

5-Oxatricyclo[5.1.0.0^{1,3}]octan-4-one, containing an enantiomorph and a racemate and not two polymorphs, is another example of a composite crystal

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This new example of a composite crystal adds to the small number previously reported among inorganic and molecular materials. Revision of the nomenclature used allows more fruitful comparison with the precedents.

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Composite crystals are formed by the ordered agglutination¹ of crystals of the same or different type; a presumed requirement is a close resemblance between the structures of the types. Alum provides one early example, quartz another. Perhaps the first recognized example among *molecular* crystals is hexabromobenzene; here the [010] axes of the two portions are parallel and there is agglutination of (001) and (301) planes, and of (100) and (10 $\bar{1}$) planes [*Composite hexabromobenzene crystals*, Boonstra & Herbstein (1963), who give references to earlier work and discuss the differences between agglutination and twinning]. Another possible example occurs with the triclinic β phase (stable above 304 K) of *p*-dichlorobenzene, for which Reynolds (1977) reported the formation of ‘bicrystals’ in about 5% of his samples (his Table 1). Only one type of crystal structure is present in these examples. A third example may well be the ‘hybrid’ made up of the two polymorphs of D,L-homocysteine thiolactone hydrochloride (Freer & Kraut, 1965); it was noted that “the *Pbca* and *Pbc2*₁ domains of the ‘hybrid’ crystals scatter X-rays independently but have their corresponding unit-cell axes oriented in the same directions”.

The structure of 5-oxatricyclo[5.1.0.0^{1,3}]octan-4-one has been reported as solved from a composite crystal containing two polymorphs (Yufit *et al.*, 2002); a ‘tiny’ single crystal of polymorph *A* has also been found (de Meijere *et al.*, 2002). The cell dimensions of the two polymorphs are very similar (our Table 1) and they have similar structures, described as follows (Yufit *et al.*, 2002): “In crystals of both modifications, molecules of [C₇H₈O₂] form loose layers, perpendicular to the [001] direction. The layers are almost identical in [the] structures of the orthorhombic (*A*) and

monoclinic (*B*) forms. However, in structure *A* the molecules of the next layer are connected to the molecules of the original layer by twofold [screw?]² axes, and in structure *B* by a *c*-glide plane. This means that structures *A* and *B* differ only by arrangement of the layers and can be regarded as polytypes”. Yufit *et al.* (2002) provide a summarizing sentence: “In the case of structure (1) [the ‘hybrid’] we are not dealing with a ‘classical’ composite crystal where both lattices are interpenetrating, but rather with a crystal containing domains of two different types corresponding to different polymorphs (polytypes, see below)”.

The resemblance to the quotation from Freer & Kraut (1965) [not referenced by Yufit *et al.* (2002)] is striking, and so there are now two examples where the agglutinated crystals are of different types. However, Yufit *et al.* (2002) used ‘polymorph’ and ‘polytype’ in ways not conforming to the usual definitions of these terms [for ‘polymorph’ see Bernstein (2002) while ‘polytypism’ is defined as ‘a special form of polymorphism that is one-dimensional and is shown by certain close-packed and layered structures, the variation occurs because identical layers of structure may be stacked in different sequences’ (Morris, 1992)]. Structure *A* is an enantiomorph, spontaneous resolution of the chiral molecules having taken place on crystallization; structure *B* is a racemate with both enantiomers crystallizing together in an ordered array. The distinction is emphasized by the fact that the layers in *A* are related by a symmetry element of the first kind (and hence are congruent), while those in *B* are related by a symmetry element of the second kind and are enantiomeric. *A* and *B* are *not* distinguished by different arrangements of *identical* layers, and should not be described as ‘polytypes’. The [010] axes of *A* and *B* are parallel, while the relation of their **a*** and **c*** axes is shown in Fig. 1

¹ ‘Agglutination’ (sticking together) is used as an overall descriptive term, without implying a particular mechanism.

² *P*₂*1**2*₁ does not have twofold axes.

Table 1
Cell dimensions (Å, °) for the *A* and *B* modifications of 5-oxatricyclo-[5.1.0.0^{1,3}]octan-4-one.

Crystal	<i>a</i>	<i>b</i> , β	<i>c</i>	Space group	<i>Z</i>
C ₇ H ₈ O ₂ - <i>A</i> enantiomer	9.9644 (8)	8.1854 (7)	7.4422 (6)	<i>P</i> 2 ₁ 2 ₁ 2 ₁	4
C ₇ H ₈ O ₂ - <i>B</i> racemate	9.9533 (8)	8.1831 (7), 108.61 (2)	7.8129 (6)†	<i>P</i> 2 ₁ / <i>c</i>	4

† $c \sin \beta = 7.4044 \text{ \AA}$.

of Yufit *et al.* (2002). The Freer–Kraut and Yufit examples differ in that the first contains agglutinated polymorphs, while the second is composed of an agglutinated enantiomorph and racemate.

Agglutination (and not twinning) clearly occurs in D,L-homocysteine thiolactone hydrochloride ('corresponding unit-cell axes oriented in the same directions') and in hexabromobenzene and 5-oxatricyclo-[5.1.0.0^{1,3}]octan-4-one ([010] axes of the two portions are parallel for both), but the

situation in γ -*p*-dichlorobenzene is not nearly as well established.

Note added in proof: Another apparent example has recently been reported by Atwood *et al.* (2002). A composite (single) crystal of composition {[*p*-*t*-butyl-calix[4]arene]-[*p*-*t*-butyl-calix[4]arene·0.60(vinyl bromide)]} was obtained by immersing the calixarene in vinyl bromide at 268 K for 10 min. Both materials 'coexist in the crystal and, owing to their similar lattice parameters, give rise to overlapping diffraction

patterns' (quote from footnote 20 of Atwood *et al.*, 2002).

References

- Atwood, J. L., Barbour, L. J., Jerga, A. & Schottel, A. (2002). *Science*, **298**, 1000–1002.
- Bernstein, J. (2002). *Polymorphism in Molecular Crystals*, pp. 2–8. Oxford: Clarendon Press.
- Boonstra, E. G. & Herbstein, F. H. (1963). *Acta Cryst.* **16**, 252–255.
- Freer, S. T. & Kraut, J. (1965). *Acta Cryst.* **19**, 992–1002.
- Meijere, A. de, Khlebnikov, A. F., Kozhushkov, S. I., Kostikov, R. R., Schreiner, P. R., Wittkopp, A., Rinderspacher, C., Menzel, H., Yufit, D. S. & Howard, J. A. K. (2002). *Chem. Eur. J.* **8**, 828–842.
- Morris, C. (1992). Editor. *Academic Press Dictionary of Science and Technology*, p. 1694. San Diego: Academic Press.
- Reynolds, P. A. (1977). *Acta Cryst.* **A33**, 185–191.
- Yufit, D. S., Kozhushkov, S. I., Howard, J. A. K. & de Meijere, A. (2002). *Acta Cryst.* **B58**, 673–676.