

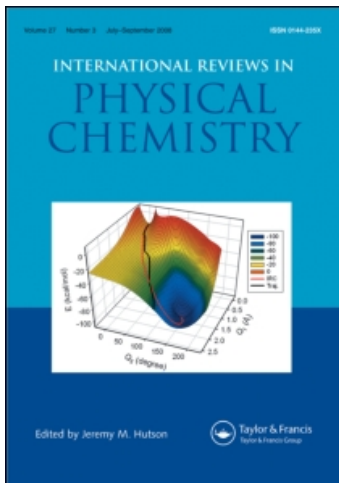
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Massimo Simonetta^a

^a Dipartimento di Chimica Fisica ed, Elettrochimica dell'Università di Milano e Centra C.N.R., Milano, Italy

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Force field calculations in structural chemistry and molecular crystallography of hydrocarbons

by MASSIMO SIMONETTA

Dipartimento di Chimica Fisica ed Elettrochimica dell'Università di Milano
e Centro C.N.R., Via Golgi 19, 20133 Milano, Italy

Empirical force field calculations (e.f.f.) provide reliable predictions of the geometrical structure of organic molecules, particularly hydrocarbons. When intermolecular interactions are combined with the intramolecular field, the influence of a condensed phase on molecular conformation can be investigated. The method can be applied rather generally to the solution and/or refinement of crystal structures and, more recently, to defining the most probable arrangements of organic molecules chemisorbed on metal surfaces. Finally, a summary is provided of how the e.f.f. technique can be used, if supplemented by calculations of lattice dynamics, in the study of phase transitions in molecular crystals.

1. Introduction

Empirical force field calculations for molecules were started long ago. Pioneering work (Dostrovsky *et al.* 1946, Westheimer 1956) investigated, respectively, the magnitude of steric effects in bimolecular substitution reactions and in the racemization of optically active derivatives of biphenyl.

The method (at that time known as molecular mechanics) was taken up again by Hendrickson (1961), who took advantage of the advent of electronic computers, in his study of the conformation of cycloalkanes. The method has since acquired considerable acceptance, especially among physical organic chemists, and many examples of its applications are now in the literature.

Force field calculations were conceived to provide a simple technique to evaluate geometries and heats of formation of organic molecules of small and medium size. The method is totally empirical but has some theoretical foundations. The steric energy of a molecule is calculated as a function of its geometry and is defined as the difference in energy between the real molecule and a hypothetical one in which all bond distances, bond angles, non-bonded distances and dihedral angles have optimum values.

It can be easily recognized that all molecules, except diatomics, are strained according to the above definition; even in a molecule as simple as methane, if the C-H bond length is defined at its equilibrium value, then non-bonded hydrogen-hydrogen distances are not those which correspond to the van der Waals energy minimum so that a compromise geometry is obtained in the real molecule. The molecular strain energy E_{str} is usually expressed as a function of the geometry in the following form:

$$E_{\text{str}} = \sum E_b + \sum E_a + \sum E_t + \sum E_{\text{nb}} \quad (1)$$

where summations of component energies are performed over bond distances (E_b), bond angles (E_a), dihedral angles (E_t) and non-bonded distances (E_{nb}). For conjugated molecules an additional term, ΔE_π can be introduced to account for any variation in delocalization energy and geometry. When elements of significantly different electronegativity are present a summation ($\sum E_{\text{el}}$) may be introduced to represent coulombic

interactions between charges on different atoms; alternatively the energy is incorporated in the other summations through adequate parametrization. Many applications of this approach are now available with, in general, each term in the various summations containing parameters which are empirically determined. Perhaps the most widely used form of equation (1) is:

$$E_{\text{str}} = \sum_b k_b (r - r_e)^2 + \sum_a k_a (\theta - \theta_e)^2 + \sum_i V_i (1 - \cos n\Phi) + \sum_{\text{nb}} [A \exp(-Br) - Cr^{-6}] \quad (2)$$

where k_b , k_a , V_i , r_e , θ_e , A , B , C are empirical parameters; k_b , k_a , r_e , θ_e are, both conceptually and numerically, very similar to stretching and bending force constants, equilibrium bond distances and angles, etc., but they must be considered only as empirical parameters.

One approach to the evaluation of these parameters is to choose an appropriate number of simple molecules of say alkanes for which the gas-phase geometry has been accurately measured; and then to minimize strain energies to give parameters with the best overall fit to observed geometries. The function and its parameters can be used subsequently to calculate geometries of new, but obviously chemically related, molecules. If one were similarly interested in heats of formation, values of standard bond energies may be introduced as new parameters, to be evaluated by an entirely equivalent procedure. The method has been parametrized in several ways, often with different purposes, and a description of the formulae that have been proposed appears in Scheraga (1968) and Williams *et al.* (1968). Paradigmatic examples are available for hydrocarbons, since the number of parameters is not large, and charge separation in these compounds is relatively small. This review accordingly restricts itself almost exclusively to this class of compounds. For gas-phase molecular structures the extensive work of Allinger (1973) should be mentioned, while for crystalline hydrocarbons the most widely used potentials are due to Williams (1966, 1967) and Williams and Starr (1977).

2. Molecules in the gas phase with little or no intermolecular constraints

The present review emphasizes applications of e.f.f. calculations to solid state arrangements and structures so that only two illustrative examples of 'isolated' molecules will be considered. Firstly, and of particular interest, is the geometry and isomerization reaction of 9,9'-bifluorenylidene and its 1,1'-dimethyl analogue (Favini *et al.* 1982). The force field parameters due to Andose *et al.* (1980) were employed with an extension to delocalized systems (Favini *et al.* 1981 a). The short contacts between hydrogen atoms bonded to carbon (1) and (8') and (1') and (8) (figure 1) require that the intramolecular strain be relieved through twisting or folding.

The parent compound has a minimum energy in a twisted conformation and its geometry compared favourably with that observed experimentally (Bailey and Hull 1978). A low energy barrier is associated with the interconversion between enantiomeric conformations: a predicted feature (Gault *et al.* 1970) in agreement with the absence of a temperature dependence in the proton magnetic resonance spectrum. The dimethyl derivative was also predicted to have a twisted conformation, in agreement with diffraction results for diisopropyl-9,9'-bifluorenylidene-1,1'-dicarboxylate (Bailey and Hull 1978), albeit in the crystal intermolecular forces might significantly influence the molecular geometry. The temperature dependence of the N.M.R. spectrum (Gault *et al.* 1970) is well interpreted as being due to the transoid (*E*)-cisoid (*Z*) interconversion, via an orthogonal transition state with an activation barrier of 18.7 kcal/mol; an

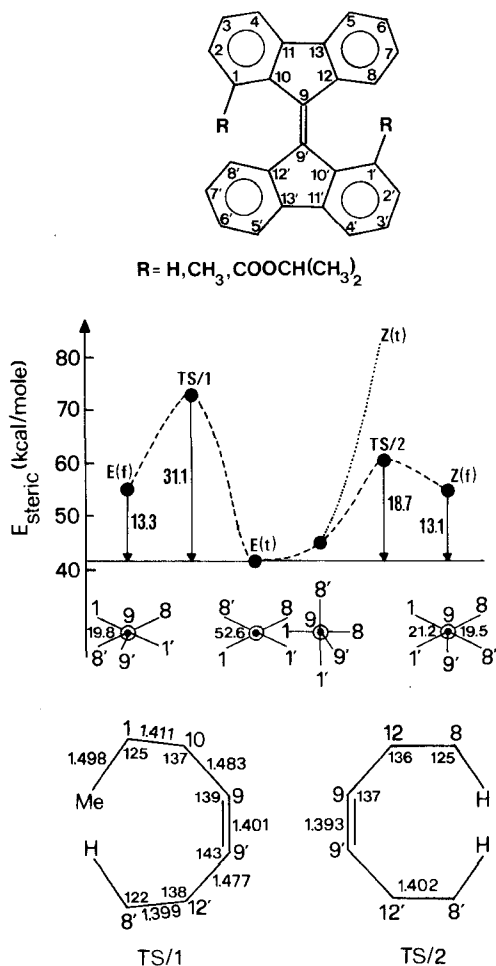


Figure 1. Energy variation along the interconversion path in 1,1'-dimethyl-9,9'-bifluorenylidene. Steric energy defined in the text. f stands for folded, t for twisted, Z is cisoid, E transoid.

experimental value of $\Delta G^\ddagger = 19$ kcal/mol was assigned to the unidentified interconversion process (see figure 1).

We next consider pentaphenylethane. For this molecule the geometry predicted from force field calculations (Hounshell *et al.* 1977, Daugherty and Mislow 1979) was not totally consistent with that determined by X-ray crystal analyses (Destro *et al.* 1978): while the central C-C bond distances were in good agreement ($r_{\text{exp}} = 1.606$ Å; $r_{\text{calc}} = 1.595$ Å), the comparison of the angles of torsion about the ethane central bond yielded differences ranging from 12.3 to 28.3° (average difference 18°).

Similar discrepancies apply when other polysubstituted ethanes are considered (Favini *et al.* 1981 b): calculated and experimental angles of rotation of the phenyl rings differ significantly (see figure 2 for 1,1,1,2-tetra-phenylethane). The X-ray data describe molecular structures and conformations in the crystal where intermolecular forces may have considerable effects on the value of torsional angles around single bonds and

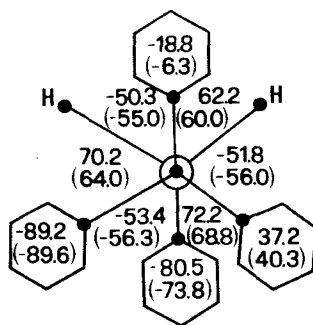


Figure 2. Calculated and (experimental) dihedral angles ($^{\circ}$) for 1,1,1,2-tetraphenylethane.

where the energy from intermolecular interactions is of the same order of magnitude on the barrier height.

Thus before comparisons between geometries calculated for the 'isolated' molecule and those obtained from X-ray crystal data can be made the non-bonded intermolecular interactions should be included. Some preliminary analyses of this kind are in hand (Favini *et al.* 1984).

3.1. Determination and refinement of crystal structures

Rather generally, the study of molecular arrangements in crystals is based on the intermolecular potential being expressed as a sum of non-bonded atom-atom interactions (Kitaigorodski 1973). Molecular format in the gas and crystalline phases can be quite different, a very well-known example being biphenyl (Casalone *et al.* 1968). This molecule is strictly planar in the solid and is torsionally twisted by 40° around the 1-1' carbon-carbon bond in the gas phase. The non-planar conformation in the gas phase results from an energetic compromise between π delocalization energy and steric repulsion between orthohydrogen atoms. A number of quantum mechanical as well as empirical calculations (see Casalone *et al.* 1968) have been produced for the restraint-free molecule; force field calculations both for the isolated molecule and for the crystal, non-bonded intermolecular interaction then being included, gave good agreement with experiment in both phases. Similarly the torsional angles and the orientation of the two chemically equivalent but crystallographically non-equivalent molecules present in *pp'*-bitolyl were satisfactorily calculated (Casalone *et al.* 1969). Intermolecular torsion angles between rigid phenyl or naphthyl groups have been used recently to optimize the parameters in torsional potential functions (Busing 1982).

E.f.f. calculations can be of value in the refinement analysis of disordered crystal structures. An example is the study of the complex of 2,4,6-trinitrophenetole with potassium ethoxide (Meisenheimer salt) (Destro *et al.* 1968). There are two molecular complexes in the asymmetric unit and hence four ethoxy chains. Three of them were easily located by standard crystallographic methods, but the fourth one was disordered; calculation of the repulsion energy between the atoms in this ethoxy group and the adjacent atoms in the crystal as a function of the angles of rotation around the $C_{\text{ring}}-O$ and the $O-C_{\alpha}$ bonds showed the existence of two points of minimum, almost equivalent in energy. Placing half atoms in the two minimum-energy positions provided better agreement with the diffraction data. The minimization of non-bonded intermolecular interactions can provide a direct solution of the phase problem for crystals built up from rigid molecules. A particularly simple case was represented by

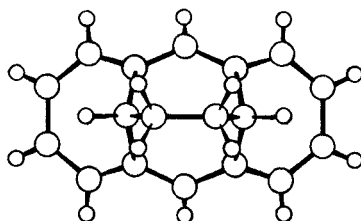


Figure 3. The configuration of 1,6:8,13-butane-1,4-diyldiene|14|annulene.

1,6:8,13-butane-1,4-diyldiene|14|annulene (Gramaccioli *et al.* 1972): the crystals are orthorhombic, space group $Fmm2$, with four molecules in the unit cell. The intramolecular geometry of the carbon skeleton was first established by energy minimization.

One then recognized that in the crystal, symmetry required that only six orientations of the molecule are possible; for five of these the crystal is unstable (packing energy of the order of $+100$ kcal/mol) while the last orientation gave a stable arrangement ($E(\text{packing}) = -2.5$ kcal/mol). Further conventional refinement of the structure was straightforward. One interesting feature that may be noted parenthetically is that the eclipsed conformation of the butane chain (figure 3) was predicted by the force field calculation and subsequently confirmed by experiment.

E.f.f. calculations for the solution of the crystallographic phase problem are entirely possible, but are largely superseded at least in any general sense by the use of direct methods. Their particular value seems related to the definition of disordered arrangements.

4. Thermal motions in crystals

It is well known that in statically disordered crystals the molecules can assume more or less randomly various orientations at the same molecular site. This situation corresponds to the existence of a many-minima surface separated by moderately high barriers. When the potential energy barriers are lower, dynamic disorder is possible with molecules jumping from minimum to minimum. Information on potential energy barriers can be obtained from X-ray data as well as from the temperature dependence of N.M.R. spectra.

The e.f.f. method can be applied also to the study of reorientational disorder. We use a simple cluster model which is formed from a reference molecule, the only one allowed to move, and a number of surrounding 'frozen' molecules, the positions of which are defined by the space group symmetry. The field experienced at any time by the reference molecule is obtained by the pair-wise addition of non-bonded interactions between its atoms and all the atoms of the surrounding molecules. The model has been successfully applied to a number of crystals where rotational disorder may be present (Gavezzotti and Simonetta 1975); figure 4 shows the potential energy curves for in-plane rotation of benzene at different temperatures and pressures (phase II is a high-pressure phase).

In figure 5 the potential energy curves for the in-plane rotation of five-membered rings are reported. The two curves for furan correspond to two different phases: one at high temperature provides an interpretation of the X-ray data given the existence of four equivalent minima while the lower temperature phase is completely ordered. The agreement of the force field calculations with the X-ray results is excellent. For thiophene the calculation predicts six equivalent minima, while the crystallographic

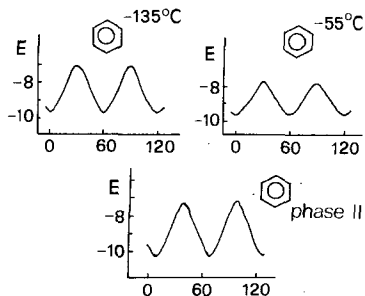


Figure 4. Potential energy curves for in-plane rotation of benzene at different temperatures and pressures.

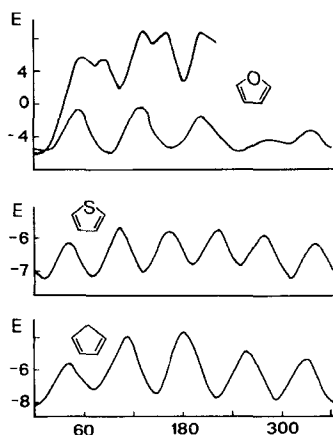


Figure 5. Potential energy curves for in-plane rotation of five-membered rings (E kcal/mole; angles in degrees).

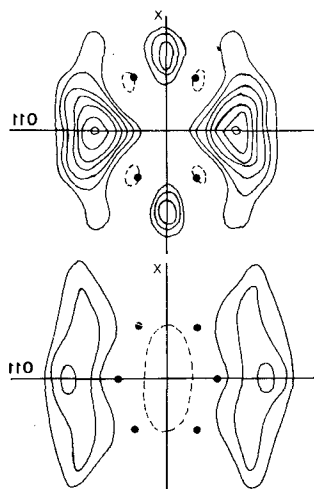


Figure 6. Difference synthesis in the molecular plane for thiophene. Above: fourfold disorder; below sixfold disorder; with sixfold symmetry the map takes a smoother appearance.

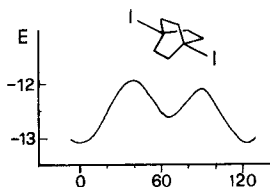


Figure 7. Potential energy for rotation of the bicyclooctane cage around the iodine-iodine axis in 1,4-diiodobicyclo[2,2,2]octane.

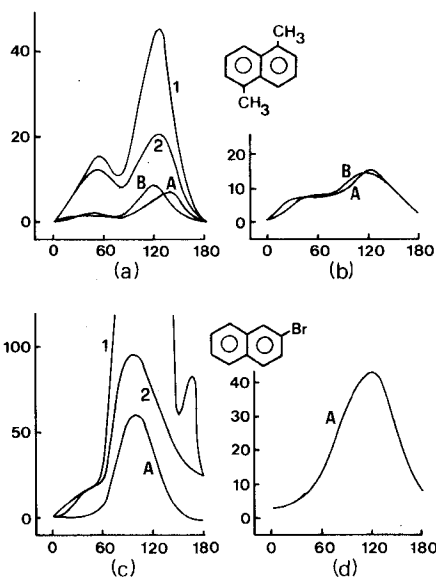


Figure 8. Potential energy and total libration curves for the in-plane rotation of 1,5-dimethylnaphthalene (a, b) and 2-bromonaphthalene (c, d). Curves A and B are the contributions due to contacts of the fundamental molecule with the two nearest neighbours.

data were interpreted assuming only four equivalent positions (Abrahams and Lipscomb 1952).

Comparison of difference Fourier syntheses (figure 6) seems to favour the six-minima potential. Figure 7 shows the potential energy curve for rotation of the bicyclooctane cage about the iodine-iodine axes in 1,4-diiodobicyclo[2,2,2]octane; it is not surprising that while the heavy atoms were easily located by crystallographic methods, the bicyclooctane cage was found to be disordered.

A more refined model considers a cluster of molecules, one of which, the reference, undergoes rotation while one or more other molecules in the cluster are allowed appropriate and correlated motions, with respect to which the cluster energy is minimized. The cluster is modelled in two shells, the first including the cooperating molecules, and the second to ensure that they experience approximately the same field as the fundamental one (Gavezzotti and Simonetta 1976). The motion of the cooperating molecules is described by means of the so-called total libration angle L

$$L = \sqrt{(\theta_1^2 + \theta_2^2 + \theta_3^2)} \quad (3)$$

where $\theta_1, \theta_2, \theta_3$ are rotational angles around the axes of inertia of the molecule. Some results are shown in figure 8, where potential energy and libration curves are shown for

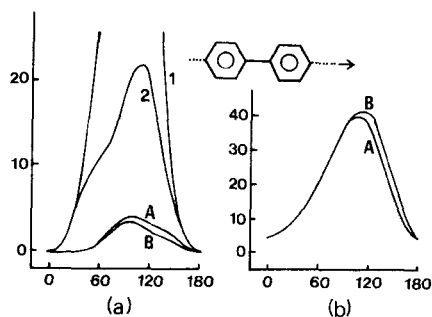


Figure 9. Potential energy and total libration curves for rotation of biphenyl around the axis shown. Curves A and B as in figure 8.

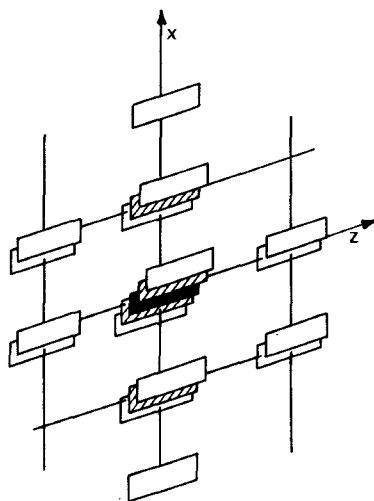


Figure 10. The 21-molecule cluster used in calculation of lattice energies of n-alkanes.

1,5-dimethylnaphthalene. Molecular rotation is predicted with an activation barrier of 20 kcal/mole but for 2-bromonaphthalene, cooperative motions are not sufficient to allow rotation. An interesting case is biphenyl (figure 9) where the fundamental molecule rotates around the axis of minimum inertia and the total librations of the neighbour molecules are again essentially rotations around the axis of minimum inertia with a gear-like motion being suggested.

Intermolecular packing energy calculations were also described for a few, even-numbered, n-alkane crystal structures (Filippini *et al.* 1981). The model cluster is shown in figure 10. In addition to rigid-body rotational energies, the energies required for crystal lattice contraction or expansion and for single- or double-kink formation along the molecular chain were determined, as well as the energy variation connected with the inclusion of a guest molecule in the crystal. Figure 11 shows potential energy surfaces for double-kink formation in n-C₁₄ while figure 12 gives the overall energy curve for formation of a double-kink structure when the intermolecular energy is included. These results are of value in the study of defect formation and of phase transitions in crystalline hydrocarbons, the implication of such phenomena in the melting of molecular solids being difficult to exaggerate (Ubbelohole 1978). I would like to mention that the concept of non-bonded packing energy can be supplemented with the

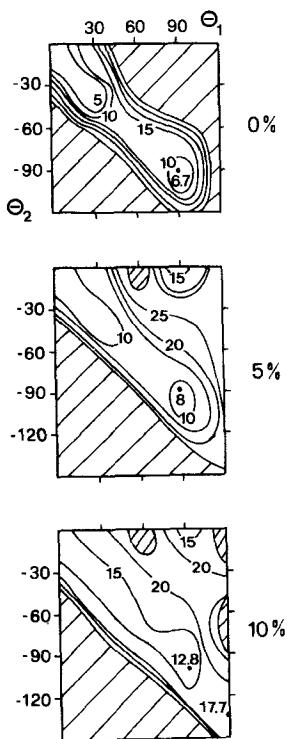


Figure 11. Potential energy surface for double kink formation in $n\text{-C}_{14}$. Percentages refer to lattice dimension change. Isoenergetic curves are drawn at intervals of 5 kcal/mole, the dashed areas being regions of very high energy.

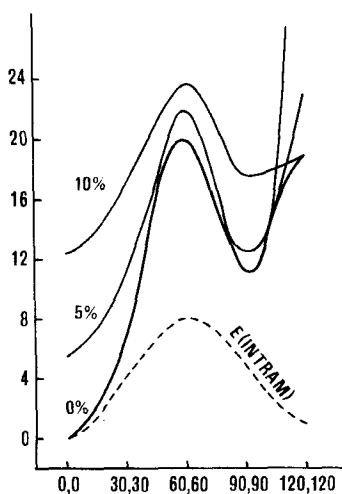


Figure 12. Overall potential energy curve for the formation of a double kink in $n\text{-C}_{14}$. Energy in kcal/mole; the abscissa is the displacement along the diagonal path in the surfaces of figure 11. Percentages as in figure 11.

calculation of molecular volumes: the combined use of packing efficiency and volume analysis can be a very efficient tool in the investigation of structured media and of solid state reactivity (see, for example, Gavezzotti 1983).

5. Thermodynamic functions and phase transitions

The motions of a rigid molecule in a crystal can be described by means of a six-dimensional displacement vector \mathbf{u} (Born and Huang 1954)

$$u_i(kl) = U_i(k\mathbf{q}) \exp i|\mathbf{q} \cdot \mathbf{r}(kl) - \omega(\mathbf{q})t| \quad (4)$$

$i = 1, 2, \dots, 6$ corresponds to the three translational and three rotational components while k labels the molecules in the unit cell ($k = 1, 2, \dots, p$) and l the unit cells in the crystal ($l = 1, 2, \dots, N$). \mathbf{U} is the amplitude, \mathbf{q} the wave vector, ω the frequency and \mathbf{r} a vector from the origin to the centre of mass of the molecule. u can be differentiated twice with respect to the time and multiplied by the mass or the appropriate inertial momentum. The resulting expression is equal to the force acting on the molecule, given, in the quasi-harmonic approximation, by

$$F_i(kl) = - \frac{\delta E}{\delta u_i(kl)} = - \sum_{j, k', l'} \left| \frac{\delta^2 E}{\delta u_i(kl) \delta u_j(k'l')} \right|_0 u_j(k'l) \quad (5)$$

where $j = 1, \dots, 6$; $k' = 1, \dots, p$; $l' = 1, \dots, N$. The derivatives must be evaluated at the equilibrium position and the approximation is quasi-harmonic since its expansion as a function of displacement is terminated at second order; the second derivatives of the energy are not constants. The energy of the crystal is given by

$$E = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} V_{\alpha\beta\gamma} \quad (6)$$

where α labels atoms in the reference molecule, β atoms in the surrounding molecules and γ the molecules in the crystal. The sum over γ included molecules within a reasonable range of distances (for example, 0–15 Å) and the atom–atom interactions $V_{\alpha\beta\gamma}$ are given by the empirical non-bonded potential used in force field calculations. A test of the quality of the potential given in equation (6) is the so-called function of merit $\sum_i (\Delta x_i)^2$ where Δx_i are the shifts of coordinates of each atom on going from the experimental position to the position found by packing energy minimization. The final form of the equations of motion is:

$$\omega^2(\mathbf{q}) m_i U_i(k\mathbf{q}) = \sum_j \sum_{k'} \sum_{l'} \Phi_{ij}(kl, k'l') \exp i|\mathbf{q} \cdot \Delta \mathbf{r}| U_j(k'\mathbf{q}) \quad (7)$$

where

$$\Phi_{ij}(kl, k'l') = \left| \frac{\delta^2 E}{\delta u_i(kl) \delta u_j(k'l')} \right|_0 \quad (8)$$

and

$$\Delta \mathbf{r} = \mathbf{r}(k'l') - \mathbf{r}(kl) \quad (9)$$

Equation (7) corresponds to an eigenvalue–eigenfunction problem and can be solved for each value of \mathbf{q} . When $\mathbf{q} = 0$ the non-zero eigenvalues represent frequencies that can be measured by Raman or infrared spectroscopy. When \mathbf{q} is varied along a direction in the Brillouin zone, phonon dispersion curves are obtained. In order that the dimension

of the calculation is restricted to a finite, reasonable size, one must proceed to a sampling within the Brillouin zone. From the eigenvectors it is possible to evaluate the translational, librational and correlational tensors which, in turn, are used to test the rigid-body motion assumption (Shomaker and Trueblood 1968) (**T**, **L**, **S** respectively). They are related to the mean square displacements of the atoms in rigid molecules:

$$W_{ij} = T_{ij} + \sum_{kl} G_{ijkl} L_{kl} + \sum_{kl} H_{ijkl} S_{kl} \quad (10)$$

where G_{ijkl} , H_{ijkl} are known functions of the atomic coordinates. The calculated W_{ij} can be compared with the experimental anisotropic temperature factors B_{ij} :

$$W_{ij} = \frac{B_{ij}}{2\pi^2} \quad (11)$$

where the **B** tensors are referred to cartesian coordinates.

Also, from the phonon dispersion curves, the density of states can be obtained:

$$g(v_j) = N \sum_i n_i(v_j, v_j + \Delta v_j) \chi_i \quad (12)$$

where the summation is over all sampling points in the Brillouin zone, n_i is the number of frequencies between v_j and $v_j + \Delta v_j$, χ_i is a weight proportional to the extension of the sampling interval and N is a normalizing factor so that $\sum_j g(v_j) \Delta v_j = 1$.

From the density of states it is possible to calculate the partition function for the lattice vibrations and hence, if the spectroscopic data for the internal frequencies are available, all thermodynamic functions for the crystal can be obtained by applying the usual machinery of statistical thermodynamics. The results for the enthalpy of sublimation, specific heat, entropy, free energy function and vapour pressure for a number of rigid crystalline hydrocarbons such as naphthalene, anthracene, pyrene, adamantane are good (Filippini *et al.* 1975 a). The evaluation of cell parameters at various temperatures through free energy minimization is also feasible (Filippini *et al.* 1975 b). This technique has been profitable when applied to the cubic α -phase of solid N_2 (Filippini *et al.* 1976). If the cell dimension was calculated at constant temperature as a function of pressure, the cell edge increased linearly up to a value, depending on temperature, where a collapse of the cell appeared. Vice versa, if the pressure were kept constant, the cell volume increased smoothly with increasing temperature, up to a sudden explosion. If the points of singularity are plotted on a P-T diagram, the range of stability of the α -phase with respect to the hexagonal β -phase and tetragonal γ -phase is obtained. In figure 13 force-field results are compared with the experimental phase diagram (Stewart 1956).

A metastable stress-induced phase transition in crystals of anthracene has recently been discovered by transmission electron microscopy (Parkinson *et al.* 1978). The triclinic phase always coexists with the stable monoclinic phase and, assuming a perfect topotactic fit at the interface, a set of unit cell parameters for the metastable phase was calculated. However, in view of the tolerance of mismatch the precise values of the cell dimensions are not known. The structure was refined by means of force-field and dynamical calculations (Gramaccioli *et al.* 1980). First, the rotation and translation of the rigid molecule and the values of the unit cell parameters were relaxed, and the packing energy minimized. Starting from different points some calculations converged to the stable phase, but a few converged to the triclinic phase, all having very similar energies. At this point calculations of the dispersion curve through the first Brillouin

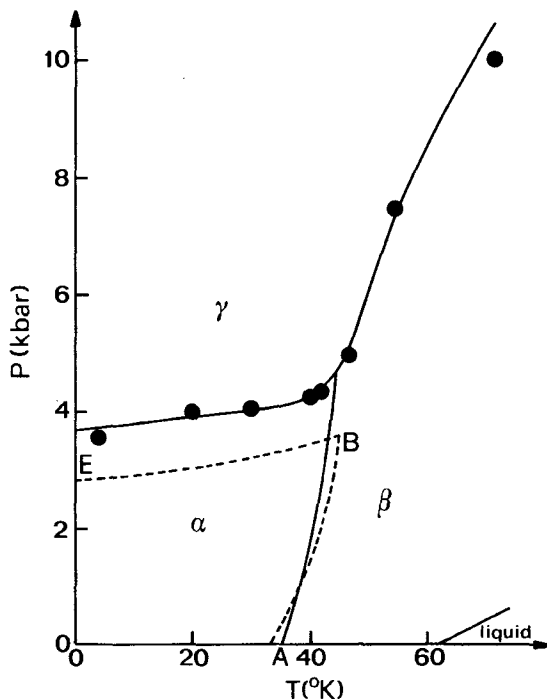


Figure 13. Experimental (solid lines) and calculated (dashed lines) phase diagram for nitrogen.

zone have shown that in all cases imaginary frequencies occurred, except for one structure, the stable one (see figure 14). In other problems the condition of molecular rigidity was relaxed and internal as well external vibrational modes were investigated (Califano *et al.* 1981). In this case an interesting issue is the evaluation of the variation of internal frequencies on going from the gas phase to the crystal (Filippini *et al.* 1984).

6. Two-dimensional crystallography

The first application of force-field calculations to a two-dimensional problem was the calculation of the surface structure for naphthalene crystals (Filippini *et al.* 1979). From low-energy electron diffraction (LEED) results (Firmant and Somarjai 1975) it was suggested that the (001) surface of naphthalene is unreconstructed, that is that it has essentially the same geometry as in the bulk. We performed calculations for this surface, shown in figure 15, using the techniques set out earlier. In order to study the surface and not the bulk structure, we used a fictional unit cell such as that illustrated in figure 16. Relaxation of the bulk structure leads to small shifts, of the order of $0.5\text{--}2^\circ$ in rotation and $0.01\text{--}0.1 \text{ \AA}$ in translation, with minimal energy variations; on moving inside the crystal, as it were, these effects fall off rapidly. The conclusion is that the (001) surface is unreconstructed, a result which holds also for the (100) surface.

Force-field calculations turn out to be extremely useful in the study of the structure of monolayers of organic molecules adsorbed on metal surfaces. Outstanding experimental techniques for the elucidation of such structures are LEED and EELS (electron energy loss spectroscopy). However, it has been pointed out that the

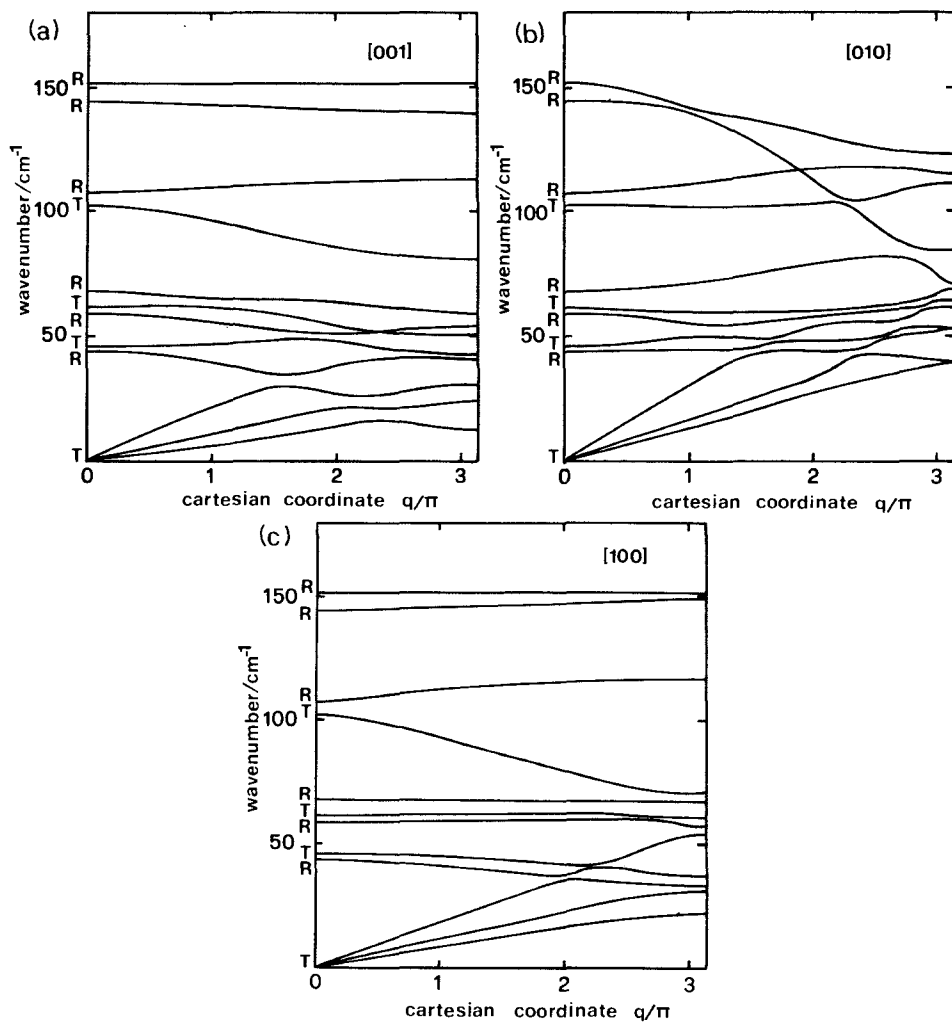


Figure 14. Dispersion curves for phase II triclinic of anthracene calculated along the (001), (010) and (100) axes.

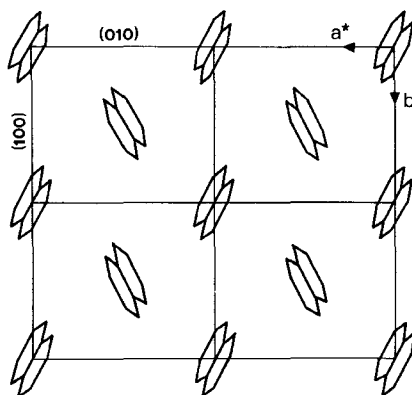


Figure 15. The (001) surface of naphthalene, as seen along c .

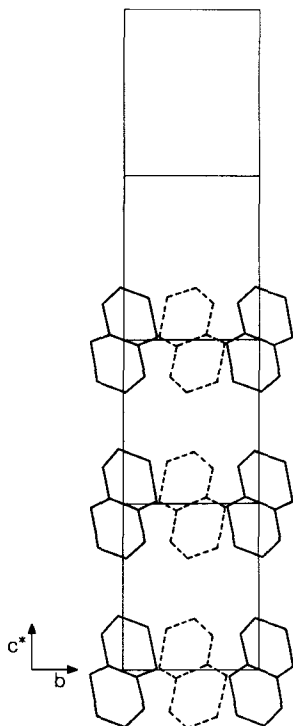


Figure 16. Unit cell for the (001) surface of naphthalene, projected along the a axis. The periodicity normal to the surface is a multiple of the corresponding one in the crystal, so that all distances between any atom in the highest layer and any atom in the cell 'above' exceeds 15 \AA .

interpretation of LEED results by means of multiple scattering theory becomes awkward and complex when more than two atoms are contained in the adsorbate unit cell (Pendry 1982). EELS, too, is much more informative on the chemical nature of the adsorbed species than on the way the molecules are arranged and registered with respect to the atoms of the metal substrate.

In our theoretical study of the structure of acetylene chemisorbed on the Pt (111) surface at low temperature (-100°C) (Gavezzotti and Simonetta 1977), the first step was to check, by means of a force field calculation, that all the orientation of the molecules arranged in a $p(2 \times 2)$ structure were energetically accessible (see figure 17). On increasing the molecular weight of the adsorbate the role of steric hindrance becomes more and more important and e.f.f. calculations can become of considerable aid in the elucidation of the structure.

The $p(2 \times 2)$, $c(4 \times 2)$, and $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure for propylidyne ($\text{CH}_3\text{-CH}_2\text{-C}\equiv$) on Rh(111) and Pt(111) have been examined. The energy as a function of the angle of simultaneous rotation of the molecules in a monolayer around the vertical C- CH_2 axis is shown in figure 18 (Gavezzotti *et al.* 1982). From the shape of the curves it can be concluded that ordering of the ethyl group may be easier for $c(4 \times 2)$ than for $p(2 \times 2)$, but still difficult, both on platinum and rhodium. The $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure is most likely ordered on both metals. Another example is the chemisorption of azulene and naphthalene on Pt(111). LEED results suggest for naphthalene a structure formed by ordered molecules lying in a plane paralleled to the

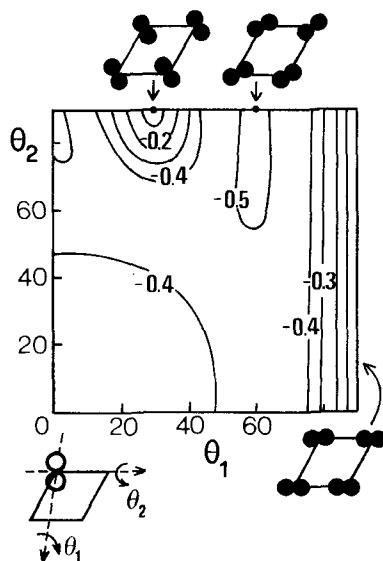


Figure 17. Packing energy for acetylene adsorbed on Pt (111) in a $p(2 \times 2)$ structure as a function of the shown angles of rotation.

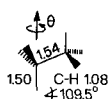
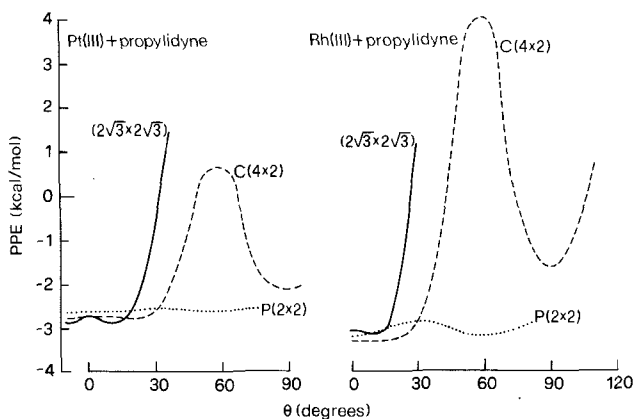


Figure 18. Packing energy for propylidyne adsorbed on Pt (111) and Rh (111) to form different structures, as a function of the shown angle of rotation.

metal surface, forming three equivalent domains of a (6×3) unit cell (Dahlgren and Hemminger 1981 a). The existence of glide planes was also suggested. Assuming that adsorbate-adsorbate interactions are predominant with respect to hydrocarbon-metal interaction in determining the ordering of molecules, the structure shown in figure 19 was found to be the most stable one (Gavezzotti and Simonetta 1982 a). In the case of azulene, no glide plane seems to exist and a reversible phase transition was discovered after annealing at about 125°C (Dahlgren and Hemminger 1981 b, 1982). The results of e.f.f. calculations (Gavezzotti and Simonetta 1982 b) show that the two

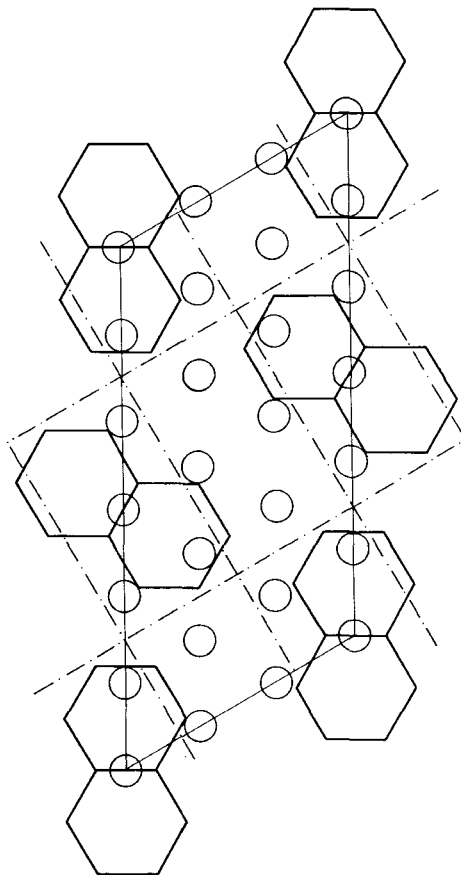


Figure 19. The unit cell (3×6) for naphthalene adsorbed on Pt(111).

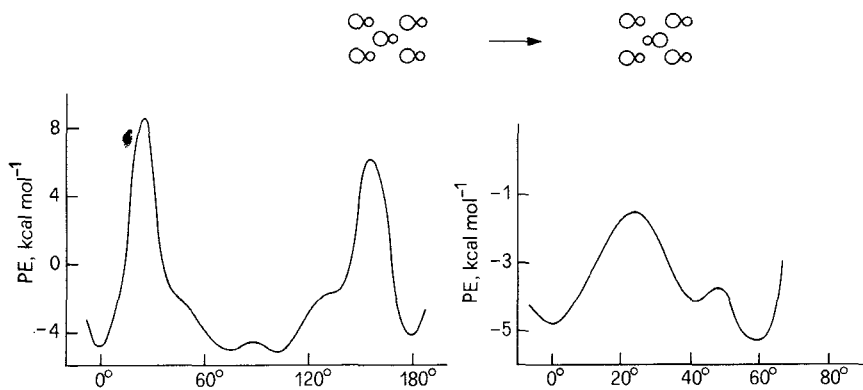


Figure 20. The variation of packing energy as a function of the angle of rotation around the axis perpendicular to the molecular plane for azulene adsorbed on Pt(111), to form structures with (right) or without (left) a glide plane of symmetry.

structures with or without glide planes, enjoy equal stability (figure 20). This different behaviour must be related to the difference in metal–hydrocarbon interactions.

Considering that both experimental (Somorjai 1981) and theoretical (Gavezzotti and Simonetta 1980) evidence suggests that the strength of bonding of organic molecules or fragments to a clean planar metal surface is rather insensitive to changes in the local symmetry of the bonding site, it can be anticipated that adsorbate–adsorbate interactions represent the dominant term in determining the structure of the overlayer. Multiple scattering theory has not graduated significantly beyond the trial and error level and the calculation for each of the numerous plausible trial structures is very time consuming. As a result the layer formation energy, as calculated by the e.f.f. method seems to represent the most efficient tool at hand at present for two-dimensional structure analyses. An automatic procedure for searching the possible structures is being developed and has been successfully applied to azulene and naphthalene on the Rh(111) surface (Gavezzotti and Simonetta (1983). It is important to note that this approach emphasizes that registry between overlay and substrate structures is one only of serendipity.

Last but not least layer formation energy results are very sensitive to the positions of hydrogen atoms, while in scattering calculations hydrogen atoms are not even included; the H...H interactions may have a paramount consequence on the choice of structure.

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