Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Angelo Gavezzotti [a]

[a] Dipartimento di Chimica Fisica ed Elettrochimica e Centre CNR, Università di Milano, Milano, Italy

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THEORETICAL STUDIES OF MOLECULAR MOTIONS AND REACTIVITY IN ORGANIC CRYSTALS

ANGELO GAVEZZOTTI
Dipartimento di Chimica Fisica ed Elettrochimica e Centro CNR, Università di Milano, Milano, Italy

Traditionally, chemists have thought of crystals as chemical systems lying in deep free energy wells with little or no chances of significant chemical evolution. It seemed obvious that the potential for transformation of a given substance could be exploited only in solution where the apparently indispensable freedom of molecular motion could be restored.

This view is now changing as subtler goals, like chiral synthesis or high synthetic selectivity, are pursued and, especially, as emphasis in chemical processes is shifting at least in part to the physical properties of organic solids as materials. Hence the desirable properties of solid substances are being engineered much as in the past decades molecular properties were. Practical applications to organic conductors, optoelectronics and other branches of materials science are foreseen. Thus, the organic solid state chemist has to work his way from molecular structure to the prediction and characterization of the structure and dynamics of the condensed phase. Disorder, static or dynamic, molecular librations and jumps among many potential energy wells and phase transitions are structural phenomena one has to deal with. It now appears that organic crystals exhibit a wide variety of structural instabilities, for which the overall definition "crystal reactions" is perhaps appropriate.

Of course it is well known that chemical reactions involving bond breaking and bond formation also occur in organic crystals. The crystal structure functions in such cases as an active or passive cradle which influences the early stages of reaction and, if in many cases it does hamper advancement of the reaction, in some cases it brings about unexpected selectivity in product formation. One is dealing in such cases with molecular reactivity under an extreme solvent effect.

Both crystal lattice reactivity and molecular reactivity in crystals involve electronic and steric effects. One must further distinguish between intra- and intermolecular factors. The energetics of bond breaking and formation can be described by usual quantum chemical methods - for example, molecular orbital theory. But as one goes from a free molecule to a molecule in a crystal, the molecular orbitals may couple intermolecularly and merge into a band. The amount of coupling depends on intermolecular coordinates such as distances between molecular stacks or angles between molecular planes. This coupling is usually small so that, for instance, low-temperature X-ray crystal structure analysis can provide accurate molecular electron density maps. When strong intermolecular orbital overlap occurs, as in charge-transfer complexes, the crystal electronic band structure can be calculated using basis functions that take into account lattice periodicity (Bloch functions). This topic will not be discussed further here since this communication deals mainly with steric effects.

To discuss the steric effects of crystal reactivity or, according to our previous definition, of structural evolution in crystals, one must first understand lattice stability. Here the concept of close-packing of Kitaigorodski is usually invoked. This is however a principle of broad scope, and more detailed models must be set up to discuss subtler effects. As an example of the study of steric factors

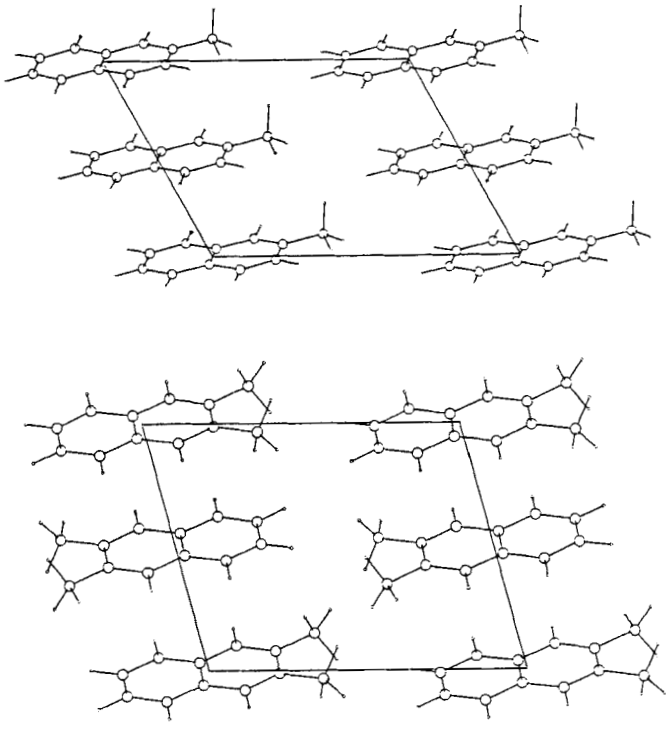
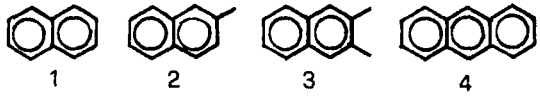


FIGURE 1. Packing diagrams for 2-methylnaphthalene (cell dimensions in ref.1) and 2,3-dimethylnaphthalene, from packing energy optimization (see X-ray structure of dimethyl derivative in ref.2).

in crystal transformations we will describe a comparative study of naphthalene, 2-methylnaphthalene, 2,3-dimethylnaphthalene and anthracene. Figure 1 shows the packing diagrams for the methyl derivatives, which were obtained by optimization of the packing energy, starting from known cell dimensions.



The four compounds 1-4 crystallize in the same space group ($P2_1/c$, Z=2) with the same relative molecular orientation (the so-called herringbone pattern). The cell dimension parallel to the axis of maximum molecular elongation corresponds to the molecular length, other cell parameters being equal. While 1 and 4 form ordered and stable crystals, 2 and 3 do not. We have undertaken a reexamination of the crystal structure of 3, whose behaviour with temperature is peculiar (Destro and Gavezzotti, to be published). A first data set was collected at room T; the structure can be interpreted in terms of strong translational librations on x, or in terms of a distribution of fractional molecules along x (Figure 2). The crystal was then brought to 220 K. Reflections become split making data collection impossible. Back at room T, the data collection was repeated. The results were the same as before cooling. Thus, the effect which produces the splitting is a reversible one, and is such that the disorder is enhanced, rather than reduced, by cooling. Cell dimensions were measured as accurately as possible as a function of temperature: the only significant effect was a shortening of c (by 0.1 Å over 70 K), which may cause some variation in the angle between molecular planes in the crystal.

The type of disorder found for dimethylnaphthalene can be explained by the potential energy curves for the slippage of molecular columns, shown in Figure 3. These curves were obtained starting from the calculated ordered structure in $P2_1$ rather than from the experimental, disordered structure. A reasonable conjecture is that at low temperatures the crystal may consist of two superimposed lattices, somehow generated by a frozen-in translational displacement along the almost flat potential energy

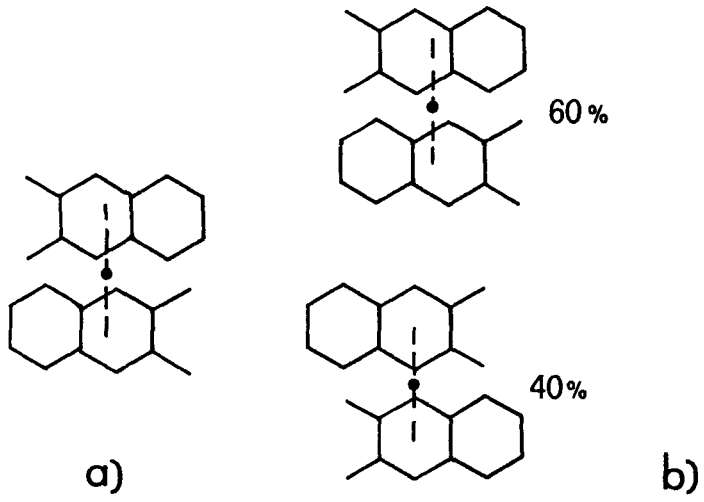


FIGURE 2. The crystal structure of 3: a) model with large translational motion (ref.2); b) model with two fractional sites along x. The black dot is the cell origin. Numbers on the right are site populations.

curve shown in Figure 3. More precise experimental work on this crystal is hampered by the difficulty of obtaining suitable crystals.

The type of motion which was simulated in Figure 3 may be a highly correlated one, as must be all translational motions which do not occur near crystal defects. From the computational point of view, one can simulate molecular motions in crystals by using various approaches to correlation. An example, the rotational motion in naphthalene crystals will illustrate this point. As the central molecule goes through the rotation around its axis of maximum inertia, one may have; a) zero cooperation, whereby the molecule moves in the static field of the surround-

ing, stationary molecules; b) self-cooperation if, at each stage of the main rotation, the molecule itself optimizes the values of the angles of tilt around the other two inertial axes; and c), full cooperation, when the first shell of molecules surrounding the rotational site cooperate by tilting motions around their own inertial axes to make way for the rotating molecule. These three models have been tested for naphthalene, and the full cooperation model is the one that gives best agreement with the experimental rotation barrier. Even the crudest model, however, gives a correct estimate of the order of magnitude of the barrier. Results on this system are shown in Figure 4.

Potential energy calculations for molecular motions in crystals can be used to analyze some aspects

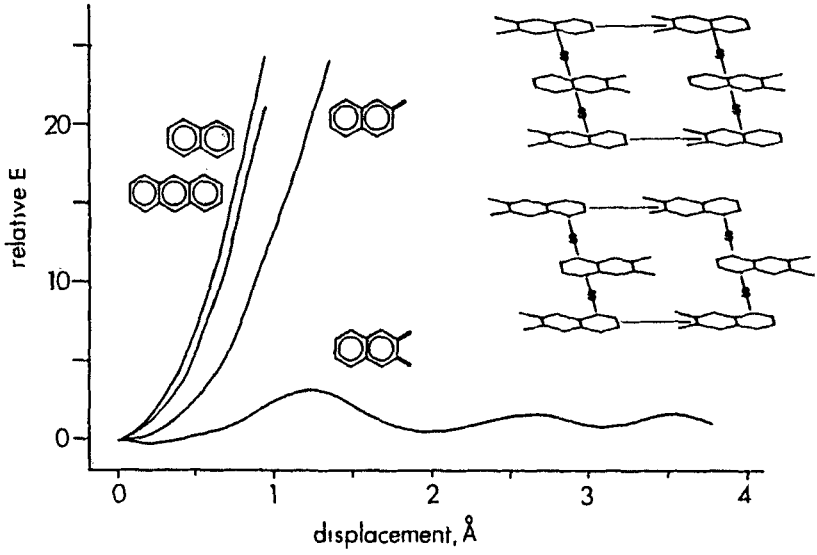


FIGURE 3. Relative packing potential energy for a molecular translational motion in crystals of 1-4. The motion (shown in the inset for 3) is such that the screw axis is preserved.

of the dynamics of crystal structures. The steric effects involved in molecular reactivity in crystals, on the other hand, can be studied by setting up a model of the reaction site, and then trying to comply at best with the space and intermolecular potential requirements of the reaction cage. An example of such calculations (Gavezzotti, McBride and Weber, to be published) will be given for the following

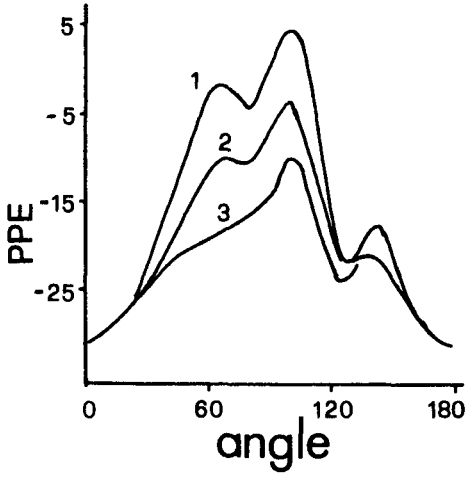


FIGURE 4. Packing potential energy (PPE) for rotation of naphthalene in its molecular plane with (1) zero cooperation, (2) self-cooperation and (3) full cooperation (Bellezza, Destro and Gavezzotti, to be published). Crystal structure of naphthalene from ref.3.

system (McBride and Weber, to be published):

$(CH_3)_3CCH_2COO(CH_2)_4OOCCH_2C(CH_3)_3$

dineopentyladipate (DNPA), crystal host

$(CH_3)_3CO\text{-}OOC(CH_2)_4COO\text{-}OC(CH_3)_3$

di-t-butylperoxyadipate (DTBPA), guest in DNPA

$(CH_3)_3CO^{\cdot} + CO_2 + (CH_2)_4^{\cdot} + CO_2 + {}^{\cdot}OC(CH_3)_3$

decarboxylation products after photolysis

In a preliminary approach, packing density maps can be fruitfully used to find empty niches in the crystal structure which could accommodate the extra volume produced by the formation of the carbon dioxide molecules. Such a map for the above system is shown in Figure 5. The crystal host matrix shows cavities into which the carbon dioxide molecules can be allocated; in the further computer simulation, the overall packing potential energy is minimized by allowing the t-butyl radical to back off slightly. The estimated activation energy (an upper threshold value, since the optimization could be pushed further) is 18 kcal/mole of carbon dioxide molecules. The effects of the first decarboxylation on the rate of the second one is less easy to assess.

References 4-8 are examples of previous work along the lines sketched in this communication, to put the reader in a better perspective. Note that eq. (3) in ref.8 is in error; it should be:

$$PPE = PPE(\text{lattice}, \text{aggregate}) + \sum E(\text{frag}_i, \text{frag}_j),$$

and the true relationship to PE is

$$PE = 1/2\ PPE + \sum E(\text{frag}_i, \text{frag}_j).$$

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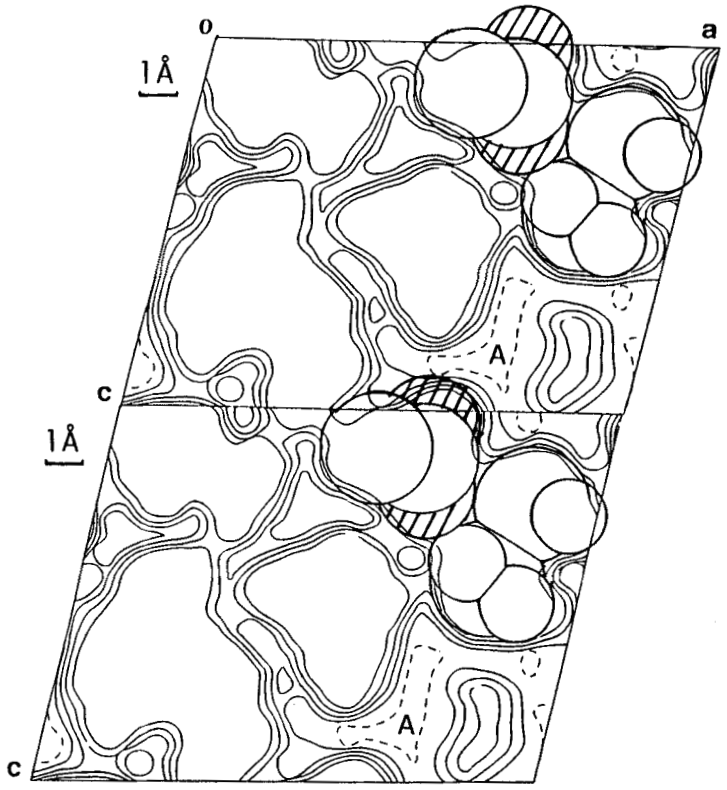

FIGURE 5. Packing density map (xz section at y= 0.10 fractional) for DTBPA in DNPA host. The carbon dioxide molecule (oxygen atoms shaded) moves into cavity A.

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