A Novel Characterisation of Organic Molecular Crystal Structures for the Purpose of Crystal Engineering

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Summary of System of Classification used for Molecular Based Cells (MBC)

1. Main Elements

MBC are formed in all planes within close-packed blocks (CPB).

A fundamental criterion is whether an MBC is of **Type 1** or **Type 2**.

For **Type 1**, glide-plane symmetry is operative, or alternatively pseudo-glide-plane symmetry applies, so that there are generally two MBC per unit cell cross-sectional area. In the former case, glide planes extend throughout the crystal, so that this symmetry applies to all MBC. In the latter case, glide planes are absent. However, in special planes of high symmetry, the two MBC are related to each by symmetry characteristic of a glide-plane, hence the terminology "pseudo glide-plane".

For **Type 2**, there is only one MBC per unit cell cross-sectional area.

Further information about the MBC is conveyed within round brackets, e.g. 1(α) or 1(α2). An important function of these symbols is to define an anchor-point in the earlier work of Desiraju & Gavezzotti (1989*a*,*b*). However, they also correlate with the geometrical characteristics of the MBC, as set out in Table 1.

Table 1. Information conveyed within the round brackets of MBC Symbols

Symbol	Description employed by Desiraju & Gavezzotti	MBC characteristics
α	herringbone	MBC Type 1 1 molecule per MBC. For *c* glide-planes, lattice translations $\parallel y$ are exploited to form MBC.
α2	sandwich herringbone	MBC Type 1 The number "2" here denotes that there are molecules per MBC. **(The number "2" may also be applied to β,γ or δ structures.)** For *c* glide-planes, lattice translations $\parallel y$ are exploited to form MBC.
γ	flattened-out herringbone	MBC Type 1 1 Molecule per MBC For *c* glide-planes, lattice translations $\parallel y$ are exploited to form MBC, as for α or α2, but the vertices translated lead to elongated MBC.
δ or δ2	Not used by Desiraju & Gavezzotti	MBC Type 1. For *c* glide-planes, lattice translations $\parallel z$ are exploited to form MBC. δ: 1 molecule per MBC; δ2: 2 molecules per MBC
||	Not used by Desiraju & Gavezzotti	An exceptional case where MBC are parallelograms instead of hexagons

The β-structural type, which was described by Desiraju and Gavezzotti as a layered structure, is associated with MBC of both Type 1 and Type 2. Definitive for a β-structure is the existence of a short unit cell axis of length ≈ 4 Å. This axis is identified by a superscript to the number 1 or 2 identifying

MBC Type. For example, the symbol $1^{\beta y}(\alpha 2)$ denotes a pair of molecules occupying an MBC of Type 1. The short axis definitive for the β structure is along y.

This superscript position may also be used in order to convey the existence of pseudo-glide, as opposed to true glide symmetry. The symbol used for this purpose is ±A. This signifies that the areas of the two MBC in the unit cell cross-section are not constrained to be equal to each other, except in the special high-symmetry planes of apparent glide symmetry.

The above notation would be complete for a consideration of polynuclear aromatic hydrocarbons (PAH) alone, which are associated exclusively with MBC of Type 1. The consideration of substituted anthracenes and anthraquinones (SAA), however, demands the definition of a new type of MBC, Type 2, which is associated almost exclusively with β-structures. Since both in-plane lattice translations are exploited in forming the MBC, the symbol ⊥ or ∠ is used to denote whether the angle between the two lattice vectors is 90° or <90°, respectively.

2. Symbols used to denote exceptional structural features

The symbols listed in this section serve to highlight exceptional structural features. They have been used in an *ad hoc* fashion.

In the exceptional case of SAA structure NTRANT01, use of the symbol ε in combination with ∠ denotes an angle of >90° between the two lattice vectors forming the MBC.

In the exceptional cases of SAA structures CANTRQ01 and BANTRQ01, the letters "JZ" denote that an MBC type of structure arises in a junction zone, rather than in a close-packed block (CPB).

The subscript "gl" used for BBCP derivatives of Crystal Structure B, as in $1^{\pm A}(\alpha)_{gl}$, denotes that true glide symmetry is operative in combination with the ±A characteristic. This is made possible by there being *four* molecules per unit cell cross-section.