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PREVIEW

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**Energetics and lattice dynamics of the 2,5-distyrylpyrazine
solid-state reaction**

Peachey, Nathaniel Mark, Ph.D.

The University of Nebraska - Lincoln, 1994

PREVIEW

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PREVIEW

ENERGETICS AND LATTICE DYNAMICS OF THE 2,5-DISTYRYLPYRAZINE
SOLID-STATE REACTION

by

Nathaniel M. Peachey

A DISSERTATION

Presented to the Faculty of
The Graduate College in the University of Nebraska
In Partial Fulfillment of Requirements
For the Degree of Doctor of Philosophy

Major: Chemistry

Under the Supervision of Professor Craig J. Eckhardt

Lincoln, Nebraska

May, 1994

DISSERTATION TITLE

Energetics and Dynamics of the 2,5-Distyrylpyrazine Solid-State Reaction

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ENERGETICS AND LATTICE DYNAMICS OF THE 2,5-DISTYRYLPYRAZINE SOLID-STATE REACTION

Nathaniel M. Peachey, Ph.D.

University of Nebraska, 1994

Advisor: Craig J. Eckhardt

With the proliferation of possible applications for condensed-phase organic materials, solid-state reactions have attracted considerable interest. Unfortunately, much of what is known about these systems is limited to geometrical considerations of the crystalline environment. In this research, the energetics and lattice dynamics of the 2,5-distyrylpyrazine solid-state reaction are investigated in order to extend the physical understanding of solid-phase reactions. The first, crystal-to-crystal, oligomerization stage is the focus of most of the study.

Low-temperature, specular reflection measurements revealed that the oligomerization of DSP is biexcitonic. Local $\pi^* \leftarrow n$ exciton-phonon coupling creates a lattice distortion which traps the delocalized $\pi^* \leftarrow \pi$ exciton to initiate the reaction. The second, polymerization, stage is induced by a single $\pi^* \leftarrow n$ excitation, connecting the unreacted styrylpyrazine ends. The pyrazine ring is crucially important in determining the reactivity of this crystal.

The phonon-assistance and chemical pressure models were investigated to determine their applicability to the DSP photoreaction. Single-crystal, polarized, Raman spectroscopy of the lattice phonon modes at varying stages of the reaction demonstrated that the changing lattice potential energy matches the expectations of the chemical

pressure hypothesis. Although several modes were found to soften early in the reaction, phonon assistance involving phonon-phonon interactions does not play an important role. This became obvious from the study of modal anharmonicity using piezomodulated Raman spectroscopy.

Structural studies were done correlating energetic and lattice dynamical changes to the structural transformations. The monomer and the partially oligomerized crystals were studied using atomic force microscopy. This allowed investigation of the local effects of the reaction, revealing that the crystal is finely segregated into domains of reacted and unreacted molecules. This agrees with the X-ray crystallography of the partially oligomerized crystal. X-ray measurements of the completely oligomerized crystal showed that the lattice changes to reflect the geometry of the oligomers. The unreacted styrylpyrazine ends are severely distorted to fit the cavity allowed by the oligomer crystal. These findings further demonstrate the effects of the evolving chemical pressure upon the crystal lattice.

To Sheri
who endured deprivation and poverty
so this endeavor could be completed,
and to
Rochelle, Yolanda, Kendall, and Ryan

PREVIEW

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Solidity is an imperfect state

Within the cracked and dislocated Real

*John Updike**

I. INTRODUCTION

Current interest in organic materials has intensified research in organic solid-state chemistry. Although some of the reactions in cinnamic acid crystals have been known for over a century, the recent interest dates from the seminal studies by G. M. J. Schmidt and coworkers.^{1,2} This attention arises from the variety of unique features inherent in the crystalline phase. The solid state provides geometric control, unavailable in other phases, that dictates both the course of the reaction as well as the structure of its products.³ This provides a predictable stereospecificity to the reaction. Unlike reactions in the fluid phases, there are seldom secondary reactions. Furthermore, the products obtained from a solid-state reaction may not be the same as those of the reaction in other phases. For example, a solid-state reaction can be the only method of synthesizing some single crystal polymers. An additional reason for understanding solid-state reactions is that they have much in common with other transformations in solids such as structural phase transitions.^{4,5} Indeed, it has been suggested that crystal to

* "The Dance of the Solids," from *Midpoint and Other Poems*, Alfred A. Knopf: New York, 1968 p 20.

crystal reactions resemble martensitic or "military" transformations while some others bear the similarities of displacive phase transitions.⁶ Thus, a more complete grasp of the principles of solid-state reactions is expected to contribute to the overall understanding of solid phase transformations.

The unique correspondence of products to structure led early researchers such as Schmidt to focus predominantly on the relationship of crystal geometry to the reactivity of the solid. This research normally consisted of X-ray structure determinations of reactant crystals and, in the infrequent cases in which they were observed, similar determinations for product crystals. The correlation of observed structural changes with the nature of the solid-state reaction was deeply rooted in chemical thinking with its emphasis on structure-reactivity relationships. From this work, many useful insights have been formulated. Chief among these is the topochemical postulate of Schmidt,⁷ later modified by Cohen,¹ where a minimum distortion of a "reaction cavity" is posited to be necessary for a solid-state reaction. Thus, it was suggested that in order for a reaction to occur in the solid state, product formation must be possible with very minimal motions of the atoms or molecules involved. Furthermore, this implies that the products resulting from the reaction can be predicted by considering the positions of the reactants in the lattice. This implies that there should always be a direct relationship between geometry and reactivity and, indeed, it has suggested that the kinetics of a solid-state reaction are crystal-structure dependent.⁷

The great success of this approach has, however, led to neglect of other important facets of these mechanisms. This is regrettable since other factors can significantly affect

the course of a solid-state reaction. Furthermore, as research has progressed, many exceptions to the topochemical postulate have been observed.⁵ One of the clearest is a comparison of the reactivity of 2,5-distyrylpyrazine (DSP) and 1,4-bis(β -pyridyl-(2)-vinyl)benzene (P2VB). The reactive double bonds of DSP are 3.939 Å apart⁸ while in the isomorphous P2VB crystal, they are separated by only 3.910 Å.⁹ A summary of their crystallographic parameters is given in Table I.1.

Table I.1
Crystallographic Data for DSP and P2VB

	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	space group	<i>Z</i>
DSP	20.639	9.599	7.655	<i>Pbca</i>	4
P2VB	21.060	9.567	7.311	<i>Pbca</i>	4

According to topochemical considerations, the P2VB crystal should be significantly more reactive than DSP, but the reverse is true. In the crystal, DSP is about 30 times more reactive than P2VB,¹⁰ while in solution, the two molecules have comparable rates of reaction.¹¹ The failure of the topochemical postulate to predict the relative reactivities of these two molecular crystals invites investigation of the energetic and dynamic processes. Indeed, on a more basic level, structure is a consequence of energetics, and, thus, investigation of the latter is needed and appropriate.

To better understand solid-state reactions, a more comprehensive approach is

required which combines structural considerations with photophysics and lattice dynamics. The interpretation of the results of such studies demands the formation of theoretical constructs that explain the observed phenomena. However, despite the intense interest in solid-state reactions, physical models which quantitatively describe them are conspicuous by their absence. This may be attributed to a paucity of investigations on the importance of the role of collective states to the reaction in the crystal. Within the last two decades, however, several qualitative models have been proposed to explain solid-state reactions, most notably steric compression¹², and phonon-assistance¹³. Steric compression posits that a force in the locus of a reaction site affects atomic motions along a reaction coordinate, although such motions need not be those of the centers participating in the reaction. The implicit philosophy of the majority of these models, including steric compression, is essentially within the traditional context of chemistry: the emphasis being on the interaction of *single* molecules and the effect of structure on this reaction. Indeed, it has been argued that molecular crystals are somehow singular in that the role of collective states is negligible.³ Nevertheless, in the solid phase, collective interactions are always present. This is particularly evident in solid-state reactions since it has been noted that such processes are invariably associated with a phase transition.^{5,6}

Local, microscopic perturbations can effect global, macroscopic transformations resulting from the collective nature of the solid. Thus, it is necessarily associated with the *aggregate* behavior of the molecules comprising the crystal. The reaction energy surface of the crystal must be some convolution of the molecular energy surface and the

crystal potential energy at each stage of the reaction. Thus, the lattice and the molecules that comprise it are intimately connected, and any complete model that treats solid state reactions must be as concerned with the lattice as with the local interactions of the reacting molecules. A naive picture would be that, somewhere in phase space, the potential energy surfaces of the reactants, products, and lattice intersect. Such a depiction is artifice but it does delineate a fundamental conceptual problem with solid state reactions that is usually ignored: the collective interactions of solids. The importance of collective excitations or states of the crystal may be regarded, along with the translational symmetry giving rise to them, as a solid's distinguishing characteristics. A phase transition is a manifestation of this collective behavior and its association with a solid state reaction compels attention to the influence of collective states.

The phonon-assistance hypothesis¹³ attempts to address this reality. By this mechanism, the collective molecular vibrations, phonons, may promote product formation analogous to the role of collisions in gas-phase reactions. Clearly, only phonons with motions along the reaction coordinate that bring the reacting molecules into a favorable position to form product could "assist" in the reaction. Such phonons are expected to shift to lower frequency with increased formation of developing product. This decrease in phonon frequency, known as mode-softening, analogous to similar behavior in phase transitions, is accompanied by an increased amplitude of the vibrational oscillations which further promote interactions of the reactants.

Although the phonon-assistance hypothesis addresses the dynamic, collective nature of the solid phase, it, along with most other models, has apparently not lent itself

easily to quantitative formulation. Recently, a theoretical model has been advanced which accounts for the effects of both the solid-state reaction and the lattice. The idea of "chemical pressure" is developed within the dielectric formalism¹⁴ which provides a convenient way to address collective interactions. This model presents a quantitative picture of how the developing products affect the lattice and how the lattice potential interacts to influence the creation of product. The chemical pressure hypothesis envisages that the developing products create strain in the reactant host crystal. The elasticity of the host lattice accommodates the strain until the interaction of the product species disrupts the host intermolecular attractions. The host lattice potential then collapses and the product interactions dominate to form a new lattice potential. Concentration fluctuations in the lattice are intrinsic to this view of solid state reactivity. The topochemical principle is embodied in this picture through the mediation of the local site deformation energy by the lattice phonons. The latter clearly involve the collective excitations of the crystal.

The importance of lattice strain in solid-state reactions has been previously suggested. Over a decade ago, Baughman developed a quantitative model for the kinetics of solid-state reactions¹⁵ in which the buildup of lattice strain was related to the reaction kinetics of polydiacetylenes. Recently, work of Hollingsworth and McBride reemphasized the importance of the developing strain in the reacting lattice.¹⁶ Although not completely unrelated, steric compression¹⁷ is more of a molecular than a solid-state based concept save for the needed confinement provided by the lattice. It does provide a conceptual link between the chemical pressure and the energetics of the

molecules. Chemical pressure can only be related to the idea of steric compression by the interplay of this resultant deformation energy with the conformation of the reacting molecules themselves.

By extending the chemical pressure hypothesis to the more general case where the lattice potentials are directionally dependent and the resulting elasticity is anisotropic, phonon modes would be expected to be differently affected by the reaction at a given fraction of conversion. Those modes having motions along the reaction coordinate should be more directly influenced by the growth of product in the lattice and thus display significant frequency shifts. Furthermore, these shifts should occur quite early in the reaction. In this manner, the evidence which is posited to support the phonon-assistance mechanism and indeed, phonon-assistance itself, can be accounted for by the chemical pressure model. To distinguish between the chemical pressure and phonon-assistance mechanisms, it is also essential to establish whether the mode-softening and concomitant increased librational oscillations are causal or merely consequential in the reaction.

To extend the physical understanding of organic solid-state reactions, this research will focus on a particular photochemical solid-state reaction, that of DSP, as an experimental test system. This study is expected not only to better establish the photophysics and lattice dynamics of the DSP reaction but may also be important for scrutiny of the various hypotheses proposed to explain solid-state reactivity. Such an investigation will assist in assessing current hypotheses dealing with solid phase transformations and is expected to point the way to a more complete physical description

of these processes, indicating what refinements are needed in theoretical descriptions of them. In this prototypical four-centered reaction, two neighboring carbon-carbon double bonds undergo a 2+2 cycloaddition to form a cyclobutane ring (Figure 1). If the crystal is irradiated with light of wavelengths between 480 nm and 400 nm, an oligomer of three to five monomer units results. The oligomer may be further irradiated with shorter wavelength illumination to yield a high polymer. Alternatively, the monomer can be irradiated with light of wavelength shorter than 400 nm and the high polymer will result directly.^{18,19} Since the first oligomerization stage is single crystal to single crystal, attention will be directed to this phase of the reaction.

To advance the analysis of solid-state reactions beyond structural considerations, this research will include studies of the energetics and lattice dynamics of the DSP reaction. The energetics are investigated using low temperature, polarized reflection spectroscopy. Reflection spectra can be used to calculate the absorption spectra using the Kramers-Kronig relationships. This provides information about the particular electronic states and exciton interactions responsible for the photoreaction. The analysis of the electronic structure of the crystal provides an explanation of the reaction mechanism. In this photoreaction, excitons do prove to be very important. Failure to recognize the crucial role that collective excited states play in the reaction has led to incomplete descriptions of the reaction mechanism. The absorption spectra of the oligomer crystal are also important to complete the description of the energetics of this reaction. The electronic structure of the oligomer crystal can be compared and contrasted with that of the monomer to provide a comprehensive characterization of the

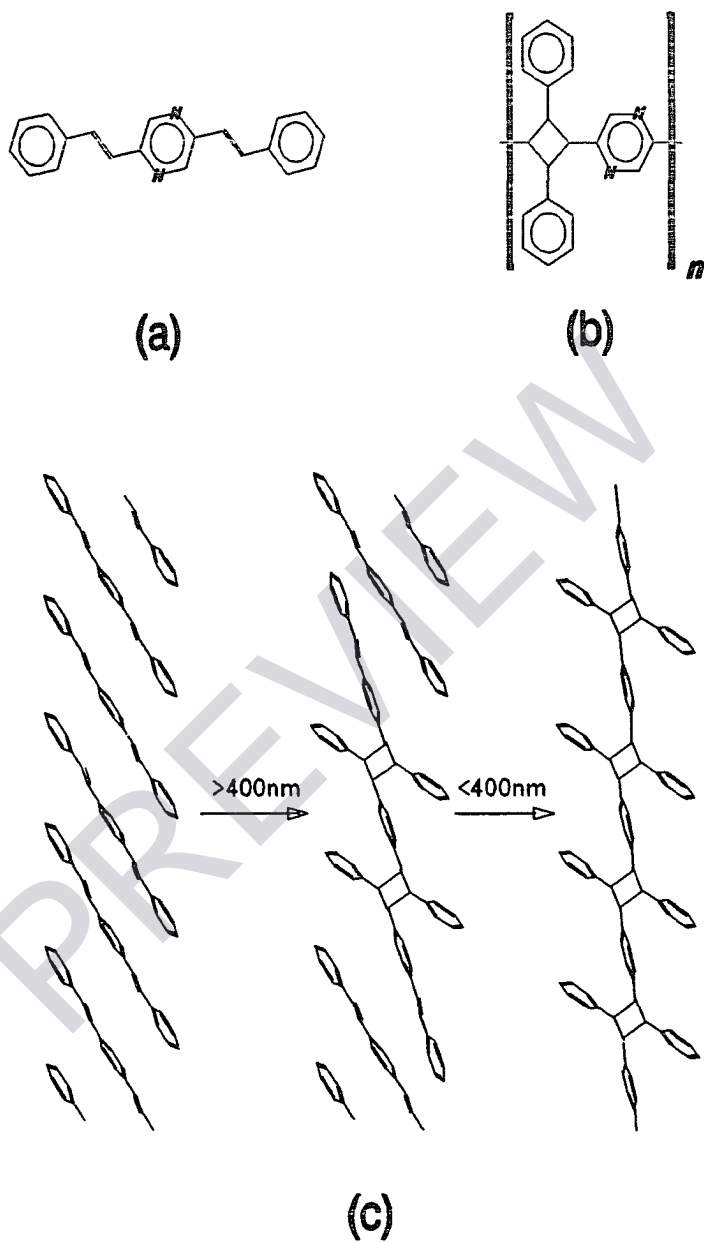


Figure 1 (a) The DSP molecule, (b) the repeat unit of the oligomer and the polymer, and (c) the two-stage DSP polymerization reaction.