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Applications of the King and Lipscomb Expression for the X-ray Scattering of a Hindered Rotor

By M. J. Bennett and W. L. Hutcheon
Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada
and Bruce M. Foxman
Department of Chemistry, Brandeis University, Waltham, Mass. 02154, *U.S.A.*

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The King and Lipscomb expression for the scattering of groups undergoing hindered rotation against a cosine potential function about an axis has been modified and incorporated into a routine full-matrix structure-factor and least-squares program. The model has been evaluated in several cases and has been found to be an excellent representation for π-bonded C_nH_n groups in organometallic compounds in that the hindered rotor representation, with only nine variables, is frequently competitive with individual atom models. The parameters of the model concerned with thermal motion have been related to the more conventional parameters to enable the deduction of good starting values for the hindered-rotor refinement. The parameter that in the formal model is associated with the height of the barrier potential function is shown to be a shape parameter that is related more properly with the root-mean-square libration about the axis. Bond lengths derived from the model are corrected for this dominant libration.

Introduction

The treatment of the scattering of groups of atoms in crystal structure analyses has been approached from two different viewpoints. First is the more rigorous approach, for example that applicable to formally rigid systems based on the rigid-body translational and rotational components of the thermal vibrations as first suggested by Cruickshank (1956). The direct refinement, in a structure-factor least-squares programme, of the T and ω tensors, together with atomic coordinates and centre of libration has been proposed and successfully applied by Pawley (1963, 1966). However, a more recent analysis of rigid-body motions by Schomaker & Trueblood (1968) shows the need to consider (1) correlations of libration and translation, and (2) non-intersection of the libration axes. This rigid model of Schomaker & Trueblood could be incorporated into a structure-factor and least-squares program. The alternative approach, which has been essentially an economy package arising from limited computer core storage and research funds, has used fixed geometries with isotropic vibration constants for such groups as the phenyl group (see for example La Placa & Ibers, 1965). This second class of rigid-body programs has found widespread use in the refinements of the structures of transition-metal complexes of phenyl-substituted phosphine ligands, which have been the subject of many recent chemical studies. Fortunately these reduced parameter descriptions of σ-bonded phenyl groups have produced relatively small increases in the conventional R index, although the independent-atom models are significantly better as judged by a Hamilton (1965) R-factor ratio test.

For transition-metal π complexes of highly symmetric ligands, such as the cyclopentadienyl group, the isotropic rigid-body models have normally been found to be unacceptable in that they fail to account for the high-amplitude librations about the metal-to-ring axes that are so common in these systems. Since the standard deviations of all parameters are approximately proportional to R (Cruickshank, 1960), the normal procedure has been to use the conventional individual-atom ellipsoid model with suitable justification from electron-density difference maps and the Hamilton (1965) statistical test. The most notable exception to this practice has been the application of a modified version of the King & Lipscomb (1950) scattering expression for a hindered rotor in the structure of the orthorhombic phase of $(\pi\text{-}C_5H_5FeS)_4$ (Schunn, Fritchie & Prewitt, 1966). In this form the hindered rotor model is highly flexible in that it allows description of groups ranging from regular rigid bodies (with a single isotropic temperature factor) in the infinite barrier limit to the free-rotor model (Bijvoet & Ketelaar, 1932) in the zero-barrier limit. This hindered-rotor refinement of cyclopentadienyl groups demonstrated the relevance of the model in situations that are encountered by crystallographers who are interested in organometallic molecules. The decrease in parameters was accompanied by a small rise in R value and an additional benefit was noted in that the bond lengths within a ring were essentially corrected for the libration about its fivefold axis. On the debit side the program developed allowed no variation of the ring orientation and hence had a complete free-atom refinement as a prerequisite. In addition the block-diagonal approach, which was used, ignored an important correlation (see below) that led to slow convergence and required the use of damping factors. The success of this partial refinement did suggest that the model of a hindered rotor was worthy of further study in a full-matrix structure-factor and least-squares program with the inclusion of the additional degrees of freedom for the ring orientation.

It should be noted that the hindered-rotor model does not contain the normal rectilinear constraints on thermal motion and offers some advantage in this respect. It was for this particular feature that we chose to use the hindered-rotor model for a reduced-parameter model rather than a rigid body with anisotropic temperature factors constrained by the point symmetry of the rigid group. The King & Lipscomb hindered-rotor model is one of several higher-order mechanistic models which have been reviewed by Maslen (1970) and by Johnson & Levy (1974) in the fourth volume of *International Tables for X-ray Crystallography*. The applications of such models are few in number (see, for example, Hamilton, Edmonds, Tippe & Rush, 1969; Kay & Cromer, 1970; Brown & Chidambaram, 1973) despite the success that has been achieved in these cases. In this paper we describe the results of using the hindered-rotor model in the refinements of several published crystal structures. This study has established guidelines for the routine application of the model. The model does not provide for the more general removal of rectilinear constraints as discussed elsewhere (see for example Johnson, 1969; Willis & Pawley, 1970; Pawley & Willis, 1970; Duckworth, Willis & Pawley, 1970). Further, we have included only an isotropic temperature factor for the hindered rotor (see below), in addition to the Lipscomb–King parameters, rather than either an anisotropic temperature factor (Chidambaram & Brown, 1973), or a translation coupled with the rotation (Kay & Cromer, 1970).

Model parameters

The scattering expression for a hindered rotor was re-evaluated for compatability with the program *SFLS5R*,* in that it seemed desirable to use expressions that are common to the simple rigid-body and hindered-rotor models. This economizes on storage and allows the use of the same rigid-body parameter analysis programme *MMMR* (Bennett & Foxman, 1967). The rigid-body routine added to *SFLS5* generates stationary sites corresponding to a selected number of sequential vertices of a regular polygon within the *XY* plane of a convenient Cartesian coordinate system. These sites are then rotated by angles *F*, *D*, and *E* radians about the *Z*, *X*, and *Y* axes respectively, and transformed to conventional fractional coordinates. The analysis of the free-atom parameters to yield the rigid-body parameters reverses this procedure. The solutions for *D* and *E* are simply obtained from the direction cosines of the normal to the least-squares plane, with respect to the Cartesian coordinate system, using the relationships $l_1 = \cos D \sin E$, $l_2 = -\sin D$, $l_3 = \cos D \cos E$. The *F* angle is determined from an analysis of the polar coordinates of the individual atoms after the least-squares plane has been rotated to bring it into coincidence with the *XY* plane. This process has proved extremely successful in giving good starting values for rigid-body refinements. The origin of the Cartesian coordinate system is chosen as the centre of generation of the rigid body which for a totally regular body is coincident with its centre of gravity. Within this framework it seemed desirable to redefine the hindered rotor as a continuously varying electron density around a circle in the *XY* plane of the chosen Cartesian coordinate system and to carry out the same rotations as for the rigid body. The cosine potential function as used by King & Lipscomb was retained.

The least-squares program was developed to use the following variables to define the ring:

g_p – an overall population factor that would allow the treatment of disorder problems and special site symmetry;
x_c, y_c, z_c – the fractional coordinates of the centre of gravity of the ring;
D, E – two angles that define the direction cosines of the normal to the ring;
F – the angle that corresponds to a potential minimum within the plane of ring;
B_d – the height of the barrier in units of $2kT$ where k is the Boltzmann constant and T the temperature;
B – an isotropic temperature factor for the ring as introduced by Schunn, Fritchie & Prewitt (1966);
r – radius of the ring in Å.

The derivation of the contribution of a hindered rotor defined by these variables follows that of King & Lipscomb. The necessary derivatives of the structure-factor amplitudes with respect to these variables were determined. Considerable caution was exercised at this point and the correctness of the calculations checked by several alternative methods. The program allows the computation of the infinite series of Bessel functions to a precision that is chosen by the user. A detailed description of the program and the derivation of all terms is available (Hutcheon, 1971).

The resulting program was then evaluated using several sets of published data where it was felt the hindered-rotor model might have been considered useful. In all cases the individual-atom models were re-refined using weighting schemes that were obtained simply from the analysis of the variation of $(|F_{\rm obs}| - |F_{\rm calc}|)^2$ with $|F_{\rm obs}|$ (Cruickshank, 1965); no $\sin\theta/\lambda$ dependence was included. It is hoped that this would

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* Basic full-matrix least-squares program (Prewitt, 1966) modified for the limited rigid-body routine by Foxman & Bennett (1967).

preclude any differences due to disparate (between the hindered rotor and individual atom models) weighting schemes. For those structures containing C_nH_n rings the hydrogen contributions to the structure factor were calculated assuming the hydrogens to be coplanar with the C_n ring. Carbon–hydrogen distances were fixed at 1·0 Å, a value that represents the trend of observed short distances for X–H bonds in X-ray diffraction studies due to the perturbation of bonding on the electron distribution (Stewart, Davidson & Simpson, 1965). In the following discussion of the results of these evaluations of the program the effect of the rotor model on the parameters of the non-rotor atoms is usually omitted in that no significant changes were observed and the discussion can be limited to the group atoms.

Results

(i) *Benzene*

The elegant study of benzene by Andrew & Eades (1953), using nuclear magnetic resonance techniques showed reorientation of the benzene molecules about the molecular sixfold axis in the solid state. Below 240°K the motion was explained by hindered rotation with an activation energy of 3·6 kcal while above 240°K the evidence suggested a considerable decrease in the effective barrier to rotation. The X-ray diffraction data at 290°K (Cox, Cruickshank & Smith, 1958) were found to be consistent with the major libration (r.m.s. 7·9°) being about the molecular sixfold axis. Benzene was chosen as the first test in that the reorientation process was known to occur (*i.e.* the hindered-rotor model had physical significance). Also the problem was small and computing costs in the development stage could be minimized.

The results of the refinement are given in Table 1. In this and subsequent tables HR denotes hindered-rotor model and IA the individual-atom models. All other atoms were treated exactly as in the original papers. R_1 and R_2, the conventional unweighted and weighted residuals, are given by:

$$R_1=\frac{\sum||F_{\text{obs}}|-|F_{\text{calc}}||}{\sum|F_{\text{obs}}|}$$

and

$$R_2=\left(\frac{\sum\omega(|F_{\text{obs}}|-|F_{\text{calc}}|)^2}{\sum\omega|F_{\text{obs}}|^2}\right)^{1/2}$$

respectively. Parameters quoted with a standard deviation of zero are constrained by symmetry. All standard deviations are given in parentheses and refer to the last digit quoted. All significance tests are based on Hamilton's (1965) treatment for comparison of residuals.

The independent-atom model is preferred at a significance level better than 0·005. This is not surprising in view of the other molecular librations which are certainly not negligible in this case. However, the derived carbon–carbon distance is in very good agreement with the corrected value from the independent-atom model – 1·391 (HR); 1·392 (1·377+0·015) Å (IA).

Table 1. *Hindered-rotor parameters for benzene*

HR	R_1 = 0·101	R_2 = 0·148	7 parameters
	x_c = 0·0 (0)	y_c = 0·0 (0)	z_c = 0·0 (0)
	D = 6·053 (33)	E = 0·8206 (29)	F = 1·7414 (35) radians
	B = 4·64 (11) Å²	B_d = 1·94 (11)	r = 1·391 (3) Å
IA	R_1 = 0·086	R_2 = 0·119	28 parameters.

(2) *π-Cyclopentadienyltricarbonylmanganese* – π-$C_5H_5Mn(CO)_3$

This structure is a good example of a π-cyclopentadienyl complex in which the ring geometry was corrected for the thermal vibrations (Berndt & Marsh, 1963). The agreement for the hindered rotor model with 36 fewer parameters matches that for the complete anisotropic model and is preferred. The parameters of interest are contained in Table 2.

Table 2. *Hindered-rotor parameters for π-cyclopentadienyltricarbonylmanganese*

HR	R_1 = 0·089	R_2 = 0·108	73 parameters
C_5 ring parameters			
	x_c = 0·3010 (7)	y_c = −0·1882 (10)	z_c = 0·1669 (7)
	D = 4·024 (7)	E = 2·998 (9)	F = 3·018 (9) radians
	B = 3·67 (17) Å²	B_d = 1·50 (12)	r = 1·211 (6)
	derived C–C 1·424 (7) Å		
IA	R_1 = 0·089	R_2 = 0·108	109 parameters
Equivalent isotropic B of Mn 3·18 Å²			
C–C 1·394 Å (uncorrected), 1·42 Å (corrected).			

This result is startling but emphasizes the advantages in removing the rectilinear constraints on groups undergoing large librations. The observation of Schunn, Fritchie & Prewitt (1966) that bond lengths appear to be corrected for thermal motion is further substantiated.

(3) *Ruthenocene* – (π-$C_5H_5)_2Ru$

(*Hardgrove & Templeton*, 1959)

The refinement of the structure of ruthenocene demonstrates the caution that is required in interpretation of the model parameters. In this case the broad-line nuclear magnetic resonance data have been interpreted in terms of an activation energy of approximately 2 kcal (Holm & Ibers, 1959). The effect of using a fixed form cosine potential function, with the barrier height as the only variable, can be investigated here (see Table 3).

The hindered-rotor model is preferred but in this case the derived C–C bond length is very little different from the independent-atom model. Since the standard deviations of the B_d parameters are so high, a rigid-body description would appear more appropriate for the constrained model.

Table 3. *Hindered-rotor parameters for ruthenocene*

HR	$R_1=0{\cdot}087$	$R_2=0{\cdot}101$	16 parameters
	x_c	y_c	z_c
Ring 1	0·3632 (18)	0·25 (0)	0·6292 (9)
Ring 2	0·1061 (19)	0·25 (0)	0·3797 (9)
	D	E	F
Ring 1	0 (0)	0·510 (13)	0 (0)
Ring 2	0 (0)	0·532 (14)	0 (0)
	B	B_d	r
Ring 1	2·14 (30)	4·5 (19)	1·239 (13)
Ring 2	2·49 (33)	5·2 (33)	1·235 (14)
Derived C–C (average) 1·453 Å			
IA	$R_1=0{\cdot}086$	$R_2=0{\cdot}105$	26 parameters
	average C–C (uncorrected) 1·447 Å.		

(4) *π-Benzenetricarbonylchromium* – π-$C_6H_6Cr(CO)_3$

The symmetry of π-C_6H_6 groups bound to transition metals has been a subject of debate (Bailey & Dahl, 1965*a*,*b*, and references therein). In comparing constrained geometry with the unconstrained geometry the hindered-rotor model could be more appropriate in that we have already shown that it can match the results of an anisotropic refinement in the case of π-$C_5H_5Mn(CO)_3$. A comparison was attempted in the case of π-$C_6H_6Cr(CO)_3$ and the pertinent results listed in Table 4.

Table 4. *Hindered-rotor parameters for benzene tricarbonylchromium*

HR	$R_1=0{\cdot}046$	$R_2=0{\cdot}052$	43 parameters
	$x_c=0{\cdot}3785$ (6)	$y_c=0{\cdot}25$ (0)	$z_c=-0{\cdot}2277$ (5)
	$D=6{\cdot}2794$ (0)	$E=2{\cdot}975$ (3)	$F=0{\cdot}5236$ (0)
	$B=3{\cdot}42$ (9)	$B_d=1{\cdot}97$ (10)	$r=1{\cdot}415$ (3)
Equivalent isotropic B of metal 2·63, derived C–C 1·415 Å.			
IA	$R_1=0{\cdot}041$	$R_2=0{\cdot}050$	64 parameters
	C–C 1·401 (uncorrected average).		

The independent-atom model is preferred at the 0·01 significance level. The large difference between the isotropic temperature factor of the ring and the equivalent isotropic temperature factor of the chromium atom is an indication of the deficiency of the hindered-rotor model (see below). This difference can result from the importance of other librations and from coordinate errors due to the geometric constraints on the ring. In this case an *ORTEP* plot of the molecule onto the plane of the benzene ring suggests that the main librations are molecular, rather than a special property of just the C_6H_6 ring and are not coincident with the metal–ring axis. Nevertheless the carbon–carbon bond length derived from the hindered-rotor treatment (1·415 Å) does show better agreement than the independent-atom value (1·401 Å) with the value 1·42 Å, observed in the more hindered hexamethylbenzene analogue (Bailey & Dahl, 1965*a*).

(5) π-$C_7H_7Mo(CO)_3C_6F_5$ (*Churchill & O'Brien*, 1969)

In this structure the thermal ellipsoids suggest a relatively large libration approximately about the metal to C_7 ring axis. The hindered rotor model closely matches the independent atom results (Table 5).

Table 5. *Hindered-rotor parameters for* π-$C_7H_7Mo(CO)_3C_6F_5$

HR	$R_1=0{\cdot}057$	$R_2=0{\cdot}062$	85 parameters
	$x_c=0{\cdot}2024$ (7)	$y_c=0{\cdot}25$ (0)	$z_c=0{\cdot}1327$ (4)
	$D=3{\cdot}1416$ (0)	$E=0{\cdot}949$ (4)	$F=0{\cdot}4488$ (0)
	$B=3{\cdot}13$ (13)	$B_d=1{\cdot}94$ (14)	$r=1{\cdot}626$ (5)
Equivalent B of molybdenum atom 2·60, derived C–C 1·411 Å.			
IA	$R_1=0{\cdot}055$	$R_2=0{\cdot}059$	112 parameters
	C–C (uncorrected) 1·407 Å.		

(6) Cs{Y[OC(CF_3).CH.C(CF_3)O]$_4$}

The previous five structures all contain carbon ring systems that would be expected to show little deviation from the assumed symmetry. The high-amplitude oscillation problem occurs for other more flexible groups where the deviations from the idealized symmetry could be a serious factor. The trifluoromethyl group is a particularly troublesome group in this respect and C–F bond length corrections of the order 0·1 Å have been estimated (Bennett, Cotton, Legzdins & Lippard, 1968). In Cs{Y[$C_5HF_6O_2$]$_4$}, there are four independent trifluoromethyl groups and the average C–F bond length (uncorrected) was found to be 1·26 Å. ($R_1=0{\cdot}076$, $R_2=0{\cdot}086$). The hindered-rotor refinement ($R_1=0{\cdot}097$, $R_2=0{\cdot}136$) can be readily rejected by a Hamilton statistical test yet it does give a carbon–fluorine distance of 1·32 Å which is in better agreement with that (1·346 Å) found in the trifluoracetate ion (Cruickshank, Jones & Walker, 1964). The prime fault in this case does appear to be due to the restriction of D_{3h} symmetry on each F_3 group. While the results for the trifluoromethyl groups may be somewhat disappointing, the model or modifications of it have been used successfully for the three hydrogen atoms of methyl groups (Hamilton, Edmonds, Tippe & Rush, 1969; Brown & Chidambaram, 1973) where refinement of anisotropic thermal parameters would not be justified.

Discussion

1. *Thermal parameters*

The parameters, B and B_d, contribute to the description of the thermal motion of the ring atoms and consequently it is not surprising to find high correlations between these parameters. Typically the correlation coefficient is of the order 0·6, which is comparable with correlation coefficients between scale factors and heavy-atom temperature factors. Within a full-matrix refinement, the problem of the B, B_d correlation should not be more serious than those encountered in routine situations. However, estimating good starting values for these parameters is certainly worthwhile and the experience gained from these hindered rotor refinements suggests the method for the deduction of suitable values from the results of an initial isotropic refinement.

The model can be related to the conventional anisotropic and isotropic model as follows. If the relative probability that a ring of order N is in a position corresponding to a rotation of θ radians from a potential minimum is represented by $P(\theta)$, then the mean-square angular deviation in radians is given by:

$$\bar{\omega}^2 = \frac{\int_0^{\pi/N} \theta^2 P(\theta)\mathrm{d}\theta}{\int_0^{\pi/N} P(\theta)\mathrm{d}\theta} .$$

The mean-square amplitude due to rotational effects alone can then be estimated to be $r^2\bar{\omega}^2$. Combining this contribution to the thermal motion with that from the isotropic temperature factor B the ellipsoid equivalent would have mean-square amplitude associated with its principal axes approximately given by:

$$\bar{u}^2_{\rm min} = \bar{u}^2_{\rm med} = B/8\pi^2;\ \bar{u}^2_{\rm max} = B/8\pi^2 + r^2\omega^2.$$

If an equivalent isotropic temperature factor, $B_{\rm eq}$, is defined by

$$B_{\rm eq} = \frac{8\pi^2}{3}\left(\bar{u}^2_{\rm min} + \bar{u}^2_{\rm med} + \bar{u}^2_{\rm max}\right) ,$$

then for the ring atoms

$$B_{\rm eq} = B + \frac{8\pi^2 r^2 \omega^2}{3} .$$

Given that $B_{\rm eq}$ would be available from an isotropic refinement of the structure the problem becomes that of estimating either B or $8\pi^2r^2\bar{\omega}^2/3$, and B appears to be the parameter for which an educated guess can be made.

In the ideal case in which librations of (i) the whole molecule and (ii) the rotor group itself (except about its n-fold axis) are negligible, then for the π-bonded organometallic systems B should correspond to the isotropic temperature factor, B_M, of the metal to which it is attached. The general trend, observed in this series of refinements, suggests that, while this is approximately true, the typical case is more likely to be represented by the relationship $B = B_M + \delta$, where $\delta \simeq 0{\cdot}5$. The suggested procedure for refinement is then to use a rigid-body representation of the C_n group while the rest of model is refined isotropically. At the stage of refinement at which anisotropy is considered the hindered rotor model can also be introduced where the ring parameter B is estimated as $B_M + 0{\cdot}5$, and if ΔB is defined as $B_{\rm eq} - B$, B_d can be readily obtained from the plots shown in Figs. 1 and 2.

It must be emphasized that while the value of B_d cannot be interpreted as a genuine activation energy, the refined values of B_d give information on the sharpness of the potential function near the minimum of the potential, since B_d is the only parameter that can accommodate the sharpness of the potential function when the form of the potential is fixed. The ruthenocene refinement can then be interpreted in terms of well-defined potential minima for the cyclopentadienyl rings. Johnson & Levy discuss the model of King & Lipscomb as an application of the circular normal distribution of von Mises (1918). We thank Dr Johnson for drawing to our attention other popular applications of the distribution (Jones, 1968) where the problem of interpretation of k_c (the parameter of concentration, B_d in this paper) is well known. Nevertheless it is difficult not to attach some marginal physical significance to the height of the potential barrier when the results seem reasonable (see for example Hamilton, Edmonds, Tippe & Rush, 1969). Hence we do not consider this warning misplaced

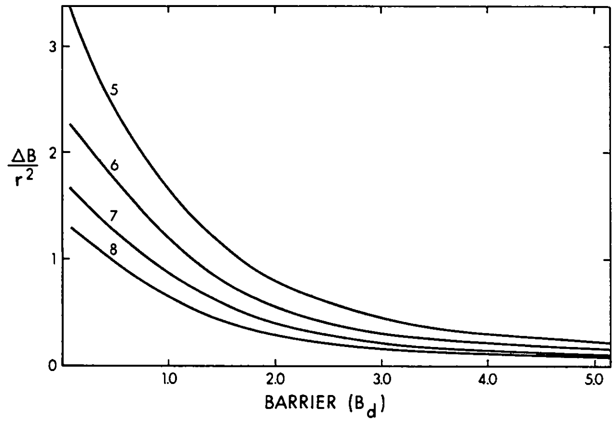

Fig. 1. General plot for estimating starting value of B_d. r is radius of the ring.

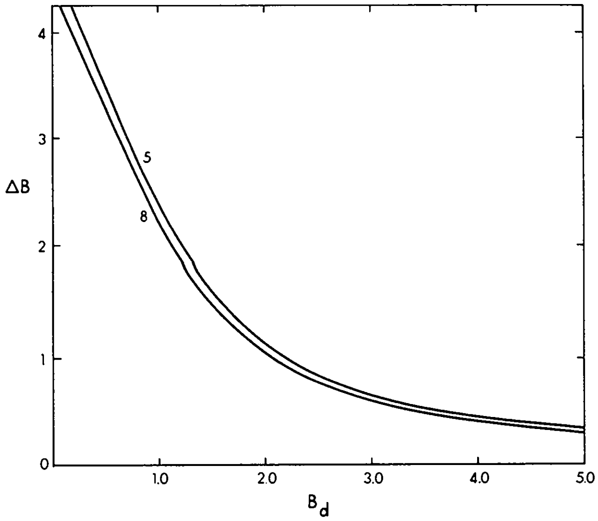

Fig. 2. Plot for estimating starting values of B_d for the common π-C_nH_n ring systems, C–C distance of 1·39 Å assumed, *i.e.* $r = 1{\cdot}39/2 \sin(\pi/n)$.

even though it is not original. Additionally we should note that the symmetry of the group is built into the potential function whereas any attempt at a more rigorous approach would rotate on a group of known geometry against a potential function that was dependent on the site symmetry. A more valid use of the B_d values is in estimating the root-mean-square angular libration about the *n*-fold axis. In this respect good agreement is obtained between the results from a β_{ij} analysis and the hindered-rotor analysis, for example, benzene 7·9° and 8·5°, and π-cyclopentadienyltricarbonylmanganese 12° and 12° (the hindered-rotor values being listed second in each pair). Fig. 3 contains plots of root-mean-square angular displacements against B_d for the common ring systems. We consider this derivation of a root-mean-square angular displacement to be as useful as an alternative treatment that yields an angular standard deviation (Stephens, 1963). For $B_d \geq 1{\cdot}0$ the two measures are essentially the same.

The model does contain features that guard against its misuse. In the case of well defined potential minima with high B_d values the standard deviations are inevitably high as a result of the form of the relevant derivatives. These high standard deviations should provide sufficient incentive to prohibit the use of a hindered-rotor model in these cases and would suggest the rigid-body approach for a constrained geometry model. High standard deviations also accompany low values of B_d ($<0{\cdot}5$), *i.e.* when the model approaches the free rotor. In the latter case the model is probably useful despite the high standard deviations and the normal working range of the model would be for $0 < B_d < 4$. The correctness of the model also required B (for the ring) $\simeq B_m$ (equivalent isotropic temperature factor of the atom to which it is attached) as discussed earlier. As yet we have no firm guidelines as to what is an acceptable discrepancy but we suggest that this feature be explored through careful examination of electron density difference maps.

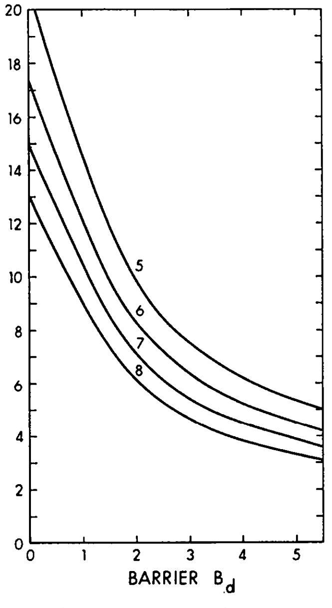

Fig. 3. Plot for evaluation of angular deviation (r.m.s.) in degrees against B_d for five- to eight-membered rings.

Computing requirements

The current version of the program *SFLS5HR* occupies 50K words of core and allows for structure factor calculations based on 60 individual atoms and 10 groups which may be either rigid groups or hindered rotors. The additional programming for the inclusion of the hindered rotors required ~2·5 K words and full-matrix refinement is limited to 195 parameters in this version. The contribution to the structure factor from a hindered rotor is relatively long, especially if high precision is used for terminating the series. The real time savings occur in the matrix build step; for example, in the case of a C_5 ring the hindered-rotor model has 36 less parameters than the anisotropic model. For structures larger than $C_5H_5Mn(CO)_3$ the hindered-rotor model saves time. When the structure is large these savings can be enormous and can delay the point at which full-matrix refinement has to be abandoned in favour of a block-diagonal approach. An example of this can be demonstrated by the refinement of the structure of $Fe(CO)_4(GeCl_2)_2CO_2(C_5H_5)_2(CO)_2$ (Bennett, Brooks, Elder, Graham, Hall & Kummer, 1970). This compound crystallizes with two molecules in the asymmetric unit. During the initial refinement cycles individual-atom models were used and the atoms of one molecule only were refined in a given cycle. Each cycle took 30 min with the parameters for nine anisotropic atoms and 22 isotropic atoms being varied with the time for refining all parameters estimated at two hours. Use of the hindered-rotor model for the four independent cyclopentadienyl groups allowed full matrix refinement of all parameters simultaneously in one hour.

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Accurate Positional and Thermal Parameters of Hexamethylenetetramine from *K*-Shell X-ray Diffraction Data

BY E. D. STEVENS* AND H. HOPE
Department of Chemistry, University of California, Davis, California 95616, *U.S.A.*

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Geometric and thermal parameters for hexamethylenetetramine have been determined from 95 unique reflections (Mo $K\alpha$, graphite monochromator) in the $\sin\theta/\lambda$ range 0·65–1·10 Å^{-1}. Both standard (second cumulant) anisotropic thermal parameters and third cumulant parameters as well as positional parameters for C and N are in excellent agreement with the corresponding neutron parameters. H atom parameters were not determined from the X-ray data. The estimated standard deviations for the X-ray parameters are generally one fifth (or less) of those for the neutron parameters. This study shows that with X-ray data it is possible to determine geometric and thermal parameters free of effects from valence electron asphericity.

Introduction

Recent interest in the experimental determination of molecular electron density distributions has renewed interest in the comparison of X-ray and neutron diffraction results. The aspherical electron distribution of atoms in molecules will influence parameters refined from conventional X-ray data. In a survey, Hamilton (1969) found significant differences between X-ray and neutron results in all cases.

When the positional and thermal parameters deter-

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* Present address: Department of Chemistry, State University of New York, Buffalo, N.Y. 14214, U.S.A.