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Some Thoughts on Choosing the Correct Space Group

BY RICHARD E. MARSH

The Beckman Institute, California Institute of Technology, Pasadena, CA* 91125, *USA*

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Abstract

Some problems that may lead to incorrect assignments of space group are identified and discussed, and some suggestions for avoiding these problems are made. Along the way, about four dozen structures listed in the Cambridge Structural Database are identified as having, almost surely, been described in space groups of unnecessarily low symmetry.

Introduction

The determination of a 'small molecule' crystal structure by means of single-crystal X-ray diffraction is one of the relatively few techniques in the physical sciences where, in most cases, the number of observations greatly exceeds the number of quantities being measured, and hence might be described as an 'exact' science. Yet, in a disturbingly large number of instances (see, for example, Herbstein & Marsh, 1982; Marsh & Herbstein, 1983; Baur & Kassner, 1992; Marsh & Bernal, 1995) the most fundamental property of the structure – the space group – turns out to have been incorrectly assigned. It is the purpose of this paper to examine some of the reasons why errors in space-group assignments may arise and to recommend some procedures for reducing the chance of such errors.

It is convenient to identify four components involved in the assignment of the correct space group: (1) The derivation of the correct space lattice – that is, the smallest *primitive* unit cell, whatever its shape, necessary to describe the translational periodicity of the structure; (2) the assignment of the correct Laue symmetry – the *centrosymmetric* (as used herein) point group consistent with the space lattice and with the full symmetry of the structure, assuming Friedel's Law to be valid; this assignment will also establish whether the unit cell is primitive or centred; (3) the identification of any systematic absences characteristic of translational symmetry elements (glide planes or screw axes); (4) the decision as to whether or not the structure is centrosymmetric. Let us discuss these four components separately.

(1) *Deriving the correct space lattice*

Prior to *ca* 1970, the majority of single-crystal X-ray diffraction experiments were carried out photographically: some combination of Laue, rotation–oscillation, Weissenberg and precession photographs was used to record the diffraction pattern. The lattice was then deduced by examining and measuring the films; the Laue group and the systematic absences were typically assigned at the same time. Such methods were surely not error-free: measurements of the photographs could be incorrect, or numbers could be altered in transcription. However, many problems could be easily recognized, including twinning, superstructures, disorder streaking and deformed or partially decomposed crystals. Perhaps more important, weak reflections were difficult to overlook, since the human eye shows high sensitivity to small intensity differentials; superstructure reflections and space-group absences were relatively simple to detect.

Today, many – perhaps most – single-crystal diffraction laboratories no longer maintain photographic facilities; while some feature modern image-plate detector systems which can produce simulated photographs, most rely entirely on conventional automated diffractometers to identify the lattice. This identification is normally carried out by programming the diffractometer to carry out a systematic search for Bragg reflections – reciprocal lattice points – by varying the orientation angles (usually χ, φ and θ) while monitoring for a high counting rate. After a pre-determined number of such diffraction maxima – perhaps 15–25 – have been found, the computer is asked to construct a space lattice that will accommodate all these maxima and to derive the largest reciprocal unit cell – and hence the smallest real cell –

Richard E. Marsh was born in Jackson, Michigan, USA, in 1922. He obtained his BS in Applied Chemistry at the California Institute of Technology in 1943 and, after a stint with the US Navy, entered graduate school, obtaining a PhD at the University of California, Los Angeles, in 1950. He then returned to Caltech, where he has been ever since; he is now a Senior Research Associate, Emeritus. His interests have been in the areas of X-ray diffraction techniques, the structures of 'small' molecules of all kinds and the flight patterns of golf and tennis balls.

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consistent with this lattice. (By usual convention, the edges of this smallest cell are taken as the three shortest, noncoplanar lattice vectors, with the three interedge angles either all acute or all obtuse.) If no satisfactory lattice and reasonable cell is found, the user is alerted that the crystal may be defective. Lacking photographic evidence of the nature of the problem, the investigator may abandon the crystal. (I note, in passing, that failure to find a reasonable space lattice may not signify a defective crystal but an especially interesting one – perhaps twinned in such a way that a set of parent reflections could be easily separated out and measured, or perhaps reflecting a modulated host–guest arrangement with important structural ramifications.)

What can go wrong with such a procedure? Probably the greatest danger is that an entire class of reflections might be overlooked during the search routine, either by chance or – more likely – because they are systematically weak. Superstructure arrangements, in which the true structure is based on small but systematic deviations from a more symmetric substructure, are not uncommon; such a superstructure will require a unit cell larger than that of the substructure and will give rise to additional weak reflections that might be overlooked during a search routine. It is impossible to estimate how many such superstructures have gone unnoticed in recent years, since the only indication that a substructure is not telling the entire story may be in the form of somewhat abnormal displacement coefficients U_{ij}.

A related problem may occur when the structure is dominated by a few very heavy atoms, whose arrangement is such that they contribute little or nothing to an entire class of reflections. For example, if a heavy atom happens to lie very close to $y = 0.25$ in the monoclinic space group $P2_1/c$, it will contribute little to reflections with l odd, since there must be an equivalent atom at x, 0.25 ($= 1/2 - y$), $z + 1/2$, and the unit cell may appear to be halved in the c direction (the space group would then appear to be $P2_1/m$). This type of event has occurred in at least one documented instance: the structure of bis[1,3-bis(diphenylphosphino)propane]-platinum, $PtP_4C_{54}H_{52}$. Originally, this structure was described in space group $C2/m$, with the Pt atom in sites of $2/m$ symmetry; the ligands appeared to be disordered across the mirror plane, and the two pairs of Pt—P bonds were appreciably unequal in length (Harvey, Schaefer & Gray, 1988). A reinvestigation (Asker, Hitchcock, Moulding & Seddon, 1990) showed a unit cell with a doubled c axis, space group $C2/c$, with the Pt atom lying on a twofold axis, but slightly displaced from $y = 0$ [0.00322(2)]; in this revised structure the ligand is ordered and the Pt—P bond lengths are equal. Asker *et al.* (1990) note that ‘all reflections with l odd tend to be weak’, and that Harvey, Schaefer & Gray (1988) ‘missed the weak reflections entirely’. It seems likely that similar events have occurred, and gone unnoticed, a number of other times.

Perhaps a more common occurrence is for heavy atoms to lie exactly on crystallographic symmetry elements which, taken alone, define a unit cell smaller than the true one. For example, a heavy atom lying on a center of symmetry in space group $P2_1/a$ will not contribute to reflections with $(h + k)$ odd; these will be systematically weak and perhaps be overlooked during the search routine. The resulting cell will appear to be C-centered (space group, $C2/m$), with the heavy atom at a site of $2/m$ symmetry and some or all of the remaining atoms disordered (since the true site symmetry of the heavy atom is lower, $\bar{1}$). I know of no documented examples of this problem; however, a search of the Cambridge Structural Database [March 1984 release, see CSD User's Manual (CSD, 1992)] for structures in space group number 5, with $Z = 2$, and with disordered ligands about a central metal atom turned up a number of instances where the trouble may have arisen. The structures of bis(isothiocyanato)bis(pyridyl)copper (Soldánova, Kabešová & Gažo, 1983), bis(4-methylpyridine)dichlorolead (Engelhardt, Patrick, Whitaker & White, 1987) and bis(methanesulfonate)tetraammine platinum(II) (Khodadad & Rodier, 1989) have all been described in space group $C2/m$, $Z = 2$, with disordered ligands coordinated to the central metal atom; in all three cases, some intermolecular distances between disordered ligand atoms are prohibitively small. If it is presumed that the true space group is $P2_1/a$, with complete ordering of the ligands, intermolecular contacts become entirely reasonable. In a fourth example, Calabrese, Jones, Harlow, Herron, Thorn & Wang (1991) note that the structure of bis(phenylethylammonium)tetraiodo lead – again, disordered in space group $C2/m$, with $Z = 2$ – might indeed involve an ‘unresolved superlattice structure’. An even more interesting example may be $(C_5H_5N)_4Yb(BH_4)_2.2C_5H_5N$ (White, Deng & Shore, 1991); here, the reported structure ($C2/m$, $Z = 2$, disordered) is properly described as orthorhombic, $Fmmm, Z = 4$, with [102] replacing [001]. In this case, one can imagine any of a number of space groups that might result if one class or another of weak reflections had been overlooked. A search for additional weak reflections might well result in a major revision of some or all of these structures.

Other possible causes for an automated search routine to overlook a class of reflections and end up with too small a unit cell include simple bad luck or too coarse a sampling interval. The bad luck might arise if, by chance, all the reflections found by the search routine show even parity for some category of indices; for example, if the list of reflections happens to contain only those with $(h + k)$ even, they can all be fitted by a unit cell that has only one-half the correct volume. For a list containing 15 reflections, the random chance of all 15 showing some systematic sort of even parity are ~1 in 4700 – hardly prohibitive in view of the number of structures being reported each year. The ‘sampling interval’ problem is also one of happenstance and is probably most important when the crystal is oriented so that a principal lattice direction is closely parallel to the φ axis of the diffractometer; entire layer lines may then be overlooked if the sampling interval in χ is too large. (Such a misfortune has occurred at least once in our laboratories and was not corrected until the resulting structure seemed questionable.) Should we not fear that at least a few of the myriad of crystal structures described in the scientific literature are based on inappropriately small unit cells, due merely to bad luck?

I am aware of two instances in which a search routine has apparently turned up too *large* a unit cell; both occurred in our laboratories. In each instance the 'lattice search' program failed to note that some linear combination of the indices assigned to the 25 defining reflections – $(h + k - l)$ or $(h - k - l)$ – was divisible by 3 and hence that the primitive unit cell derived by the computer was too large by a factor of 3. In one instance the problem was not noted until the final structure (with $Z = 6$, space group $P\bar{1}$) showed the additional translational relationships. Has this occurred in other laboratories as well?

What might be done to ensure that the correct lattice has been found? Many workers take the time either to collect intensity data at intermediate fractional reciprocal-lattice points or to record continual θ–2θ scans along principal reciprocal lattice rows, searching for additional reflections that would indicate a larger unit cell. Such procedures should prevent most errors. Yet one can fear that additional reflections might still be present, perhaps at irrational lattice points (in the case of modulated structures) or along unsampled lattice rows. Systematic examination of the *entire* reciprocal lattice, as can best be done photographically, remains the method of choice for establishing the correct space lattice. It seems particularly desirable that photographs be prepared and examined whenever serious disorder appears to be present, since diffuse streaking along reciprocal lattice rows may be of great help in deducing the nature of the disorder [see, for example, James (1948), pp. 239–267].

(2) *Assigning the Laue symmetry*

In our automated world, much of the task of assigning the Laue group may be relegated to the controlling computer, by asking it to fit each of the 14 standard unit cells ('Bravais lattices') to the space lattice it has already found; it then reports to the user which of these standard cells might provide an adequate fit. Alternatively, the computer may list the angles between all pairs of reasonably short lattice vectors, from which the user may deduce the highest-symmetry unit cell available. In any event, the information available to the user consists of the axial lengths and the interaxial angles corresponding to a number of possible Bravais lattices and the precision estimates of these lengths and angles (as obtained by the quality of fit to the orientational angles θ, φ and χ previously measured for the 15–25 fiduciary reflections). On the basis of this information, the user must decide – perhaps once and for all – on the most appropriate lattice type.

This is surely a dangerous procedure, since it is not the shape of the unit cell that determines the lattice type but, rather, the symmetry of the diffraction intensities. Obviously, a unit cell may have two or even three interaxial angles as close to 90° as desired, whereas the structure has no symmetry whatsoever and must be described as triclinic. If the investigator assumes, on the basis of two angles being approximately equal to 90°, that the structure is monoclinic and, hence, that the Laue symmetry is $2/m$ (and if pressure exists to produce a structure as rapidly as possible), he or she may elect to collect no more than a single quadrant of intensity data – an 'asymmetric unit' for a monoclinic structure – and not find out until later (or, perhaps, not at all) that a hemisphere of data should have been collected in order to arrive at the correct triclinic structure. More difficult decisions arise in higher-symmetry crystal systems, where two or more Laue groups may be compatible with a single lattice type. Thus, a hexagonal unit cell may represent any of five Laue symmetries ($\bar{3}$, $\bar{3}m1$, $\bar{3}1m$, $6/m$ and $6/mmm$); the correct choice must depend upon intensity comparisons and until this choice is made the asymmetric unit of data cannot be determined. I have encountered in the crystallographic literature (but failed to document) quite a number of instances where a tetragonal, trigonal or hexagonal structure has been reported on the basis of obviously incomplete intensity data.

There is another problem which may arise if a choice of lattice type is made merely on the basis of the unit-cell shape. This problem is associated with the fact that the uncertainties in the unit-cell dimensions, as reported by the controlling computer, are merely measures of *precision* – of how well the derived unit cell matches the measurements of the orientation angles of the small set of fiduciary reflections. (Typically, these precisions are of the order 0.01% in cell lengths and 0.01–0.02° in cell angles.) If these precision estimates are interpreted as 'standard deviations' and accepted as reliable indicators of true accuracies, an incorrect assessment of the lattice symmetry may result. For example, an angle of 90.20 (2)° might be considered to be so far from 90° – 10 e.s.d.'s – as to rule out orthogonality when in fact the deviation is no greater than the true experimental error. The actual uncertainties in the measured cell dimensions may be far larger than the precision indicators (see Taylor & Kennard, 1986), for a variety of reasons. The diffractometer may lose its alignment as the characteristics of the X-ray tube or the monochromator change (or for other reasons, as those of us in earthquake-prone California know), or the crystal may be mis-centered. Special problems arise if the crystal is highly absorbing, so that much of the diffraction takes place at its surface rather than at its center and the effective radius of the instrument is incorrect. All of these problems are exacerbated if the fiducial reflections – the 15 or 25, or whatever, reciprocal lattice observations that may constitute the entire body of experimental data available – have been chosen so as to cover only a narrow region of reciprocal space, so that correlations between the derived cell dimensions are large and systematic errors are enhanced.

Another source of error in assigning the appropriate Laue group surely arose a few years ago – and perhaps is still prevalent today – when one or two of the popular computer routines that were relied upon to indicate possible choices of lattice type were flawed, seemingly being reluctant to produce centered monoclinic cells (or, perhaps, severely oblique rhombohedral ones). This problem, which may have been associated with early versions of the program *TRACER*, has apparently been corrected in newer releases.

That the assignment of an incorrect Laue group is not an infrequent occurrence is, I believe, clearly indicated in Table 1, which represents the results of a hasty search of the Cambridge Structural Database [March 1994 release, see CSD User's Manual (CSD, 1992)] of all triclinic crystal structures with more than one molecule in the asymmetric unit ($Z > 1$ for $P1$, $Z > 2$ for $P\bar{1}$). I estimate that there are ~5000 separate entries of this type; of them, I have identified the 33 structures in Table 1 as being properly described in higher Laue symmetries. (The assignment of higher symmetry was made on the basis of the atom coordinates provided in the CSD and, usually, checked in the original reference. In all cases these coordinates conformed to the symmetry requirements of the revised space group within very small tolerances – typically 0.01–0.02 Å.) In some cases, deviations of the revised unit-cell angles from 90° are quite large (for example, Bailey, Berlin & Holt, 1984; Tochtermann, Olsson, Sczostak, Sonnichsen, Frauenrath, Runsink, Peters, Peters & Von Schnering, 1989; Sakaguchi, Anzai, Furuhata, Ogura & Iitaka, 1979), yet the symmetry of the structure – and hence the symmetry of the diffraction intensities – is unquestionable.*

A particularly instructive example of the sort of problem that may arise in the assignment of Laue symmetry is provided by *JOGRUS* (Lotz, Kiel & Gattow, 1991). Here, the authors measured all three unit-cell angles as 90.0 (1)°, and became convinced that the Laue symmetry was *mmm*. They then searched for a structure in 17 different orthorhombic space groups, but reported that they could find no complete molecule in six of these space groups and could not achieve refinement in the other 11. They then reported the structure as triclinic, space group $P1$, with two independent molecules in the asymmetric unit. (They apparently failed to notice that these two molecules are related, very closely, by a lattice-centering translation.) The final refinement was admittedly unsatisfactory, with large parameter correlations between the two molecules and a final R of 0.27. In fact, the structure they report is entirely consistent with the monoclinic space group $I2/m$, with one of the cell angles close to 90° only by accident.

The many examples in Table 1 of failure to deduce a centered monoclinic lattice may well result from the program deficiencies alluded to above. However, the true symmetry of all these structures could – and *should* – have been deduced from the final atomic coordinates, since in all cases there were strongly suggestive relationships between the coordinates of corresponding atoms of 'different' molecules.

Routine application of a program such as *MISSYM* (Le Page, 1988), as is now the policy at the Editorial Offices of *Acta Crystallographica*, would undoubtedly have caught all these errors prior to publication.] However, a far more sensible procedure would be to select the correct Laue symmetry early on, either by examining diffraction photographs or image-plate simulations or by collecting an entire set of intensity data – a complete sphere of reflections – and carrying out a systematic search for the true symmetry at that stage of the investigation. Surely the solution and refinement of a structure is more straightforward if it is carried out in the correct crystal system!

(3) *Determining the systematic absences*

In principle, this should be a straightforward procedure; most computer installations have, I believe, standard routines for displaying or analyzing the intensities of the various categories of reflections whose absence might indicate translational symmetry elements. (Indeed, in some software packages these symmetry elements are combined so as to arrive at recommendations as to probable space groups.) Nevertheless, there are pitfalls in this procedure. Perhaps the most common occurrence is that a small number of reflections of a given category appear, erroneously, to have intensities so far above the measured background as to provide conclusive proof of the absence of the symmetry element (and it is a solid tenet of crystallography that even a single violation of an extinction condition should be taken as proof that the symmetry is not present). Such erroneous observations occur quite commonly as a result of the 'Renninger effect' (Renninger, 1937) – reflection from, in turn, two strongly-diffracting sets of planes so oriented that the resulting diffracted beam is in the direction of a third reflection. (A necessary, but by no means sufficient, condition is that the indices of the first two reflections sum to those of the third.) Another

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* Atomic coordinates for the revised structures have been deposited with the IUCr (Reference: AN0514). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Structures originally reported as triclinic that are more accurately described in higher symmetries*

Included are the original and the revised space groups (S.G.) and number of formula units per cell (*Z*), the revised cell dimensions (Å, °), and the 'Reference codes' assigned by the Cambridge Structural Database System (Version of March 1994), from which most of the data were obtained.

	Original		Revised								
Formula	S.G.	*Z*	S.G.	*Z*	*a*	*b*	*c*	*α*	*β*	*γ*	Ref.
$C_{36}H_{32}O_4Mo_2$	$P\bar{1}$	4	$C2/c$	8	35.573	10.065	19.095	89.99	118.16	90.04	(*a*)
$C_{12}H_{27}P_3$	$P\bar{1}$	4	$C2/c$	8	34.265	6.256	18.162	89.99	120.53	90.01	(*b*)
$C_{18}H_{20}N_3OS_3I$	$P\bar{1}$	6	$R3$	6	26.127	26.129	26.131	119.53	119.52	119.53	(*c*)
$C_{24}H_{36}N_2SbCl_5$	$P\bar{1}$	4	$C2/c$	8	32.459	7.497	24.335	89.97	94.42	89.97	(*d*)
$C_{28}H_{46}O_2Sm$	$P\bar{1}$	4	$C2/c$	8	21.941	20.910	16.141	90.01	130.15	90.01	(*e*)
$CH_8O_9S_2Ca$	$P\bar{1}$	4	$P2_1/n$	4	5.764	19.438	7.727	89.98	92.96	90.04	(*f*)
$CH_8O_9S_2Cd$	$P\bar{1}$	4	$P2_1/n$	4	5.616	19.230	7.596	90.06	90.61	89.96	(*g*)
$C_{126}H_{106}OP_7Au_7$	$P\bar{1}$	8	$C2/c$	16	68.18	15.45	55.19	90.13	127.85	89.89	(*h*)
$C_{18}H_{32}N_{14}O_4FeK_3$	$P\bar{1}$	4	$C2/c$	8	20.806	19.096	18.926	89.93	127.58	90.04	(*i*)
$C_{14}H_{20}NO_6SCl$	$P\bar{1}$	4	$C2/c$	8	33.614	6.917	15.720	89.65	116.71	90.11	(*j*)
$C_{17}H_{22}N_2O_7Cu_2$	$P\bar{1}$	4	$C2/c$	8	23.981	11.961	15.769	89.99	116.96	90.01	(*k*)
$C_{26}H_{26}N_6S_2Cd$	$P1$	3	$R\bar{3}$	3	16.490	16.494	16.492	114.99	114.96	114.99	(*l*)
$C_{18}H_{24}O_5$	$P\bar{1}$	4	$P2_1/c$	4	11.81	18.70	8.09	89.90	107.50	89.61	(*m*)
$C_5H_{10}N_3O_3P$	$P\bar{1}$	8	$C2/c$	16	26.676	7.653	18.817	90.03	114.65	89.99	(*n*)
$C_{36}H_{40}N_4O_7Cu_2$	$P\bar{1}$	4	$C2/c$	8	29.488	15.641	18.379	89.96	126.70	90.01	(*o*)
$C_{16}H_{47}N_2O_3Cl_9Mo_2$	$P1$	2	$C2/m$	4	20.776	11.271	16.364	89.99	115.49	90.02	(*p*)
$C_{14}H_{14}N_4S_2Cd$	$P\bar{1}$	4	$C2/c$	8	20.646	9.284	19.430	90.04	114.71	89.94	(*q*)
$C_{20}H_{32}N_{10}O_{13}S_4Na_2Mo_2$	$P\bar{1}$	1	$C2$	2	13.279	13.330	23.721	90.12	92.97	89.95	(*r*)
$C_{15}H_{14}N_4O$	$P\bar{1}$	4	$C2/c$	8	23.776	9.360	12.864	89.93	92.82	89.97	(*s*)
$C_{12}H_6O_{17}Mo_4K_4$	$P\bar{1}$	8	$C2/c$	16	23.721	13.196	37.156	90.00	97.23	89.94	(*t*)
$C_{14}H_{14}N_4OCu$	$P\bar{1}$	6	$R3$	6	15.421	15.428	15.432	115.05	114.96	114.92	(*u*)
$C_{15}H_{18}O_7Fe$	$P\bar{1}$	4	$C2/c$	8	25.579	11.346	13.534	89.99	116.49	89.89	(*v*)
$C_{26}H_{14}O_{12}S_3Fe_4$	$P\bar{1}$	4	$C2/c$	8	30.108	13.701	17.030	90.15	109.58	90.03	(*w*)
$C_{17}H_{12}N_2OSFe_4$	$P1$	4	$C2/c$	8	22.108	13.429	16.018	90.02	133.09	89.97	(*x*)
$C_{10}H_{22}N_8O_5Cl_2Cu$	$P\bar{1}$	2	$Fdd2$	8	27.835	18.705	7.205	90.03	89.87	90.15	(*y*)
$C_{10}H_8N_2O_2Cl_2$	$P\bar{1}$	6	$C2/c$	12	31.672	14.849	6.902	89.97	91.63	90.00	(*z*)
$C_5H_8N_4O$	$P\bar{1}$	4	$I2/m$	4	7.971	6.709	12.303	90.0	90.0	90.0	(*aa*)
$C_{13}H_{14}N_4O_4$	$P1$	4	$P2_1/n$	4	7.026	18.344	10.973	89.99	107.42	90.06	(*bb*)
$C_{24}H_{34}N_4O_6F_6Co$	$P\bar{1}$	2	C2/c	4	19.670	11.119	14.897	89.99	113.85	90.00	(*cc*)
$C_{14}H_4N_4S$	$P\bar{1}$	4	$C2/c$	8	20.215	7.540	16.084	90.02	104.00	90.01	(*dd*)
$C_{11}H_{10}Cl_2Ti$	$P1$	2	$C2/c$	4	11.939	10.902	8.461	89.88	109.97	90.11	(*ee*)
$C_{16}H_{19}NO_2BiFe$	$P\bar{1}$	4	$C2/c$	8	35.209	8.383	13.267	89.96	111.38	90.05	(*ff*)
$C_4H_9O_2S_2Sb$	$P\bar{1}$	4	$C2/c$	8	19.512	6.449	15.183	90.04	121.39	90.19	(*gg*)

(*a*) *AZMMOB*. Tetracarbonyl-bis(η^5-cyclopentadienyl)(μ_2-η^2-di-*p*-tolylmethylidene)dimolybdenum toluene solvate (Curtis, Messerle, D'Errico, Solis, Barcelo & Butler, 1987). (*b*) *BIMBAA*. Tri-*t*-butyl-cyclotriphosphane (Hahn, Baudler, Krüger & Tsay, 1982). (*c*) *BORYEM*. 3-(2′-Phenyl-2,4′-bithiazole-4-carboxamido)propyldimethylsulfonium iodide (Kuroda, Neidle, Riordan & Sakai, 1982). (*d*) *BPCLSB*. Bis(4-benzylpiperidinium)-pentachloroantimony(III) (Cariati, Panzanelli, Antolini, Menabue, Pellacani & Marcotrigiano, 1981). (*e*) *CALCEX*. Bis[(η^5-pentamethylcyclopentadienyl)(tetrahydrofuran-*O*)]samarium (Evans, Bloom, Hunter & Atwood, 1981). (*f*) *CAMSOA*. Calcium methanedisulfonate trihydrate (Charbonnier, Faure & Loiseleur, 1979). (*g*) *CAMSOB*. Cadmium methanedisulfonate trihydrate (Charbonnier, Faure & Loiseleur, 1979). (*h*) *CENJUA*. Heptakis(triphenylphosphine)heptagold hydroxide (Van der Velden, Beurskens, Bour, Bosman, Noordik, Kolenbrander & Buskes, 1984). (*i*) *CIWJOH*. Catena[tetra-aquo-hexacyano-bis(*N*-hexamethylenetetramine)tripotassium iron(III)] (Meyer & Pickardt, 1988). (*j*) *CUDNAQ*. *N*-Benzyl-3-thia-7-azabicyclo[3.1.1]nonan-9,9-diol perchlorate (Bailey, Berlin & Holt, 1984). (*k*) *DEXNEZ*. (μ_2-Acetato-*O*,*O*′)(μ_2-3,11-diacetyl-5,9-diazatrideca-2,4,9,11-tetraene-2,7,12-triolato-*O*,*O*′,*O*″,*N*,*N*′)dicopper(II) (Nishida & Kida, 1986). (*l*) *DEXYIO*. *Trans*-bis(isothiocyanato)-tetrakis(4-methylpyridine-*N*)cadmium(II) 4-methylpyridine clathrate hydrate (Pervukhina, Podberezskaya, Bakakin, Kislikh, Chekhova & Dyadin, 1985). (*m*) *DIHCOM*. 8-Formyltricyclo[6,2,1,$0^{1,5}$]undec-9-en-9,10-diarboxylic acid diethyl ester (Tochtermann, Olsson, Sczostak, Sonnichsen, Frauenrath, Runsink, Peters, Peters & Von Schnering, 1989). (*n*) *DIYMED*. 1,3-Dimethyl-2-methylamino-1,3,2-diazophospholidine-2,4,5-trione (Hutton, Modro, Niven & Scaillet, 1986). (*o*) *FADSIM*. [μ_2-1,2,3,4-Tetrakis(salicylideamino-2,3-dimethylbutano)]dicopper(II) ethanol solvate dihydrate (Mikuriya, Izumitani, Okawa & Kida, 1986). (*p*) *FAFSOU*. [Bis(tetraethylammonium)tris(μ_2-chloro)bis(trichloromolydenum(III)] hydroxonium dihydrate (Spitsyn, Kazin, Subbotin, Aslanov, Zhirov, Zelentsov & Felin, 1986). (*q*) *FAPCOO*. *catena*-[Bis(4-methylpyridine-*N*)bis(μ_2-thiocyanato-*N*,*S*)]cadmium(II) (Taniguchi, Shimoi & Ouchi, 1986). (*r*) *FEBMUU*. Disodium(μ_2-oxo)bis(μ_2-xanthopterine-*N*,*O*,*O*′)bis(dioxomolybdenum)dimethyl sulfoxide tetrahydrofuran solvate (Burgmayer & Stiefel, 1986). (*s*) *FOWVUI*. *N*-Benzoyl-3,3-dimethyl-3*H*-pyrazolo(3,4-*c*)pyridine-5-amine (Klinger, Foulon, Gesche, Strub & Streith, 1987). (*t*) *GALGEF*. Tetrapotassium tetrakis-[($\mu_3$hydroxo)tricarbonylmolybdenum] monohydrate (Bazhenova, Ioffe, Kachapina, Lobkovskaya, Shibaeva, Shilov & Shilova, 1978). (*u*) *GEBHOK*. *catena*-[(4-Imidazolyl)methyliminopropylsalicylideneiminato-*N*,*N*′,*N*″,*N*‴,*O*]copper(II) (Matsumoto, Yamashita, Ohyoshi, Kohata & Okawa, 1988). (*v*) *GICSIU*. Tricarbonyl-(η^4-methyl-7,8-epoxy-6-hydroxyundeca-2,4-dienoate)iron (Lellouche, Breton, Beaucourt, Toupet & Gree, 1988). (*w*) *GIHGAF*. (μ_4-Sulfido)bis[(μ_2-benzylsulfido-*S*,*S*)hexacarbonyl-diiron (Ruji, Licheng, Honggen, Kadiata & Jitao, 1988). (*x*) *HAGPAG* 2-Acetylmethylidene-3-(2,4-dibromophenyl)-5-phenyl-2,3-dihydro-1,3,4-thiadiazole (Pandya, Basile, Gupta, Hand, Maclaurin, Mohammad, Ratemi, Gibson & Richardson, 1993). (*y*) *HZPYCU*. Aqua-bis(2-hydrazino-4-hydroxy-6-methylpyrimidine)copper(II) dichloride dihydrate (Sakaguchi, Anzai, Furuhata, Ogura & Iitaka, 1979). (*z*) *JEWSUZ*. 3,7-Dichloro-4,6-(1,4-tetramethylene)-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione (Marciano, Baud'huin, Zinger, Goldberg & Kosower, 1990). (*aa*) *JOGRUS*. 2-Amino-4-methoxy-6-methyl-1,3,5-triazine (Lotz, Kiel & Gattow, 1991). (*bb*) KEYYUI. 3-Hydroxy-6-(4′-nitro)phenylazopyridine ethanol clathrate (Ramachandra, Krishna & Desiraju, 1989). (*cc*) *LACFAW*. [(μ_2-Butyleneglycol)bis(1-oxy-2,2,5,5-tetramethyl-4-(3,3,3-trifluoropropenyl-2-olato)-3-imidazoline]cobalt(III) (Romanenko, Ovcharenko & Podberezkaya, 1992). (*dd*) *LADLUX*. 1,3,Dihydro-1,3-bis(dicyanomethylene)isothianaphthene (Lorcy, Robinson, Okuda, Atwood & Cava, 1993). (*ee*) *MYCPTI*. (η^5,η^5-1,1′-Methylene-dicyclopentadienyl)dichlorotitanium (Smith, Von Seyerl, Huttner & Brintzinger, 1979). (*ff*) *TBAFEB*. (1-*t*-Butyl-3-methyl-2-phenyl-η-1,2-azaborolinyl)dicarbonyl-iodo-iron (Schulze, Boese & Schmid, 1980). (*gg*) *VENCOG*. 2-(β-Hydroxyethylthio)-1,3,2-oxathiastibolane (Sen Gupta, Bohra, Mehrotra & Das, 1990).

possible cause for an erroneous violation of systematic extinctions is the cutting off of background intensity of a low-angle – typically, first order – reflection: if data are being measured by an θ–2θ scan technique, the low-angle background may be intercepted by the beam catcher and the resulting net intensity will be artificially enhanced.

A particularly interesting example of the artefactual appearance of additional 'reflections' [and an example that properly belongs in (1), discussing the assignment of the space lattice] is that of $[Fe([9]aneN_3)_2]Cl_3.5H_2O$. Here, the original authors (Boeyens, Forbes, Hancock & Wieghardt, 1985) assigned the space group as *P*3 with three almost equivalent molecules per asymmetric unit; the primitive hexagonal lattice was needed in order to accommodate a number of weak but apparently significant violations of the rhombohedral-centering condition ($h - k - l = 3n$). A reinvestigation (Marsh, 1987), which included oscillation and Weissenberg photographs and intensity measurements on a hemisphere of the reciprocal lattice, showed that these apparent violations were not real; they had probably resulted from scan overlap involving neighboring strong reflections. An improved structure was then obtained in space group *R*32, with all three molecules being structurally equivalent (and having additional twofold symmetry).

Other recent examples, where the appearance of a few relatively weak violations of systematic extinctions led the original authors to select an incorrect space group, include *bis*(dipicolinato)ferrate(III) dihydrate, where the choice of *Pnn*2 (Cousson, Nectoux & Rizkalla, 1992) was revised to *Pnna* (Marsh, 1993), and α-dicalcium silicate hydrate, where the choice of $P2_12_12_1$ (Yano, Urabe, Ikawa, Teraushi, Ishizawa & Udagawa, 1993) was later revised to *Pbca* (Marsh, 1994*b*); in both cases the revised structure was considerably more satisfactory than that reported when the space-group assignment was incorrect.

Assignment of systematic absences is much less ambiguous if diffraction photographs are available; not only can scan overlap or truncation problems be avoided, but Renninger effects can usually be recognized – either by the peculiar shapes of most double-reflection spots or by the non-equivalence of symmetry-related reflections in different regions of the photograph. Recognizing Renninger effects on a diffractometer usually involves measuring a particular reflection at various orientations of the crystal; this is seldom done.

(4) *Centrosymmetric or not?*

This is probably the most irksome problem affecting all crystallographers (excepting those who deal exclusively in chiral molecules). For many of the most common pairs of space groups – *P*1 and $P\bar{1}$, $P2_1$ and $P2_1/m$, *Cc* and *C*2/*c*, and $Pna2_1$ and *Pnam* come immediately to mind – the choice between the two is not dictated by any set of systematic absences and depends only on whether or not the resulting structure is centrosymmetric. The number of molecules in the unit cell (as indicated by the density of the crystals) and the presumed symmetry (or lack thereof) of the molecule may provide a clue; and, of course, the molecule may be known to be chiral so that a centrosymmetric space group is impossible. In many cases, however, a definitive answer cannot be made until the final structure has been arrived at (and even then the choice may not be unambiguous, as we shall discuss later).

It is common practice to make an initial decision as to whether or not a structure is centrosymmetric by examining, at a very early stage, the distribution of the measured intensities; this distribution should, in theory, be appreciably different for the two cases (Howells, Phillips & Rogers, 1950; Karle, Dragonette & Brenner, 1965). However, such statistical tests can be *very* deceptive. For instance, if, within a noncentrosymmetric structure, there is a centrosymmetric array involving some of the atoms – particularly heavy ones – the intensity distribution may well suggest a centrosymmetric space group. But a far more dangerous – and common – result works in the opposite sense, falsely indicating a noncentrosymmetric space group. This result can arise in two separate ways: (1) If the primitive unit cell contains a small number of dominating scatterers, the intensity statistics will be distorted toward a noncentrosymmetric indication (Hargreaves, 1955). Indeed, if the 'small number' is 2 – as often occurs in $P\bar{1}$ and $P2_1/m$ – the indication of noncentrosymmetry may be completely convincing (even though the two dominating atoms, taken alone, must define a centrosymmetric array). (2) If a significant number of weak intensities has been deleted before the statistical test is made, the resulting distribution will again be distorted toward a noncentrosymmetric indication (Marsh, 1981). I have encountered many instances – far too many to cite – of authors being misled into incorrectly assuming a noncentrosymmetric space group on the basis of these misleading intensity statistics; in most of these instances the incorrect space-group assignment has persisted through the entire structure analysis and into the final publication.

What are the consequences of an incorrect decision at this early stage? In the first instance – a false indication of centrosymmetry – the consequences will probably be extreme difficulty in arriving at a satisfactory trial structure; if a partial solution is obtained (presumably because a portion of the structure is, indeed, approximately centrosymmetric), refinement will surely be unsatisfactory. There is little danger that a centrosymmetric description of a demonstrably noncentrosymmetric structure will find its way into the literature. However, I must add a caveat here: there are many examples, particularly in the world of mineralogy, where structures have been described as centrosymmetric and disordered whereas subsequent investigations, perhaps by noncrystallographic methods, have shown them to be noncentrosymmetric and ordered. As we shall see later, the distinction between the two cases by diffraction methods alone is difficult and sometimes impossible. An excellent discussion of the situation, including recommendations as to how to refine almost centrosymmetric structures, has recently been given by Watkin (1994).

The opposite result – an indication that a centrosymmetric structure is noncentrosymmetric – may lead to serious consequences that are never resolved. The overwhelming difficulty in attempting to describe a centrosymmetric structure in a noncentrosymmetric space group is that meaningful refinement is not possible. This has been well recognized for at least a generation, perhaps beginning with the note by Ermer & Dunitz (1970), who said: 'It is impossible to distinguish by means of a least-squares analysis between a centrosymmetric structure and a corresponding non-centrosymmetric one by simple expansion of the set of parameters over the questionable inversion centre', and adding: 'Small, random shifts may be applied to the centrosymmetric set of parameters so as to make it only approximately centrosymmetric, but then the occurrence of an ill-conditioned set of normal equations has to be reckoned with'. On occasion, investigators have presumed to remove the ill-conditioning by resorting to block-matrix refinement, but any apparent profit from such a procedure is purely chimeral: near-singularities do not disappear simply by being ignored. [Watkin (1994) emphasizes that: 'Blocking the matrix can never be recommended as a cure for singularities unless their source is well understood'.] The result of any such block-matrix refinement must surely be nonconvergence. However, perhaps even more important: if the off-diagonal terms that represent the near-singularities are removed from the refinement matrix, the resulting parameter e.s.d.'s may appear to be quite normal when in fact these parameters are effectively undetermined. In other words, the investigator may be deluded into believing that a satisfactory structure, with reasonable e.s.d.'s, has been found when in fact it has not. This point should be made again and again, as loudly and as clearly as possible: *ignoring a center of symmetry can – and usually does – result in errors in the atom coordinates that are several times larger than the nominal e.s.d.'s.* In such instances it is not unusual to read, in reputable journals, of C—C distances in a fully aromatic benzene ring ranging from ~1.25–1.55 Å, in the face of reported e.s.d.'s of ~0.01 Å. I find such results indefensible.

In perusing, rather rapidly, those structures in the Cambridge Structural Database showing space group No. 1 ($P1$) with $Z \geq 2$, I noted the 16 examples given in Table 2 where the atom coordinates are closely compatible with a center of symmetry; in all probability, these structure should correctly be described in $P\bar{1}$, space group No. 2. Included in Table 2 are, for each example, the coordinates of the average center of symmetry relating each pair of corresponding atoms, as well as the scatter e.s.d.'s of the individual centers. This latter 'scatter e.s.d.', which measures how closely each atom pair conforms to the overall center of symmetry, is also a measure of how much the original $P1$ coordinates depart from the symmetry of $P\bar{1}$ – typically, several hundredths of an Ångstrom unit. Since the nominal e.s.d.'s in the atom coordinates are considerably smaller – typically ~0.01 Å – one might argue on statistical grounds that the structures cannot be centrosymmetric. However, this is exactly the point: the 'nominal e.s.d.'s' simply cannot be trusted, because of the problem of near-singularity. Further evidence that the original $P1$ descriptions were inappropriate lies in the molecular structures themselves: in all these 16 cases, chemically equivalent bond lengths (and angles) in the $P1$ description are severely discrepant, by amounts represented by the scatter shown in Table 2. Accordingly, although I have not performed the conclusive experiment of re-refining these 16 structures in $P\bar{1}$, there is little doubt that all these structures belong in $P\bar{1}$ and that such re-refinements would lead to far more reasonable molecular dimensions than originally reported.

However, one point must be strongly emphasized: *it simply cannot be determined, by diffraction methods alone, whether a particular structure is centrosymmetric or only approximately so.* The reason for this lies in the inherent singularity in the situation: the diffraction intensities are completely insensitive to any small distortion from centrosymmetry. As one collects more and better data for the very weak reflections, one can reduce the region of uncertainty – the amount of distortion that cannot be detected – to smaller and smaller values, but not to zero; the strong correlations between the various parameters describing these antisymmetric distortions will remain. What is one to do? It remains my strong conviction that the most reasonable procedure is to describe such a structure in the centrosymmetric space group if at all possible, for the centrosymmetric refinement will not suffer from near-singularities and should converge normally. If the resulting structure is unsatisfactory in some obvious way – that is, if the agreement between observed and calculated intensities is manifestly unsatisfactory, or if some atoms show such peculiar displacement parameters as to suggest that they might be split into ordered pairs – it may well be profitable to search for a noncentrosymmetric alternative. However, in so doing, one should be fully aware of the dangers involved in refining an almost centrosymmetric structure in a non-centrosymmetric space group. And, finally, I caution – as Baur & Tillmanns (1986) have already done – against relying on Hamilton's (1964) R-ratio test in an attempt to resolve the ambiguity: the additional parameters needed to create a noncentrosymmetric model may well be able to compensate for systematic errors in the data and hence reduce the residual, either weighted or unweighted, by an

Table 2. *Structures originally reported as triclinic, space group* $P1$, *that probably are correctly described in the centrosymmetric space group* $P\bar{1}$

The fractional coordinates x_c, y_c and z_c (with scatter e.s.d.'s in parentheses) are those of the average center of symmetry relating *n* pairs of corresponding atoms; r.m.s. is the root-mean-square deviation of the *n* individual centers from the average center, in Å. (This 'average' center defines the origin in space group $P\bar{1}$.) H atoms were omitted from the calculations. Included in the references are the 'Reference Codes' assigned by the Cambridge Structural Database System (Version of March 1994).

Formula	*n*	*Z*	x_c	y_c	z_c	r.m.s.	Ref.
$C_{23}H_{22}O$	24	2	0.0063 (23)	0.1155 (13)	0.5025 (21)	0.020	(*a*)
$C_{18}H_{42}O_6P_3S_6Ir$	33*	2	0.7599 (103)	0.5570 (93)	−0.2334 (53)	0.097	(*b*)
$C_{20}H_{12}O_6Fe$	27	2	0.0009 (59)	0.0001 (89)	−0.0008 (107)	0.092	(*c*)
$C_{17}H_{17}NO_6P_2S_3Mn_2$	31	2	0.5015 (78)	0.4996 (42)	0.5006 (30)	0.047	(*d*)
$C_{27}H_{26}NO_5Br$	34	2	0.8516 (52)	−0.1122 (32)	0.9170 (50)	0.051	(*e*)
$C_{18}H_{56}N_{15}P_3B_6$	42	2	0.6217 (71)	0.3207 (40)	0.5309 (47)	0.064	(*f*)
$C_{23}H_{19}NClPSPd$	28	2	−0.1985 (31)	−0.1163 (61)	−0.1426 (55)	0.053	(*g*)
$C_{15}H_{13}N_3O$	19	2	0.4306 (31)	0.4978 (24)	0.4871 (18)	0.022	(*h*)
$C_{28}H_{46}N_4O_6F_6Ni$	45	2	0.0017 (100)	0.0004 (70)	0.0025 (67)	0.104	(*i*)
$C_{38}H_{48}N_3O_2B$	44	2	0.4983 (35)	0.4995 (31)	0.4970 (42)	0.046	(*j*)
$C_{12}H_{14}N_4O_4S$	21	2	0.6980 (66)	0.7689 (47)	0.6247 (45)	0.048	(*k*)
$C_{10}H_{10}N_2O_3$	30	4	0.0603 (20)	0.5310 (30)	0.5185 (16)	0.022	(*l*)
$C_{10}H_{13}NO_3S_2$	16	2	0.0732 (78)	1.0606 (105)	−0.1345 (143)	0.096	(*m*)
$C_6H_6O_4Cl_4$	21	3	0.6980 (28)	0.6362 (43)	0.9657 (36)	0.035	(*n*)
$C_{12}H_{15}NO_6$	19	2	0.6947 (24)	0.2202 (35)	1.0396 (42)	0.030	(*o*)
$C_{20}H_{26}N_3O_5Cl$	28†	2	0.5004 (23)	−0.0001 (7)	0.0001 (13)	0.015	(*p*)

* In the original paper, the coordinates of C(23) are obviously incorrect; this atom has been omitted from the averaging.

† In the original ($P1$) description, two of the water molecules – O*w*5 and O*w*6 – are unrealistically close together, at 1.97 Å; their midpoint deviates by ~0.5 Å from those of the other atoms. These two atoms have been deleted.

(*a*) *BEFFEX*. (1-(*p*-Methoxyphenyl)-*trans*-1,2-diphenylbut-2-ene (Cutbush, Neidle, Foster & Leclercq, 1982). (*b*) *BUVMIO*. Tris(*O,O'*-diisopropyldithiophosphate-*S,S'*)iridium (Tkachev & Atovmyan, 1983). (*c*) *CBZEFE*. Tetracarbonyl(*trans*-α, β-dibenzoylethylene)iron (Andrianov, Struchkov, Rybinskaya, Rybin & Gubenko, 1972). (*d*) *CEVJES*. 1,1,1,6,6,6,-Hexacarbonyl-5,5,8,8-tetramethyl-2-phenyl-4,7λ^3,9λ^3-trithia-2λ^4-aza-5λ^4,8λ^5-diphospha-1,6-dimanganatricyclo[4.2.1.$0^{3,9}$]nona-2,7-diene (Lindner, Krieg, Hiller & Hübner, 1984). (*e*) *FAGHIE*. (*Z*)-*N*-*p*-Bromobenzoyl-6,7-dimethoxy-1-(3,4-dimethoxyphenylmethylene)-1,2,3,4-tetrahydroisoquinoline (Noyori, Ohta, Hsiao, Kitamura, Ohta & Takaya, 1986). (*f*) *JANDAD*. *gem*-Bis(pentamethylborazinylamino)tetrakis(dimethylamino)cyclotriphosphazene (Welker, Manners, Parvez & Allcock, 1989). (*g*) *JUHWIS*. Chloro(pyridine-2-thiolato)(triphenylphosphino)palladium(II) (Nakatsu, Nakamura, Matsumoto & Ooi, 1992). (*h*) *JUXLIX*. 4'-Cyano-2,6-dimethyl-4-hydroxyazobenzene (Sarma, Dhurjati, Bhanuprakash & Ravikumaro, 1993). (*i*) *LEDTUJ*. Bis(2,2,5,5-tetramethyl-1-oxy-3-(3,3,3-trifluoro-2-oxy-1-propenyl)-3-imidazoline)bis(*N*-butanol)nickel (Romanenko & Podberezskaya, 1993). (*j*) *SARZUG*. 2-Ethylammonio-*N*-(pivaloyl-D,L-prolyl)ethylamine tetraphenylborate (El Masdouri, Aubry, Sakarellos, Gomez, Cung & Marraud, 1988). (*k*) *SFDMOX*02. Sulfadimethoxine (Narula, Haridas & Singh, 1987). [Note: the revised $P\bar{1}$ structure is essentially identical, after choosing a different set of cell axes and a different origin, with the structure reported earlier by Patel, Tiwari, Patel & Singh (1983) – *SFDMOX*01 – and, even earlier, by Koo, Kim, Yoon & Suh (1975) – SFDMOX]. (*l*) *SIDXUY*. Ethyl 2-methyl-5-cyano-1,6-dihydro-6-oxo-3-pyridinecarboxylate (Mosti, Menozzi, Schenone, Dorigo, Gaion, Benetollo & Bombieri, 1989). (*m*) *SILHAW*. 3-Carbomethoxy-5-(2,2-dimethylpropylidene)rhodanine (Ohishi, Mukai, Nagahara, Yajima, Kajikawa, Miyahara & Takano, 1990). (*n*) *SILRIO*. *trans,trans-meso*-4,4',5,5'-Tetrachloro-2,2'-bi-1,3-dioxolane (Huang, Ogata, Sakai & Sim, 1990). (*o*) *SOXWOR*. Benzoyl-L,D-glutamic acid monohydrate (Zhukhlistova, Smirnova, Nekrasov & Tishchenko, 1991). (*p*) *VELZER*. 9,10-Dimethoxyphenylpyrimido(6,1a)isoquinoline-2-iminium chloride trihydrate (Korbonits, Horvath, Kiss, Simon & Kolonits, 1990).

unrealistic amount. The bottom line, I believe, is the following: if a centrosymmetric description – even one that involves disorder – provides adequate agreement between observed and calculated intensities, there is no profit in searching further. (The experimentalist – and not a computer – should decide on what is 'adequate'.) If small deviations from centrosymmetry are present, they must be detected by other means.

Discussion

Of the four components in a space-group assignment that I have discussed here, the two that are the most frequent sources of error are the assignment of the correct Laue group and the decision as to whether or not a center of symmetry is present; I believe that the frequency of errors is approximately the same for these two components. However, the consequences are far different, particularly when the major interest is in the molecular structure. (I use the term 'molecular structure' only as a convenience, with no intent to exclude nonmolecular compounds. However, I also note that the frequency of space-group errors in nonmolecular crystals, such as minerals and inorganic compounds, appears to be lower than for the purely molecular species – perhaps because the crystals tend to be harder and the structures better defined, but perhaps, also, because workers in such fields are often more concerned about properties of the crystals other than mere atomic connectivity, and hence are apt to be a bit more painstaking in their efforts.). The assignment of an incorrect Laue group, whether it be an incorrect lattice type or an incorrect assignment of symmetry within a lattice type, should lead to no important changes in the positions of the atoms; refinement should proceed normally, with no more than a small increase in the coordinate e.s.d.'s due to the increased number of parameters (Schomaker & Marsh, 1979). On the other hand, failure to notice a center of symmetry may have far more serious consequences: not only will the atom positions be unreliable, but the very identities of the atoms may be confused, leading to an incorrect identification of the compound (*e.g.* Marsh, 1986, 1990).

The other two categories of space-group problems – failure to identify the correct space lattice or the systematic absences – appear to be less common; on the other hand, it is difficult to detect such errors without repeating the entire experiment. How many examples are there where the reported structure is only a superstructure, in which additional weak reflections – if they had been identified – would have indicated the systematic and significant perturbations? And how many clathrate structures, in which the arrangement of enclathrated species is incommensurate with that of the host structure, have gone undetected? The failure to correctly identify the systematic absences is usually associated with other errors in the reported structure, most commonly by a centrosymmetric structure being reported as noncentrosymmetric: the observation of a few apparent violations to the glide-plane extinctions characteristic of the centrosymmetric space group $P2_1/c$ lead well to the assignment of the noncentrosymmetric $P2_1$, with large distortions in the resulting structure (Marsh, 1994*a*). However, it is difficult to presume, without careful examination of intensity data, that the assignment of extinctions is incorrect; most such examples will surely go undetected.

What can be done to minimize the chance of error? Baur & Tillmanns (1986) recommend nine procedures; my recommendations (which also total nine) are, for the most part, similar.

(1) Hold onto, and use, that old photographic equipment (or that new image-plate system). Initial diffraction photographs, besides allowing rapid identification of twinned, decomposed or otherwise unsatisfactory specimens, will surely reduce the incidence of overlooked superlattices and disorder streaking, misidentified systematic absences, and incorrect Laue symmetry. A side benefit is that when that synthetic chemist comes around to ask why you have been unable to solve the structure, it is far more convincing to produce a photograph with obviously unsuitable reflections than merely some printed output suggesting that a satisfactory cell cannot be found.

(2) Do not depend upon a computer to tell you the correct lattice symmetry, particularly if the only data available to it are the setting angles of a few reflections. (It is not the computer that is blamed when the structure turns out to be incorrect.) I think it is far wiser to collect a complete sphere of intensity data, perhaps at an increased scanning rate, and to assess the Laue symmetry in the appropriate manner – by establishing the intensity symmetry of these data.

(3) Examine carefully for systematic absences. I believe that, in most data-processing routines, there are provisions for tabulating the average intensities for various categories of reflections. If one of these categories shows weak but, perhaps, nonzero intensities, it is usually a simple matter to examine the questionable reflections at various orientation angles; if the intensities disappear at some settings, the Renninger effect is undoubtedly at work. However, of course, this survey must be done at an early stage – before the crystal is removed from the instrument.

(4) Measure and retain the intensities of *all* reflections, not only the strong ones. This can be absolutely crucial: if the weak reflections are not available, not only will the intensity statistics be biased but, in addition, the chances of making an intelligent decision between a centrosymmetric and a noncentrosymmetric space group will be sharply diminished (Marsh, 1981).

(5) In carrying out least-squares refinements, I urge that the quantity minimized be based on the F^2 values rather than on F. This will allow all reflections – not only those with positive net intensities – to be retained, with correct weights, which is particularly important not only when there is a possible ambiguity between centrosymmetry and noncentrosymmetry, but also in those cases where the decision about systematic absences is borderline.

(6) Carry out full-matrix refinements if at all possible and examine the resulting correlation coefficients with care. Large coefficients are usually a cause for worry; they should always be of interest.

(7) If block matrix is necessary, do not be satisfied with less than full convergence (surely the maximum value of shift/sigma should be less than 0.1). If convergence is slow, perhaps the parameters in the various blocks should be interchanged, so that other covariance terms can have their influence. Also, avoid the temptation to place similar atom groupings, such as entire molecules, into separate matrixes; they will usually show the largest correlations.

(8) Do not forget about anomalous dispersion and the effect that an incorrect choice of handedness may have on the resulting structure – particularly in a polar space group (Cruickshank & McDonald, 1967). This is another reason for collecting an entire sphere of intensity data: if anomalous dispersion by any of the constituent atoms is appreciable, suitable merging of the data may well indicate the most appropriate point group at a very early stage, distinguishing, for example, between 222, *mm*2 and *mmm*.

(9) Finally, when the structure appears to be complete, examine it carefully. Use of symmetry-checking programs such as *MISSYM* (Le Page, 1988) can be of great help, but other checks are advisable. Are any of the unit-cell angles greater than 120° or less than 60°? – if so, shorter and more nearly orthogonal axes can be found, perhaps leading to a different Laue symmetry. Is there anything unusual about the coordinates – values such as 0.2500 or similarities between atoms in different asymmetric units – which might indicate higher symmetry? (This is the way that the entries in Table 2 were

found.) Are there any unusual U_{ij}'s? Such considerations, being mostly subjective, can be made far more reliably by a person than by a computer.

Concluding remarks

There is little that is new in this paper, other than a couple of moderately extensive lists of structures that have, almost surely, been erroneously described. These lists are far from exhaustive, since the only effort I made to uncover the various examples was a quick, visual survey of the cell dimensions and of a few coordinates of those entries in the Cambridge Structural Database which showed more than one formula unit per asymmetric unit, space group $P1$ or $P\bar{1}$. Thus, the survey effectively excluded all those examples with only one molecule per asymmetric unit, but with *molecular* symmetry that might have been compatible with a higher-symmetry space group – surely a very large category. Also, of course, it excludes all examples in which the basic lattice was incorrectly determined, perhaps due to a superstructure. The 49 examples in Tables 1 and 2 comprise $\sim 1\%$ of the entries surveyed and I have little reason to doubt the estimate of Baur & Tillmanns (1986) that 'about 3% of all recently published crystal structures were described with too low symmetry'. If anything, I suspect that their estimate is conservative. A few journals – *Acta Crystallographica* is a more notable example – are now making increased efforts to assure that crystal structures are carefully checked before being accepted for publication; at the same time, however, many other journals are relaxing their standards in many ways, including relegating crystallographic results to footnotes or even to supplementary material, selecting referees with little or no experience in crystallography and making it quite clear to their readers that, basically, any crystallographic details beyond a drawing of the molecule are unnecessary and boring. In such journals I have absolutely no doubt that the percentage of incorrect results is appreciably larger than 3%.

In closing, let me return to my opening thought – that small-molecule single-crystal diffraction experiments are, almost invariably, well over-determined and the results should be unassailable; a 3% frequency of errors seems unacceptable. These errors cannot – *must not* – be blamed on computer programs. Nor should they be blamed on the pressures of time. Almost invariably the synthesis of the compound and the preparation of the crystals require far more time (and, probably, far more effort) than the entire structure determination. [I cannot avoid wondering how much time was spent just in assigning a name to the molecule in *CEVJES* (Lindner, Krieg, Hiller & Hübner, 1984).] Spending a bit more time to critically assess the results, and asking a diffractometer to spend a bit more time to collect a definitive set of intensity data, seem entirely reasonable procedures if the result is a minimization of the chance of error. We should not be deluded, by those who want immediate results, into believing that incorrect symmetry or incorrect bond lengths are of no importance so long as the atomic connectivity is correct. If crystal-structure results are to be published in the open literature or deposited in open facilities such as the Cambridge Structural Database, investigators should take adequate pains to ensure that these results are correct. Any other course is indefensible.

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