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Packing Analysis for Reactive Crystals

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PACKING ANALYSIS FOR REACTIVE CRYSTALS

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Abstract A technique for the analysis of packing density in crystals is presented, based on simple and intuitive models of molecular structure.

Quantum mechanics can in principle give a full description of the electronic structure of an infinite crystal. If the solid is such that discrete molecular entities can be recognized, it may be useful to reduce this description to a superposition of intermolecular effects. These in turn may be reduced to atom-atom non-bonded empirical potentials, which have met a considerable success in the calculation of many properties of molecular solids. The ultimate approximation consists in describing atoms and molecules as mere envelopes of electrons, that is reducing quantum mechanics to molecular volume and shape. These concepts have been fruitfully exploited in many fields of chemistry and biochemistry. In what concerns crystal chemistry, the idea that molecular shape leads to mutual recognition has given rise to the close-packing principle, stating that a crystalline edifice is built so as to leave as little free space as possible[1].

Volume and shape somehow define a sort of molecular 'valence' (i.e., ability to coordinate other molecules) whose theory is far from the sophistication of the intramolecular valence theory. Partial quantification of this idea comes from the non-bonded potentials; some aspects of this volume/shape/cohesion energy connection have been examined[2]:

$$\text{cohesion en.(Kcal/mol)} \simeq 0.1 \text{ mol.volume } (\text{Å}^3)$$

Notable exceptions to this rule of thumb come from twisted or folded molecules (a shape effect), besides of course those crystalline systems for which the non-bonded potentials are not accurate - such cases falling mostly under the broad definition of partially ionic crystals.

If and how the elements of this schematic discussion apply to crystal reactivity is the main concern of this note. One obvious requirement for a reaction to occur in a molecular solid is that either a bond breaking with subsequent disproportionation or recombination of fragments occur, such as is the case in many photochemical radicalizations, or that the molecules packed in the crystal carry in their structure both termini of the reaction process, such as is the case in intermolecular dimerizations or cyclizations. These factors and their energetics are to be analyzed by the usual theories of molecular electronic structure. In order to examine the special elements of solid-state reactivity, one might start from the hypothesis that the same factors which, when present, make a crystal stable, should make it unstable when absent.

This does not imply that a crystal must be loosely bound or low-melting in order to be reactive: packing coefficients for many organic crystals, including reactive ones, have been calculated[2], and found to bear no specific relationship to reactivity. The peculiarity of solid-state reactions is spatial orientation - a concept merging with that of topochemistry - so that one possibility is that reactivity is favored, if not entirely originated, by local and specifically oriented breakdowns of the close-packing principle. The crystal packing should then be analyzed to spot such features. The ideal cases in which this method applies are those reactions that involve large displacements of molecular fragments in the initial stages; at the other extreme are cases in which proper juxtaposition of reaction termini causes reaction with little or no displacement.

Close packing can be analyzed in the very simple terms of space occupation by molecules made of rigid spheres of given radius. Each point in cell space, described by a vector $\underline{s}$, can be either inside or outside one or more of the atomic spheres. By sampling the cell space by systematic variation of $\underline{s}$, all points in the cell or in a given zone of the cell can accordingly be labelled as either free or occupied. If the number of free and occupied points is N_{free} and N_{occ}, respectively, the total occupied volume in the cell (or in a given zone of the cell) can be computed as:

$$V_{occ} = V_C \frac{N_{occ}}{N_{occ} + N_{free}}$$

where V_C is the total volume of the explored zone; the packing coefficient is then

$$C_K = V_{occ} / V_C$$

If only a zone is explored, this number may be called the packing density in that zone. Typically, 1000 points/Å^3 must be explored to reach a good accuracy.

Packing density maps can be obtained by dividing the cell space in a number of zones, and calculating the packing density in each zone. Cell zones about 0.5-1.0 Å^3 wide are used. This allows a prompt visualization of local breakdowns of close packing, in the form of cavities or channels of free space. Two examples of this analysis, carried out in critical zones of reactive crystals, are shown in Figures 1 and 2.

The total volume of a hole can be computed as

$$V_{hole} = \sum_{i,hole} V_i(1 - D_i)$$

where V_i is the volume of zone i, within the hole, and D_i is the packing density. This calculation can be important in cases in which small product molecules form during the reaction, since the hole volume indicates whether or not the guest molecule

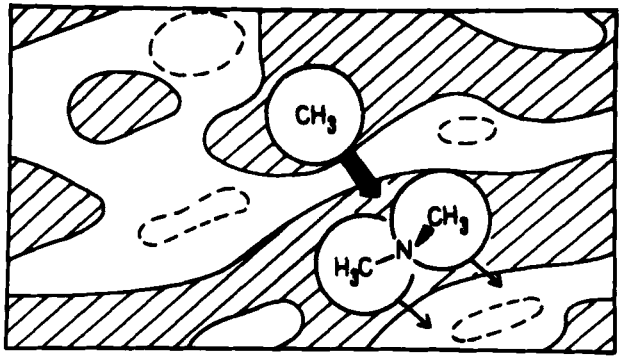

FIGURE 1. Packing density map for section z=0.435 in methyl p-dimethylaminobenzenesulphonate (Bergman et al.,J.Am.Chem.Soc.99,851(1977)). Broken lines contour zones with density < 0.1. Loose packing around ester methyl group is evident; the amino methyl group bends back as reaction proceeds.

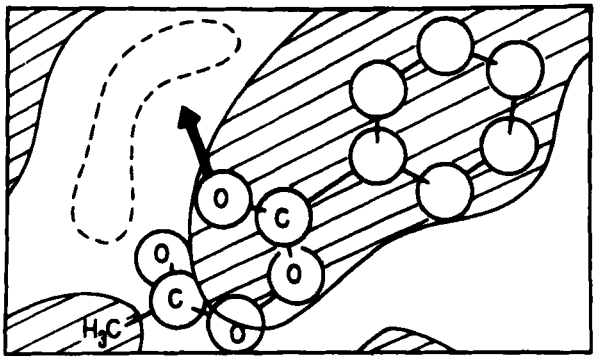

FIGURE 2. Section y=0.25 of the map for acetylbenzoylperoxide (McBride et al.,J.Am.Chem.Soc.97, 6729(1975)). Benzoyl radical rotation in its plane after O-O bond breaking is favored by free space.

can be hosted in the crystalline lattice. Applications of the above technique to various cases of crystal reactivity have been carried out with encouraging results; work in this direction is in full progress in our laboratory.

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