Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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A. J. Campbell [a b] , C. A. Fyfe [a b] , D. Harold-smith [a b] & K. R. Jeffrey [a c]

[a] Guelph-Waterloo Centre for Graduate Work in Chemistry

[b] Guelph Campus, Department of Chemistry, University of Guelph, Guelph, Ontario, Canada

[c] Guelph Campus, Department of Physics, University of Guelph, Guelph, Ontario, Canada

To cite this article: A. J. Campbell , C. A. Fyfe , D. Harold-smith & K. R. Jeffrey (1976): An Investigation of the Dynamic Structures of Ferrocene, Ruthenocene and Dibenzenechromium in the Solid State and in Solution, Molecular Crystals and Liquid Crystals, 36:1-2, 1-23

To link to this article: http://dx.doi.org/10.1080/00268947608084827

*Mol. Cryst. Liq. Cryst.*, 1976, Vol. 36, pp. 1–23

Printed in Holland

# An Investigation of the Dynamic Structures of Ferrocene, Ruthenocene and Dibenzenechromium in the Solid State and in Solution

A. J. CAMPBELL,[‡] C. A. FYFE,[†‡] D. HAROLD-SMITH,[‡] and
K. R. JEFFREY[§]

*Guelph-Waterloo Centre for Graduate Work in Chemistry; Guelph Campus,*
*Departments of Chemistry and Physics, University of Guelph, Guelph, Ontario, Canada*

(*Received February 23, 1976*)

Pulse nuclear magnetic resonance measurements have been used to determine the activation enthalpies for the reorientation of the organic rings in ferrocene, ruthenocene and dibenzenechromium. The contribution from non-bonded interactions to the total potential for reorientation of the rings has been calculated and is compared to the experimental activation enthalpies. The results indicate that there is no contribution to the potential from the non-bonded interactions between the two rings on a single molecule and that the observed potential barrier is due to a combination of crystal packing forces and bonding forces within the molecule.

The crystal structure of ferrocene is thought to be disordered above 135°K, and a model is proposed for the order-disorder transition in the solid state. On this basis, dynamic models are proposed for the structures of the three metallocenes in solution.

## INTRODUCTION

Considerable work has been done to investigate the structures of metallocenes, much of the work being done on the solid state. Of the compounds with unsubstituted aromatic rings, the structures of ferrocene, ruthenocene and dibenzenechromium have been the most thoroughly investigated.

The first detailed report on the structure of ferrocene was the single crystal X-ray diffraction study of Dunitz *et al.*[1] Despite a large *R* factor (17.5 %) and the fact that a difference synthesis indicated some electron density between

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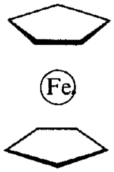
[†] Author to whom enquiries should be addressed.

[‡] Department of Chemistry.

[§] Department of Physics.

the calculated positions of the carbon atoms, it was concluded that the molecular structure of ferrocene were of approximate $D_{5d}$ symmetry with the rings in a staggered conformation (**1**).



(**1**)

This structure is still generally accepted, although several other studies have indicated that this is not necessarily a complete description of the structure.[2–18]

A study of the thermodynamic properties of ferrocene[9,10] revealed the presence of a $\lambda$ point transition in the heat capacity ($C_p$) at 163.9°K. X-ray diffraction studies down to 95°K showed that the lattice dimensions are continuous functions of temperature. The mechanism suggested for the $\lambda$ point transition was that of rotational disorder of the rings. It was also concluded that the close relationship of the room temperature and low temperature X-ray data was consistent with the low temperature (below the $\lambda$ point transition) structure being an ordered lattice of staggered molecules.[9] However, a complete structure determination was not carried out.

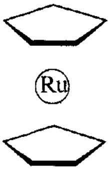
A neutron diffraction study of ferrocene was made by Willis[11,12] using a limited number of reflections. Although no data or results were presented, it was concluded in this study that there is disorder in the orientation of the molecules: that is, the molecules have the staggered configuration (structure 1); but there are two orientations (related by a 36° rotation about the C5 axis) presented in the proportion 2 : 1. This is in quantitative agreement with the specific heat measurements.[9]

The dynamic aspects of the structure of ferrocene in the solid state have been investigated by continuous-wave NMR. The second moment was measured between 68° and 300°K, and correlation times derived from progressive saturation experiments were reported for a similar temperature range. It was concluded that the cyclopentadienyl rings were undergoing rotation in the plane of the ring. A discontinuity in the plot of the correlation time ($\tau_c$) against $1/T$(°K) was observed by Holm and Ibers;[8] they concluded that, at temperatures above the discontinuity, the motion could no longer be described by a single correlation time.

Churchill and Wormald[17] have summarized the solid-state structural data available for ferrocene and its derivatives. It was noted that the conformation of the rings varied from completely staggered to eclipsed, and they concluded that the conformation of the rings were dependent on the balance between the intramolecular carbon-carbon repulsions and the intermolecular packing forces. Krukonis *et al.*[18] extended the list of structural data on these compounds, and concluded, in agreement with Palenik,[19] that the eclipsed form was the "normal" conformation of the cyclopentadienyl rings in ferrocene and its derivatives. There is some direct evidence that ferrocene is eclipsed in the absence of intermolecular forces:

Electron diffraction studies[13–16] on ferrocene in the gas phase have been interpreted in terms of an eclipsed molecular structure with a barrier to rotation of approximately 0.9 kcal/mole.

The structure of ruthenocene has been determined, in the solid state, by X-ray diffraction[21] and the conformation of the rings was found to be eclipsed.



**(2)**

Structure of ruthenocene as determined by X-ray diffraction studies.[21]

The structure of ruthenocene in the gas phase has also been studied by electron diffraction. Unlike ferrocene, however, it proved impossible to choose between the staggered and eclipsed forms for ruthenocene.[16] It has been shown by NMR that there is motion of the cyclopentadienyl rings in ruthenocene in the solid state at temperatures above ~100°K.[2,8] However, there was no observed discontinuity in the plot of $\tau_c$ against $1/T(°\mathrm{K})$[8] as in the case of ferrocene. Hence, it has been concluded that the motion of the rings is about their $C_5$ axis, via a series of 1,2 shifts.†

Dibenzene chromium, has been extensively investigated by both X-ray[22,26] and neutron diffraction[27,28] studies. There has been some dispute as to the symmetry of the molecule. Jellinek concluded that the symmetry was $D_{3d}$[24–26] whereas Cotton *et al*[23] and Ibers[22] maintained that it was $D_{6h}$. Recent neutron diffraction studies[26,27] are consistent with a $D_{3d}$ structure.

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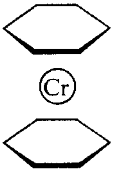
† The errors in these determinations are, however, very large.



(3)

Structure of dibenzene chromium.

Hence, it is concluded that the structure described by Jellinek[24–26] is the correct one: *i.e.*, the molecule has $D_{3d}$ symmetry with the benzene rings being approximately planar and having alternate long and short bonds (The difference in bond lengths being about 0.07 Å).

Motion of the benzene rings in this complex has been detected by solid state NMR[2]; however, to date there has been no detailed investigation of this compound using these techniques.

Recently it has been shown that it is possible to theoretically predict the barriers to reorientation of molecules in the solid state with acceptable accuracy using non-bonded atom-atom potential functions.[32] The first compounds studied were benzene and other polycyclic aromatic compounds.[32a] For these compounds the problem is comparatively simple since

1) there are no internal motions to be considered and

2) the molecules are planar so that one rotational axis is *a priori* favoured over the others.

The second more complex type of molecule treated was cage-like aliphatic molecules such as adamantane and hexamethylenetetramine.[32b,c] In these cases, the molecules are still rigid, but there are several probable axes. In the case of adamantane[32c] it was also possible to provide a detailed and specific dynamic model for the order-disorder transition observed for this solid. It should be possible to extend these calculations to the reorientation of molecules where there are internal motions possible, provided the dependance of the intramolecular bonding on the internal conformation is small or can be determined. It was hoped that the metallocenes would be of this type.

The purpose of the work was thus three-fold: firstly, to determine the solid-state activation energies for the reorientation of the organic rings in ferrocene, ruthenocene and dibenzenechromium using pulse-nuclear magnetic resonance spectroscopy; secondly, to calculate the activation energies produced by the non-bonded interactions in the crystal; thirdly, by combining all the relevant data for these compounds, to attempt to explain the order-disorder transition in ferrocene and the variety of conformations exhibited by these compounds in the solid and gaseous states.

## EXPERIMENTAL

Pulse NMR measurements were made at 18 MHz using a spectrometer constructed in the laboratory. Samples were sealed in 10 mm o.d. thin walled glass tubes, and temperature variation was achieved using a gas-flow system. Details of the instrument design, measurement techniques, and sample preparations have already been given.[33]

All potential energy and other computer calculations were performed with programs written by the authors; additional details of the programs and of the models upon which they are based have also been given elsewhere.[32,33]

## RESULTS AND DISCUSSION

### A Spin-lattice relaxation time measurements

*(i) Ferrocene*

$T_1$ was measured over the temperature range 296–90°K and was found to be very temperature dependent (Figure 1). A discontinuity in $T_1$ was observed at about 163°K which is consistent with the $T_1$ results of Holm and Ibers[8] and the thermodynamic study of Edwards *et al.*[10] It was concluded that at temperatures above the transition the motion could not be described by a single correlation time; hence only values of $T_1$ below 150°K were used in the computer fit[33] of the experimental results to equations (1) and (2):

$$T_1 = C\left[\frac{\tau_c}{1 + \omega_0^2\tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2\tau_c^2}\right] \tag{1}$$

$$\tau_c = \tau_\infty \exp(E_a/KT) \tag{2}$$

A good fit was obtained in the region below 150°K as indicated by the solid curve in Figure 1. The resulting values of $E_a$, $\tau_c$ and $C$ are given in Table I.

TABLE I

Values of $E_a$, $\tau_\infty$, and $C$

| Compound | $\tau_\infty$ (sec) | $C$ (sec$^{-2}$) | $E_a$ (kcal/mole) |
|---|---|---|---|
| Ferrocene | $6.16 \times 10^{-13}$ | $2.21 \times 10^9$ | 1.99[a] 1.8[b] 2.3[c] |
| Ruthenocene | $2.10 \times 10^{-13}$ | $2.81 \times 10^9$ | 4.51[a] 2.3[b] |
| Dibenzene Chromium | $1.67 \times 10^{-13}$ | $3.38 \times 10^9$ | 4.56[a] |

[a] Values obtained in the present study.
[b] From reference 8.
[c] From reference 6.

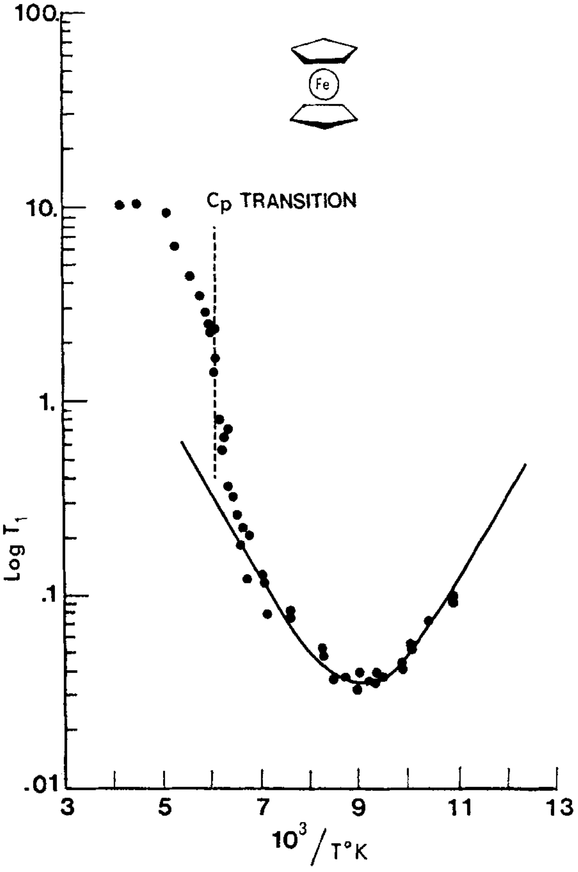


FIGURE 1 Proton spin-lattice relaxation times of ferrocene measured at 18 MHz. The solid curve is a computer-calculated best-fit to the experimental points.[33]

### (*ii*) *Ruthenocene*

$T_1$ was measured over the temperature range 301–152°K and was found to to be very temperature dependent. The value of $T_1$ was found to pass through a minimum at about 215°K. Values of $E_a$, $\tau_\infty$ and $C$ were obtained from a computer fit[33] to the experimental $T_1$ results and are given in Table I. The value of $E_a$ is considerably larger than that reported previously.[8] It is, however, in good agreement with the value reported from a detailed analysis of the "thermal errors" in the X-ray diffraction measurements using a hindered rotor model.[35]

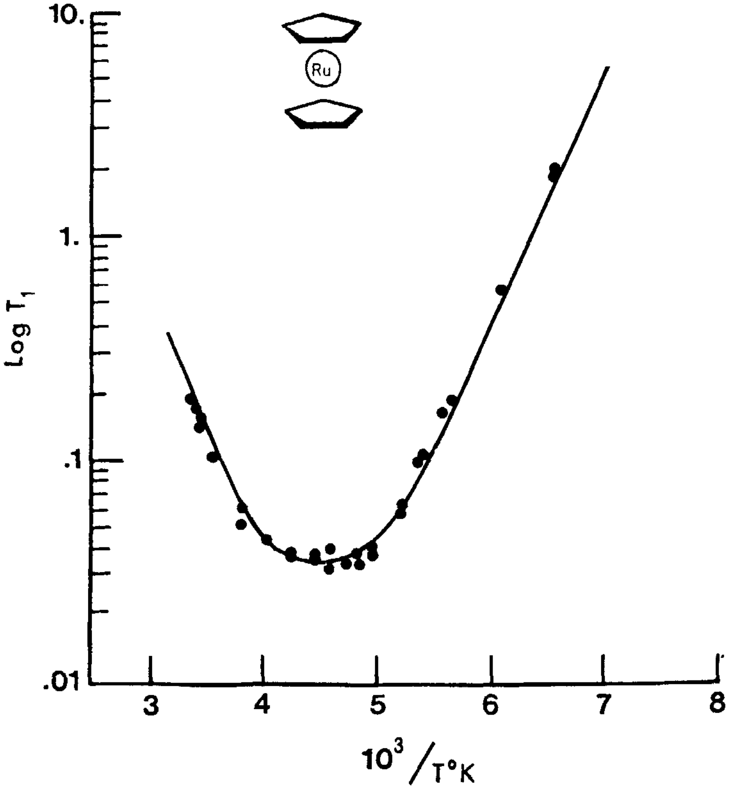


FIGURE 2 Proton spin-lattice relaxation times of ruthenocene measured at 18 MHz. The solid curve is a computer-calculated best-fit to the experimental points.

The complete experimental data together with the theoretical curve are shown in Figure 2.

*(iii) Dibenzene Chromium*

Results very similar to those of ruthenocene were obtained, the $T_1$ minimum occurring at about 220°K. A computer fit[33] to the experimental data yielded values of $E_a$, $\tau_\infty$ and $C$ (see Table I).

The complete experimental data together with the theoretical curve are shown in Figure 3.

The results obtained in the present work are compared with previously obtained values in Table I. The value of $E_a$ for ferrocene is in good agreement with the value obtained by Holm and Ibers;[8] hence the value of 1.9

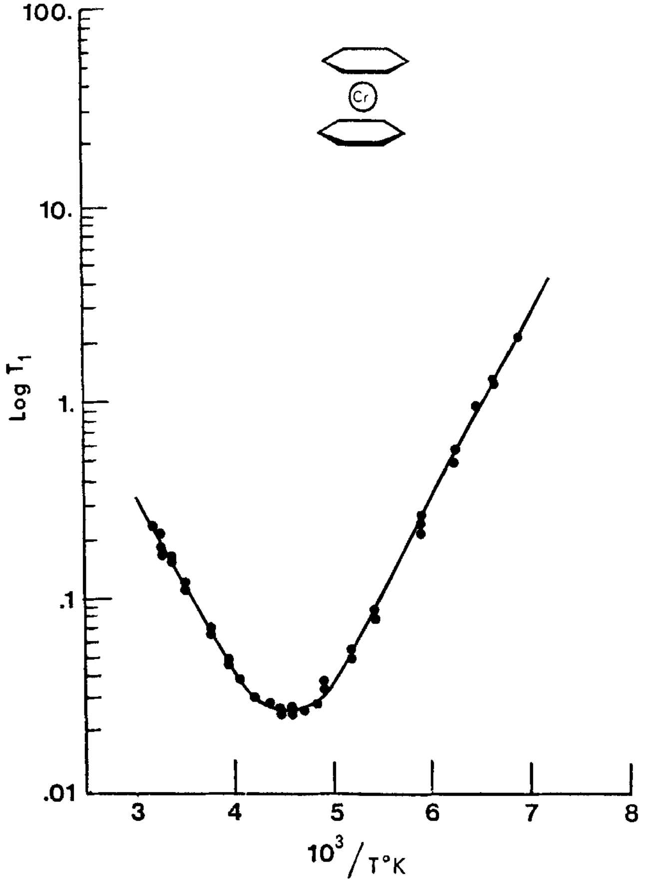


FIGURE 3 Proton spin-lattice relaxation times of dibenzenechromium at 18 MHz. The solid curve is a computer-calculated best-fit to the experimental points.[33]

kcal/mole is thought to be an accurate value for the energy barrier. In the case of ruthenocene there is a noticeable difference between the value obtained in the present work and the value obtained by Holm and Ibers.[8] Since the technique used in the present work is subject to fewer errors than the progressive saturation technique of the earlier work, the value of 4.51 kcal/mole is considered more accurate.† The value of $E_a$ for dibenzene chromium, 4.56 kcal/mole, is also considered accurate, and is similar to the activation enthalpies for rotation of the benzene ring which have been determined for benzene-metal ion complexes.[29]

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† A similar value has been deduced from a refinement of the X-ray data treating the rings as rigid-body oscillators.[35]

These results will be discussed further and compared to the results from the calculations of the potential energy between the non-bonded atoms.

## B Potential energy calculations

### (*i*) *Choice of potential functions and model*

(*a*) *Potential Functions* In these calculations the potential energy of interaction between any two non-bonded atoms in a crystal lattice is assumed to be a function dependent only on the nature of the two atoms and the distance between them, to be independent of the nature of the rest of the molecules of which the individual atoms are a part, and to be unaffected by the presence of non-bonded atoms on a third molecule with which the two atoms under consideration may be simultaneously interacting. In the present work two types of function were used to describe these interactions. For C—C, C—H and H—H interactions the exponential −6 function was used,

$$V = Ar^{-6} + B\exp(-\mathrm{C}r), \tag{3}$$

where $V$ is the potential energy of interaction between the non-bonded atoms; $r$ is the distance between them; and $A$, $B$ and $C$ are empirically determined parameters which are dependent on the pairs of interacting atoms. The experimental information used to obtain these parameters is the crystal structures for a series of molecular crystals and their enthalpies of sublimation.[30] The values of the parameters $A$, $B$, $C$ for Eqn. (1) which were used in the present work are listed in Table II. The "6-exp" function is generally considered to be the best description of the non-bonded interactions. Unfortunately there were insufficient experimental data available to enable the values of the parameters $A$, $B$ and $C$ to be evaluated for the interactions involving the metal atoms, i.e., between M—M, M—H, and M—C (where M=Fe, Re and Cr). Hence an alternate equation, the Lennard-Jones "6-12" potential, was used:

TABLE II

Parameters used in Equation 3

| Atom pair | $A$ (kcal/mole Å$^6$) | B (kcal/mole) | $C$ (Å$^{-1}$) |
|---|---|---|---|
| C—C | −535 | 74461 | 3.6 |
| H—H | −36 | 4000 | 3.74 |
| C—H | −139 | 9411 | 3.67 |

$$V = 4\varepsilon\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \tag{4}$$

Here $\sigma$ is the finite distance at which the potential energy is zero, and $\varepsilon$ is the absolute value of the depth of the potential well. $\sigma$ and $\varepsilon$ differ for the interaction between different atoms. Approximate values for these constants can be obtained from an extension of Badger's Rule.[31]

$$R_e = a_{ij} + b_{ij}[\log_{10} Fs - 5] \tag{5}$$

$R_e$ is the equilibrium distance between the two atoms, $a_{ij}$ and $b_{ij}$ depend only on the row and column of the periodic table for the two atoms being bonded and $Fs$ is the stretching force constant. From Equation (5) it can be shown that the value of $r$ at minimum energy is,

$$R_e = 2^{1/6}\sigma. \tag{6}$$

The stretching force constant is the second derivative of $V$ with respect to $r$ evaluated at $r > R_e$ and is

$$Fs = \frac{72}{2^{1/3}\sigma}. \tag{7}$$

Hence from a knowledge of the equilibrium distance between homonuclear atoms it is possible to calculate value for $\sigma$ and $\varepsilon$. For hetronuclear interactions combination rules apply.

$$\begin{aligned} \varepsilon_{ij} &= (\varepsilon_{ii} \cdot \varepsilon_{jj})^{1/2} \\ \sigma_{ij} &= 1/2(\sigma_{ii} + \sigma_{jj}) \end{aligned} \tag{8}$$

Hence values for $\sigma$ and $\varepsilon$ for M—C and M—H can be calculated.

Several different values of $\sigma$ and $\varepsilon$ were calculated using different values for $R_e$. The best values obtained are given in Table III. The Lennard-Jones 6-12 equation is more empirical than the exponential-6 function, and therefore less reliable. In the course of these calculations, however, it became

TABLE III

Values for $\varepsilon$ and $\sigma$ used in Equation 4

| Atom pair | $\varepsilon$ (kcal/mole) | $\sigma$ (Å) |
|---|---|---|
| Fe—Fe | 0.323 | 3.48 |
| Fe—C | 0.262 | 3.26 |
| Fe—H | 0.109 | 2.34 |
| Ru—Ru | 0.457 | 3.83 |
| Ru—C | 0.309 | 3.45 |
| Ru—H | 0.147 | 2.99 |
| Cr—Cr | 0.323 | 3.48 |
| Cr—C | 0.262 | 3.26 |
| Cr—H | 0.109 | 2.34 |

apparent that the C—C, C—H and H—H interactions determined the shape and height of the potential barrier. The M—M, M—C and M—H interactions were found to be independent of the rotation of the ring in its plane, and they affected the absolute value of the potential but not the height of the energy barrier.

(*b*) *Choice of Model* The model chosen was the simplest one possible. Each of the compounds studied has two organic rings. In the molecule under study, one of these rings was considered to move in its plane whilst the other ring in the molecule and all other rings and metal atoms on other molecules were kept static in the lattice. Thus no concerted motions were considered, nor distortions in the lattice around the molecule under study. The justification for such a simple model comes entirely from the agreement it gives with experiment.[32] Hence, while concerted motions and oscillations may well occur, they would appear to have an effect which is within experimental error.

In the application of this model, the molecule of interest was placed in the correct position as indicated by X-ray diffraction measurements in a unit cell which itself was placed primarily at the centre of twenty seven unit cells. However, in certain cases, for example, ferrocene, half the molecule lies outside the central unit cell and a second layer of unit cells was added on the sides closest to the molecule under study.

The potential energy from the non-bonded interactions of the atoms in this molecule with the atoms of all the other molecules in its own unit cell and those of all the molecules in the surrounding unit cells was evaluated as a sum of the appropriate pair potentials. For distances $>8$ Å the potential was assumed to be zero for C—C, C—H and H—H interactions. The cut-off value for M—M, M—C and M—H was taken as distances $>10$ Å.

When the molecule is thus located in the position given by the X-ray structure, the intermolecular potential evaluated corresponds to the experimentally measurable sublimation energy $\Delta H_{\mathrm{subl}}$.

Ring (1) of the molecule under study was then rotated by an angle $\theta$ round a chosen axis to a new set of coordinates, with all the other atoms in the surrounding molecules kept in their original positions. The intermolecular potential between the molecule under study and all the other molecules was then evaluated. From a series of such calculations, the variation of the intermolecular potential for the motion of the ring (1) around a given axis can be found as a function of the angle of rotation. The difference in energy between the zero rotation and the maximum energy obtained on rotation was equated to the activation energy for motion about this axis. This value plus any barrier to rotation from bonding can then be compared with that obtained from experimental data.

### (*ii*) *Results of first-order calculations*

The sublimation energies and activation energies for reorientation calculated as described above for ferrocene, ruthenocene and dibenzene chromium are presented together with the appropriate experimentally observed values in Table IV. In each case, the theoretical rotation was about the axis through the center of both rings. The agreements between the observed and calculated values of the sublimation energy for ferrocene and dibenzene chromium are within 10% and were taken as a general indication of the validity of the parameters used, especially those in the Lennard–Jones "6-12" equation.

The calculated values for the activation energies are also in good agreement with those obtained from solid-state NMR, considering the simple model assumed.

The characteristics of the different systems studied will be discussed individually:

(*a*) *Ferrocene* Primarily the atomic coordinates for ferrocene were taken from the X-ray structure determination of Dunitz *et al.*[1] The coordinates of the hydrogen atoms were generated from the carbon positions at an assumed bond length of 1.08 Å. The results of this calculation of potential energy as a function of angle for the in-plane rotation about the $C_5$ axis for one ring

TABLE IV

Calculated Effects of Neighboring-Ring Reorientation on the Barrier to Ring Rotation in Ferrocene

| $R$ (Å) | $\Delta V_{Mi}$ (k.cal./mole)<br>$\theta_M = 0°$ | $\theta_M = 36°$ |
|---|---|---|
| 3.30 | 0.0 | 0.0 |
| 4.83 | 0.4 | 0.5 |
| | 0.0 | 0.1 |
| 5.45 | 0.0 | 0.0 |
| | 0.1 | 0.1 |
| 5.75 | 0.4 | 3.5 |
| | 0.3 | 3.4 |
| 5.75 | 0.1 | 1.6 |
| | 0.1 | 0.1 |
| 5.94 | 0.6 | 0.0 |
| | 0.1 | 0.7 |

$R$ is the center-to-center distance between the test ring, $M$, and the neighboring ring $i$. $\Delta V_{Mi}$ is the change in the ring pair potential when ring $i$ is rotated from the orientation which is two-thirds occupied ($\theta = 0°$) to the orientation which is one-third occupied ($\theta = 36°$). $\Delta V_{Mi}$ is listed for two orientations of the test ring, $\theta_M = 0°$ and $\theta_M = 36°$

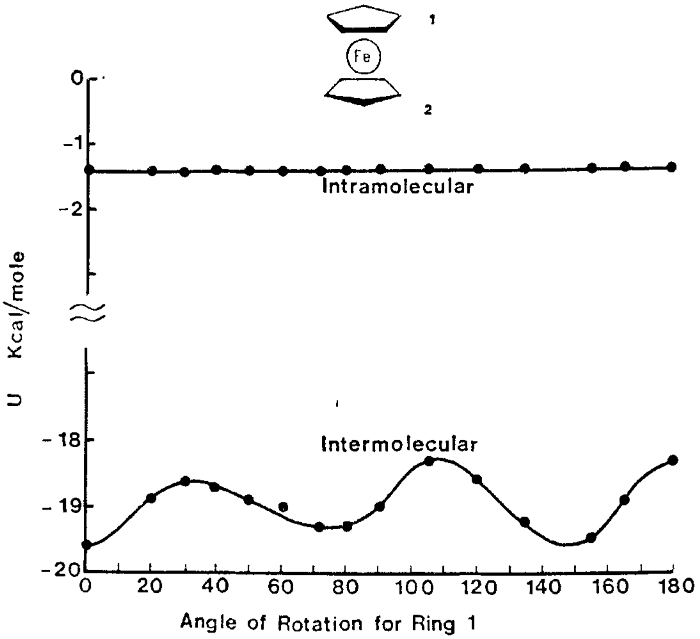


FIGURE 4 Lower curve: Calculated potential for the rotation of one of the rings of a ferrocene molecule, with all other atoms in the lattice held motionless. Upper curve: Angular dependence of the non-bonded potential between the two rings of a ferrocene molecule.

in a ferrocene molecule are given in Figure 4. Distinct minima are observed at 0° and multiples of 72°, as expected from the five fold symmetry of the ring. These correspond to the position of minimum potential energy in the lattice. Maxima are observed at ±36°, ±108° and 180°.

There is reasonable agreement with the measured $\Delta H_{\mathrm{subl}}$[9] and the calculated value of 0° rotation. The value for the activation energy obtained is very low ~1 kcal/mole, which is consistent with the value obtained from the solid-state NMR data. Since the calculations are based on a room temperature structure and the NMR measurements are made at lower temperatures, the calculated values should be lower than the experimentally observed ones due to contraction of the lattice on cooling.

There may also be a small barrier to rotation due to the electronic contribution; this and the temperature effect will be considered subsequently.

Also shown in Figure 4 is the result of the calculation of the potential energy due to non-bonded interactions between the two rings of the ferrocene molecule. The potential is *independent of the angle of rotation* and has a weak attractive influence. This would tend to negate the arguments put forth by Churchill and Wormald[17] that the structure of ferrocene and ferrocene derivatives are dependent on the balance between the carbon-carbon repulsion and the intermolecular packing forces. From these calculations it is concluded that the observed crystal structure is dependent on a balance between the *bonding* forces within the molecule (which favour an eclipsed structure) and the intermolecular packing forces within the lattice. In the case of ferrocene these latter forces are the dominant ones, and the observed crystal structure is not a true indication of the gaseous molecular structure.

The implication of these results will be discussed further when the data from the other calculations designed to test the validity of the current treatment have been presented.

(*b*) *Ruthenocene* The atomic coordinates for ruthenocene were taken from the X-ray structure determination of Herdgrove and Templeton.[21] The hydrogen coordinates were generated at an assumed bond length of 1.08 Å. The result of the calculation of potential energy as a function of angle for the in-plane rotation about the $C_5$ axis for one ring of the molecule under study is given in Figure 5. A distinct minimum occurs at 36°, and this pattern is repeated every 72°.

There is no available experimental value for $\Delta H_{\text{subl}}$ for ruthenocene; hence, the values of $\sigma$ and $\varepsilon$ used in the Lennard-Jones 6-12 equation cannot be checked. However, these values are not critical to the determination of the energy barrier since the ruthenium atoms are symmetrically displaced about the rings. The calculated activation energy is in agreement with the experimentally determined value (Table IV). Also shown in Figure 5 is the result of the calculation of the potential energy between the two rings of the ruthenocene molecule. This intramolecular potential is independent of the angle of rotation and is slightly greater than the force between the rings in ferrocene. This supports the conclusion that for these compounds the crystal structure is determined by the packing of the molecules and hence is not necessarily the molecular structure in the gas or in liquid phases.

(*c*) *Dibenzene Chromium* The atomic coordinates for dibenzene chromium were taken from the X-ray structure determination. The results of this calculation of the potential energy as a function of angle for the in-plane rotation about the hexad axis for ring 1 in the molecule under study are given in Figure 6. As expected from the ring symmetry, distinct minima were obtained at 0° and 60°; and a maximum occurred at 30°.

There is reasonable agreement between the measured $\Delta H_{\text{subl}}$ and the calculated value for the potential energy at 0° rotation. Similarly, there is reasonable agreement of the activation energy from solid-state NMR with the value obtained from the calculations, considering changes in lattice

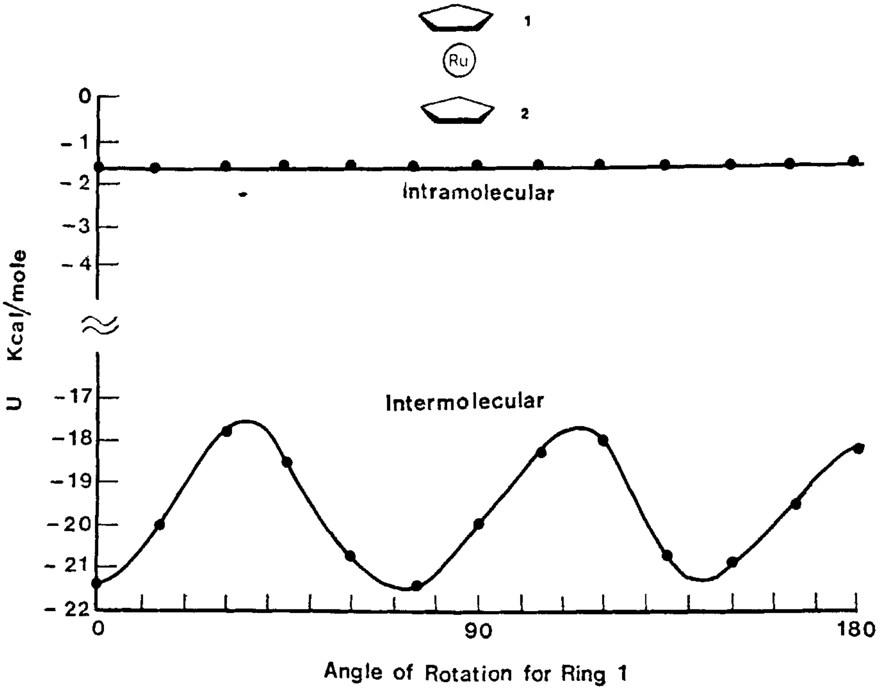


FIGURE 5 Lower curve: Calculated potential for the rotation of one of the rings of a ruthenocene molecule, with all other atoms in the lattice held motionless. Upper curve: Angular dependence of the net non-bonded potential between the two rings of a ruthenocene molecule.

dimensions and the small, unknown contribution from the bonding. As for ferrocene and ruthenocene, the intramolecular potential between rings was also calculated (Figure 6) and found to be independent of angle, which is consistent with the results for the other two compounds.

### (*iii*) *Results of "second-order" calculations and inclusion of intramolecular bonding contributions*

The results of the previous section indicate that approximate values for the activation energies for ring reorientation can be obtained by treating the non-bonded interactions only. They show that the crystal packing forces are the dominant factors in determining the molecular conformations in the solid state, and that these structures may well not be those found in solution, where the conformation will be determined *entirely* by the *bonding* forces within the molecule. The inclusion of such forces into the calculations for reorientation in the solid should also be made for a complete description

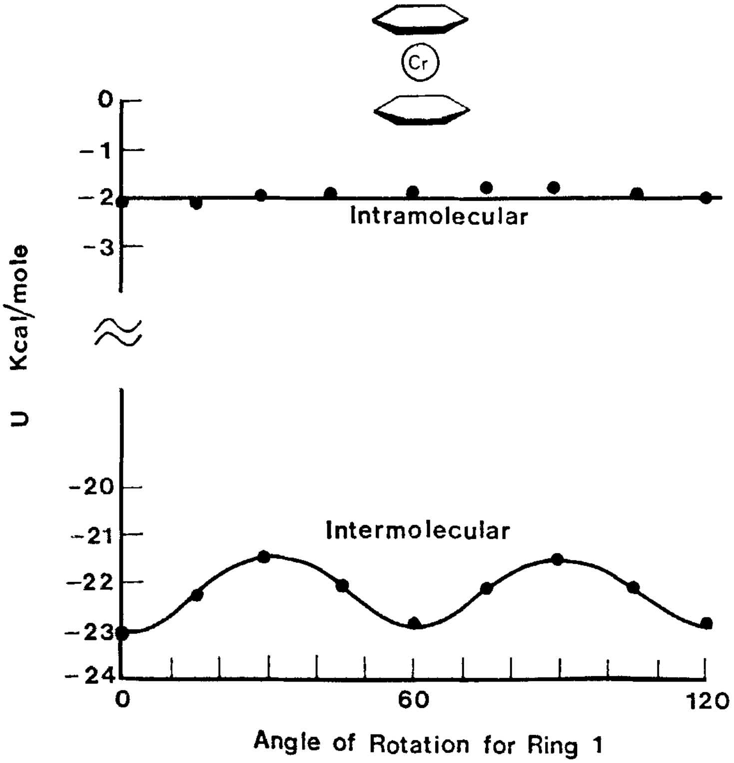
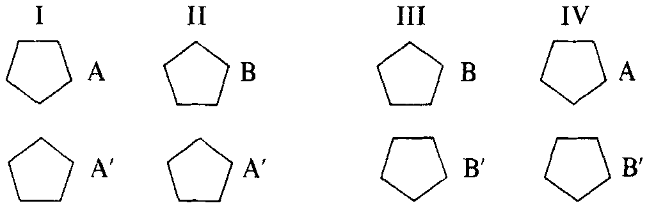


FIGURE 6 Lower curve: Calculated potential for the rotation of one of the rings of a dibenzenechromium molecule, with all other atoms in the lattice held motionless. Upper curve: Angular dependence of the net non-bonded potential between the two rings of a dibenzenechromium molecule.

of the dynamic structures. In the case of ferrocene, an explanation must also be found for the order-disorder transition and the 2 : 1 occupancy of the two disorder sites.

(*a*) *Ferrocene* As indicated above, although the first-order calculations give an approximate description of the contributing factors in the solid-state structure, there are still experimental observations for which an explanation must be found. The most obvious of these is the existence of a higher-order specific heat transition at low temperatures in the case of ferrocene and the implied existence of a disordered phase at room temperature for this compound. A redetermination of the room temperature X-ray structure clearly indicates that there exists two possible orientations for each cyclopentadienyl ring and that there is a statistical 2 : 1 occupancy between them.[34]

The 2 : 1 occupancy can be resolved on a molecular basis in terms of the structures I–IV where AA′ is the major contributing statistical occupancy as indicated by the original X-ray investigation.[1]



Qualitatively, an examination of the original structural data indicates that there are some very short intermolecular contacts introduced into the lattice by the combination BB′ and its occurrence may be considered much less probable.[9] Thus the 2 : 1 occupancy could be represented by the equal occurrence of I, II, IV.

Alternatively, we can describe the disorder in terms of the behaviour of the individual cyclopentadienyl rings. In this description a *single ring* must experience a general potential of the type shown in Figure 7 imposed on it by the surrounding lattice, where there is a subminimum at 30° rotation of similar energy to that of the 0° rotation.

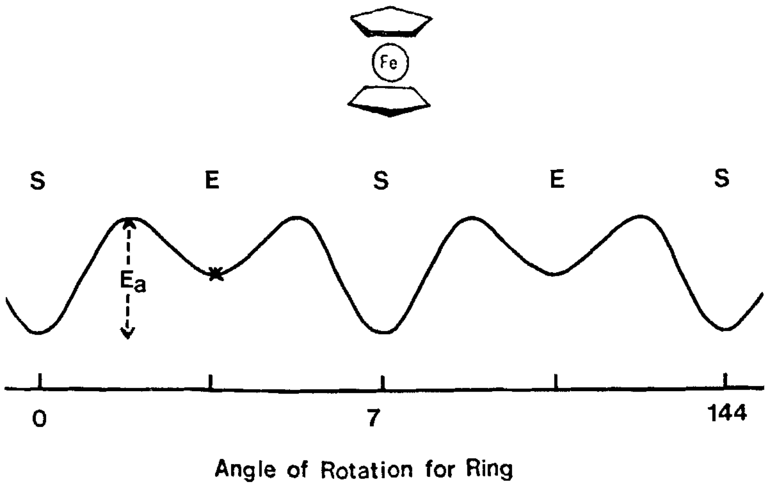


FIGURE 7 Schematic representation of the average potential for the rotation of a single ring in a ferrocene molecule in the plane of the ring, needed to produce the observed disorder. The zero rotation represents the staggered (major) arrangement of the two rings in a ferrocene molecule.

In the case of solid adamantane, a successful molecular description of the mechanism of the order-disorder transition was obtained using the same general methods of calculation as used here.[32c] The explanation predicted both the occurrence of disorder and also the particular axis about which the disorder would occur, by calculating "second-order" effects in which the effect on the test molecule of populating the metastable orientations of the surrounding molecules in the lattice was investigated. In the case of adamantane, the first order calculations indicated subminima in the potential energy curves which corresponded to metastable orientations of the molecules in the lattice. In the case of reorientation about one axis (the one about which the disorder occurred) the population of the metastable orientation was "self-propagating" i.e. the energy difference was lowered and subsequent population of the metastable orientation became more likely until a statistical disorder was introduced. For all other axes, the population of metastable orientations was found to be "self-quenching", i.e., the energy difference increased and further population of these orientations became less probable.

Inspection of the potential deduced from the structure AA′ reported by the original X-ray determination[1] indicates no such subminimum at 36° (Figure 4). However, although the presence of such a subminimum would make the occurrence of disorder about the axis intuitively more reasonable, it need not be considered an essential requirement, especially if the barrier were very low.

Second order calculations were therefore carried out to investigate the effect on the test molecule of populating the surrounding lattice with the configuration corresponding to a 36° rotation from the equilibrium position, i.e., to the maximum in Figure 4. The results are presented in Table IV.

As can be seen from the Table there is no interaction between the test molecule and the surrounding molecules in the lattice in which the energy difference between the 0° and 36° orientations of the ring drops or where even a barrier between these two orientations is introduced. The source of the disorder *cannot* therefore be the non-bonded interactions between the molecules in the crystal/lattice and the test molecule and must, therefore, within the uncertainty of the calculations, be ascribed to bonding interactions *within the ferrocene molecule.*

The types of function necessary to produce the correct total potential function for a single ring may be deduced from the results of the potential energy calculations in Figure 4 and the function in Figure 7 and are shown in Figure 8.

As can be seen, the function describing the bonding within the ferrocene molecule must have the eclipsed orientation more stable than the staggered. It need not have the staggered at a subminimum of energy, but if it does not,

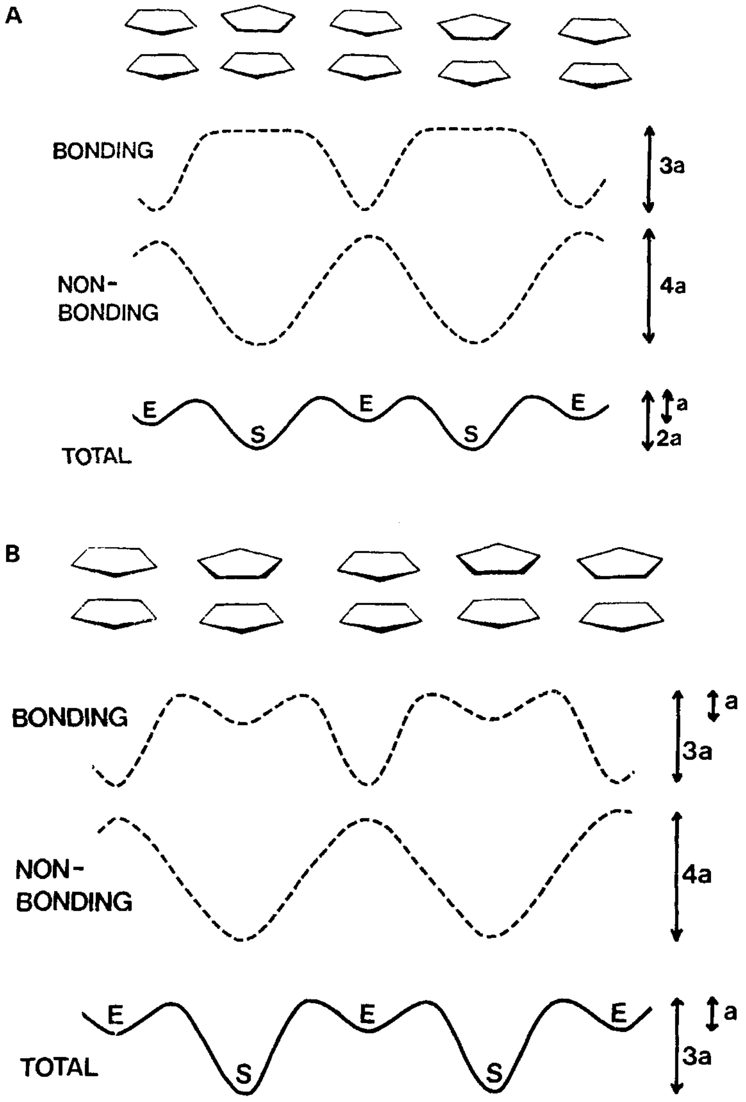


FIGURE 8 Schematic representation of the addition of two intra-molecular bonding functions to the calculated non-bonding interaction shown in Figure 4 to produce a total potential energy function qualitatively similar to that shown in Figure 7. In this case, the bonding function has the eclipsed form the more stable, and no subminimum at the staggered configuration.

then the shape of the function must change from that of the *non-bonded* interactions and have a much narrower shape about the energy minimum.

The molecular structure of ferrocene has been investigated in the gas phase by electron diffraction techniques, and it was proposed from these studies that the eclipsed were more stable than the trans conformation. The data were fitted by a variety of functions like 8B. (It is not clear that the electron diffraction measurements require a maximum in the potential for the staggered conformation; it may only be necessary that the eclipsed form be more stable than the staggered.) Thus the suggestion that potential functions from the intramolecular bonding are involved is in accord with other experimental data.†

The introduction of a contribution to the total potential from the bonding within the molecule has an important use in that it provides a basis for rationalizing the mechanism of the order/disorder transition: Thus, of the two contributions to the total potential, that from the bonding would be temperature independent. However, the contribution from the non-bonded interactions will be temperature dependent as it will depend on the expansion of the lattice with temperature. For example, in the case of benzene, where both low and high temperature structural data are available, the activation energy changes from a low temperature value of $E_a$ (138°K) = 3.5 kcal/mole to a high temperature value $E_a$ (270°K) = 1.5 kcal/mole.

Calculations of the energy barrier to rotation of the cyclopentadienyl ring in ferrocene as a function of temperature have been carried out by taking the high temperature structure[34] and the cell dimensions determined by Mason and co-workers[9] at different temperatures. These indicate similar changes in the barrier height with temperature to those observed previously for benzene and are listed in Table V.

Thus the total potential energy as a function of temperature may be predicted, at least qualitatively, as shown in Figure 9. At low temperatures, where the contribution from the non-bonding interactions within the lattice is at a maximum, there is no subminimum corresponding to the metastable orientation at 36°. As the contribution from the lattice forces decreases, the relative contribution from the intramolecular bonding increases, reaching a limiting contribution corresponding to the room-temperature distribution between the two sites.

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† In principle, the contribution to the potential from bonding within the molecule could be evaluated from M.O. calculations but it would depend on accurately calculating a difference in energy of less than 1 kcal/mole in a total energy of several hundred kcal/mole. It is difficult to argue from group theory as to the shape of the potential energy profile and the stabilities of the conformers as the only common symmetry element is the $C_5$ axis and this exists for all intermediate orientations also.

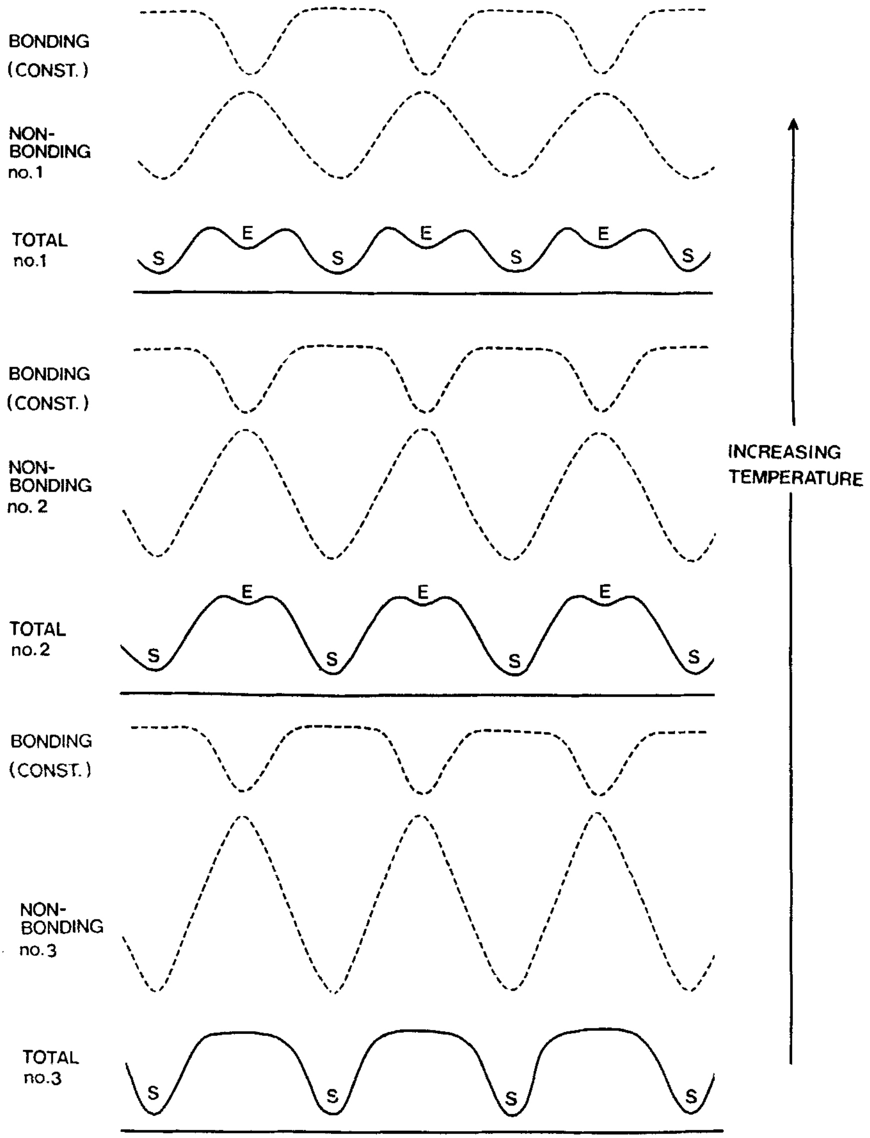

FIGURE 9 Schematic representation of the temperature dependence of the total potential enery function for the rotation of a single cyclopentadienyl ring in ferrocene. The intramolecular bonding contribution remains constant, while the inter-molecular contribution from lattice interactions increases as the temperature decreases. At the lowest temperature (bottom function) the staggered configuration is present alone; the appearance of the subminimum at the eclipsed configuration with increasing temperature (upper functions) corresponds to the introduction of disorder into the lattice giving the room-temperature distribution between the two forms represented by the top function.

TABLE V

Temperature Dependence of the Calculated Non-bonded Barrier to Ring Rotation in Ferrocene

| $T$ (°K) | $E_a$(kcal/mole) |
|---|---|
| 5 | 2.64 |
| 135 | 1.93 |
| 298 | 1.16 |

(*b*) *Ruthenocene and Dibenzenechromium* A similar explanation may be given here for the contribution to the total potential from bonding forces within the molecule and the implied temperature dependence of the total potential. Two factors are important:

(*i*) The barriers to rotation imposed by the non-bonding lattice forces are much larger and thus the contribution from the bonding within the molecule will be much less important.

(*ii*) If (as in the case of ferrocene) in the gas the eclipsed forms are the more stable, then there will just be a small increase of the barrier height in the solid as the two potentials will complement each other. If the staggered is the more stable, then the barrier would become slightly smaller, as the functions would oppose each other, but no subminimum would be introduced.

Thus the occurrence of order-disorder transitions is not expected for these compounds, in contrast with the situation for ferrocene. The available data from electron diffraction studies suggest that in the gas the eclipsed forms are the more stable,[6] but this information cannot be deduced from the solid state results for these compounds.

## CONCLUSIONS

The potential energy calculations presented here are thought to provide a rational framework in the understanding of the many available and sometimes seemingly contradictory experimental data on the metallocenes, including the observed X-ray structures and the occurrence of an order-disorder transition for ferrocene in the solid state: They also provide an important bridge between the observed solid state structures and those in the gas-phase and in solution.

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