diketone malonates can be highlighted.

Remarkably H···O inside and outside interactions are depicted in the fingerprint plots of the 1,5-diketones **1a**–**g**, Fig. 6. It is noticeable that inside interactions are slightly greater than outside contributions, the first mainly attributed to the carbonyl group of the 1,5-diketones and the functional group –COO in the malonate to the -C–H of the molecule by supporting the kite-like topology. In addition, outside con-

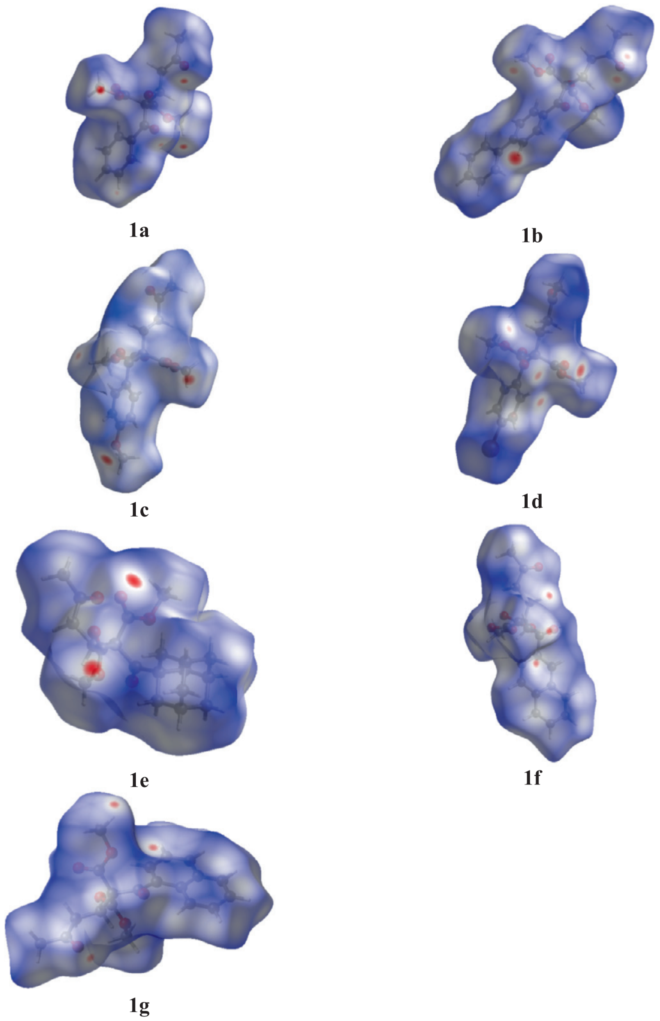

1a **1b** **1c** **1d** **1e** **1f** **1g**

Fig. 7 The Hirshfeld surface of 1,5-diketones **1a** – **g** mapped with dnorm.

tributions represent C–H···O hydrogen bond interactions with intermolecular hydrogen bonds (dimers, synthons and macrocycles). Fig. 7 describs the Hirshfeld surfaces for the diketones, enhancing the inside interactions, Fig. 8 shows the surfaces for dimers synthons.

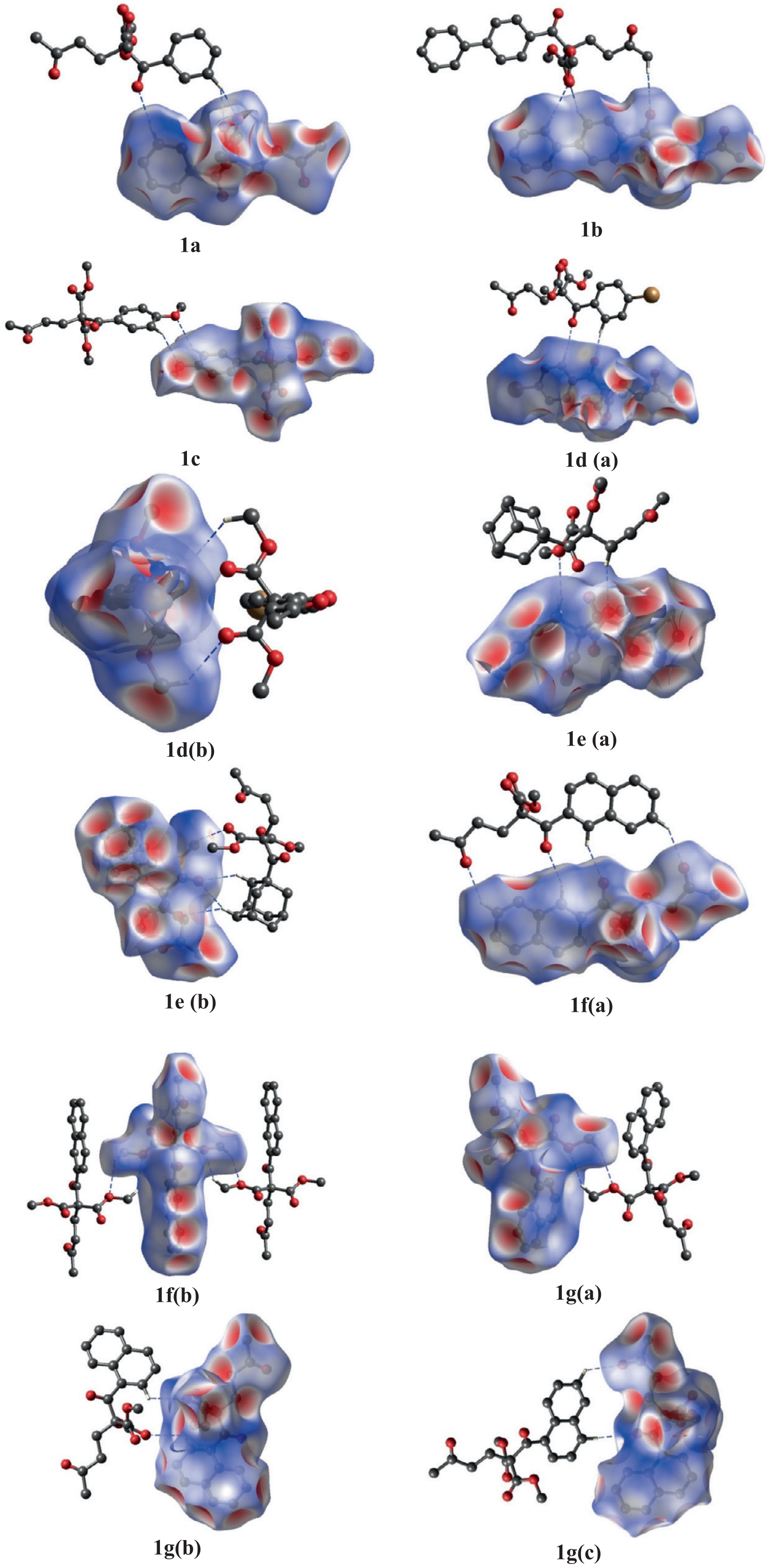
3.4. Supramolecular architectures

Highlighting the importance of intramolecular c–h···o hydrogen bonds in the primary kite-like conformation, the intermolecular C–H···O hydrogen bond interactions in dimer motifs for the 1,5-diketone malonates are also important non-covalent interaction at different levels of hierarchy in crystal engineering. (Sutor, 1963, Desiraju, 2003) a small library of supramolecular architectures in diketones 1**a-g** can be described in the crystal structures in conjunction with the cooperative C–H···O hydrogen bonds, Fig. 9.ing the importance of intramolecular C–H···O hydrogen bonds in the primary kite-like conformation, the intermolecular C–H···O hydrogen bond interactions in dimer motifs for the 1,5-diketone malonates are also important non-covalent interaction at different levels of hierarchy in crystal engineering. (Sutor,1963, Desiraju, 2003) A small library of supramolecular architectures in diketones **1a-g** can be described in the crystal structures in conjunction with the cooperative C–H···O hydrogen bonds, Fig. 9.

According to Fig. 9, the motif dimers **1a** and **1b** with intermolecular hydrogen bonds show a supramolecular chain through 6 hydrogen bond interactions **C(6)** represented by stick model topology, $\mathbf{C}(6)\boldsymbol{R}_2^3(16)$ for **1a** and $\mathbf{C}(6)\boldsymbol{R}_3^3(20)$ for **1b.** The **1c** supramolecular synthon shows a two-dimensional supramolecular structure with three interactions. The **1c** synthon is represented by two series of molecules in parallel using the sticks model, $\boldsymbol{R}_2^2(8)$. The compound **1d**, with two dimers, generated a supramolecular structure with four **C(4)** interactions represented by the sticks model, $\mathbf{C}(4)\boldsymbol{R}_2^2(10)\boldsymbol{R}_2^2(14)$.

The supramolecular structure (with adamantyl moiety) of **1e** has a macrocycle in conjunction with the supramolecular synthon. This structural unit has 4 molecules that form a 1D zigzag supramolecular structure with five interactions each, $\boldsymbol{R}_2^2(10), \boldsymbol{R}_3^3(16)$.

For compound **1f**, the three synthons generated a 3D supramolecular structure with four interactions represented by the sticks model, $\boldsymbol{R}_2^2(10), \boldsymbol{R}_2^2(24), \boldsymbol{R}_2^2(6)$. In the case of **1 g**,



1a 1b

1c 1d (a)

1d(b) 1e (a)

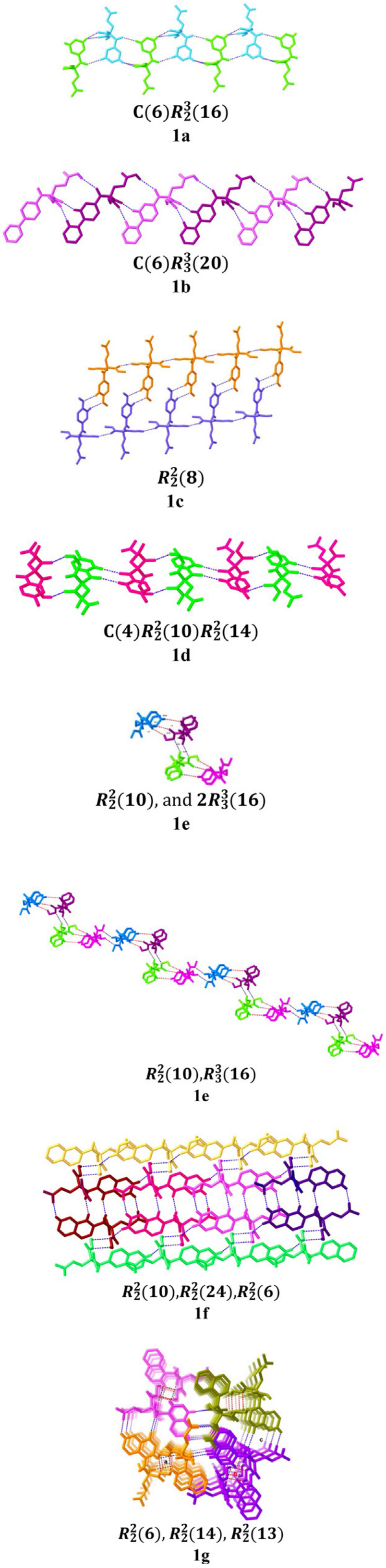
1e (b) 1f(a)

1f(b) 1g(a)

1g(b) 1g(c)

Fig. 8 The Hirshfeld surface of 1,5-diketones **1a**–**g** of dimers synthons and macrocycles.

$\boldsymbol{R}_2^2(6), \boldsymbol{R}_2^2(14), \boldsymbol{R}_2^2(13)$**,** the interaction of four stick motifs is notable.



C(6)R_2^3(16)
1a

C(6)R_3^3(20)
1b

R_2^2(8)
1c

C(4)R_2^2(10)R_2^2(14)
1d

R_2^2(10), and **2R_3^3(16)**
1e

R_2^2(10),R_3^3(16)
1e

R_2^2(10),R_2^2(24),R_2^2(6)
1f

R_2^2(6), R_2^2(14), R_2^2(13)
1g

Fig. 9 Supramolecular structures through hydrogen bonds of 1,5-diketones **1a-g**.

4. Conclusions

In conclusion, the 1,5-diketone malonates **1a-g** are illustrative examples of crystal packing determined exclusively by weak C–H···O hydrogen bonds. The plausible route of construction of crystalline solid has been explored to understand the mechanism of crystallization: a) Intramolecular C–H···O interactions provide 1,5-diketone malonates **1a-g** a kite-like topology because the seven intramolecular hydrogen bonds constituted, on average, the two perpendicular molecular axes. b) The intermolecular interactions of C–H···O generate molecular recognition by forming ten synthons and four macrocycles as structural units in the crystallization process. c) The supramolecular architectures of compounds **1a-g** are three-dimensional and obtained from the conjunction of cooperative hydrogen bonds C–H···O at different hierarchy levels.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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CCDC number: 2204857, 2204858, 2204859, 2204860, 2204861, 2204862, 2204863, for the reported structures (1a - g) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/data_request/cif.

CRediT authorship contribution statement

Domingo Salazar-Mendoza: Conceptualization. **José Luis García-Gutiérrez:** Investigation. **Federico Jiménez-Cruz:** Conceptualization, Writing – original draft.

Appendix A. Supplementary data

Supplementary information: data associated with X-ray and ^{1}H and ^{13}C NMR data and spectra for 1,5-diketone malonates **1e-g**.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.arabjc.2023.104843.

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