Liversidge Research Lecture

No. 23
1982

MOLECULAR CRYSTALS AND LIGHT: CHEMICAL REACTIONS IN CAGE

D.P. CRAIG

The Royal Society of New South Wales

David Parker Craig

Liversidge Research Lecturer No. 23, 1982.

DAVID PARKER CRAIG 1919 - 2015

David Parker Craig was born on 23 December 1919 in Sydney, N.S.W. His secondary education was at the Sydney Church of England Grammar School, then he went to the University of Sydney, graduating B.Sc. (1st. class Hons) in 1940; as a Commonwealth Science Research Scholar, he graduated M.Sc. at the same Institution in 1941. For the period 1941-1944 he was engaged in War Service. In 1945 he was appointed as Lecturer in the Chemistry Department, University of Sydney, then in 1946 he went to University College, London as a Turner and Newell Research Fellow to work with Professor C.K. Ingold on energy levels of conjugated and aromatic molecules. He graduated Ph.D. (London) in 1949 and continued on at University College. In 1952 he was appointed to the Chair of Physical Chemistry at the University of Sydney, then in 1956 he returned to University College London as Professor of Theoretical Chemistry which position he occupied until 1967. In the mid-sixties he was invited to be an advisor to the Australian National University on the establishment of a new Research School of Chemistry. At the start of the school in 1967 he was appointed to be one of the two Foundation professors (with A.J. Birch), and was Dean of the School for the periods 1970-1973 and 1977-1981. While on periods of study leave he was Visiting Professor, University College, London (1967-); Visiting Professor at University College, Cardiff (1975-1985); and Visiting Foreign Professor, University of Bologna (1984). He has been Emeritus Professor since retirement in 1985, and for the period 1985-1988 he was a University Fellow at the Australian National University.

David Craig was a Member of Executive, CSIRO for the period 1980-1985, and during 1985-1988 he was actively involved in affairs of the Commonwealth Department of Science as Chairman of its Bilateral Programs Committee, and as a Member of its International Science Policy Adsvisory Committee. For the period 1990-1994 he was President of the Australian Academy of Science. He has served in various capacities on a number of other Australian and international bodies concerned with science and technology.

Honours and Awards (Pre 2001)

1953	FRACI (Fellow of the Royal Australian Chemical Institute)
1956	D.Sc. (London)
1959	British Council Lecturer in USSR and Czechoslovakia
1963	Nuffield Foundation Lecturer in Canada
1966	Venable Lecture, University of North Carolina
1968	FRS
1968	FAA
1969	Corday-Morgan Lecturer in South East Asia, Chemical Society (London).
1971	Seaver Memorial Lecture, University of Southern California

1972	H.G. Smith Medal, RACI
1974	Chemical Society (London) Lecturer in Australia
1982	Liversidge Research Lecture, Royal Society of New South Wales
1983	B.D. Steele Lecture, University of Queensland.
1985	Dr. Chem. (Hon.), University of Bologna
1985	D.Sc. *honoris causa*, University of Sydney
1985	Honorary Member, Royal Society of New South Wales
1985	Russell Grimwade Lecture, RACI
1985	Officer, Order of Australia (AO)
1986	D.P. Craig Festschrift, *Int. Rev. Phys. Chem.,* (1986), **5**, 91-317.
1987	Honorary Fellow, Royal Society of Chemistry
1989	'Professore in Contratto', University of Bologna
1991	A.E. Leighton Medal, RACI
1993	T.G.H. Jones Lecture, University of Queensland
1995	Special Issue of *Chemical Physics* dedicated to D.P. Craig (75th. birthday).

Biographical Source

Personal Communication

Australian Academy of Science web site: www.science.org.au/educatio/dc.htm

Scientific Publications by D.P. Craig

Between 1940 and1999 D.P Craig published some 192 papers on physical chemistry, as well as 2 books and 8 book chapters.

MOLECULAR CRYSTALS AND LIGHT: CHEMICAL REACTIONS IN CAGES*

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ABSTRACT. The kinetics, mechanisms, and stereochemistry of solid state photochemical reactions are different in fundamental ways from reactions in fluids, and constitute a distinct set of problems. Molecules in crystals below the melting point are confined by intermolecular forces to sharply defined regions, or 'cages'. Reactions take place between molecules within such cages in positions and orientations known from crystal structure analysis or in positions related to the perfect crystal structure by dislocations or local disordering.

New concepts are being developed to advance understanding in this field. The best known is that of 'topochemistry', which is that static lattice constraints restrict the products of a photochemical reaction to those preformed in the parent crystal. Also recent theory leads to the proposal that there may be impulsive molecular displacements following light absorption and lasting only a few picoseconds that bring neighbour molecules close together and promote chemical change or excimer formation. The theory of this concept of 'dynamical preformation' is described and possible examples discussed.

Introduction

The Will of Archibald Liversidge is the source from which we seek the true intention of these lectures. From Professor David Mellor's splendid biographical note (Mellor, 1957) we learn that '... the lectures shall not be such as are termed popular lectures dealing with generalities and giving mere reviews of their subjects nor such as are intended for the ordinary class or lecture room instruction ... but shall be such as will primarily encourage research ... '. The lectures are to be about new knowledge, and not generalities but generalizations are called for because they so often mark new insights and newly recognized connections between observations. In research we aim to replace isolated observations, often seemingly mysterious, by a network of facts fitting together straightforwardly, leading to general conclusions, and enabling the working of a physical system to be understood in terms of accepted principles. The advances in knowledge of photochemical reactions in solids provide just such possibilities.

Photochemical reactions in crystalline solids have exceptional interest in that the processes of light absorption, energy transfer to the reactants and the reactions themselves occur under conditions made simpler by reason of the ordered structure of the crystal. Of leading importance is the elimination of collisions, which so complicate the understanding of chemical reactions in fluids.

The replacement of collisions as the mechanism by which energy is made available at a reacting site has profound consequences for the nature of chemical change in solids. In a

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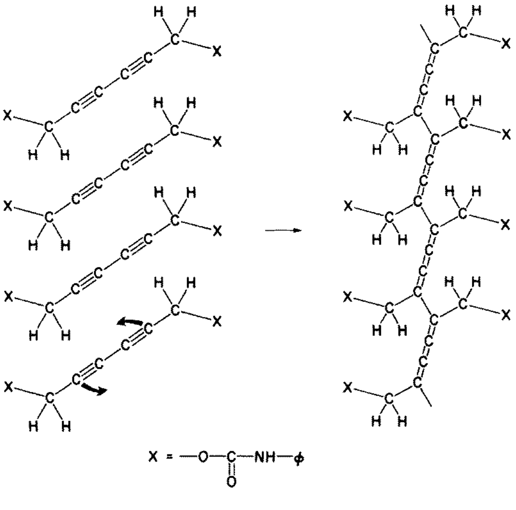
particular way it makes thermal reactions harder to study than in solution or in the gas phase and gives a special advantage to photochemical reactions. If there are no collisions to activate a molecule, the activation of a thermal reaction must come by the chance accumulation of vibrational motions of the lattice and of the molecule. There is no collisional kinetic energy for conversion to potential energy. For this reason a thermal reaction in a crystal rarely occurs at isolated single locations at a controlled rate. When a crystal is heated to induce a thermal reaction, thermal activation often occurs at a large number of sites almost at the same temperature. Autocatalysis is common, as the result of a thermal reaction at one site releasing heat to activate the same reaction at neighbouring sites.

On the other hand in a photochemical change it is possible to control the rate of activation of molecules in the solid by varying the light intensity. This varies the rate at which energy is supplied to produce the activation necessary for a chemical change. Also energy collection is highly efficient. When light falls on a crystal it excites it as a whole and, as a second stage, the available energy is trapped at sites at which chemical change is possible. The available energy is 'scavenged' by molecules capable of reaction and can be used with high efficiency. This contrasts with photochemical reactions in gases and liquids in which a molecule can react only by itself absorbing a photon. Solid state photoreactions are in many cases cooperative in this sense.

It is at once obvious that the range and variety of chemical reactions is very limited compared with other phases. Because the molecules in a solid are in fixed positions chemical reactions tend to be confined to molecules which are nearest neighbours, and for a reaction between two different molecular species the molecules must have been combined in a mixed crystal as host and guest. However one should not underestimate the possibilities. Wegner and colleagues (1972) synthesized photochemically and thermally long chain stereoregular polymers which up to the present have not been made by any other means. This reaction does not go in solution and in the crystal goes only in that crystal modification in which the molecules are stacked as shown in Figure 1. Here the polymer is preformed and small rotations only about the centres of mass are required to achieve the precise structures



Wegner, *Die Makromoleculare Chemie*, **154**, 35, (1972)

FIGURE 1

essential for polymerisation. Such polymers are important technically, possessing interesting semiconducting properties. The structural characteristics of the starting crystals, apart from preformation of the product, are that the triple bonds of adjacent molecules are very close (about 0.3 nm) and thermally induced vibrations can bring the reacting entities close enough to combine. Photochemical activation is also facile. The central idea in this example is that of topochemical preformation, namely that the molecules which will react together are already held in the original lattice in a configuration which is a natural precursor of the product.

Topochemical Preformation

The systematic study of photochemical reactions in solids began in the late thirties. Its first major result was the generalization deduced from a range of studies by Schmidt and coworkers (1964) which they called the principle of topochemistry, to which reference has just been made. One of its clearest examples is the solid state photochemistry of *p*-substituted cinnamic acids (Figure 2). These acids for various substituents in the *p*-position of the phenyl group form crystals with a range of molecular packings, with variations in the relative orientations and separations of nearest neighbours. The photochemical reactions, where they occur, are dimerisations proceeding to form one or other of the two structures shown on the left hand side of Figure 2 and in their approximate crystal registrations on the right-hand side. The reaction is the cyclisation of the pair of double bonds. Where the separation of these bonds exceeds a critical value there is no photochemical reaction; where the separation is less than the limiting value there is photodimerisation, leading in every case to the dimer performed by the crystal packing of the parent. This remains one of the classic studies of topochemistry.

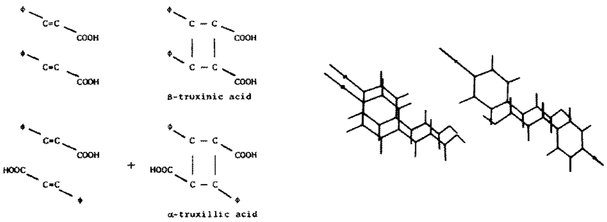


FIGURE 2. Dimerisation of the cinnamic acids showing the chemical products (left-hand) and structural registry in the crystals (right-hand) for *cis*- and *trans*-dimers.

Later findings have added much to this general understanding of solid state reactivity. It was shown that even in cases where a dimer was preformed in the monomer crystal, and the packing was close and in correct registration, there need be no reaction if opposing steric constraints were strong enough. Thus in the crystal of 9-cyanoanthracene there is preformation of the *cis*-dimer, in which the 9 and 9' carbons, and 10 and 10', are expected to bridge as in the well known dimer of anthracene itself. No *cis*-dimer forms. Instead, in a remarkable variant, in a slow and auto-catalysed reaction, there is formation of the 'wrong', i.e. the *trans*, dimer (Craig and Sarti-Fantoni, 1966). This is the first of many examples of

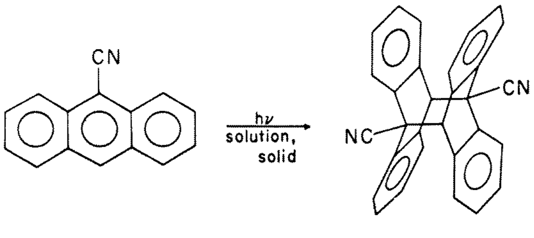


FIGURE 3. Monomer and *trans*-dimer structures for 9-cyanoanthracene. The *cis*-dimer is not known.

non-topochemical reactions, for which a general explanation has become accepted. The initial rate of such reactions is increased in crystals lacking perfect crystalline order. The reactions can often be shown to have occurred at these zones of imperfection and at surfaces. Their autocatalysis has in a few examples been connected with the growth of dimer bodies, causing increasing disturbances to the host structure, and thus inducing further loss of order.

Consideration of the course of photoreactions not taking place in the ordered crystal bulk is incomplete without reference to their highly selective and localized nature. After irradiation, the absorbed energy is transferred within the crystal and trapped at 'reactive' sites, which, as in the examples already referred to, may be misoriented molecules in a pure crystal, or may be chemical impurities in a doped crystal. Cases are known of photoreactions confined to impurities present only in parts-per-million concentrations. In anthracene crystal for example 2-hydroxyanthracene (2-OHA) is a photoreactive impurity, forming with one molecule of anthracene a pair compound joined in the 9-9' and 10-10' positions to give a structure similar to the 9-cyanoanthracene dimer in Figure 3 (Craig and Rajikan, 1977). The reaction can be followed in some detail, because the radiation absorbed at the wavelength characteristic of the host anthracene crystal, even at 2-OHA concentrations of less than 10 parts per million, is largely trapped by the impurity. At low temperatures the radiation is emitted at frequencies characteristic of 2-OHA; at higher temperatures the energy is dissipated in processes leading to formation of the pair molecule. On closer study the details contain much information illustrated in Figure 4. In a crystal of the anthracene space group $P2_1/a$ replacement of a host molecule by an impurity of symmetry C_{1h} may be made in two distinct ways. The local atom-atom contacts between impurity and host make different contributions

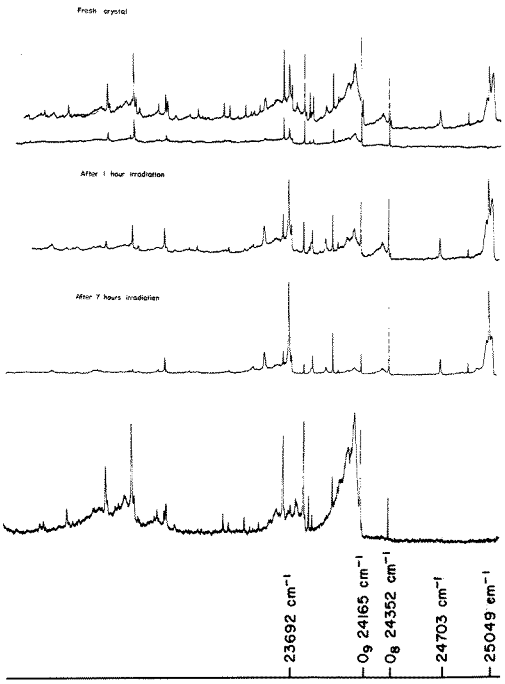


FIGURE 4. Fluorescence spectra at 5 K of anthracene crystal doped at <10 ppm with 2-hydroxyanthracene. In the two orientations of 2-OHA there are different emission origins, at 0_8 and 0_9. Under suitable conditions, irradiation depletes 0_9 only, by photochemical reaction. The bottom spectrum is of a fresh heavily doped crystal. Taken, with permission, from *Chem. Phys. Lett.,* 1977, **47**, 20.

to the total crystal energy. The consequences are that one packing orientation is more probable than the other, and that the energy of the radiation required to excite them is different. Thus an easy experimental method, the measurement of fluorescence frequencies and intensities, is available to find the relative concentrations, and the rates of photoreaction. As shown in Figure 4 both orientations trap radiation absorbed by the host anthracene crystal but photoreactivity is confined to one only. The explanation is not known. Calculations of the local packing do not agree with the idea that there is topochemical preformation in either case (Craig and Markey, 1980). Probably both impurity packings are disordered, one but not the other preforming the reaction product.

Static and Dynamic Topochemical Preformation

Preformation is a more complex concept than at first appears. It is well established by measurements of lattice vibrations, and supported by calculations of the force system holding a molecule in place at its lattice site, that the 'cage' in a lattice containing a molecule is a stiff structure, limiting its motion to small excursions from a mean position and orientation even at temperatures within a few tens of degrees of the melting point. There are obvious exceptions to this statement, as in molecules with an axis of rotation (CO_2) and also where there is an axis of high order (C_6H_6), but in molecules like naphthalene and anthracene the centres of mass oscillate with amplitudes of only a few tens of picometres and axes of inertia by a few tenths of a radian. How this picture changes when the molecule is electronically excited is not known experimentally but calculations suggest that while there may be a change in the equilibrium positions the motional amplitudes, which depend on the same cage as in the ground state, are not much changed. Thus in a broad sense one has no difficulty in rationalizing the topochemical principle. It is not so easy to understand the steps following excitation in a dynamical context. The atoms of adjacent molecules which are to be bonded to one another (9,9' and 10,10' in the anthracene dimers) have to get much closer than they are in the crystal. If the crystal distance is too great, as noted in Section 2 for the cinnamic acids, there is no reaction even if the molecules are favourably registered. Thus it is not possible to avoid analyzing motional and dynamic aspects as well as the static problems of cage structure and local packing.

Instabilities as an Aspect of Dynamical Preformations

The force system maintaining the local packing in a molecular crystal is well described by summing the dispersion attractions and the closed shell repulsions due to electron exchange. These two are often referred to jointly as van der Waals forces, although sometimes the term is applied to the dispersion force alone. The repulsion energy is fairly well represented over a range of interatomic separation R by an exp(-cR) dependence. The dispersion energy between molecules a and b, denoted by D_{ab}, is accounted for on the Heitler-London theory in terms of the intermolecular coupling of virtual transitions according to equation (1)

$$M_{ab} = -\sum_{i(a)} \sum_{j(b)} \frac{\underset{\sim}{M}^2_{oi} \; \underset{\sim}{M}^2_{oj}}{\Delta E_{oi} + \Delta E_{oj}} \left(I^{ij}_{ab}\right) \qquad (1)$$

where, in the notation Craig *et al.* (1965) $\underset{\sim}{M}_{oi}$ is the transition moment and ΔE_{oi} the excitation energy for the transition to the i-th excited state from the ground state of the molecule. I^{ij}_{ab} is a geometrical factor depending on the positions of the two molecules and on the polarization directions of the $i \leftarrow 0$ and $j \leftarrow 0$ transitions. The energy (1) varies with the distance ρ separating the molecules as ρ^{-6}. Where the total interactions are represented as sums of interatomic parts, the dispersive terms are empirically set to obey an R^{-6} relation between atomic centres. In that case, in what has become the usual treatment of intermolecular forces in studies of crystal packing, the potential energy is the sum of interatomic terms of the 'exp-6' form

$$V_{ij} = -a(ij)R_{ij}^{-6} + b(ij)\exp\{-c(ij)R_{ij}\} \quad ..... \quad (2)$$

With the help of some rather crude approximations the dispersion energy can be written as a function of the polarizabilities of the coupled molecules. The polarizabilities are measured quantities, and allow comparison of actual and computed dispersion energies. Computations based on measured polarizabilities rarely give more than 60% of the true values, but are still of great value. In particular, by using the polarizability of an excited molecule, we get a measure of the forces acting to move and reorient it within the cage. In most crystals electronic excitation increases the attractive forces (dispersion forces) so that the excited molecule is more tightly bound to its environment. It is quite a good approximation to say that the closed shell repulsions are not altered, inasmuch as the excitation affects the states of electrons not much involved in the repulsions. Thus excitation of the π-electrons in an aromatic molecule leaves the hydrogen-hydrogen atom repulsions more or less unchanged, and these are mainly responsible for the repulsive, structure-maintaining, forces in the crystal.

There are examples, notably in crystals of pyrene and perylene, where the structure consists of eclipsed pairs of molecules, which on excitation form excimers, or close-spaced excited molecule-pairs, with characteristic spectral properties, but with no tendency to form chemical dimers. The increased attractive force on excitation accounts for the movement of molecules closer together in such structures. In others such as 9-cyanoanthracene the structure is not by pairwise molecular association; the molecules are in stacks, and it is not at once easy to see how excimers, which are observed, would form. In yet other cases there are similar problems in accounting for the formation of photochemical products.

Some of these difficulties would be removed if it were the case that, following excitation, impulsive forces were generated which, over short time intervals, caused displacements of molecules, or perhaps only the excited molecule, away from the ground state equilibrium positions, so predisposing the molecules for excimer or dimer formation in a process that one can describe as dynamical topochemical preformation. After the impulsive motion is damped out, the excited molecule and its neighbours settle into a new equilibrium, in which the packing may be unsuitable for excimer or dimer formation. We may readily show that such short-term instabilities are feasible by taking a simple model system of three molecules in a straight line, held in equilibrium by balanced dispersive and repulsive forces. The repulsive term will be given by a power law, rather than an exponential, dependence on distance so that the attractions and repulsions vary with distance respectively as R^{-6} and R^{-12}. The pairwise potential is thus

$$V = -\alpha/R^6 + \beta/R^{12} \quad .... \quad (3)$$

α and β being constants for the scale of the attractive and repulsive energy functions. If the equilibrium separation is at $R = \rho$, β can be eliminated, giving

$$V = -\alpha/R^6 + \alpha\rho^6/2R^{12} \quad .... \quad (4)$$

and if on excitation the dispersive constant is changed to α^* we have for the excited state potential function

$$V^* = -\alpha^*/R^6 + \alpha\rho^6/2R^{12} \quad \text{..........} \quad (5)$$

given in terms of ρ, the ground state equilibrium spacing. To test the consequences for the 3 molecule system

$$\dot{1} \qquad\qquad \dot{2} \qquad\qquad \dot{3}$$

one can take two extreme assumptions. If molecule 2 is excited, and atoms 1 and 3 allowed to relax freely, the system will come to a new symmetrical equilibrium structure with separation changed from ρ to ρ^*,

$$\rho^* = \rho(\alpha/\alpha^*)^{1/6} \quad \text{...........} \quad (6)$$

The other extreme is to follow the motion of the central atom in the short period before molecules 1 and 3 can move. Figure 5 shows how the potential for the central atom depends on the ratio α^*/α. For small changes in α^* the centre position remains the equilibrium position. For larger changes there is instability, the central atom being driven away from its site at the centre to one of two equivalent displaced configurations with close approach to one or other neighbour. There is thus pre-formation of a dimer pair, in the short term, which could prepare the system for chemical change or excimer formation. If there is no chemical change long term equilibration would follow to the symmetrical structure described before.

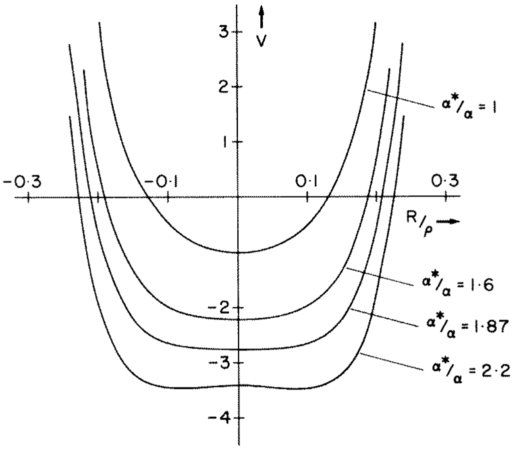


FIGURE 5. Potential curves for an excited atom in a triatom configuration with fixed outside atoms. R is the displacement from the ground state equilibrium. α^*/α is the ratio of excited state to ground state dispersive constants in equations (4) and (5). Taken, with permission, from *Chem. Phys.* 1982, **65**, 129.

While the three molecule system gives a useful view, a much more detailed picture can be had by taking a one-dimensional 'crystal' consisting of equally spaced atoms (Figure 6) in which one molecule is to be excited. The force system controlling the response of the excited system can now be followed realistically, taking account of the propagation along the chain of the impulsive forces caused by excitation. The extremes are shown in Figure 6; there can be a symmetrical contraction (c) (or, in principle, expansion) about the excited atom, and after sufficient time this will certainly be the result. In short periods an unsymmetrical (dimer preforming) motion (d) is a possibility. Also it is necessary to simulate in the calculations another feature of real systems, which is that, depending on temperature, there will be vibrational motion in the initial state of the system.

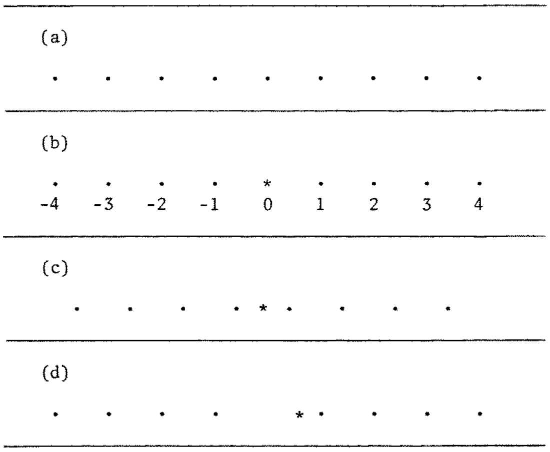


FIGURE 6. One-dimensional atomic lattice: (a) ground state, (b) excited atom shown as * in ground state configuration, (c) symmetrical long-term relaxation, (d) asymmetrical short-term distorted lattice

Calculations (Craig and Collins, 1981) of the one-dimensional system by classical mechanics (semi-classical method) are illustrated by the results in Figure 7. The calculations are made for a range of initial motions of the inner (u_0) and one of the outer (u_1) atoms, and the time development of the system after excitation of the atom labelled 0 in Figure 6. In (a) with initial motion of atoms 0 and 1, those atoms oscillate as a pair over long periods, atom -1 being more or less unaffected. This is the typical dynamical pre-formation of the dimer pair.

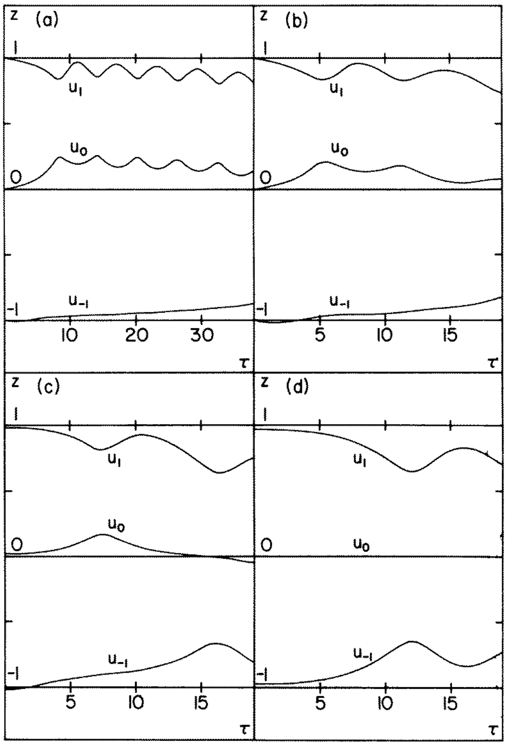


FIGURE 7. Motions of the inner (u_0) and outer (u_1 and u_{-1}) atoms in the excited atomic chain. Taken, with permission, from *Chem. Phys.* 1981, **54**, 305.

In (b) with small initial velocities the same behaviour is found. Successively, in (c) and (d) , the dynamics changes to symmetrical collapse. It is thus confirmed that the unsymmetrical short-term displacement, reflecting instability, occurs in a range of circumstances.

Instabilities in Real Crystals

The extension of such kinematic arguments to three-dimensional systems is difficult, though possible in atomic lattices of simple structure, such as crystalline argon (Collins and Markey, 1982). For molecular crystals calculations of the kind sketched for the three-atom system can be made, leading to potential energy functions. One can predict instabilities and the magnitudes of short-term and equilibrium displacements, but cannot follow the time-evolution leading to these configurations with present theories.

There are well-established procedures for calculating the equilibrium properties, structural and dynamic, of the crystals of simple molecules especially, but not only, hydrocarbons. The starting point is a set of atom-atom potentials of the 6-exp form in which the repulsive part of the potential is an exponential function. Given atom-atom potentials found by fitting a few known crystal structures, other crystal structures can be accounted for with good accuracy. The potentials used are of the form given in equation (2) and in the following work the constants are taken from Williams set IV (Williams, 1966). Early efforts to account for known structures were in many cases based on observed lattice spacings, and minimized the total atom- atom potential energy with respect to angles of orientation. Later, lattice dimensions were included as variables, again with good results. To deal with the effects of excitation of one molecule on local structure is much harder, and is similar to finding the effect on local packing of an impurity molecule or of a vacancy. All three can be done only if local structural relaxation can be allowed for, with loss of the simplifying features that come from translational symmetry of a lattice, and permitting independent position and angle variations of molecules in a neighbourhood of the foreign molecule (Craig and Markey, 1980). In the present problem of calculating the forces produced by molecular excitation the calculations are of two types. First, the energy is minimized with respect to centre-of-mass movement and orientation changes of the excited molecule only, the environment being kept fixed. This simulates the short-term energetics, and brings to light any instabilities, in the manner of the three-atom system in Section 4. In the second calculation the energy minimization includes relaxation of the environment molecules, and simulates the long-term energetics, after any instability has been damped out.

The procedures and results are well illustrated in the crystal of 9-cyanoanthracene, one molecule of which is assumed to be excited. The excitation is known to delocalize to a greater or less degree, moving from site to site, but we shall assume it to be trapped. The polarizability of the excited molecule exceeds that of the normal molecule, as is known from the spectral red shift that takes place between solution and crystal. The magnitude of the increase is taken to be equal to that of anthracene, which has been measured (Liptay and Schlosser, 1972; Liptay *et al.* 1971; Mathies and Albrecht, 1974), but because the measured quantities is an average over three components, its composition over these components must be treated as a variable, and calculations of structure made for a range of values. The results show that for a large part of the range the excited molecule in a fixed environment is unstable at its normal equilibrium position and is displaced towards one or other of its neighbours in the stack, in a manner to perform an excimer. This finding is illustrated in Figure 8, in which the initial molecular positions are shown in full lines, and the energy minimized positions by dashed lines. The right-hand diagram, for the largest changes of the force system on excitation, shows a large asymmetric displacement of the excited molecule in a manner predisposing its participation in excimer formation with one neighbour.

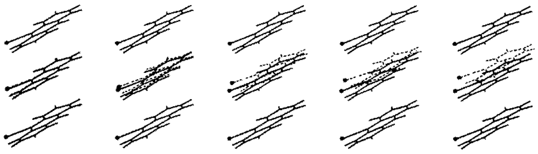


FIGURE 8. The effect of allowing an excited molecule of 9-cyanoanthracene (dashed line) to relax in a fixed lattice for a range of excited-unexcited coupling strengths. The nitrogen atom is shown by a full circle. The coupling strengths increase from left to right; even for rather small values the excited molecule is unstable at its equilibrium position and moves towards one neighbour. The projection is along the a-axis of the crystal. Taken, with permission, from *Chem. Phys*. 1982, **65**, 129

Figure 9, giving the results including relaxation of the environment, shows quite large displacements of near neighbours of the excited molecule, but in a nearly symmetric manner, as expected.

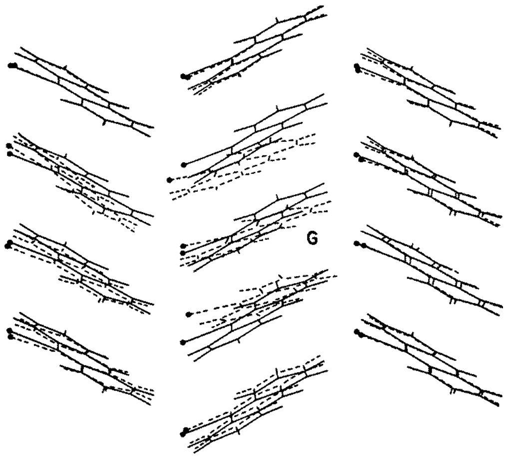


FIGURE 9. 9-Cyanoanthracene crystal structure as modified by the presence of an excited molecule (shown as G) with allowance for environment molecules to relax. The crystallographic structure is shown by full lines, and the relaxed structure by dashed lines. The nitrogen atom is shown by a full circle. Taken, with permission, from *Chem. Phys*. 1982, **65**, 129.

Conclusion

The instabilities that arise in the model three-atom system, and in the example of 9-cyanoanthracene in Section 5, are not general, and not essential as a step in the formation of excimers or chemical dimers. They do not appear in calculations on crystalline anthracene either in the normal $P2_1/a$ structure or in the metastable $P\bar{1}$ structure, nor in 9-methylanthracene (Craig and Mallett, 1982). Excimers in the classical examples of perylene and pyrene are associated with pairwise stacking in the normal crystal, and not with dynamic instabilities, though perhaps with other dynamic features. However in structures with stacks of translationally equivalent molecules like 9-cyanoanthracene instabilities can be expected in many cases, and their occurrence provides a new insight into excimer formation, which was puzzling before. There is another and varied class of mixed crystals, not discussed in this lecture, in which instability will be a common feature. An example studied by methods like those described (Craig and Mallett, 1982) is that of 9-methoxyanthracene as an impurity in 9-cyanoanthracene. The calculated instability gives a useful clue to the nature of excimer formation recently found experimentally (Berkovic and Ludmer, 1981). In the more general context one sees that the dynamic properties of lattices must be included in theories of photochemical change in crystals, as well as already recognized static properties, and that we need to reckon with dynamic topochemical preformation as a newcomer to the array of concepts that help understanding of the radically new features of chemical change in solids.

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