On the Relationship between Crystallographic and Spectroscopic Evidence of Dynamic Processes in the Solid State: the Cases of *cis*- and *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ †

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The reorientational motion of the C_5H_5 ligands, evidenced in solid *cis*-and *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ by magic angle spinning n.m.r. spectroscopy, has been examined by means of atom–atom pairwise potential-energy calculations. The results are compared with the *X*-ray crystallographic indications of extensive librational motion of the ligands around their five-fold axes in both species. A thermal motion analysis has been carried out showing that the mean-square displacement parameters contain relevant information on the occurrence of dynamic processes in the solid state.

Nowadays the fact that groups of atoms or entire molecules can undergo reorientation and/or rearrangement in the solid is commonly accepted in solid-state crystal chemistry.[1] For instance, molecular motions of even large and complex organic molecules have been demonstrated by various means including diffraction studies, spectroscopic experiments (mainly i.r. and n.m.r.),[1] and theoretical approaches.[2] The combined efforts of all these methods have provided a good insight into the factors controlling the occurrence of dynamic phenomena in the condensed state of matter. In the organometallic field, however, the idea that a crystal is not only a simple ordered packing of frozen entities which are allowed not more than limited displacements around their equilibrium positions is still regarded with suspicion by many chemists. Nonetheless there is a growing interest in work aimed at correlation between the information (sometimes 'old') obtained by diffraction experiments on some of the most fundamental organometallic species and the recent developments of solid-state n.m.r. spectroscopy [mainly ^{13}C MAS magic angle spinning (m.a.s.)].[3] This latter technique has provided extremely interesting information on the occurrence of dynamic processes in solid transition-metal carbonyl clusters and many other organometallic species.[4] Difficulties in the interpretation of the spectroscopic results in the light of known crystal structures arise mainly from the conceptual difference between a diffraction experiment, which yields an image of the molecular structure averaged over time and space,[5] and a spectroscopic experiment which delivers information on a time-averaged object depending on the span of the electromagnetic frequencies employed.[6] This 'time-scale' problem has led to many controversies which are still matters of debate.[7]

We now intend to show that a direct correlation between single-crystal *X*-ray diffraction and n.m.r. spectroscopy is possible and that 'dynamic' information is also contained in the results of *X*-ray analyses of organometallic species. For this purpose the two isomers *cis*- and *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2(CO)_2]$ have been selected. Solid-state ^{13}C m.a.s. n.m.r. data have been reported for both species showing that, while no exchange process involves the CO groups, the C_5H_5 (hereafter cp) groups undergo rapid rotation on the n.m.r. time-scale.[8] Starting from the known crystal structures of both species, it is not only possible to show that the arrangement of the molecules in the solid (crystal packing) controls the dynamic processes as detected by n.m.r. spectroscopy, but also to provide qualitative information on the heights of the energy barriers and on the shapes of the potential-energy functions associated with the cp reorientation. What is more, it is possible to demonstrate that there is a strict agreement between both n.m.r. and potential-energy calculations and those structural parameters which contain 'dynamic' information, namely the mean-square-displacement amplitudes (m.s.d.a.s) of the atoms undergoing thermal motion.[9]

The evaluation of the energy terms mentioned above is approached by applying the pairwise potential-energy method widely used in organic solid-state chemistry,[10] and which has also recently been used to investigate analogous dynamic phenomena for some transition-metal carbonyl clusters.[11]

Results and Discussion

The Pairwise Potential-energy Method and the M.S.D.A. analysis.—The crystal packing of neutral organometallic species of the kind discussed herein is assumed to be dominated by purely van der Waals interactions.[12] The potential energy of a molecule in the crystal is obtained as a simple function of the intermolecular separation by summing attraction and repulsion potential-energy (p.e.) terms between a reference molecule and the surrounding ones distributed in the crystal according to space-group symmetry and falling within a certain distance (a cut-off of 10 Å has been adopted in our calculations) from the reference one.[2,10] Bond polarities or coulombic interactions between permanent atomic charges are, to a first approximation, neglected. This is justified also by the fact that the barriers in which we are interested originate from the motion of a hydrocarbon fragment. A problem is posed by the value of the coefficients *a*, *b*, and *c* to be used in the p.e. expression (1) ‡ which

$$\text{p.e.} = \Sigma_i\Sigma_j a e^{-br_{ij}} - cr_{ij}^{-6} \qquad (1)$$

are known for atoms such as H, C, N, and O, but not for transition metals.[2,10] However, if no absolute value of the potential energy is sought (as in the cases discussed here) and attention is focused only on the *relative* ratios of the p.e. values and on the *relative* heights of the p.e. barriers to motion, the problem can be overcome by neglecting altogether the metal atom contribution. This may appear to be a drastic assumption. We have tested it by attributing to the Fe atoms the coefficient for the corresponding noble gas (Kr). The curves obtained with and without metal contribution are shown together for comparison. It will be seen that, while the absolute value of the

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† *Non-S.I. unit employed:* cal = 4.184 J.

‡ r_{ij} is the atom-atom intermolecular distance.

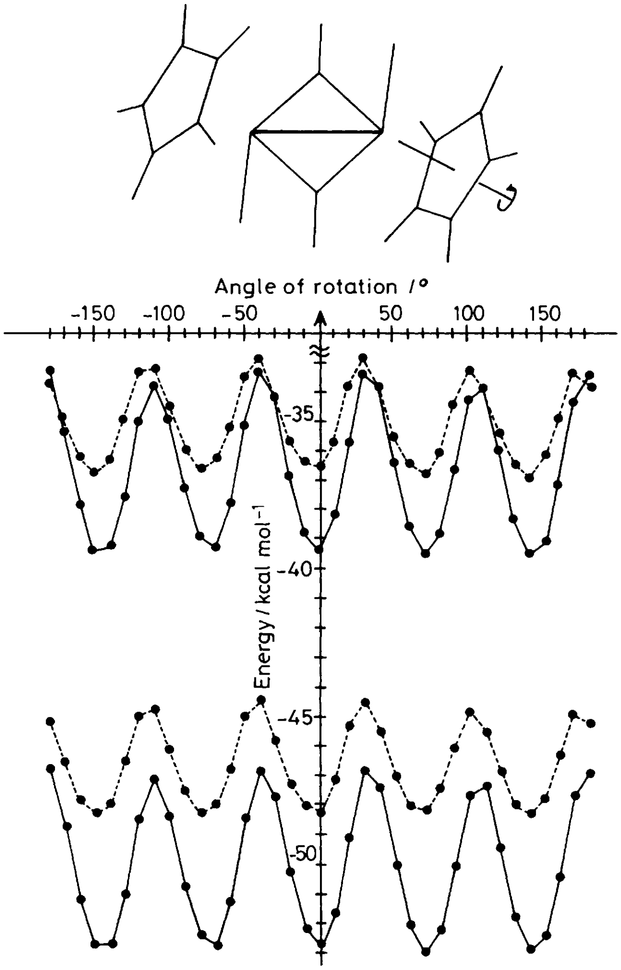

Figure 1. Potential-energy barriers to rotation of the cp-ligand for *trans*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ obtained from room-temperature (broken lines) and 74 K *X*-ray determinations. Top, without metal contribution; bottom with metal contribution

p.e. minima decreases by about 10—15 kcal mol^{-1} on adding the metal contribution, the shapes of the energy profiles and heights of the energy barriers are not affected.

Reorientation of the cp rings is simulated by allowing rigid-body rotation between −180 and 180° of the ligand as a whole around its five-fold axis and by calculating the p.e. value, as described above, at 10° steps. The molecular environment is considered static during their motion; in such a way the molecular packing around the reorienting fragment retains the crystallographic symmetry and no co-operation by the neighbouring molecules is involved.

Atomic co-ordinates and space groups were taken from the original structural reports. Potential-energy calculations have been performed by using a modified version of the program OPEC.[13] The reader seeking more details of the computational method is addressed to refs. 2, 10, and 13.

The available atomic thermal parameters were used to carry out a rigid-body motion analysis based on the translation, libration, and correlation tensors (TLS approach),[14,15] in order to evaluate the mean-square amplitudes for the cp librational motion around their idealized five-fold axes. In such calculations the contribution of the Fe atom co-ordinated to each cp had to be included to avoid the singularity problem associated with regular pentagonal molecules.[16] The principal librational axes were always found to fall within a few degrees of the axes joining the cp centres and the corresponding Fe atoms, these axes being roughly coincident with the axes of maximum inertia of the C_5H_5 systems.

The m.s.d.a.s were also used to perform a rigid-bond analysis based on the Hirshfeld postulate[17] which states that the difference between the mean-square displacements of pairs of atoms evaluated along the bond axis ($\Delta_{A,B} = Z^2_{A,B} - Z^2_{B,A}$) should approach zero if the atom pair is linked by a substantially rigid bond. In the case of the cp rings, the average $\Delta_{A,B}$ should approach zero even in the presence of extensive in-plane thermal vibration if the ligand oscillates as a rigid body. M.s.d.a. analysis was performed by using the program THMAIO.[18]

trans-$[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2(CO)_2]$. The structure of the *trans* isomer has been subjected to two independent crystallographic studies,[19] the latest carried out by both neutron and low-temperature *X*-ray diffraction in order to study X-N electron deformation density maps.[19b] The species crystallizes in the monoclinic space group $P2_1/c$ with $Z = 2$, the molecule lying on a crystallographic centre of symmetry placed midway along the Fe–Fe bond. In such a way the molecule has crystallographically imposed C_i symmetry which, *inter alia*, renders the two cp groups crystallographically equivalent. Carbon-13 m.a.s. n.m.r. spectroscopy[8] has been reported to show a single sharp resonance for the cp carbon atoms thus indicating that, at room temperature, an exchange process involving these atoms is taking place in the solid. The bridging and terminal CO ligands show, on the contrary, distinct resonances. On these bases, rapid rotation of the cp groups around their C_5 axes has been inferred.

The potential energies associated with the static structure and with the rotational motion of the cp ligands have been calculated for both low- and room-temperature *X*-ray data sets and are reported together in Figure 1. The cp ring reorientation has been performed, as mentioned above, by allowing rotation around an axis passing through the centre of mass of the ring and the Fe atom bearing the ligand as indicated in Figure 1. The results of the calculations allow the following conclusions.

(*i*) The p.e. profiles show minima of almost identical energy every 72° rotation which correspond to site swapping between the C atoms of the cp ligand in agreement with its five-fold symmetry.

(*ii*) The p.e. barrier for each rotational jump is about 6.0 kcal mol^{-1} for the low-temperature structure while it decreases to about 3.4 kcal mol^{-1} on passing to the room-temperature structure.

(*iii*) The p.e. barriers associated with the motion do not differ whether the metal contribution (bottom of the figure) is taken into account or not.

(*iv*) The absolute minima calculated with and without metal contribution differ by about 13 kcal mol^{-1} for the low-temperature structure. This difference is reduced to 11 kcal mol^{-1} in the room-temperature case.

(*v*) The p.e. barrier shows an increase of *ca.* 3 kcal mol^{-1} if neutron-derived co-ordinates are used instead of those obtained from the low-temperature *X*-ray experiment (see Table). This behaviour must be ascribed to the different H-atom positioning yielded by the two kinds of experiments[19b] (average C–H taken from the original papers, 0.97 and 1.08 Å, for *X*-ray and neutron, respectively) which causes an appreciable underestimation of the p.e. barrier in the *X*-ray case. A value of 1.08 Å was instead used to add H atoms in calculated positions for the room-temperature structure.

It is interesting to compare this evidence with the m.s.d.a. obtained for the cp ring in the two cases. ORTEP projections in the cp plane are shown in Figure 2(a). Although care must be taken in relying on a 'visual inspection' of thermal ellipsoids to

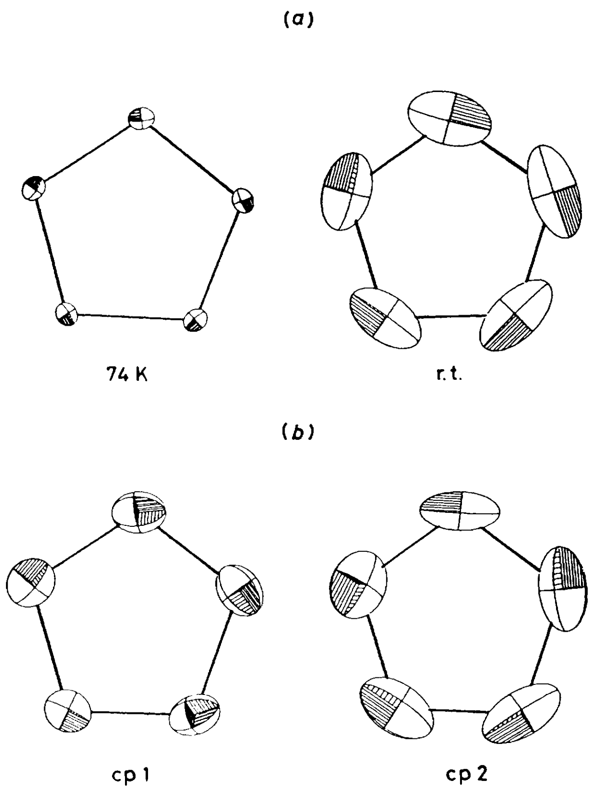

Figure 2. ORTEP projections in the plane of the cp ligand. (*a*) The cp ligand in *trans*-[$Fe_2(\eta$-$C_5H_5)_2(CO)_4$] at 74 K (*X*-ray determination) and room temperature (r.t.); (*b*) comparison of the two independent cp groups in *cis*-[$Fe_2(\eta$-$C_5H_5)_2(CO)_4$]

evaluate the extent and direction of atomic displacements,[9] the agreement with the p.e. curves is striking, the smaller displacements being associated with the higher barriers calculated for the low-temperature structure. Since there is no hint of a double-well structure for the p.e. profile, these observations strongly indicate that the thermal vibrations reflect true atomic motions, and that static disorder is unlikely.

As expected the cp ligand in the low-temperature determination truly satisfies the rigid-bond test ($\Delta_{A,B} = 1.0 \times 10^{-3}$ Å^2) as can be seen in the Table, which collects all basic information. Interestingly, $\Delta_{A,B}$ is also very low (6.5×10^{-3} Å^2) in the room-temperature case, though expectedly higher than in the more accurate low-temperature determination. This difference is due to the more accurate thermal vibration definition at low temperature allowed, *inter alia*, by the very large θ range scanned with respect to the room-temperature determination [$(\sin \theta/\lambda)_{max.} = 1.15$ and 0.70 respectively].

The root mean square (r.m.s.) librational amplitudes (see Table) are also in agreement with these observations: not only the librational motion is very anisotropic ($L_1 \gg L_2 \approx L_3$), but also it is drastically reduced on lowering the temperature to 74 K. Similar relationships among the L tensors and the temperature dependence of the m.s.d.a. have been previously observed for several metallocene species subjected to *X*-ray studies at different temperatures.[20]

It should be emphasized, at this stage, that there is no direct relationship between the height of the p.e. barriers and the extent of libration, this latter being rather related to the 'shape' of the p.e. surface at the bottom of the p.e. well. Nonetheless a relatively smooth p.e. curve certainly implies that the atoms can 'spend more time' in positions associated with the transition state than in the case of a barrier with steeply rising walls.[7]

cis-[$Fe_2(\eta$-$C_5H_5)_2(\mu$-$CO)_2(CO)_2$]. The *cis* isomer represents an even more interesting case. The species crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ so that the whole molecule lies in a general position in the unit cell.[21] Although the idealized molecular symmetry is C_{2v}, the site symmetry is only C_1 thus rendering the two cp rings crystallographically independent. As shown in the original paper, the two cp rings show different extents of thermal motion [see Figure 2(*b*)] corresponding in both cases to an extensive in-plane oscillation of the ligands.

Carbon-13 m.a.s. n.m.r. spectra are nicely in accord with this picture: in contrast with what is observed for the *trans* isomer (whose cp groups are crystallographically equivalent), two distinct resonances in the cp region are recorded. In addition, both sets of C atoms appear to be equilibrated on the n.m.r. time-scale thus indicating that an exchange process is occurring in the solid. Distinct signals are otherwise observed for the terminal CO groups, while one signal is observed for the bridging CO groups (this latter is convincingly attributed to accidental degeneracy of the two resonances).

On these premises it should be clear that the *cis* isomer represents an interesting test for the pairwise p.e. method not only because of the dynamic process evidenced by n.m.r. spectroscopy, but also because it offers an opportunity for checking the sensitivity of the method in the presence of small differences in the results of both diffraction and n.m.r. experiments.

Results of p.e. calculations are shown in Figure 3 for both cp rings; the p.e. profiles calculated by treating Fe as Kr are also reported for comparison. These results allow the following conclusions.

(*a*) As previously shown for the *trans* isomer, the effect of neglecting the metal-atom contribution is seen *only* in the absolute value of the p.e. minima (which differ by about 11 kcal mol^{-1}), neither the shape nor the height of the energy barriers is affected.

(*b*) Minima of equivalent energy are seen for both cp groups every 72° jump.

(*c*) The most interesting feature is the relative height of the two energy barriers to rotation which differ by about 2 kcal mol^{-1} between the two cp rings, the lower being associated with the cp ring undergoing more extensive thermal vibration (cp 2).

The Hirshfeld rigid-bond test (see Table) also affords useful information: the Δ values calculated for the two cp groups 1 and 2 are different: while Δ(cp 1) is small (7.9×10^{-3} Å^2) and comparable with the value obtained for the *trans* isomer at room temperature, Δ(cp 2) is much larger (15.8×10^{-3} Å^2) thus indicating that the m.s.d.a. definition for this latter cp is worse, in agreement with the structural report. Nonetheless the r.m.s. librational amplitudes (see Table) afford a comforting picture: both the relative ratio of L_1, L_2 and L_3 for each cp and the ratios between the two independent cps are in good agreement with a model of more extensive librational motion for cp 2 than for cp 1. Furthermore the value of Δ considerably increases (33.2×10^{-3} Å^2) when averaged between C(cp 1)–C(cp 2) pairs (rigid-molecule test) thus indicating that the two moieties librate independently in the crystal.

Comparison of the Two Isomers and Conclusions.—It is also interesting to compare the packing efficiencies of these species in the solid and to discuss them in the light of the above results. Packing coefficients can be calculated as the ratio $(V_{mol}Z)/V_{cell}$. Molecular volumes (V_{mol}) can be evaluated by applying the method of the intersecting caps proposed by Kitaigorodski[22] and further developed by Gavezzotti,[13] by considering a molecule as a collection of atomic spheres of given radii. Once again we are interested only in the relative ratios of these quantities and not in their absolute values so that the problem of attributing correct radii to all species involved is not

Table. Potential-energy minima, energy barriers to rotation, and results of thermal motion analysis for *trans*- and *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$

	trans		*cis*	
	Room Temperature	Low Temperature	cp 1	cp 2
p.e. min. (Fe as Kr)/kcal mol^{-1}	−47.93	−52.74	−43.36	−43.36
p.e. min. (no metal contr.)/kcal mol^{-1}	−36.51	−39.37 (−38.5)*	−32.29	−32.29
p.e. barrier (Fe as Kr)/kcal mol^{-1}	3.6	5.9	4.2	1.9
p.e. barrier (no metal contr.)/kcal mol^{-1}	3.6	6.0 (9.0)*	4.2	1.9
10^{-3} Δ/Å^2	6.5	1.0	7.9	15.8
L_1/°	18.7	2.7	7.9	17.4
L_2/°	2.7	1.1	3.6	7.3
L_3/°	1.4	0.6	2.8	3.4
p.c. (packing coeff.)	0.55	0.58	0.53	0.53

* neutron determination (74 K).

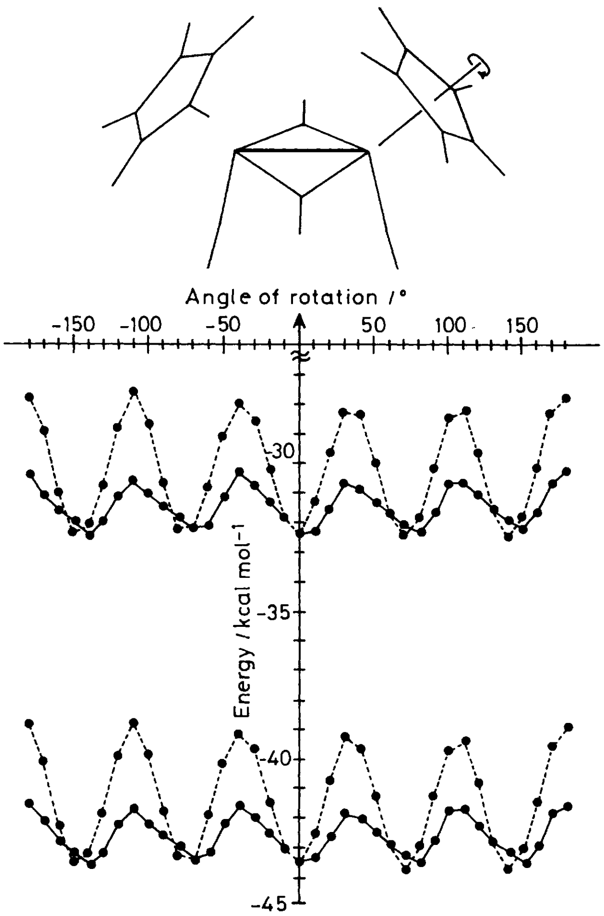

Figure 3. Potential-energy barriers to rotation of the two independent cp ligands [(cp 1) broken lines, (cp 2) solid lines] in *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$. Top, without metal contribution; bottom, with metal contribution

dramatic. In our calculations van der Waals radii were used for H, C, and O atoms, while Fe atoms were treated as Kr.

The Table reports the packing coefficient (p.c.) values for the two species showing that the *cis* isomer, whose cp groups undergo more extensive thermal vibration, appears to be more loosely packed than the *trans* isomer. What is more, the effect of decreasing the temperature to 74 K for the *trans* isomer causes a decrease in the cell volume (665.1 *versus* 622.0 Å^3) and an increase in the packing efficiency (0.55 *versus* 0.58). This behaviour is in keeping with the increase of the energy barrier to rotation discussed above.

Altogether these results afford a consistent picture: not only is a convincing, semiquantitative agreement found between the spectroscopic evidence for facile reorientation in the solid of the cp rings and the energy barriers associated with these motions, but also between this information and the direct crystallographic evidence for extensive in-plane thermal vibrations of the atoms involved in the motion.[23] Also demonstrated is the ability of the method to discriminate between only slightly different rotational sites. On these premises, it can be safely stated that, also in the field of organometallic complexes, p.e. calculations, even when based on some rather crude assumptions and approximations, are a powerful support to work aimed at correlation between spectroscopic and diffraction techniques. More than that, they provide a reliable tool for checking, on the basis of knowledge of the *X*-ray structure, hypotheses on the occurrence of dynamic processes in the solid state.

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References

1 N. G. Parsonage and L. A. K. Stavely, in 'Disorder in Crystals,' Oxford University Press, Oxford, 1978; 'Organic Solid State Chemistry,' ed. G. Adler, Gordon and Breach, New York, 1969.
2 A. Gavezzotti and M. Simonetta, *Chem. Rev.*, 1982, **82**, 1.
3 C. A. Fyfe and R. E. Wasylishen, 'Solid State Chemistry Techniques,' eds. A. K. Cheetham and P. Day, Clarendon Press, Oxford, 1987, ch. 6, p. 190.
4 B. E. Hanson, E. C. Lisic, J. T. Petty, and G. Iannacone, *Inorg. Chem.* 1984, **23**, 4062; B. E. Hanson and E. C. Lisic, *ibid.*, 1986, **25**, 716 and refs therein.
5 J. D. Dunitz, '*X*-Ray Analysis and the Structure of Organic Molecules,' Cornell University Press, Ithaca, New York, 1978.
6 E. L. Muetterties, *Inorg. Chem.*, 1965, **4**, 769; E. Band and E. L. Muetterties, *Chem. Rev.*, 1978, **78**, 639.
7 R. E. Benfield, D. Braga, and B. F. G. Johnson, *Polyhedron*, 1988, **7**, 2549.
8 H. C. Dorn, B. E. Hanson, and E. Motell, *J. Organomet. Chem.*, 1982, **224**, 181.
9 J. D. Dunitz, V. Schomaker, and K. N. Trueblood, *J. Phys. Chem.*, 1988, **92**, 856.
10 A. Gavezzotti and M. Simonetta, *Acta Crystallogr., Sect. A*, 1973, **31**, 645; A. Gavezzotti, *Nouv. J. Chim.*, 1982, **6**, 443 and refs. therein.
11 D. Braga and F. Grepioni, *Polyhedron*, in the press.
12 A. J. Pertsin and A. I. Kitaigorodski, 'The atom–atom potential method,' Springer, Berlin, 1987.
13 A. Gavezzotti, *J. Am. Chem. Soc.*, 1983, **105**, 5220.

14 V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, 1968, **24**, 63.

15 B. T. M. Willis and A. W. Pryor, 'Thermal Vibrations in Crystallography,' Cambridge University Press, London, 1975.

16 D. W. J. Cruickshank, *Acta Crystallogr.*, 1956, **9**, 754.

17 F. L. Hirshfeld, *Acta Crystallogr., Sect. A*, 1976, **32**, 239; see also D. Braga and T. F. Koetzle, *Acta Crystallogr., Sect. B*, 1988, **44**, 151; D. Braga and B. T. Heaton, *J. Chem. Soc., Chem. Commun.*, 1987, 144.

18 K. N. Trueblood, THMAIO, Thermal Vibration Analysis Computer Program, University of California, Los Angeles, 1986.

19 (*a*) R. F. Bryan and P. T. Greene, *J. Chem. Soc. A*, 1970, 3064; (*b*) A. Mitschler, B. Rees, and M. S. Lehmann, *J. Am. Chem. Soc.*, 1978, **100**, 3390.

20 P. Seiler and J. D. Dunitz, *Acta Crystallogr., Sect. B*, 1980, **36**, 2255, and refs. therein.

21 R. F. Bryan, P. T. Greene, M. J. Newlands, and D. J. Field, *J. Chem. Soc. A*, 1970, 3068.

22 A. I. Kitaigorodski, 'Molecular Crystals and Molecules,' Academic Press, New York, 1973.

23 E. Maverick and J. D. Dunitz, *Mol. Phys.*, 1987, **2**, 451.

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