

***P1* or $P\bar{1}$? Or something else?**

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The October 1998 release of the Cambridge Structural Database (1992) contains structural details (unit-cell dimensions and atom coordinates) for nearly 1300 distinct entries under space group *P1* (No. 1); for 279 of these entries, the space-group designation is incorrect. The most common type of error, occurring for 157 entries with $Z > 1$, seems to have resulted from a simple misprint – the omission of the ‘overline’ in the symbol $P\bar{1}$ as it appears in the original publication; in these cases the reported coordinates, when applied to space group $P\bar{1}$ rather than *P1*, lead to reasonable intermolecular distances and to apparently reliable structures. In the remaining 123 cases the space group is incorrect for more fundamental reasons and the atom coordinates should be revised. In approximately one-third of the structures in which chiral molecules crystallize in *P1* with $Z = 2$, the two molecules are related by an approximate center of inversion. In some cases this pseudocenter is surprisingly exact, with r.m.s. deviations from centrosymmetry as small as 0.1 Å, and may result in the same sort of refinement difficulties that inevitably arise when truly centrosymmetric structures are mistakenly refined in space group *P1*. It appears as though, for typical molecular compounds, standard crystal-structure techniques may be unable to distinguish between *P1* and $P\bar{1}$ if the r.m.s. deviation from centrosymmetry is less than ~ 0.1 Å.

1. Comment

I have carried out a survey of a recent (October, 1998) release of the Cambridge Structural Database (1992; CSD), examining all structures reported for space group No. 1 (*P1*, usually, but a few structures are based on centered lattices). After rejecting duplicate reports and a number of obviously unsatisfactory ones, I find a total of approximately 1280 presumably reliable entries. Closer examination indicates that 279 of these structures should be described in space groups other than *P1*. Most of the errors occur for structures having $Z > 1$, where the space group is reported incorrectly over one-third of the time.

The most common cause of the space group being incorrectly reported as *P1* is, apparently, nothing more than a simple misprint – a missing ‘overline’ in the

symbol for the correct space group, $P\bar{1}$; the misprint usually occurs in the original paper, but may also have been introduced in the supplementary material supplied to the CSD. A disproportionate number of these apparent misprints have occurred in the more recent entries – when electronic word processors have become prevalent – and it seems apparent that many investigators have found it difficult or inconvenient to create the appropriate symbol ‘ $P\bar{1}$ ’ when producing the final manuscript. In many of these cases there are clear signals, in the original journal publications, that the correct space is $P\bar{1}$: words such as ‘the centrosymmetric space group *P1*’, or ‘space group *P1* (No. 2)’, or, perhaps, tables of intermolecular distances that involve a center of inversion. In quite a few cases the original journal article clearly specifies the space group as ‘ $P\bar{1}$ ’; in these cases, I suspect that the ‘overline’ was omitted when supplementary material was submitted to the CSD. All of these ‘misprint’ errors (Table 1) occur for structures listed in the CSD as having $Z > 1$.

In 123 entries the reported space group (*P1*) is in error for other reasons; the authors (or, perhaps, their computers) were incorrect in the choice of space group. In 45 of these cases the errors have previously been reported. (In such cases the CSD typically notes the corrected space group and includes a reference to the journal article describing the revised structure, but often does not include the revised coordinates, so that the only structural material available in the CSD remains incorrect.) As far as I am aware, the other 78 errors (Table 2)† have not previously been noted.

The revised space groups cover a wide range. Not surprisingly, the most common is $P\bar{1}$; in 76 cases the original authors failed to realise that the structure contains a center of inversion. In essentially all of these cases the *P1* coordinates lead to some very peculiar bond lengths and angles, owing to the well known problem of effective singularity when a centrosymmetric structure is described in a non-centrosymmetric space group. Typically, the scatter among chemically equivalent bond lengths may be of the order 0.2–0.3 Å in the face of reported s.u.’s of 0.01 Å or so; occasionally the discrepancies are much larger. In these cases, symme-

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK0068). Services for accessing these data are described at the back of the journal.

trizing the coordinates across the center of inversion in $P\bar{1}$ invariably leads to far more reasonable molecular geometry. (The severe covariance terms in the $P1$ refinement must lead to large uncertainties in the differences between related bond lengths, but not in their average values; see, for example, Marsh *et al.*, 1998). Only very occasionally did the original authors point out that some of the bond lengths were unsatisfactory or questionable.

The second most frequent space-group revision is to $C2$ (23 cases). In such cases, when the Laue group is changed but no center of inversion is added, refinement difficulties and large covariance terms are not to be feared (Schomaker & Marsh, 1979); the symmetrized bond lengths in these structures differ little from the individual values obtained from the $P1$ coordinates. Other revised space groups are: Cc (seven examples), $C2/c$ (six), $Fdd2$ (two), $R3$ (two), $P3_121$ (two), $P2_1/c$, $C2/m$, $P2_12_12_1$, $Cmc2_1$ and $R3$ (one each). Approximately 4% of the structures with $Z = 1$ and 13% (plus the 'misprint' cases) of those with $Z > 1$ should be revised. Two entries, 'KOKNUT' and 'YORTII', warrant special notice; I shall discuss them later.

Of the 483 valid examples of space group $P1$ with $Z > 1$, approximately 90% are chiral compounds. (I was occasionally unable to tell whether the compound was formally chiral, perhaps by synthesis, or whether chirality was induced during crystallization.) As I examined these structures, I soon noted a tendency for pairs of these chiral molecules to be related by an approximate center of inversion. Accordingly, I surveyed them more systematically, searching for approximate centers; in perhaps one-third of the entries I could find such a center. In some cases it was surprisingly exact; for the compound aqua(1,10-phenanthroline-L-serinato)-copper(II) nitrate (ZAMBEU; Moreno-Esparza *et al.*, 1995) the r.m.s. deviation of the centers of all pairs of equivalent atoms from their global center is less than 0.07 Å. (The chiral α -C atoms of the serinate ligands, of course, show a larger deviation.) In the case of JAPMES ($C_{26}H_{23}BrO_7$; Giordano & Lanzetta, 1989) the authors noted an approximate center of inversion which led to large correlation coefficients and unsatisfactory refinement; in the final refinements they imposed an exact center between all pairs of atoms except for the chiral atom and its five neighbors. The final r.m.s. deviation from centrosymmetry is ~ 0.08 Å.

A common theme in the nearly centrosymmetric pairing of chiral molecules is that the external portions of the molecules find a means of achieving centrosymmetric packing and the interior portions, typically including the chiral atoms, adjust as they see fit. Another method of attaining approximate centrosymmetry, particularly for amino acids, is for an N atom and an O atom to interchange places in an otherwise centrosymmetric coordination or hydrogen-bonding arrangement. In chirally substituted ring systems, different modes of

Table 1. CSD entries listed under space group $P1$ ($Z = 2$) rather than $P\bar{1}$, apparently because of misprints

The atomic coordinates supplied for these compounds, when applied to space group $P\bar{1}$, lead to reasonable structures (see text).

Refcode	Refcode	Refcode
DUJCOA	LEXPIN	TAXPAJ
DUTHUV†	NAJWEA	TEBBEH†
DUWDAA	NANMOE	TENCAQ
EABPOM†	NAZBEV	TEPJIH
EABPUS†	NETXIT	TEXHUZ†
FABRIJ01†	NIBDIL	TIVPAP
FAFGIC	NIDVOL	TOFYOC‡
FASCIL	NIJHOD	VAWZIC†
FECNAC	NIZR0D	VAXHEH
FEPCAE†	NOFBEP	VEHSUW†
FEVNI0	PAJBUX	VELYOA
FEXDAN	PAJMES§	VICKAT
FIBKIK†	PAJMOC	VICVEI
FIBKOO†	PAKSOJ	VOLFAV†
FOLSOO	PALDOV01	VOMLIS†
FUYFEK	PEJGAM	VONSAS
HARLOB	PEZHAD	VONSIA
HEWVEL	PIZXEB	VOVKAS
JAPXU01†	POLTUF†	VOZGAS
JATMEW†	RARYEO†	VULNOF†
JAXJUN	RAWSIR	VUPMEY
JEDXIZ†	REFLAP†	VUSTAE
JISSOT	REJBIR†	WAFCOV†
JOGJOE	RERBOF	WAFDAI
JOPSEM	REWMEL	WALRIK
JOYFUY	RILCIY	WEMCOG
JUFWEM10	RILCUK	YAFHOC†
JUGMON	ROCHEA†	YAGLEX
KARYEH10	RODLEB	YAGRUT†
KAYWOW†	ROKHOO	YAGZOV†
KECPOX	ROPCAA	YIGMUW
KEDXOG	RUFHEF	ZACCEL
KEFTIY†	RUPYIK	ZAVPIV
KEHBII	RUQJIW	ZEQHAE
KESXAH	RUQQUP	ZIDKEC†
KEYKOO	SEFGUF	ZIRTAV†
KEZSUD	SETLOS†	ZIXDAL
KIHVIG	SIHMAX	ZIZTEH
KIJDAI	SILNUW	ZONGUE†
KJUREA	SIMRUB	ZOPXOR
KIKYAE†	SIRLAG	ZORCUE
KIKZOT†	SOHJII†	ZOWBUI†
KOGFAN†	SUGLEL	ZOXLAZ†
KOTXIA†	SUGSIW	ZOYQEQ
KUMZIB†	SUJYUR	ZOYQIN†
KUPZOK	SUMBOR	ZUBJEL
KURZUS†	TACNAM†	ZUBJIP
KUXNAS	TADSEW	ZUBJOV†
LADSUE	TAFCUY†	ZUCGAF†
LAPCIO	TAKJUK	ZUKSED†
LECLUA	TAXHIJ†	ZUSRIO
LEVMEE	TAWMAF	ZUXXAR

† Dr David Watson has informed me that these 48 entries have been revised in the April 1999 release of the CSD as a result of correspondence with me in late January 1999, and that the remaining entries in the list will be revised in the October 1999 release. ‡ Reported in space group $F1$; should be $F\bar{1}$. § The correct value of Z is 1.

ring puckering can lead to approximately centrosymmetric pairing. However, I have not examined in any detail the various techniques that pairs of chiral mole-

Table 2. CSD entries, not previously noted, that are listed incorrectly under space group $P1$ for reasons other than misprints

In these cases the atomic coordinates should be revised

Refcode	Space group	Z
BUTHPN	$C2$	4
CIKDOP	$P\bar{1}$	2
DARNUF	$C2$	2
DISRAY	$P\bar{1}$	1
DUPFEZ10	$P\bar{1}$	2
ENCOMA10	$C2$	2
FEWCIT	$P\bar{1}$	2
FUJFOF10	$P\bar{1}$	2
FUMROU	$P\bar{1}$	1
FURGAA01†	$P\bar{1}$	2
GALYOH‡	$P\bar{1}$	2
GAZYAH	$C2$	4
GIPTAA	$P\bar{1}$	2
HICMUB	$P\bar{1}$	2
HPHGER	$P\bar{1}$	1
JELFIP	$P\bar{1}$	1
JIFYAY	$C2$	4
JIYKAD	$P2_12_12$	2
JOHRAZ	$P\bar{1}$	2
JORMIM	$C2$	4
KECRIT	$P\bar{1}$	8
KERVEI	$C2$	4
KOPKOP	$C2$	4
KUCTEH	$P\bar{1}$	2
LACFIE	$P2_1/c$	2
LEMZAE	$P\bar{1}$	1
LIKXOS	Cc	4
LIKXUY	Cc	4
MBDARP	$C2$	4
NICBOQ	$C2$	4
NIXQAM	$C2$	4
NOQBUQ	$Cmc2_1$	4
PABYIA	Cc	4
PACDAY	$P\bar{1}$	2
PADWOG	$C2$	4
PBBTAZ01	$P\bar{1}$	2
POPKUA	$P\bar{1}$	2
RAFWAW	$C2$	4
RIGSEF	$P\bar{1}$	2
RIQHAA	$P\bar{1}$	2
RISZIC	$P\bar{1}$	2
ROBCEQ	Cc	4
SEWZAV	$P\bar{1}$	2
SIHLOK	$P\bar{1}$	2
SIJDUK	$P\bar{1}$	1
SILREK	$C2/c$	4
SMOCUC10	$P\bar{1}$	2
SOHROW	$C2$	4
SUKJOX	$C2$	4
TEBLUH	$P\bar{1}$	2
TEFDUD	$P\bar{1}$	2
TEVZAV	$C2$	4
TIYVIG	$P\bar{1}$	2
TIZWAA01	$C2/c$	4
TOJTER	$P\bar{1}$	2
TOJTIV	$P\bar{1}$	2
TOQJAK	Cc	4
VEBPIB	$P3_12_1$	3
VEBPOH	$P3_12_1$	3
VEMSAH	$C2$	4
WENGAX	$Fdd2$	8
WEPWUJ	$P\bar{1}$	2

Table 2 (cont.)

Refcode	Space group	Z
WIMG0010	$P\bar{1}$	1
YADJAO	$P\bar{1}$	2
YAHYIP	Cc	4
YEPBAW	$P\bar{1}$	2
YIBBOA	$P\bar{1}$	2
YIWSAY	$P\bar{1}$	4
YOPSOL	$P\bar{1}$	2
YOWBIV	$P\bar{1}$	2
YOYPUX	$P\bar{1}$	1
YUCHAF	$P\bar{1}$	1
ZADCAI	$P\bar{1}$	1
ZASTES§	$P\bar{1}$	1
ZEDCAM	$C2$	4
ZIYPUS	$P\bar{1}$	1
ZOWFAS	$P\bar{1}$	2
ZUBDAB	$C2$	4

† FURGAA01 and FURGAA02 are separate entries in the CSD, both listed as space group $P1$, $Z = 4$, but with different cell dimensions; they are reported as two separate modifications of 9-ethyl-8-hydroxyguanine monohydrate (Doi *et al.*, 1991). Both sets of coordinates represent lattice-centered structures which can be reduced to the same primitive lattice and to the same structure in space group $P\bar{1}$, $Z = 2$. The entry FURGAA contains the correct unit cell and space group, but no coordinates. ‡ Originally reported in space group $I1$, $Z = 4$. § Reported in the CSD as space group $P1$, $Z = 2$. In the original paper (Sokol *et al.*, 1995) the space group is reported as $P\bar{1}$, $Z = 2$; coordinates are given for an entire, approximately centrosymmetric molecule. The cell is too small to contain more than one molecule.

cules may resort to in attempting to achieve centrosymmetric packing arrangements. Nor do I have much of an idea as to how ‘approximate centrosymmetry’ might be defined. In general, I have applied it to arrangements in which the r.m.s. value of the deviations of the individual centers between pairs of related atoms from the global center is less than about 0.5 Å; but there remains the bothersome question as to whether or not a pair of ‘related atoms’ need be chemically identical as they obviously are not when N must be paired with O, and in several other examples as well. Nevertheless, the general tendency seems clear: crystal structures prefer to be centrosymmetric (Brock & Dunitz, 1994), even when they cannot be exactly so.

2. Experimental

My survey was a personal inspection of the cell coordinates and cell dimensions of all CSD entries designated as space group No. 1. (Computer programs are available to carry out such inspections much more quickly and conveniently; however, I fear that they may fail to pick up some special cases, such as those where different pairs of chemical entities are related by different symmetry elements, or the structure is polymeric or the coordinates of some disordered atoms are omitted.) With few exceptions I ignored H atoms, since in most cases they were either placed in calculated positions or, if allowed to shift, ended up in untenable

sites. In almost all cases of a previously unnoted space group error I inspected the original publication in an attempt to learn the reason for the error; I was seldom successful.

In those 156 cases where the report of space group $P1$ was the apparent result of a misprint (for $P\bar{1}$), the first sign of trouble was that the number of atoms for which coordinates were available was less than that expected from the value for Z (or from the unit-cell volume). Sometimes the original paper provided a clue that the correct space group was $P\bar{1}$; often there was no such clue. In all cases I calculated interatomic distances, out to 3.2 Å, based on the coordinates in the CSD, but presuming the space group to be $P\bar{1}$ rather than $P1$; in no case were there any unusual contacts (as would surely have been the case if the space group were actually $P1$ and the authors had provided coordinates for only one formula unit).

The search for an approximate center of inversion in structures of chiral compounds was based, primarily, on a program written by V. Schomaker (Marsh *et al.*, 1998), slightly modified for space group $P1$ rather than $Pna2_1$ or $Pca2_1$. In this program the moment centers of the two independent molecules are calculated and moved to a common origin; attempts are then made to match, across this origin, each atom of one molecule with an atom of the second molecule within some specified tolerance, such as 0.5 Å; if desired, a specific pairing of atoms can be designated. For structures containing disordered atoms, counter ions, water molecules or other solvents, individual attention was often needed. This program was also of help in searching for centers of symmetry in achiral cases where a preliminary inspection of coordinates suggested that the space group might be incorrect. However, in most of these latter cases, particularly when the corrected space group was other than $P\bar{1}$, the averaging in the higher-symmetry space group was performed with simple Fortran programs.

2.1. KOKNUT

This compound, with empirical formula $(Cr_4S_4Cp_4) \cdot [(Cr_3VS_4Cp_3(MeCp)]$ (Cp = cyclopentadienyl), is reported in space group $P1$ with $Z = 1$. In this description the unit cell contains two distinct metal complexes, each consisting of a tetrahedral cluster of metal atoms with an S atom bonded to each tetrahedral face and a cyclopentadienyl group attached axially to each of the four metal atoms. One cluster contains four Cr atoms, while the other contains one V and three Cr atoms; the Cp ring attached to the V atom is methylated at one position. However, the coordinates derived for this structure are unsatisfactory. The most serious problems involve the Cp rings, for which the C—C bond lengths range from 0.96 to 1.98 Å with one severe outlier at 2.49 Å. (While it is possible that this latter value results from a misprinted coordinate, it is not clear which

atom is at fault: the entire ring is severely distorted.) In the methylated Cp ring the methyl group is displaced by $\sim 30^\circ$ from its expected direction. The Cr—S distances, while not so dramatically disparate, cover a range from 2.10 to 2.38 Å. Clearly, something is quite wrong. Indeed, the authors (Pasynskii *et al.*, 1988) note that ‘the inadequate quality of the single crystals ...precluded a highly accurate determination of the geometrical parameters’ (the final R was 0.075.)

The triclinic cell can be transposed to a C-centered cell with dimensions $a = 17.639$, $b = 8.074$, $c = 16.707$ Å, $\alpha = 90.63$, $\beta = 117.55$, $\gamma = 89.71^\circ$. Here, the values of α and γ differ from 90° by amounts that would appear to be prohibitive: the s.u.’s given by Pasynskii *et al.* (1988) are ~ 0.001 Å in the cell lengths and 0.009° in the angles. However, such ‘standard uncertainties’ are measurements of precision rather than of accuracy and it is well known that the actual errors may be far larger (Taylor & Kennard, 1986; Marsh, 1995). The atomic coordinates, when transformed to the C-centered description, can be averaged (in sets of four) according to space group $C2/c$ within an r.m.s. deviation (from the additional symmetry elements) of 0.10 Å. This $C2/c$ -averaged structure is far more reasonable than the original one, with effectively identical Cr—S bond lengths of 2.258 (9) Å and a narrower range of C—C bond lengths in the Cp rings, 1.34–1.68 Å. (The latter distance includes, in the averaging, the pair of atoms separated by 2.49 Å in the $P1$ description.)

If the proper space group is $C2/c$ and the empirical formula is correct, the V atom and the associated Me-Cp ring must be disordered. In any event, it is clear that a definitive description of the structure is not available. I have not included it in Table 2.

2.2. YORTII

This is an even more puzzling structure. The compound, $C_{16}H_{19}N_3O_3 \cdot H_2O$, comprises a 4-methylcyclohexanedione(2,6) ring linked to an *N*-methylpyridine ring by a $-\text{CH}=\text{N}-\text{NH}-\text{C}(\text{O})-$ grouping; it is described as a monomer with two molecules (plus two water molecules) per cell. However, the coordinates (Strakov *et al.*, 1993) lead to a distance of 1.56 Å between an O atom of the cyclohexanedione group in one molecule and a methyl C atom of the cyclohexanedione group in a neighboring molecule, suggesting that the compound may have polymerized. (The original authors make no mention of this short distance nor of any polymerization.) However, this atomic arrangement is so unusual as to be, almost certainly, incorrect: the C(ring)—C(methyl)—O ‘bond’ angle is approximately linear, 174° , whereas the angle at the O atom is approximately tetrahedral and the C(ring) atom has four tetrahedrally arranged neighbors. I cannot imagine what sort of bonding might lead to such a grouping of atoms. In addition, one of the two water molecules of

crystallization seems to be in a peculiar position, its closest neighbors being two C atoms (at 2.82 Å) rather than some of the potential hydrogen-bonding groups.

What might be going on? The final R reported by Strakov *et al.* (1993) was high, 0.149; moreover, equivalent bond lengths in the two molecules are highly disparate, by as much as 0.64 Å. Except for four pairs of atoms, there is an approximate center of inversion relating the two molecules; the four exceptions are the water molecules of crystallization and the $C(CH_3)_2$ groupings in the cyclohexanedione rings, which include the C(ring) and C(methyl) atoms noted above. When the coordinates of the remaining atoms (those related by the approximate center) are averaged across that center, the resulting bond lengths are much more reasonable. Perhaps, then, I may be allowed to conjecture that the entire structure is centrosymmetric, space group $P\bar{1}$, and that the peculiar positions derived for the dimethyl grouping and the water molecule resulted from difficulties associated with refining the structure in the non-centrosymmetric $P1$. In any event I believe that the entries for YORTII, as well as for KOKNUT, should be noted as unreliable.

3. Final comments

There is one important point that must be considered: when (and how) can one be certain that a structure should be described as exactly centrosymmetric (space group $P\bar{1}$) rather than only approximately so ($P1$)? I believe that the correct answer, in the absence of conclusive non-crystallographic evidence, is 'never' (and 'in no way'). Incremental distortions from centrosymmetry are without influence on the diffraction intensities. Small but finite distortions affect principally the very weak reflections, which are typically measured relatively inaccurately (because of background effects) and are often omitted. Moreover, if the distortions are small the correlation coefficients between the parameters of related atoms are large, so that convergence is difficult or impossible to achieve and uncertainties in the correlated values are meaningless. (As noted earlier, bond-length and bond-angle differences between related entities become more uncertain than their sums or average values.)

There is also the question as to whether one would expect the energy minimum in a molecular crystal to favor a truly centrosymmetric arrangement or a slightly non-centrosymmetric one – whether the intermolecular potential function would have a single or a double minimum. To calculate (with confidence) such a function for anything but a very simple crystal is a daunting task that must await future generations. There are many examples of superstructures, often forming at low temperature, where small, systematic shifts from a symmetric arrangement are clearly evidenced by weak superlattice reflections or by small violations of space-

group absences; in most such cases, I believe, the anti-symmetric shifts are 0.5 Å or more for at least some atoms. If the separation between energy minima were appreciably smaller than that, perhaps of the order 0.1–0.2 Å, one might well expect a disordered (either static or dynamic) structure; except at low temperatures, such disorder might be adequately modeled with anisotropic displacement parameters and would probably go unnoticed.

An interesting example of this $P1$ – $P\bar{1}$ ambiguity is provided by FUYCOR, a crown ether (15-crown-5) complex with $Mg(SCN)_2$ (Wei *et al.*, 1988); it is not included in Table 2. Here, the two molecules in the triclinic cell are paired across a common center of symmetry within an r.m.s. deviation of ~ 0.08 Å. However, two pairs of C atoms have mismatches (across the common center) of ~ 0.3 Å and electron density maps in $P\bar{1}$ showed these atoms to occupy two sets of half-populated positions. The choice was then between an ordered structure in $P1$ or a disordered structure in $P\bar{1}$. The authors opted for the former, since an electron density map phased from the ordered $P1$ structure showed only one position for each of these C atoms. (From my experience, this is a false argument. When deviations from centrosymmetry are small, Fourier maps reflect very faithfully the antisymmetric component of the assumed structure and cannot be used as reliable indicators as to whether the antisymmetry is real or only a result of the assumption.) Final refinement in $P1$ was rather unsatisfactory: convergence was not reached [$(\Delta/\sigma)_{\max} = 1.06$], B 's for related atoms were disparate and R was large at 0.093. In this case a definitive choice between $P1$ and $P\bar{1}$ probably cannot be made. Also, perhaps the choice is unimportant, so long as only the average structure of the molecule is wanted and differences between the two molecules (which reach 0.13 Å) are ignored. However, refinement in $P\bar{1}$ might have been preferable, with fewer parameters and normal convergence.

Another interesting example is TAMLAU, $[C_9H_{18}N_3][NbClO_4(H_2O)]$ (Schäfer *et al.*, 1991). Here, an approximate center relates pairs of equivalent atoms within r.m.s. deviations of less than 0.1 Å for all three coordinates; the maximum deviation for any pair of atoms is ~ 0.3 Å. Yet, satisfactory convergence was reached in space group $P1$ and all the heavy-atom parameters, including anisotropic U^{ij} 's, were reasonable (except for the coordinates of some of the H atoms). Corresponding bond lengths involving related atoms are in agreement almost within the reported uncertainties, indicating that correlations were not serious. I have attempted refinement in space group $P\bar{1}$, based on the original F_{obs} values, with unsatisfactory results: R remained high (0.125; the original authors report a value of 0.034 for their $P1$ refinement), U^{ij} ellipsoids were large and anisotropic, and difference maps clearly suggested that several atoms should be split into two

separate sites. $P1$ is clearly the appropriate choice. In this case the authors collected and retained the entire sphere of intensity data, including the weaker reflections – a procedure that increases the chances of distinguishing between $P1$ and $P\bar{1}$.

In all the examples listed in Table 2 there are two features that have convinced me that the centrosymmetric $P\bar{1}$ description is to be preferred.

(i) The original $P1$ descriptions lead to some unacceptable bond lengths, which are invariably improved when the coordinates are symmetrized.

(ii) The deviations from centrosymmetry are relatively small; almost invariably the r.m.s. deviations of the two-atom centers from the global center are less than 0.1 Å.

In some chiral systems, as noted earlier, r.m.s. deviations are as small as 0.1 Å and only occasionally do the authors note refinement difficulties. Therefore, it appears that, for normal X-ray diffraction data, the borderline at which the space group $P1$ can be successfully distinguished from $P\bar{1}$ lies at an average mismatch of ~ 0.1 Å. However, this value of 0.1 Å is surely an arbitrary number which must depend upon such things as the quality and quantity of data, the hardness and perfection of the crystal, and the temperature of the experiment. In any event, the moral is clear: if an approximate center is present, extra care must be taken.

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