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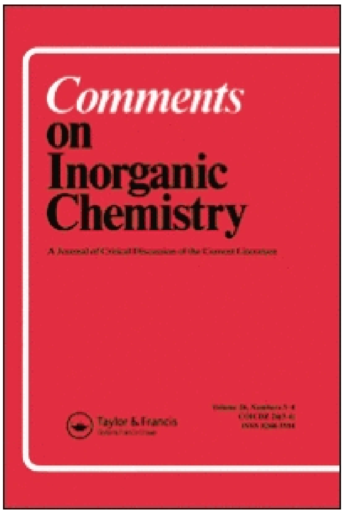

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Generation of Organometallic Crystal Architectures

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Generation of Organometallic Crystal Architectures

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Organometallic crystal architectures have been examined in terms of extramolecular interactions between molecules and ions. Attention has been focused on the modelling of van der Waals crystals by means of empirical atom–atom pairwise potential energy calculations and on the possibility of generating theoretical crystal structures to be compared with those experimentally determined. Examples of crystal generation techniques for simple binary carbonyls have been reviewed. It has also been shown that organometallic crystal enginnering takes advantage of both the great structural flexibility of organometallic molecules as well as of the possibility of linking ligands via hydrogen bonds. The importance of charge assisted. C–H——O hydrogen bonds in the construction of supramolecular aggregates is stressed.

Key Words: *crystal engineering, intermolecular interactions, organometallic molecules and crystals*

INTRODUCTION

Molecular crystal engineering is the planning of a crystal structure from its building blocks.[1] The building blocks are molecules or ions chosen on the basis of their size, shape and extramolecular bonding capacity. The

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engineering of molecular crystals as well as the construction of supramolecular aggegates are both concerned with intermolecular interactions; hence crystal engineering and supramolecular chemistry are conceptually connected.[2] The most representative process of molecular self-recognition and self-assembling is the very nucleation and growth of a molecular crystal. Moreover, as the supramolecular chemical behavior of a supermolecule is governed by weak non-covalent interactions, the chemical and physical properties of a molecular crystal are controlled by the intermolecular, or interionic in the case of charged species, interactions. On this premise, a molecular crystal can be viewed as a *solid supermolecule*.

Crystals are the most accessible systems for a detailed study of the geometric and energetic features of non-covalent interactions. However, until now, studies of crystal engineering have been essentially confined to organic solids. For this reason, a few years ago we initiated at Bologna a systematic investigation of organometallic solids.[3] We have observed important differences between organic and organometallic molecular crystals arising from the presence of metal atoms and from the electronic nature of ligand–metal bonds. In addition, organometallic crystals are often made of charged species, *viz.* the interaction between size, shape, and charge of anions and cations needs also to be considered. These were the aspects that attracted our interest most.

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Solid organometallic complexes can be regarded as a bridge between molecular solids of the organic type and inorganic solids and bulk metals so that the properties of solid organometallic materials show dependence on the electronic nature of the metal(s), besides that on the patterns of intermolecular interactions established by the ligands, most often organic molecules or fragments. It is important to appreciate that information on extramolecular interactions obtained from solid state studies can be transferred to supramolecular aggregates in solution or to molecule–substrate investigations.

We pointed out before how molecular aggregation and crystal stability depend on the complex interplay between intramolecular bonding and intramolecular non-bonding interactions (*internal interactions*) and intermolecular interactions between neutral atoms, molecules, or ions present in the crystal (*external interactions*). This interplay becomes crucial when dealing with structurally non-rigid organometallic molecules.[4] Although highly desirable in crystal modelling, it is, in most cases, very difficult, if at all sensible, to try to separate the two types of contributions. Indeed the molecular structure observed in the solid state is the result of a compromise between energetic terms which need not be convergent, i.e., which do not lead to a unique solution. This is well evidenced by the existence of crystal isomers and polymorphs for the same molecule.[5]

In this paper we elaborate on some aspects of our approach to organometallic crystal engineering. We will briefly discuss (i) database analysis; (ii) crystal cohesion estimate; (iii) modelling of theoretical crystal structures; and, finally, some example of engineering of supramolecular organometallic crystals (iv). We reckon that this is the basic *mental* algorithm to use in the construction and modelling of molecular solids.

What are the goals? Crystal engineering is primarily a process of learning: by studying how molecules interact, cling one to another, and self-organize, the experimentalist can conceive ways to *direct* the crystal building process towards a given architecture. The objective is that of developing a methodology of organometallic crystal engineering, via systematic synthesis and characterization of bioinorganic, organometallic and bio-organometallic materials to establish structure, thermodynamic properties and organization in the solid state. In the case of organometallic species the corollary is that of preparing systems incorporating transition metal atoms in different valence states via complementary intermolecular interactions (mainly but not exclusively hydrogen bonding) in mixed organic–organometallic and bioinorganic systems to obtain conducting and ferromagnetic materials as well as materials for non-linear optical properties.[6] Further, one may wish to discover and learn how to make channelled and/or nanoporous materials[7] for uptake of gas (to be utilized, for example, in the construction of gas sensors) or to study molecular diffusion and solid state reactivity.[8]

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THE CAMBRIDGE STRUCTURAL DATABASE (CSD): A TOOL TO STUDY NON-COVALENT INTERACTIONS IN CRYSTALS

Fundamental to devising a crystal engineering strategy is the knowledge of the factors controlling the interaction between the building blocks. In Desiraju's *synthon* approach[8] this is made possible by supramolecular retrosynthesis, *viz.* by working out backwards how a given molecule or molecular fragment participates in intermolecular interactions to form networks.

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The CSD[9] represents the most accessible depository of information on atom–atom interactions in molecular crystals. Of course one may object that only molecules in the solid state can be studied, *viz.* the sampling of atom–atom interactions is biased by the physical state of the systems. While this objection is essentially correct, it should also be kept in mind that non-bonded distances between atoms in crystals represent equilibrium separations, i.e., the best compromise between attractive and repulsive interactions of van der Waals and Coulombic types (see next section). A statistical basis for structural analysis is of indisputable importance because it allows the study of the behavior of a given functional group, a whole molecule, or ions in a variety of crystal environments. This is essential when dealing with flexible organometallic molecules.

If the relationship between the structure of the individual molecular entity and that of a collection of molecules can be understood, then modification to either molecular or supramolecular structures can be engineered. The April 1996 version of CSD collects 152,464 crystal structures, 75,385 of which are organometallic compounds. The very abundant storage of crystal structures contains information not only on all possible extramolecular interactions, on their strength, and on their geometric features, but also on the robustness of a given interaction, on its transferability from crystal to crystal, and on the extent of deformability.

As an example of the utilization of CSD to investigate intermolecular interactions we discuss the distribution of intermolecular C–H——O distances in organometallic crystals of neutral molecules carrying CO-ligands and C–H groups belonging to organic ligands. The Lewis basicity of CO is a well studied phenomen, and there are a number of examples of compounds in which the CO ligand can act as a base towards a Lewis acid or a proton acid.[10] The CO-basicity depends on the degree of electron delocalization onto the CO-ligand and follows the order face-bridging > edge-bridging > terminal. This is the reverse order of the CO stretching frequencies on changing the CO-bonding mode. We have demonstrated recently that the higher basicity of the CO-ligand in bridging bonding mode with respect to the terminal coordination is reflected in the average (C)H——O separations in the solid state. The histograms of $(C)H——OC_{terminal}$ and $(C)H——OC_{bridge}$ separations in the case of cobalt complexes, taken as representative examples of transition metal carbonyl complexes, are shown in Figs. 1a, and 1b, respectively.

The CSD has also been successfully used to investigate organometallic salts.[11] It is important to appreciate that the occurrence of charged

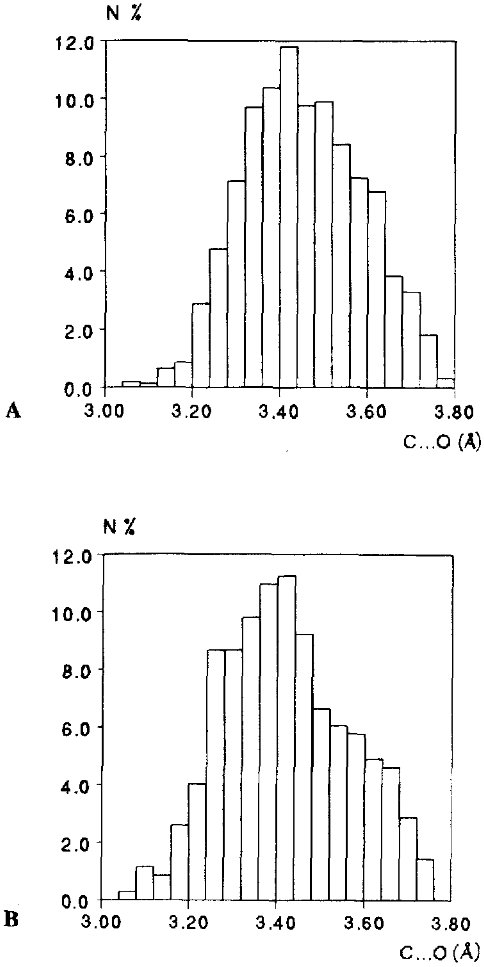

FIGURE 1 Histograms of C——O distance distributions for intermolecular (C)H——OC hydrogen bonds: (a) Co-complexes carrying terminal ligands, (b) Co-complexes carrying μ_2-CO ligands bound to Co and to another generic transition metal atom.

species is much less common in organic chemistry than in organometallic chemistry, where, thanks to the variable valence state of transition metals, many complexes are isolated as ions. In the case of molecular salts the crystal architecture is controlled by the interplay between size

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and shape of the component ions as well as by the actual ionic charge. We have shown that predefined ionic arrangements in the solid state can be attained by adequately choosing the counterions. For example, large transition metal cluster anions can be driven towards anisotropic arrangements in the solid state by crystallization with small counterions, so that anion piles or layers can be constructed. The CSD affords a readily available tool to examine the effect of a given counterion choice on a large number of crystal structures.

THEORETICAL APPROACH: THE COHESION OF A CRYSTAL EVALUATED BY ATOM–ATOM POTENTIAL ENERGY CALCULATIONS

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The atom–atom potential energy method, in use for more than 50 years in the organic solid state chemistry field, still represents a simple and highly transferable method to estimate non-covalent interactions of the van der Waals type in crystals.[12] This approach has recently included hydrogen bonding interactions,[13] thus overcoming one of the major limitations to its application to hydrogen bond controlled crystal engineering and supramolecular chemistry. This is not to claim that the atom–atom approach is superior to more sophisticated theoretical approaches for the study of bonding and non-bonding interactions available nowadays. The atom–atom method, however, is extraordinarily flexibile and transferable. Portability makes it a method of choice for the estimate of the cohesive energy of molecular crystals: it has been shown in a number of instances that, with very small changes, the method can be applied to a great variety of crystalline systems, from the simplest noble gas or organic crystal to the most complex organometallic cluster. In this latter case there are, of course, limitations arising chiefly from the lack of suitable parameters for the metal atoms, although the problem can be circumvented by attributing to metal atoms the potential parameters of the corresponding nobles gases. This may appear as a severe approximation but does not seriously affect the calculations because the metal atom(s) is usually deeply embedded in a sheath of ligands and screened from the surroundings to the extent that their contribution to crystal cohesion is often minor if not negligible. The periphery of organometallic complexes is, in most cases, made of "organic" atoms for which potential parameters are available and well tested.

The most commonly used expression for the empirical estimate of the packing potential energy (PPE) of a molecular crystal is called the 6-exp-1 potential, with PPE = $\Sigma_i\Sigma_j(Ae^{-\mathrm{B}r_{ij}}-\mathrm{C}r_{ij}^{-6} + q_iq_jr_{ij}^{-1})$.[12,14] In this expression, index i runs over all atoms of the reference molecule in the lattice and index j over the atoms of the surrounding molecules distributed according to crystallographic symmetry; r_{ij} is an atom–atom intermolecular distance, q_i and q_j are the formal atomic charges if a Coulombic term is included in the calculations. The basic assumption underlying the use of most atom–atom potential calculations is that only central forces operate between pairs of atoms and that the total interaction energy is the sum of the interactions between all atomic pairs. Excessive approach of atoms giving rise to repulsions is taken into account by the exponential function. A number of independent tabulations for the coefficients A, B and C, for each type of atom–atom contact for organic substances, are available in the literature.[13] They are obtained either by fitting observed crystal properties (heat of sublimation and known crystal structures) or via *ab initio* calculations of the intermolecular potential energy.[12]

It should be stressed that the atom–atom potential energy method provides information of essentially enthalpic nature. Entropy is not taken into account. This is not a severe problem in most cases because the entropy contribution is small in crystals, but it can become fundamental when comparing polymorphs, for example, or when dealing with disordered crystals in which dynamic processes take place. Packing energy calculations of this type have been successfully applied to several families of organometallic crystals, such as the binary transition metal carbonyls[15] and the metallocene complexes.[16] In all these cases, rather than extracting exact values of crystal packing potential energies or molecule–molecule cohesive energy, the method has been fundamental in the rationalization of structural analogies and differences, including the dynamical behavior in the solid state, between the members of the families.

PACKING GENERATION THEORY AND PRACTICE AND SPACE GROUP FREQUENCY

The construction of organometallic crystals requires a profound knowledge of the factors that control molecular recognition. The generation of hypothetical crystal structures[17] is therefore logically connected to *ab initio* calculations of molecular structures. Hence, as it is becoming

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almost routine to accompany the laboratory synthesis of molecules with theoretical calculations to *rationalize* or *model*, if not *predict*, the structure (and chemical behavior) of the product, the analogous approach to crystal synthesis requires a combined use of *theory and practice*. As in the case of atom–atom potential energy calculations, the algorithms and softwares for this goal have been initially developed in the field of organic solid state chemistry.[18]

It has been amply demonstrated in studying organic solids that there is no unique way to organize the "web" of intermolecular interactions that generates packing arrangements unless very strong and directional forces (such as some strong intermolecular hydrogen bonds) are present. It requires little differences in free energy to attain alternative yet chemically and crystallographically acceptable packing modes. Our work in the field[19,22] of theoretical crystal structure generation has contributed to demonstrate that a large number of polymorphic modifications are, in principle, available for even the simplest molecular shape with energy difference falling within a very narrow range. We have used the term *crystal isomerism* to indicate isomeric forms in different crystal structures.

Knowledge of the molecular shape allows the investigation of the way molecules self-recognize and self-assemble in the solid state and the identification of the most frequent interlocking motifs between ligands or groups of ligands. Such an analysis is based on the inspection of the *enclosure shell* formed by the molecules in the immediate neighborhood of the one molecule chosen for reference. Crystal structure decoding can be easily achieved by calculating the intermolecular interactions energies via atom–atom potentials and by ranking the molecules in order of decreasing contribution to the total cohesive energy of the crystal.[23] In this way differences and analogies between apparently very different crystals can be appreciated more efficiently than with "traditional" crystallographic tools. The second level of the packing decoding is concerned with the interlocking of atomic groupings belonging to neighboring molecules. The crystal is reconstructed starting from pairs of molecules generated via most common symmetry operators. The energetic analysis allows recognition of the most relevant structural sub-units in the experimental crystal structures. Information of this type is useful for the investigation of self-recognition and nucleation processes, and it is transferable to other molecules containing similar structural sub-units.

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TABLE I

Most common space groups obtained by combining inversion (I) and screw-axis (S) symmetry operators with translational symmetry (T).

Initial Dimolecular Nucleus	Symmetry Operator	Space Groups
T	T	$P1$
I	I+T	$P\bar{1}$
S	S+T	$P2_1$
S	S+I+T	$P2_1/c$
I	I+S+T	$P2_1/c$
S	S+S+T	$P2_12_12_1$

In order to construct theoretical crystals one needs finally to combine symmetry operators and translational symmetry to obtain three-dimensional arrangements, *viz.* crystals. Examples of how symmetry operators can be combined to generate space groups are given in Table I.

Clearly the generation of all 230 space groups would represent an incredibly demanding task. This is not necessary, though. We have compared space group frequencies in organic[24a] and organometallic crystals[24b] (see Table II) by analyzing the structures deposited in the April 1996 version of CSD. The search was carried out on the 55,480 crystal structures formed by neutral mononuclear and polynuclear organometallic molecules. From Table II it is immediate that there is no need to worry about 230 space groups. The relative majority of organometallic crystals crystallizes in the monoclinic space group

TABLE II

Comparison of the observed space group frequencies.

Space Group Symbol	Organomet.s %	Organics % (24a)	Organics & Organomet.s % (24b)
$P1$	1.4	1.5	1.2
$P\bar{1}$	22.1		13.4 16.9
$P2_1$	2.4	10.0	6.4
$P2_1/c$	38.6	37.1	36.6
$P2_1/a$			
$P2_1/n$			
$P2_12_12_1$	4.6	18.1	11.0
Pbca	3.6	4.8	4.2
Pnma	1.4	1.1	1.6
$Pna2_1$	1.1	1.8	1.6
C2/c	7.3	5.6	7.0

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TABLE III

Comparison of packing potential energy values and of packing coefficients for observed and calculated crystal structures of $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$.

Structure	PPE kcal.mol^{-1}	PC	a	b	c	α	β	γ	V/Å^3
Altern. Setting[a]	Space Group		a′	b′	c′	α'	β'	γ'	V′/Å^3
Ni–OBS	–19.4	0.66	10.897	–	–	–	–	–	1293.96
Ni	–18.02	0.67	7.220	7.863	7.278	62.12	88.88	116.01	314.84
Orthorh.	F		10.351	13.912	10.151	90.	90.	90.	1461.82
FE–OBS	–24.3	0.67	11.785	6.828	9.388	90.	107.62	90.	719.99
Monocl	C2/c								
Fe	–24.13	0.68	6.859	6.696	10.019	70.52	96.74	60.57	354.93
Monocl	C		11.948	6.696	9.287	90.	107.15	90.	709.96
Cr–OBS	–38.72	0.68	11.769	11.092	6.332	90.	90.	90.	826.6
Orthorh	Pnma								
Cr	–37.7	0.68	11.1191	6.142	12.187	90.	90.	90.	832.3
Orthorh	$P2_12_12_1$		1.119	12.187	6.142	90.	90.	90.	

[a] Niggli reduced cells or alternative settings based on the primitive cells.

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TABLE IV

Comparison of packing potential energy values and of packing coefficients for observed and calculated crystal structures of $Fe_3(CO)_{12}$, and $Ru_3(CO)_{12}$.

Structure	PPE kcal.mol^{-1}	PC	a	b	c	α	β	γ	V/Å^3
Altern. Setting[a]	Space Group		a′	b′	c′	α′	β′	γ′	V′/Å^3
FE3–OBS	–62.1	0.67	8.359	11.309–	8.862	90.	97.0	90.	831.5
Monocl	$P2_1/n$								
FE3	–58.2	0.65	9.403	9.322	9.809	85.88	90.14	88.92	857.4
Tricl	P–1								
RU3–OBS	–75.3	0.71	8.117	14.863	14.614	90.	100.7	90.	1732.6
Monocl	$P2_1/n$								
RU3	–46.4	0.62	14.830	8.152	16.172	90.	90.	90.	1955.1
Orthorh	$P2_12_12_1$		14.830	16.172	8.152	90.	90.	90.	1955.1

[a] Niggli reduced cells or alternative settings based on the primitive cells.

P2_1/c, whereas "second best" is the centrosymmetric triclinic space group P$\bar{1}$. These two space groups only account for almost 60% of all know organometallic crystal structures characterized to date. It is also interesting to note that the number of non-centrosymmetric crystals is lower in organometallics than in organics probably because of the lower incidence of chiral molecules.

Theoretical crystal structures have ben calculated for the simple binary carbonyl complexes $Ni(CO)_4$,[19] $Fe(CO)_5$,[19] and $Cr(CO)_6$[20] as representative of the classes of tetrahedral, trigonal bipyramidal, and octahedral complexes (see Table III). In all cases it has been possible to retrace, among other solutions of similar cohesive energy, the experimentally determined crystal structures. The intermolecular interlocking and crystal packing for the experimentally observed structures as well as for the most cohesive theoretical crystals obtained by the procedure outlined above are compared in Figs. 2, 3, and 4 for Ni, Fe, and Cr carbonyl complexes.

In the cases of the dinuclear complexes $Co_2(CO)_8$ and of $Fe_2(CO)_9$[21] the method has allowed us to demonstrate that the similarity between the molecular arrangements in the crystals of the two species arises from the stereoactivity of the lone pairs on the Co-species which occupy the space taken by the two additional carbonyl ligands in the structure of the Fe-complex.

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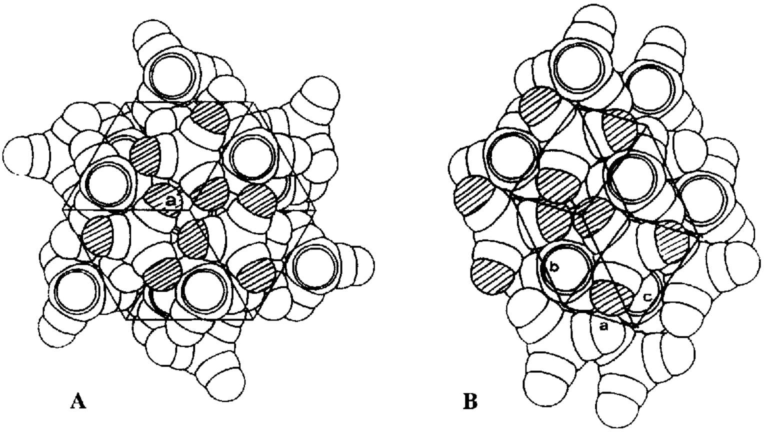

FIGURE 2 (a) The packing in the experimental crystal structure of $Ni(CO)_4$; (b) a projection down the *pseudo* three-fold symmetry axis in the calculated crystal structure of $Ni(CO)_4$. Note the similarity to the observed structure.

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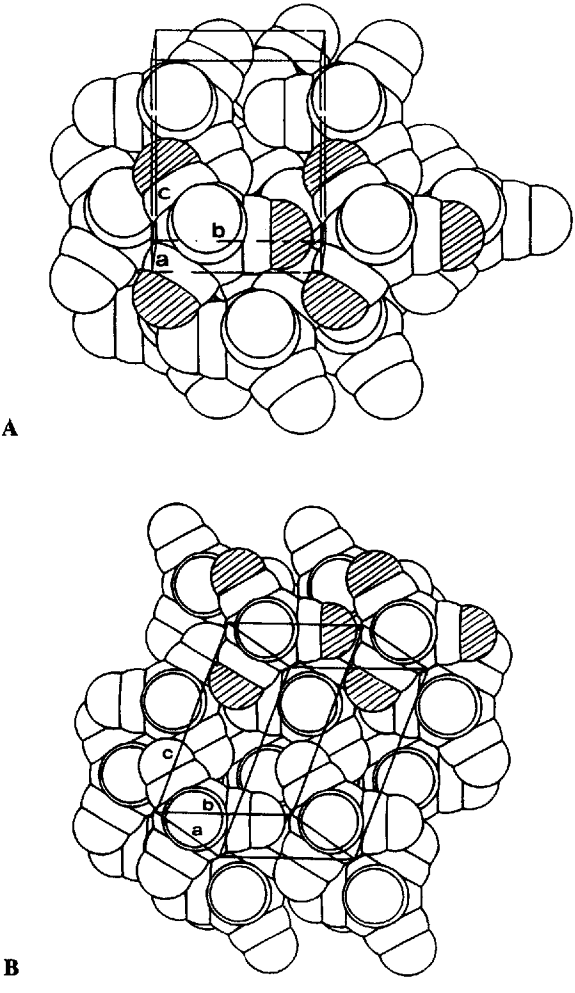

FIGURE 3 (a) The crystal structure of $Fe(CO)_5$: each molecule is surrounded by twelve next neighbors; (b) calculated crystal structure of $Fe(CO)_5$: the structure retraces the observed crystal structure.

When the approach is extended to higher nuclearity complexes, however, the limitations inherent to the description of the metal atoms become more and more severe. In the case of crystalline $Fe_3(CO)_{12}$[22a] and $Ru_3(CO)_{12}$ [22b] the experimental crystal structures could also be retraced and compared with other theoretical ones, although the PPE of the theoretical crystals were invariably higher than the expected range (see Table IV). Theoretical and experimental structures are compared in Figs. 5 to 6 for Fe and Ru clusters.

Lattice energy minimization starting from random molecular arrangements have also been successfully used to generate unknown crystal structures of some metallocene and substituted metallocene complexes.[25] In all cases, however, rigid molecules were used as input. The lack of a sufficiently general intramolecular force field and the necessity of combining and scaling intramolecular versus intermolecular energy terms represent, at present, the limit of organometallic crystal structure generation procedures.

We reckon that, besides the interest in theoretical crystal structure generation, there is scope in studying how molecules can be linked together in the solid by optimizing intermolecular cohesion even if confined to oligomolecular units. In doing so we gain access to information on the factors responsible for crystal stability and cohesion as well as on the interplay between molecular shape and crystal organization.

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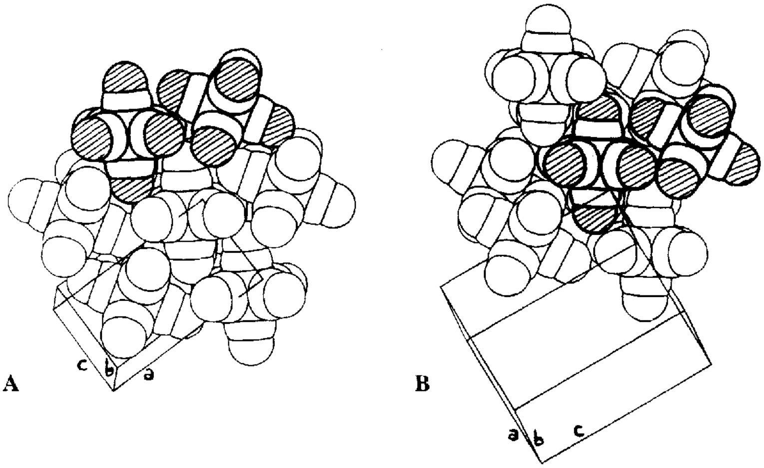

FIGURE 4 (a) Space-filling representation of the experimental crystal structure of $Cr(CO)_6$; (b) calculated crystals structure of $Cr(CO)_6$.

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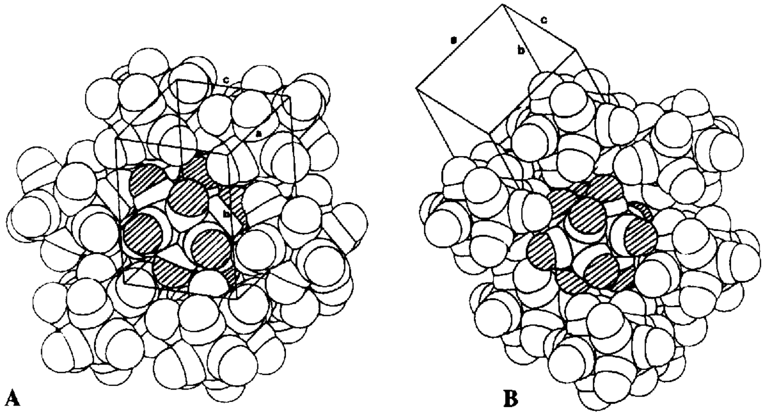

FIGURE 5 (a) The ideally ordered monoclinic P2_1 crystal obtained from the experimental structure of $Fe_3(CO)_{12}$ by "removing" the center of inversion; (b) intermolecular interlocking and molecular arrangement in the theoretical crystal structure of $Fe_3(CO)_{12}$ in space group P$\bar{1}$.

ORGANIC–ORGANOMETALLIC CRYSTAL ENGINEERING: SOME EXAMPLES

As mentioned in the Introduction, the idea of constructing crystalline materials with predefined molecular arrangements is attracting much interest because of the potentialities in materials chemistry. The objective of this section is that of providing examples, coming from our own work as well as from that of other authors, of the enormous potential of organic–organometallic crystal engineering as a means to *combine* structural and chemical features of molecules in the two fields. Most of the work done in the field of molecular crystal engineering is in the domain of organic chemistry, whereas solid state organometallic chemistry is still a mostly uncharted territory.

The examples selected for this section all take advantage of hydrogen bonds, mainly of the O–H——O, N–H——O, and N–H——N types, but also of the C–H——O type. These interactions are at least an order of magnitude stronger than any van der Waals interaction and are directional.[26] Strength and directionality allow *desk modelling* of supramolecular aggregates formed by molecules carrying adequately chosen donor and acceptor groups.[27]

In devising organic–organometallic crystals we have utilized two basic concepts of molecular modelling: (i) the "shape analogy" between organic molecules and those organometallic molecules which carry the same organic fragments as ligands and (ii) the complementarity role of strong and directional hydrogen bonds (such as O–H——O) to selectively and tightly link together organic molecules and of diffuse networks of weak C–H——O hydrogen bonds and anion–cation interactions to link the organic and organometallic fragments in the crystal. The organic–organometallic shape analogy concept is chiefly the recognition that solid state interactions between molecules or ions are governed by the type and distribution of peripheral atoms, with marginal contribution from the atoms "inside" which are screened from the surroundings. Hence, molecules with similar shape and size are organized in the solid state in similar manner irrespective of the chemical composition. A good example of "shape analogy" is afforded by the close similarity between the crystal structures of benzene and dibenzene chromium.[23b] Both crystal structures are based on herring bone patterns that allow C–H——ring interactions to be maximized, as shown in Fig. 7.

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Interesting results of supramolecular solid state chemistry have been recently obtained by Walther and collaborators who have been able to isolate bis(alkyne)Ni(0) complexes thanks to the stabilization afforded in the solid state by hydrogen bonds between alkynediol and alkynol groups.[28] Complementary triple hydrogen bonds have been employed by Mingos *et al.* to synthesize bifunctional transition metal complexes that could be co-crystallized with organic bases in order to construct solid-state sheet and tape structures.[29] It has recently been pointed out that the supramolecular concept is effectively a bridge between organic, inorganic and organometallic crystal chemistry.[30]

We have recently reported the results of our design of supramolecular aggregates between the paramagnetic cations $[(\eta^6\text{-arene})_2\text{Cr}]^+$ (arene = benzene and toluene) and the 1,3-cyclohexane-dione (CHD) with the participation of water in the intermolecular hydrogen bonding patterns. The aggregation of the CHD system in super-anions and/or in extended hydrated aggregates is based on strong hydrogen bonds, whereas the interaction between organic aggregates and the organometallic complexes is based on weak C–H——O hydrogen bonds reinforced by the different polarity. The synthetic idea behind this "crystal synthesis" stems from the recognition that C–H——O interactions, though "soft" in comparison to hard O–H——O and

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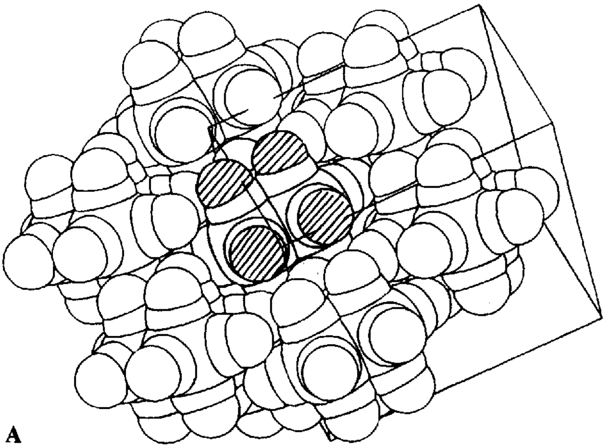

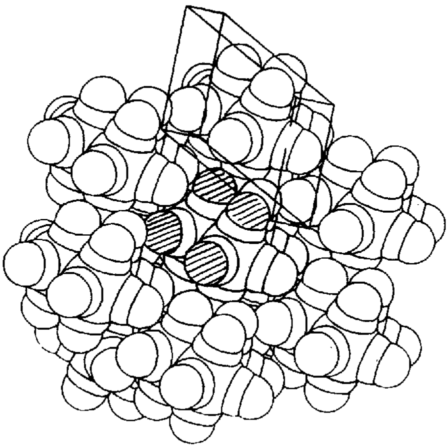

FIGURE 6 (a) The monoclinic $P2_1/n$ crystal obtained from the experimental structure of $Ru_3(CO)_{12}$; (b) calculated crystal structure of $Ru_3(CO)_{12}$ in space group $P2_12_12_1$.

N–H——O bonds, can be determinant for crystal cohesion because of the profusion of C–H donors carried by the ligands in organometallic molecules and of acceptors, such as the CO ligand in its various modes of bonding.

The crystal of the hydroxide $[(C_6H_6)_2Cr][OH]\cdot 3H_2O$ shows the importance of C–H——O_{water} interactions and affords a remarkable example of the supermolecule–crystal analogy: the non-covalent aggregation of water and of two simple ions such as OH^- and $[(C_6H_6)_2Cr]^+$ generates a highly specialized superstructure in which layers of opposite sign alternate and result in a system with *sides* of completely different chemical composition. The hydrated hydroxide is constituted of a stacking sequence of layers containing $[(C_6H_6)_2Cr]^+$ cations intercalated with layers of water molecules and OH^- groups (see Fig. 8a). The $\{[OH]\cdot 3H_2O\}_n$ layer is formed of a slightly puckered hexagonal network containing three water molecules and one OH^- group per formula unit, with the O-atoms hydrogen bonded to three neighbors. The interlayer link is provided by three C–H——O interactions between each crystallographically independent oxygen atom and the benzene ligands above and below the hydrated layers.

The structure of the hydrated $[(C_6H_6)_2Cr][CHD]\cdot 3H_2O$ salt is strictly related to that of the hydroxide $[(C_6H_6)_2Cr][OH]\cdot 3H_2O$. The CHD system terminates the hexagonal water layers via O(water)H——O(CHD) links. The resulting packing arrangement is reminiscent of that of the hydroxide, being composed of a stacking sequence of cations and of strings containing water and CHD^- anions (see Fig. 8b).

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CONCLUSIONS AND FUTURE PERSPECTIVES

With this paper, rather than discussing specific scientific results, we have tried to show to the reader a way of planning his/her research project in organometallic crystal engineering. The crystal engineer is a chemist with an interdisciplinary background ranging from organometallic synthesis to crystallography and computational chemistry. The synthetic strategy needs first to be planned via computer graphics, modelling, and database analysis; then supermolecules and solids are produced and the crop characterized by solid state spectroscopic and diffraction techniques, such as solid state NMR, variable temperature X-ray diffraction, neutron diffraction, EXAFS, IR and Raman. The second stage requires selection and test of the "best" materials in terms of solid state properties including non-linear optical behavior, conductivity, etc.; solid-state reactivity, gas-uptake, bulk–surface relationship, nucleation and crystal growth can also be investigated. At the same time, rationalization of molecular and crystal structures can be attempted via computational methods so that new syn-

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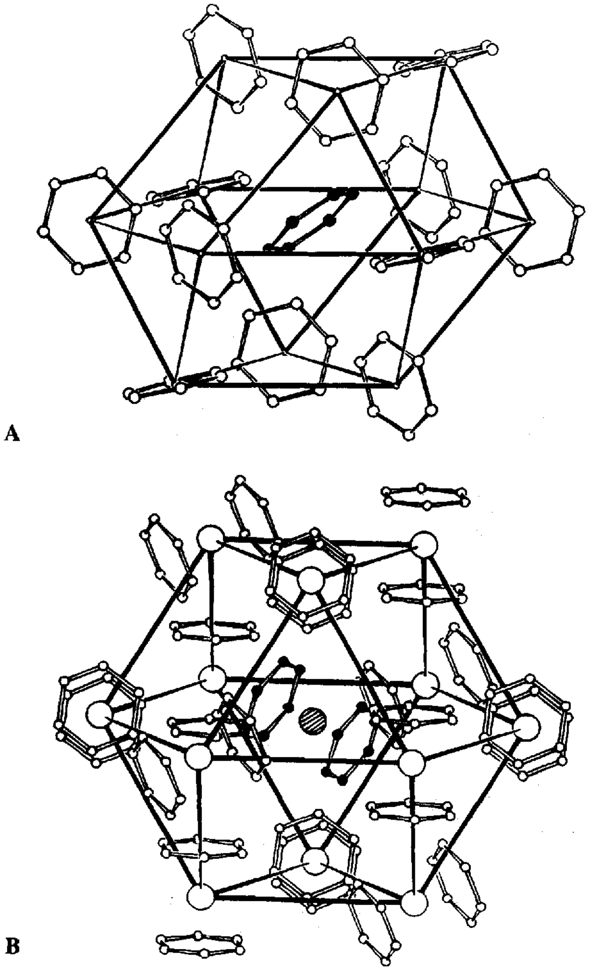

FIGURE 7 Comparison of the arrangements in crystals of (a) benzene and of (b) bis-benzene chromium. Note how the molecules are distributed in a similar way around the molecule chosen for reference.

thetic strategies can be planned. This type of approach has many possible applications. Indeed, the same way of thinking can be extended to other systems such as *bio*-organometallic crystal engineering: for example, the interaction between metal complexes and natural amino acids may be exploited to build new aggregates in chiral space groups.

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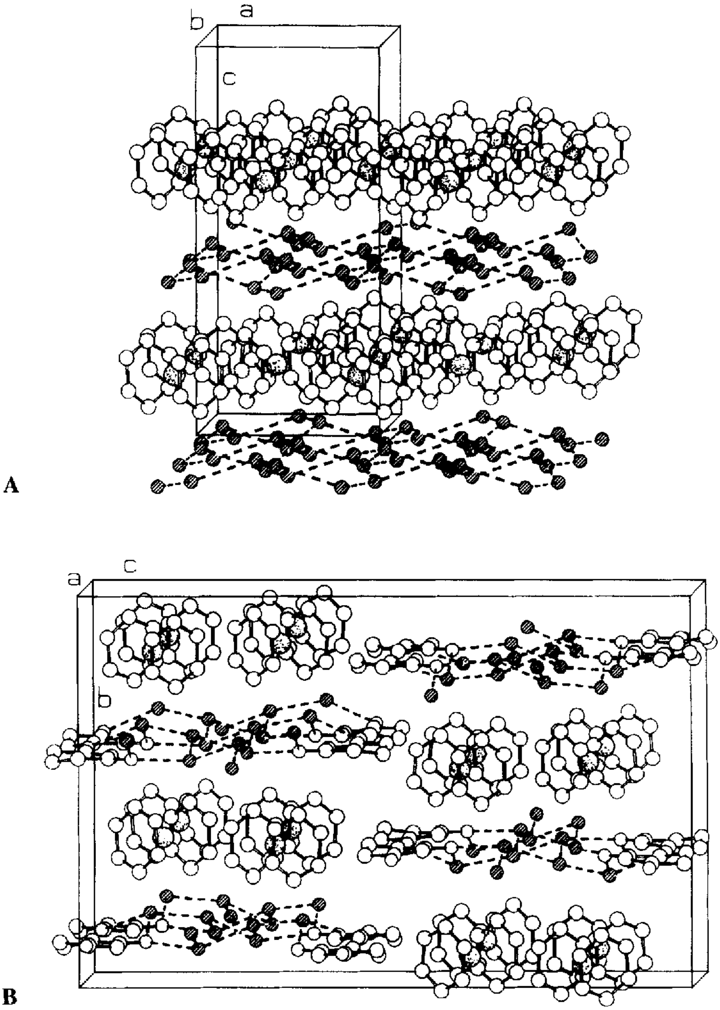

FIGURE 8 (a) Ball and stick representation of the stacking along the *c*-axis in crystalline $[(\eta^6\text{-}C_6H_6)_2Cr]$ [OH]·$3H_2O$: (b) the stacking along the *a*-axis in crystalline $[(\eta^6\text{-}C_6H_6)_2Cr]$ [CHD]·$3H_2O$. Dashed atoms represent O_{water} atoms.

The master key interaction in crystal engineering is hydrogen bonding. Hydrogen bonds are sufficiently strong and directional as to allow choice of intermolecular patterns, co-crystallization of organometallic and organic molecules via complementary hydrogen bonding, use of chiral organometalllic partners to prepare non-centrosymmetric crystals for NLO studies.

However, if hydrogen bonds are also the most facile way to crystal engineering, there are many areas to which the imagination of the experimentalist may lead. For example the crystallization in varied conditions of pressure, temperature, solvents of the same species to attain different packing arrangements, hence the study of conformational polymorphism of organometallic molecules, in the case of molecules possessing extensive structural freedom of having higly fluxional behavior in solution, is almost completely unexplored.

The construction of nanoporous and channeled compounds where stiff organic frameworks are combined with strong hydrogen bonding links may bring within the crystal architecture electron deficient metal atoms or metals with vacant coordination sites for coordination of gas molecules. This may lead to monitoring via IR or NMR or other physical means of gas uptake, i.e., to the utilization of organometallic solids as gas sensors and/or to the study of solid state reactivity in microenvironments.

Finally, this approach can be exploited to prepare bioinorganic and bio-organometallic cocrystals by means of crystallization of functionalized molecules carrying different metal atoms, heterometallic cocrystals involving transition metal cluster complexes of high nuclearity, small metalloproteins and peptides, cocrystallization of van der Waals solids based on shape and size analogy *viz.* neutral complexes possessing similar outer ligand distribution but with different metallic cores.

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References

1. (a) Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647. (b) Sharma, C. V. K.; Desiraju, G. R. in *Perspective in Supramolecular Chemistry. The Crystal as a Supramolecular Entity*, Ed. Desiraju, G. D., Wiley, **1996**. (c) Etter M. C. *Acc. Chem. Res.* **1990**, *23*, 120. (d) Braga, D.; Grepioni, F. *Acc. Chem. Res.* **1994**, *27*, 51.
2. (a) Lehn, J.-M.; Mascal, M.; Fisher, J. *J. Chem. Soc. Chem. Commun.* **1990**, 479; (b) Whitesides, G. M.,; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37. (c) Etter, M. C. *J. Amer. Chem. Soc.* **1982**, *104*, 1095.
3. For an overview of recent results see Braga, D.; Grepioni, F. *J. Chem. Soc. Chem. Commun.* **1996**, 571.
4. Braga D. *Chem. Rev.* **1992**, *92*, 369.
5. For a recent (and brilliantly written!) overview of polymorphism see Dunitz, J.; Bernstein, J. *Acc. Chem. Res.* **1995**, *28*, 193 and references therein.
6. Some entry points: (a) Marks, T. J.; Ratner, M. A. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 155; (b) Kanis, D. R.; Ratner, M. A., Marks, T. J. *Chem. Rev.* **1994**, *94*, 195; (c) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Acc. Chem. Res.* **1988**, *21*, 114; (d) Gatteschi, D.; Pardi, L.; Sessoli, R. *Mater. Sci.* **1991**, *17*, 7. (e) Rouxel, J. *Acc. Chem. Res.* **1992**, *25*, 328; (f) Moore, J. S.; Lee, S. *Chemistry and Industry* **1994**, 556. (g) Ghadiri, M. R.; Kobayashi, K.; Granja, J. R.; Chadha, R. K.; McRee, D. E. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 93. (e) Etter M. C. *Acc. Chem. Res.* **1990**, *23*, 120.
7. (a) Subramanian, S.; Zaworotko, M. J. *Coord. Chem. Rev.* **1994**, *137*, 357. (b) Dance. I in *Perspective in Supramolecular Chemistry. The Crystal as a Supramolecular Entity*, Ed. Desiraju, G. D., Wiley, **1996**.
8. Desiraju, G. R. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2311.
9. Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Watson, D. G. *J. Chem. Inf. Comp. Sci.* **1991**, *31*, 204.
10. (a) Braga, D.; Grepioni, F.; Sabatino, P.; Desiraju. G. R. *Organometallics* **1994**, *13*, 3532. (b) Biradha, K.; Desiraju, G. R.; Braga, D.; Grepioni, F. *Organometallics* **1996**. (c) Braga, D.; Biradha, K.; Grepioni, F.; Pedireddi, V. R.; Desiraju, G. R. *J. Am. Chem. Soc.* **1995**, *117*, 3156. (d) Braga, D.; Grepioni, F.; Tedesco, E.; Desiraju. G. R.; Biradha, K. *Organometallics* **1996**, *15*, 1284.
11. (a) Braga, D.; Grepioni, F.; Milne, P.; Parisini, E. *J. Amer. Chem. Soc.* **1993**, *115*, 5115. (b) Braga, D.; Grepioni, F.; Marshall, P.; Parisini, E. *Inorg. Chim. Acta* **1993**, *213*, 121. (c) Braga, D.; Grepioni, F.; Parisini, E. *J. Chem. Soc. Dalton Trans.* **1995**, 287.
12. (a) Kitaigorodsky, A. I. "*Molecular Crystal and Molecules*", Academic Press, New York, 1973; (b) Pertsin, A. J.; Kitaigorodsky, A. I. "*The Atom-Atom Potential Method*", Springer-Verlag, Berlin **1987**; (c) Gavezzotti, A.; Simonetta, M. *Chem. Rev.* **1981**, *82*, 1.
13. (a) Gavezzotti, A.; Filippini, G. *Acta Crystallogr. Sect. B* **1993**, *B49*, 868. (b) Gavezzotti, A.; Filippini, G. *J. Am. Chem. Soc.* **1995**, *117*, 12299.
14. Gavezzotti, A. **OPEC**, "*Organic Packing Potential Energy Calculations*", University of Milano, Italy; see also Gavezzotti, A. *J. Amer. Chem. Soc.* **1983**, *195*, 5220.
15. Braga, D.; Grepioni, F.; Sabatino, P. *J. Chem. Soc. Dalton Trans.* **1990**, 3137.
16. Braga, D.; Grepioni, F. *Organometallics* **1992**, *11*, 711.
17. Gavezzotti, A. *Acc. Chem. Res.* **1994**, *27*, 309. (b) Gdanitz, R. J. *Chem. Phys. Lett.* **1992**, *190*, 391.
18. Williams, D. E. **PCK83**, "*A Crystal Molecular Packing Analysis Program*", Quantum Chemistry Program Exchange n. 481, Indiana University, Bloomington, Indiana, USA. Gavezzotti, A. **PROMET** "*A Program for the Generation of Possible Crystal*

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Structures from the Molecular Structure of Organic Compounds", Gavezzotti, A. *J. Am. Chem. Soc.* **1991**, *113*, 4622.

19. Braga, D.; Grepioni, F.; Orpen, A. G. *Organometallics* **1994**, *13*, 3544.
20. Braga, D.; Grepioni, F.; Tedesco, E.; Orpen, A. G. *J. Chem. Soc. Dalton Trans.* **1995**, 1215.
21. Braga, D.; Grepioni, F.; Sabatino, P.; Gavezzotti, A. *J. Chem. Soc. Dalton Trans.* **1992**, 1185.
22. (a) Braga, D.; Calhorda, M. J.; Grepioni, F.; Lopes, P.; Tedesco, E. *J. Chem. Soc. Dalton Trans.* **1995**, 1215. (b) Braga, D.; Grepioni, F.; Tedesco, E.; Dyson, P. J.; Martin, C. M.; Johnson, B. F. G. *Trans. Met. Chem.* **1995**, *20*, 615.
23. Braga, D.; Grepioni, F. *Organometallics* **1991**, *10*, 2563.
24. (a) Scaringe, R. P. in "*Electron Cyrstallography of Organic Molecules*", NATO ASI Series, Edt.s Fryer, J. R.; Dorset, D. L. Kluwer Academic Publishers, Dordrech, **1991**, pp. 85. (b) Baur, W. H.; Kassner, D. *Acta Cryst. Sect. B* **1992**, *B48*, 356.
25. Schmidt, M. U.; Englert, U. *J. Chem. Soc. Dalton Trans.* **1996**, 2077.
26. (a) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures* Springer-Verlag, Berlin, **1991**. (b) Bernstein, J.; Davis, R. E.; Shimoni, L.; Chang, N.-L. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1555. (c) *Structure Correlation*, Bürgi, H.-B.; Dunitz, J. D. Ed.s, ch. 11, p. 431–500, VCH, Weinheim, **1994.** (d) Brammer, L.; Zhao, D.; Ladipo, F. T.; Braddock-Wilking, J. *Acta Cryst. Sect. B* **1995**, *B51*, 632. (e) Aakeröy, C. B.; Seddon, K. R. *Chem. Soc. Rev.* **1993**, 397.
27. see for example (a) Shekhar Reddy, D.; Craig, D. C.; Desiraju, R. G. *J. Amer. Chem. Soc.* **1996**, *118*, 4090. (b) Shekhar Reddy, D.; Ovchinnikov, Y. E.; Shishkin, O. V.; Struchov, Y. T.; Desiraju, R. G. *J. Amer. Chem. Soc.* **1996**, *118*, 4085.
28. Walther, D.; Klettke, T.; Schmidt, A.; Görls, H.; Imhof, W. *Organometallics* **1966**, *15*, 2314.
29. Burrows, A. D.; Chan, C.-W.; Chowdry, M. M.; McGrady, J. E.; Mingos, D. M. P., *Chem. Soc. Rev.* **1995**, 329.
30. Desiraju, G. R. *J. Mol. Struc.* **1996**, *374*, 191.
31. Braga, D.; Grepioni, F.; Byrne, J. J.; Wolf, A. *J. Chem. Soc. Chem. Commun.* **1995**, 1023.
32. Braga, D.; Costa, A. L.; Grepioni, F.; Scaccianoce, L.; Tagliavini, E. *Organometallics* **1996**,*15*,1084.

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