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Tetrahedron 59 (2003) 8445–8455

TETRAHEDRON

26 Space group changes and 6 crystallographic puzzles found in Tetrahedron journals[☆]

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Received 18 April 2003; revised 3 July 2003; accepted 30 July 2003

Abstract—The November 2002 release of the Cambridge Structural Database (CSD) contains unit-cell dimensions and atom coordinates for 121 compounds reported in Tetrahedron family journals under space group $P1$ (No. 1) and 1170 under space group $P2_1$ (No. 4). Twenty six of these compounds have been revised to space groups of higher symmetry. Seven have been originally described in space group $P1$, 18 in space group $P2_1$ and one in a non-standard setting of space group $P2_1$. The most common revisions are $P1 \rightarrow P\bar{1}$, $P2_1 \rightarrow P2_1/c$ and $P2_1 \rightarrow P2_12_12_1$. We must add to these 26 compounds four other compounds that has been already re-interpreted in other journals, bringing the total number of $P1$ and $P2_1$ incorrect structures to 30. Thus the percentage of incorrect structures is 2.32%. Evidence favouring higher symmetry is equivocal for four other compounds, thus they are not included among the incorrect structures. Two other structures containing other mistakes are also noted. The consequence of incorrect space group assignment on the molecular structure will be discussed.

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1. Introduction

We have collected and studied the crystal and molecular structures having space group (SG) $P1$ (No. 1) or $P2_1$ (No. 4) described in Tetrahedron, Tetrahedron Letters and Tetrahedron: Asymmetry in order to continue our efforts[1] to understand: (a) the reasons why a crystal structure is described in a space group with lower symmetry than the true one; (b) the kind of symmetry elements that are lost; (c) what relation between molecular and crystallographic symmetry leads to the determination of an incorrect space group. The great number of chiral structures contained in Tetrahedron journals have induced us to study the crystal structures reported, thus increasing the probability of detecting unusual space group changes. A survey of the version 5.24 of the Cambridge Structural Database[2] (CSD-update November 2002, 272000 entries) was carried out for the space groups mentioned above. Not considering the crystal structures without atomic coordinates, we have found that the total number of structures described in SG=$P1$ is 121 while there are 1170 in SG=$P2_1$.

2. Methods, conventions and definitions

The abovementioned structures were at first examined using ADDSYM function in program PLATON.[3] This program checks cell dimensions and atom coordinates, within default tolerances, for missed symmetry and suggests the probable higher symmetry space group. This automatic search provided a list of many possible candidates for the revision of space group. Many chiral compounds with approximately centrosymmetric structures were rejected as non centrosymmetric, while the others were submitted to the following further four tests using two programs written by us: FSCC.FOR and MEAN.FOR.

(1) FSCC.FOR has been already described by us.[1] It produces a reflection data file NAME.HKL, which is adapted for use with SHELXL.EXE[4] program. For the compounds that increase the Laue class the program LAUE.EXE[5] was used to merge the equivalent reflections and to obtain an R_{int} factor (on F_o). If this R_{int} factor is greater than 5% the structure is not further analysed unless disorder is present, this R_{int} factor will be reported, when appropriate, as R_{laue} for each compound in Table 1.

[☆] In this paper the atomic names, the relative coordinates and the name (REFCODE) of the compounds are taken from the CSD system. The reading will be more comfortable editing the CSD file and using the REFCODE, thus the numbering scheme and the graphical scheme of the compound under study will be apparent on the screen.

Keywords: space group change; missed symmetry; revised molecular structure.

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0040–4020/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0040-4020(03)01233-X

Table 1. Structures originally described in space groups $P1$ or $P2_1$ that are more properly described in higher symmetries. Included are refcode, reference number, original space group, revised space group, original (Z) and new (Z') number of formula units per cell

Refcode	Reference number	Original space group	Revised space group	$Z \rightarrow Z'$	Formula unit	Maximum shift (Å)[a]	R_{shelx}[b] (%)	R_{laue}[b] (%)	Transformation vectors	Coordinate transformations	Revised cell parameters					
											a	b	c	α	β	γ
DOCKUB	**14**	$P1$	$P\bar{1}$	1→1	$C_{30}H_{30}N_2O_4$	0.001	1.54	–	[0 0 1][$\bar{1}$ 0 0][0 $\bar{1}$ 0]	$x'=z-1/2$; $y'=-x+1/2$; $z'=-y$	8.162 (7)	8.530(3)	9.586(4)	77.86(2)	81.44(5)	79.22(4)
HOFVED	**15**	$P1$	$P\bar{1}$	3→3	$C_{12}H_6Se_8$	0.197	6.31	–	[0 0 1][$\bar{1}$ 0 0][0 $\bar{1}$ 0]	$x'=z-0.0600$; $y'=-x+0.2595$; $z'=-y+0.3645$	8.759 (1)	10.249(1)	15.559(2)	72.550(9)	79.54(1)	74.93(1)
JOBLOB	**16**	$P1$	$P\bar{1}$	2→2	$C_{35}H_{31}NO_3P_2$, H_2O	0.650	13.70	–	[0 0 $\bar{1}$][0 $\bar{1}$ 0][$\bar{1}$ 0 0]	$x'=-z-0.0002$; $y'=-y+0.0001$; $z'=-x+0.0003$	10.057(9)	12.390(11)	14.136(13)	115.80(1)	98.30(1)	100.40(1)
WATCID	**18**, **19**	$P1$	$P\bar{1}$	1→1	$C_{14}H_{24}N_4O_2$	0.055	7.31	–	[0 0 $\bar{1}$][1 0 0][0 $\bar{1}$ 0]	$x'=-z+0.2618$; $y'=x-0.4961$; $z'=-y+0.1204$	5.015 (2)	8.123(5)	9.341(6)	67.18(5)	87.56(5)	74.40(4)
ZECRAA ZECRAA01	**20**, **21**	$P1$	$P\bar{1}$	1→1	$2(C_{28}H_{16}O_3)$, $C_6H_6O_6$, C_6H_6	0.136	7.64	–	[0 0 1][1 0 0][0 1 0]	$x'=z-0.2664$; $y'=x-0.2929$; $z'=y-0.3926$	8.818(1)	11.779(3)	12.747(2)	101.86(3)	107.14(1)	92.59(3)
YAFLEW	**22**	$P2_1$	$P2_1/m$	4→4	$C_{12}H_{10}Cl_2N_2O$	0.120	4.67	–	[1 0 0][0 1 0][0 0 1]	$x'=x$; $y'=y-0.4907$; $z'=z$	As the original					
ZEBZAH	**23**	$P2_1$	$P2_1/m$	2→2	$C_{20}H_{17}BrN_2O$	0.099	2.43	–	[1 0 0][0 1 0][0 0 1]	$x'=x-1$; $y'=y+0.6685$; $z'=z-1$	As the original					
DAWSUP	**24**	$P2_1$	$P2_1/c$	2→2	$C_6H_6N_2O_2$	0.189	12.26	–	[0 0 1][0 $\bar{1}$ 0][1 0 0]	$x'=z-1/2$; $y'=-y-0.0005$; $z'=x-3/4$	4.570(3)	13.617(4)	5.261(3)	90.00	104.58(5)	90.00
HOSJUU	**27**	$P2_1$	$P2_1/c$	2→2	$C_{22}H_{22}F_4O_2$	0.200	12.90	–	[0 0 1][0 $\bar{1}$ 0][1 0 0]	$x'=z-1/2$; $y'=-y+0.2229$; $z'=x+1/4$	19.3163	6.0136	8.6979	90.00	95.00	90.00
GUMRIP	**30**	$P2_1$	$P2_1/c$	2→2	$C_{26}H_{20}O_4S_4$	0.060	2.89	–	[1 0 0][0 1 0][0 0 1]	$x'=x$; $y'=y+0.3574$; $z'=z-1/4$	As the original					
VIZVIJ	**31**	$P2_1$	$P2_1/c$	4→4	$[C_{16}H_{24}N_2]^{2+}$, 2 Cl^-, 2 H_2O	0.240	6.90	–	[1 0 0][0 1 0][0 0 1]	$x'=x$; $y'=y-0.4067$; $z'=z-1/4$	As the original					
ZUXNAI	**32**	$P2_1$	$P2_1/c$	2→2	$C_{32}H_{34}N_2O_8$	0.140	10.81	–	[0 0 1][0 $\bar{1}$ 0][1 0 0]	$x'=z-1/2$; $y'=-y+0.3660$; $z'=x+1/4$	16.455(4)	9.552(4)	9.551(5)	90.00	105.35(3)	90.00
FIKBUW	**33**,**34**	$P2_1$	$P2_1/n$	4→4	$C_{14}H_{16}O_6$	0.290	15.55	–	[1 0 0][0 1 0][0 0 1]	$x'=x-1/4$; $y'=-y+0.0269$; $z'=z-1/4$	As the original					
UBEKOB	**35**	$P2_1$	$P2_1/n$	4→4	$C_8H_{10}N_2O_3S$	0.048	2.45	–	[1 0 0][0 1 0][0 0 1]	$x'=x+1/4$; $y'=y+0.0238$; $z'=z-1/4$	As the original					
YEGLEB	**36**	$P2_1$[c]	$P2_1/n$	4→4	$C_{29}H_{29}N_3O_6$	0.162	4.65	–	[1 0 0][0 1 0][0 0 1]	$x'=x+3/4$; $y'=y+0.6125$; $z'=z+3/4$	As the original					
ZULBEN	**37**	$P2_1$	$P2_1/n$	4→4	$C_{19}H_{35}BF_3O_3PS$	0.320	14.10	–	[1 0 0][0 1 0][0 0 1]	$x'=x-1/4$; $y'=y-0.2783$; $z'=z-1/4$	As the original					
SEZMAL	**43**	$P1$[d]	$P2_1$	2→2	$C_{20}H_{29}NO_3$	0.151	7.07	7.70	[0 1 0][$\bar{1}$ 0 0][1 0 1]	$x'=y+0.0151$; $y'=-x+z$; $z'=z+0.4608$	11.021	5.466	16.293	89.97	99.574	90.00
CACTAC	**47**	$P2_1$	$P2_12_12_1$	4→4	$C_{31}H_{35}Cl_3N_3Rh$	0.016	0.57	1.20	[0 $\bar{1}$ 0][1 0 0][0 0 1]	$x'=-y+0.4975$; $y'=x+1/2$; $z'=z-1/2$	10.9370(5)	15.8410(9)	16.9940(10)	90.13(1)	90.00	90.00
NOTQIW	**48**	$P2_1$	$P2_12_12_1$	4→4	$C_{15}H_{24}O_4$	0.006	1.94	0.70	[0 $\bar{1}$ 0][1 0 0][0 0 1]	$x'=-y+0.6476$; $y'=x+1/4$; $z'=z-1/2$	6.478(2)	13.400(3)	16.382(3)	90.10(2)	90.00	90.00
RIGCUF	**49**	$P2_1$	$P2_12_12_1$	4→4	$C_{25}H_{32}Cl_4O_5$	0.027	0.97	1.60	[0 1 0][$\bar{1}$ 0 0][0 0 1]	$x'=y-0.1839$; $y'=-x+3/4$; $z'=z-1/2$	13.255(8)	13.570(10)	14.893(8)	90.43(4)	90.00	90.00
RISYOH	**52**	$P2_1$	$P2_12_12_1$	4→4[e]	$C_{29}H_{46}N_2O_4S$	0.061	2.54	7.10	[0 $\bar{1}$ 0][1 0 0][0 0 1]	$x'=-y+0.8260$; $y'=x+1/4$; $z'=z+1/2$	10.817(5)	11.848(5)	23.466(5)	90.550(5)	90.00	90.00
WAQZAP	**53**	$P2_1$	$P2_12_12_1$	4→4	$C_{16}H_{12}O_3$, H_2O[f]	0.119	2.02[g]	5.70[g]	[0 1 0][0 0 1][1 0 0]	$x'=y-0.3470$; $y'=Z+1/4$; $z'=x$	18.817(4)	11.579(2)	7.273(2)	89.96 (3)	90.00	90.00
WIPJAG	**54**	$P2_1$[h]	$P2_12_12_1$	4→4	$C_{16}H_{11}N_3$	0.008	0.0084	0.005	[0 $\bar{1}$ 0][1 0 0][1 0 1]	$x'=-y-0.3146$; $y'=x-z+1/4$; $z'=z-1/2$	9.9397(9)	7.4872(4)	16.6174(11)	90.010(5)	90.00	90.00
ZECPOM	**55**	$P2_1$	$C222_1$	4→8	$C_{42}H_{36}Fe_4$	0.055	0.18	2.80	[$\bar{1}$ 0 1][1 0 1][0 1 0]	$x'=-1/2x+1/2z-1/4$; $y'=1/2x+1/2z+1/4$; $z'=y-0.4128$	26.931(5)	20.048(6)	13.094(3)	90.00	90.00	89.88(2)
UBUFIG	**56**	$P1$	$R\bar{3}$	1→3	$[RuL_2]^{2+}$, $L=C_{27}H_{24}N_6O_3$, PO_4^{2-}, H_3O_3P, 14 H_2O[i]	0.060	9.33	2.40	[$\bar{1}$ 0 0][0 1 0][2 $\bar{1}$ $\bar{3}$]	$x' = -x - \frac{2}{3}z - 0.2679$; $y' = y - \frac{1}{3}z + 0.2791$; $z' = -\frac{1}{3}z + 0.0806$	12.276(3)	12.278(3)	36.023(3)	90.01(2)	90.10(2)	119.99(2)
JECREO	**58**	$P2_1$	$P2_1$	4→2	$C_{21}H_{25}NO_2S$	0.439	10.61		Non-space group translation along a	$x'=-2x+z+1$; $y'=-y+3/2z$; $z'=z$	5.947(6)	12.261(10)	14.290(3)	90.00	100.12(3)	90.00

[a] Only the shifts regarding the non-hydrogen atoms are reported.

[b] R_{shelx} and R_{laue} are defined in the text.

[c] The original authors have reported this compound as monoclinic, space group $P2_1/n$ with $Z=4$. However, CCDC have changed the space group to $P2_1$ with $Z=4$, because the original authors have deposited at CCDC the fractional coordinates of two molecules instead of only one.

[d] Since the space group reported in the original publication is exactly $P1_1$ (and also without the number) we use the space group reported by CSD.

[e] The original authors report $Z=2$, but with a formula unit $C_{58}H_{82}N_4O_8S_2$, i.e. containing two molecules (note H_{82} must be replaced by H_{92}).

[f] We report here the same formula unit reported in the CSD file, however, it should be $C_{16}H_{12}O_3$, 2 H_2O because the coordinate list contains four water molecules for two $C_{16}H_{12}O_3$ unit.

[g] Since the water molecules are disordered, the R_{shelx} and R_{laue} are calculated without their contribution.

[h] $P2_1$ but in a non-standard setting (see text).

[i] We report here the same formula unit reported by the CSD file, but something is wrong because the phosphate group cannot be PO_4^{2-}, probably it is HPO_4^{2-}, see text for a more detailed discussion about this point.

(2) MEAN.FOR calculates atomic shifts[†] necessary to achieve the higher symmetry and compares them with the standard uncertainties (s.u.) averaged over (now) crystallographic equivalent atoms. The maximum shift will be reported for each compound in Table 1.

When systematic errors (such as absorption, miscentering of the crystal, misalignment of the diffractometer) are not present and the only error is the incorrect space group, three possibilities occur for the usual value of the atomic shifts:

(a) They are in the range 0.2–0.3 Å, but occasionally may reach a value of 0.5–0.6 Å, when a centre of symmetry goes unrecognised.[6–8] or when a non-space group translation is present.[7]

(b) They are moderate, up to 0.1–0.2 Å, when the space group change concerns two chiral space groups containing a chiral molecule (usually a large molecule with only one stereogenic centre) that is nearly related to its enantiomeric form by a centre of symmetry, thus obtaining a nearly centrosymmetric space group. We do not report here examples of this type but see QELPUS in Ref. 1.

(c) They are low, up to 0.04–0.05 Å, in all the other cases. However, it is still interesting to find the correct space group for the analytic, spectroscopic and physical implications.

(3) A structure factor calculation is performed using SHELXL.EXE,[4] it reads the file NAME.HKL and the coordinates transformed to the new space group and averaged. If the space group change is correct the R factor must be less than 15% in case (a), 6–8% in case (b) and 3% in case (c), this R factor will be reported as R_{shelx} for each compound in Table 1.

(4) Finally the most important test is the comparison of the distances and angles obtained in the new space group with those normally accepted in the literature. In particular we use the tables of bond lengths reported in Ref. 9.

In one instance (DAWSUP) we obtained a listing of observed structure factors and re-refined the structure in the revised space group.

The key parameter changes have been summarized in Table 1, furthermore Supplementary Information contain further details of the structural changes.

Lists of revised coordinates and additional data as bond lengths and angles has been submitted as REFCODE.CIF file for each compound to Cambridge Crystallographic Data Centre (CCDC).[10] In this paper we use the metric criterion of the reduced basis[11] when it is not in conflict with the symmetry-controlled basis criterion. In particular the triclinic cells are transformed to type-I or type-II cells.

3. Results

The results for each space group change are now classified according to their symmetry properties.

3.1. Category 1: add a center of symmetry

3.1.1. From $P1$ (No. 1) to $P\bar{1}$ (No. 2). FUMROU[12] belongs to this SG change and it has been already re-interpreted by Marsh.[13]

3.1.1.1. DOCKUB[14]—13,14-dibenzyl-3,9-bis(methoxycarbonyl)-13,14-diazatricyclo (6.4.1.1^{2,7})tetradeca-3,5,9,11-tetraene. This compound was reported as triclinic, SG=$P1$ but with SG number: (#2). Thus it is obvious that the original authors meant SG = $P\bar{1}$ (No. 2), i.e. $P1$ and # are only misprints. Moreover the original authors stated that *Z value*: 2, i.e. there are two $C_{30}H_{30}N_2O_4$ molecules in the cell, and in accordance with this they calculate a density of 2.51 g cm^{-3}. But this density is too high for such an organic compound, its density must be 1.258 g cm^{-3} and Z=1. Moreover the original authors have deposited with CCDC the atomic coordinates of the whole molecule, thus it is evident that the original authors suppose to have a crystal with SG = $P\bar{1}$ (No. 2) and Z=2. However, the CSD file report SG=$P1$ (No.1), and Z=1 and calculated density= 1.258 g cm^{-3}, i.e. with one $C_{30}H_{30}N_2O_4$ molecule in the cell. Nobody is right, in fact another interpretation became clear, the space group is $P\bar{1}$ (No. 2) and Z=1, in fact a survey of the original coordinates suggest that the molecule is centrosymmetric and lies on the centre of symmetry at (1/2 1/2 1). We note that the original authors stated "the simple signal patterns in the ^{1}H and ^{13}C NMR spectra of 6 implied a symmetrical structure," i.e. the molecule is also centrosymmetric in solution.

3.1.1.2. HOFVED[15]—bitetraselenafulvalene. This structure is better described in SG = $P\bar{1}$ (No. 2) and Z=3. Two molecule of bitetraselenafulvalene are related by the centre of symmetry at (0,0,0) while the third one lies on the centre of symmetry at (1/2,0,0), thus explaining the sentence reported by the original authors "Two of the crystallographycally independent molecules, wich dimerize, are found to have essentially the same zig-zag conformation, whereas the third one has an almost planar structure."

3.1.1.3. JOBLOB[16]—4,5-bis(diphenylphosphinooxide)-2-phenyl-1-aza-7-oxabicyclo (2.2.1) heptane monohydrate. The original authors noted that "the two crystallographically independent molecules in the unit cell are chemically equivalent enantiomers [C3 is chiral R while C38 is chiral S] and, except for the conformations of some phenyl rings the whole structure approximates to the centrosymmetric space group $P\bar{1}$ (No. 2)." We may confirm that the two molecules are indeed nearly related by a centre of symmetry at (0,0,0), in fact the average shift is 0.069 Å. However, the pairs of equivalent phenyl rings (C6–C11)/(C41–C46) and (C18–C23)/(C53–C58) show very large shifts, as great as 0.65 and 0.55 Å, respectively. The disorder of the phenyl rings is not fortuitous but is due to the different torsion angles of the equivalent benzene rings around the C–C or P–C bond that links them to the rest of the molecule. However the improvement in molecular geometry has convinced us that the change of space group is appropriate, thus we have deposited the JOBLOB.CIF file with SG = $P\bar{1}$ (No. 2).

[†] We define the shift necessary to achieve the higher symmetry as one half of the distance between the two atoms that became crystallographically equivalent after the space group change.

3.1.1.4. WATCID[18,19]—1,6,10,15-tetra-aza-3,12-dioxa-pentacyclo(9.7.1.1^{2,6}.0^{10,20}.0^{15,19}) icosane 6,12-dioxa-3a, 6b,9a,12b-tetra-azaperhydroperylene. The transformation vectors lead to atomic coordinates that are related by a centre of symmetry at (0,0,0), in fact this molecule is an achiral *meso* form. The improvement in the interatomic distances is noteworthy.

3.1.1.5. ZECRAA and ZECRAA01[20,21]—bis(1-(9-anthryloxy)anthraquinone) hydroquinone benzene clathrate. Two refinements are reported for this compound, a pre-liminary communication[20] and a final publication.[21] Since there is not a substantial difference between the two determinations, apart from an origin shift, we describe only ZECRAA. This three-component clathrate compound is better described in SG $= P\bar{1}$, in fact, the two (1-(9-anthryloxy)anthraquinone) molecules are related by a centre of symmetry, while the hydroquinone molecule lies on the centre of symmetry at (0,1/2,1/2) and the benzene ring lies on the centre of symmetry at (1/2,0,0).

3.1.2. From $P2_1$ (No. 4) to $P2_1/m$ (No. 11).

3.1.2.1. YAFLEW[22]—5,6-dihydro-4*H*-benzo(*de*)-6,8-dichloro-2-methyl(2,7)naphthyridin-1-one. The two independent molecules are practically identical and also planar. In fact the maximum deviation from the mean plane is 0.08(2) Å for C3 in the first molecule and 0.12(5) Å for C19 in the second molecule. Only C6 in one molecule and C20 in the other molecule deviates considerably from the mean plane, 0.64(2) and 0.60(2) Å, respectively. Considering that the two molecular planes are both perpendicular to the *b* axis and shifting all the atoms by $\Delta y = -0.4907$, the SG$=$ $P2_1/m$ is obtained. Moreover C6 and C20 atoms are disordered across the mirror plane at $y=1/4$ (C20 is disordered also in the original structure). Thus they must be refined with occupation site factor=0.50 as suggested by Marsh.[13,17]

3.1.2.2. ZEBZAH[23]—3-(4-bromophenyl)-7-methoxy-1,1-dimethylcyclo-penta(*b*) quinoxaline. This compound is better described in SG$=P2_1/m$. In fact the original paper states "all the single rings are planar in the experimental errors and also the whole molecule is planar," considering that this molecular plane is perpendicular to the *b* axis and shifting all the atoms by $\Delta y=0.6685$, one obtains the SG$=$ $P2_1/m$. The two equivalent distances C9–C18=1.60(4) and C9–C19=1.46(4) become now 1.528 Å (C_{sp^3} (overall)$=$ 1.53 Å[9]).

3.2. Category 2: add a center of symmetry and systematic absences

3.2.1. From $P2_1$ (No. 4) to $P2_1/c$ (No. 14).

3.2.1.1. DAWSUP[24]—3,6-dimethylene-piperazine-2,5-dione, cyclo-bis(dehydro-alanyl). This cyclic dipeptide was refined in SG$=P2_1$ to $R=0.071$ for 385 reflections with $I>2.5\sigma(I)$. Moreover, as noted also by the original authors, the molecule presents nearly a point group $2/m$ (C_{2h}), but the chemically equivalent bond lengths are very disparate. However, interchanging *a* and *c* axes and shifting the origin on the centre of hexaatomic ring, the structure can be described as monoclinic, SG$=P2_1/c$. We have obtained 385 F_o values from the British Library as Supplementary Publication (Document No. SUP 45,267). and have transformed the Miller indices according to $h'=l$, $k'=-k$, $l'=h$. Only one violator is present (4 0 5) but its intensity is extremely week (0.4% of the strongest reflection). The standard deviations on intensities were assigned according to Ref. 25. Least squares refinements based on 46 variables lead to an R of 0.0781 for 333 reflections with $F_o>4.0\sigma(I)$. This R factor is slightly greater than the R factor (0.071) of the earlier $P2_1$ model thus the Hamilton test suggest the $P2_1$ model as more probable than the $P2_1/c$ model, however, it is well known that this 'significance test' is unreliable in such situations especially when the weak intensities are not present (as in the present case) in the data set.[8,26] Moreover, in $P2_1/c$ model the distances are reported in the normal range. The previous authors stated "Rather surprisingly, however, molecules are not centrosymmetric; this is to be ascribed to intermolecular interactions, in particular to hydrogen bonds." However, it is well known that hydrogen bonds are not able to modify so markedly chemically equivalent covalent bonds and less than ever inside an hexaatomic ring. Moreover, the two hydrogen bonds reported are effectively the same crystallographic hydrogen bond. We note also that the piperazine rings translated along *a* are very close packed, their distance is 3.105(5) Å. Moreover the previous authors stated "the non-centrosymmetric structure has only a pseudo-centre of symmetry, but also atoms O(1) and O(2), N(1) and N(2), C(5) and C(6), are related by a pseudo-binary screw axis along *x*, thus the difficulty of refinement." These difficulties are usually found when a centre of symmetry goes unrecognised.[6–8]

3.2.1.2. HOSJUU[27]—(*meso*)-(*trans*,*trans*)-2,2,2′,2′-tetrafluoro-3,3′-bis(benzyloxymethyl)bicyclo-propane. The bond lengths of this *meso*-form compound are manifestly unsatisfactory as can be inferred studying the compounds FOMWEJ[28] and TPCLPR[29] containing a bycyclo-propane group. Moreover the chemically equivalent bond lengths are disparate. However, considering that the molecule presents a centre of symmetry between C(10) and C(12) and shifting the cell origin on this centre, one can describe this structure as monoclinic, SG$=P2_1/c$. The molecular geometry is only slightly improved, but the original structure is quite distorted, not only by the omission of the centre of symmetry but probably also because this rod-like molecule possess an high libration motion. However a new refinement is needed to achieve a better centrosymmetric structure.

3.2.1.3. GUMRIP[30]—25,27-dimethoxythiacalix(4)-arene, 1,2-alternate conformation. This compound was reported as monoclinic, SG$=P2_1$, with one molecule in the asymmetric unit. However, the molecule presents an almost perfect centre of symmetry, thus shifting the cell origin on this molecular centre the SG$=P2_1/c$ is obtained. The $P2_1/c$ description leads to a noticeable improvement in bond lengths and angles.

3.2.1.4. VIZVIJ[31]—1,8-diazoniapentacyclo(10.2.2.2^{5,8}.0^{1,10}.0^{5,8})octadeca-3,10-diene di chloride dihydrate. The two independent molecules are related by a centre of symmetry. The structure can be reformulated in SG$=P2_1/c$ shifting the origin to this centre. While the shifts in the $[C_{16}H_{24}N_2]^{2+}$ cations and in the Cl1–Cl2 pair are low, the water pair O3 and O4 presents a larger shift (0.13 Å). The situation for the remaining atoms is still more complicated because there is also disorder, namely the Cl3 ion is centrosymmetric related to O1 water molecule (shift=0.16 Å) and Cl4 ion is centrosymmetric related to O2 water molecule (shift=0.24 Å). Although such anomalies could probably be clarified with the structure factor tables at hand, we describe them below:

(1) The O3–O4 distance reported in the original publication is 1.65(2) Å, too short for a hydrogen bond between two water molecules. This feature is due to the presence of the (unrecognised) centre of symmetry in the middle of the O3–O4 pair. Clearly the position and the occupancies of these atoms must be re-determined.

(2) A chloride ion is equivalent to an oxygen atom in the Cl3–O1 and Cl4–O2 atomic pairs, an unrealistic situation that must be clarified. Since only two Cl^- ion must be contained in the asymmetric unit of $P2_1/c$ and one Cl^- ion is already well determined, we propose that the remaining Cl^- ion is equally distributed over the two sites of Cl3 and Cl4 ions, i.e. with an occupation factor of 0.50, this also explains why a chloride ion is equivalent to an oxygen atom.

We note that the distances in $P2_1/c$ become more regular.

3.2.1.5. ZUXNAI[32]—tetramethyl 5,16-diazatricyclo-(18.2.2.2.[9,12])hexacosa-2,7,9,11,13,18,20,22,23,25-decaene-3,7,14,18-tetracarboxylate. Considering that a centre of symmetry is present in the middle of the large cavity of this cyclophane, the structure of this compound can be reformulated in SG=$P2_1/c$. The $P2_1/c$ structure shows a convincing improvement in molecular geometry.

3.2.2. From $P2_1$ (No. 4) to $P2_1/n$ (No. 14). We prefer to use the $P2_1/n$ variant of $P2_1/c$ when it gives the three shortest translations of the monoclinic lattice.

3.2.2.1. FIKBUW[33,34]—dimethyl 8-oxo-(6)(2,5)furanophane-3,4-dicarboxylate. The two purportedly independent molecules are related by a diagonal *n*-glide, thus this structure can be better described in SG=$P2_1/n$. The shifts for achieving the higher symmetry are low (0.02–0.11 Å), but the pair O2–O8 presents a shift of 0.29 Å. This large shift is probably due to a misprint on the coordinates of the O2 atom, in fact the original angles around the sp^2 carbon atom C7 [C6–C7–O2=147.6(9)°; C8–C7–O2=97.7(1.1)°] are very different from the expected value of 120° or from those around the C21 atom (equivalent to C7), but became a little better in $P2_1/n$, 134.0 and 107.7°. The $P2_1/n$ structure lead to a more reasonable molecular geometry.

3.2.2.2. UBEKOB[35]—2-methyl-3,4,5,7-tetrahydro-2*H*-pyrrolo(3,4-*f*)(1,2)thiazepin-5-one 1,1-dioxide. This compound was described as monoclinic, SG=$P2_1$, with Z=4 (note that the original paper reports Z=2, however, the original Figure (Compound **10**) shows two molecules in the asymmetric unit and the CSD file contains the coordinates of two molecules, thus we consider Z=2 a misprint). It is properly described as monoclinic, SG=$P2_1/n$, with Z=4. The new space group reveals that the two purportedly independent molecules are related by a centre of symmetry. The atomic shifts are lower than expected when a centre of symmetry goes unrecognised, in fact the maximum shift is 0.048 Å for the atomic pairs: O5–O1.

3.2.2.3. YEGLEB[36]—*N*-methyl-2,5-bis(methoxycarbonyl)-3,4-bis(*N*-methyl-5-methoxy-indol-3-yl)-pyrrole. This natural and achiral compound was originally reported in the monoclinic SG=$P2_1/n$, with Z=4. However, the CSD file contains the fractional coordinates of two molecules (instead of only one) and the SG is $P2_1$. Our study reveals that the two purportedly independent molecules are related by a centre of symmetry and that the structure can be described in SG=$P2_1/n$. The improvement in molecular geometry is noteworthy.

3.2.2.4. ZULBEN[37]—tricyclohexylphosphino(trifluoromethanesulfonyloxy)borane. The two purportedly independent molecules are related by a *n*-glide perpendicular to *b*, thus this structure is better describe in the SG=$P2_1/n$. The F atoms deserve special mention, in fact they cannot be simply averaged as the other atoms because the twist angle around the S–CF_3 σ-bond is different for the two independent (in $P2_1$) molecules (max. shift F2–F4=0.32 Å). Similar situations were already described by Marsh.[13,17] Consequently the six F atoms have been inserted in the ZULBEN.CIF file without averaging their coordinates but with an occupation site factor equal to 0.5. In the new space group the bond distances become more realistic.

3.2.3. From $P2_1$ (No. 4) to $P2_1/a$ (No. 14). We have not reported examples of this SG change because $P2_1/a$ is not a conventional choice, but it has been described for 1*H*-Indole-3-propionic acid. In fact this acid was initially reported as $P2_1/a$ (INDPRA[38]), then was re-determined as $P2_1$ (INDPRA02[39]) and finally was definitively and correctly determined as $P2_1/a$ (INDPRA01[40]).

3.3. Category 3: Change in Laue group

This space-group changes requires that the new α', β', γ' angles differ from the expected value only by a few s.u., however, this is only rarely reached because the accuracies in the original cell dimensions are appreciably worse than represented by the reported s.u. In fact, the so-called standard uncertainties on the cell parameters are usually obtained through an automated centering routine on a computer-controlled diffractometer, but such a procedure is not able to correct the numerous mistakes that can be introduced at this point such as absorption, mis-centering of the crystal, poor choice of reference reflections, but above all misalignment of the instrument. What we really obtain with this procedure are the precisions rather than the accuracies on the cell parameters. This question resolves itself into the problem of estimating two distinct quantities, namely precision and accuracy as is well explained by Frank Herbstein[41] or by Edward Prince.[42]

3.3.1. From $P1$ (No. 1) to $P2_1$ (No. 4).

3.3.1.1. SEZMAL[43]—(2*S*,6*S*,7*R*,9*S*)-2-phenyl-7,9-dibutyl-1-aza-4,8-dioxabicyclo(4.3.0)nonan-5-one. This chiral compound was reported in the original publication as monoclinic, but with a SG not defined, in fact the reported SG is exactly $P1_1$(?) (also the SG number is not given). The original cell parameters are: a=5.466 Å, b=11.021 Å, c=17.188 Å, β=108.57°, Z=2, D_x=1.390 g cm^{-3}, V=966.50 Å^3. First, the previous cell has V=981.51 Å^3 and also D_x does not correspond with the calculated density. Moreover, the CSD file reports the following triclinic cell: a=5.466 Å, b=11.021 Å, c=17.188 Å, α=99.071°, β=108.57°, γ=90.00°, SG=$P1$ (No. 1) and Z=2. The unit cell was calculated by Cambridge with a method[44] involving fitting the bond lengths reported by the authors to the bond lengths calculated from the given atomic coordinates and hence calculating a new unit cell. Thus we continue the crystallographic analysis with the CSD data, furthermore we note that CSD reports the fractional coordinates of two independent molecules. The transformation vectors (Table 1) reveal that the two purportedly independent molecules are related by the 2_1 axis along *b* of the new cell (i.e. the old *a* axis) with a mean shift of 0.026 Å. The $C_{sp}3-C_{sp^3}$ distance C11–C14 becomes 1.16 Å in the new SG and remains still very short, but no more than this can be expected when the starting equivalent distances are so short. However, the shifts are so small that we have no doubt that the SG change is correct.

3.3.2. From *P*1 (No. 1) to *C*2 (No. 5).

Two structures PADWOG[45] and VEMSAH[46] have been already re-interpreted by Marsh, obtaining PADWOG01[13] and VEMSAH01.[13]

3.3.3. From $P2_1$ (No. 4) to $P2_12_12_1$ (No. 19).

3.3.3.1. CACTAC[47]—trichloro-(2,6-bis(8-methyl-5,6,7,8-tetrahydro-5,8-(2-propano)quinolin-2-yl)pyridine-*N*,*N*′,*N*″)-rhodium. This chiral C_2-symmetric $Rh(L_2)Cl_3$ complex has been described as monoclinic, SG=$P2_1$, with β=90.13(1)°. However, the two molecules in the asymmetric unit are related by an almost perfect 2_1 screw-axis, thus this structure is properly described as orthorhombic, SG=$P2_12_12_1$. The deviation (0.13°) of α' from 90° seems to be significantly larger than the reported s.u. (0.01°) but convincing evidence of orthorhombic symmetry comes from the necessary shifts for achieving the higher symmetry, they range from 0.001 Å for Rh1–Rh2 pair to 0.017 Å for C29–C52 pair. Since the shifts are so low there are no significant changes in bond lengths or angles.

3.3.3.2. NOTQIW[48]—6-acetyl-3,12-dihydroxy-2,9-dimethyl-4-oxatricyclo(6.3.1.0^{5,12})dodecane. This chiral compound, obtained by reduction of artemisin (an active natural anti-malarial compound) was described in the monoclinic SG=$P2_1$ with β=90.10(2)°. However, considering that the two molecules in the asymmetric unit are related by an almost perfect 2_1 screw-axis, the orthorhombic SG=$P2_12_12_1$ can be obtained. The deviation (0.10°) of α' from 90° seems to be significantly larger than the reported s.u. (0.02°) but convincing evidence of orthorhombic symmetry comes from the necessary shifts for achieving the higher symmetry, they range from 0.0008 Å for O1–O2 pair to 0.006 Å for C23–C24 pair. Since the shifts are so low there are no significant changes in bond lengths or angles.

3.3.3.3. RIGCUF[49]—(1*S*,2*S*,3*R*,6*S*,7*R*,8*R*)-1,8,9,10-tetrachloro-11,11-dimethoxy-6-(((1′*R*,2′*S*,4′*S*,6′*S*,7′*S*)-1′,10′,10′-trimethyl-3′-oxatricyclo(5.2.1.0$^{2',6'}$)decan-4′-yl)oxy)-tricyclo(6.2.1.0^{2,7})undeca-4,9-dien-3-ol. This chiral compound has been described as monoclinic, SG=$P2_1$, with β=89.57(4)°. However considering that the two molecules in the asymmetric unit are related by an almost perfect 2_1 screw-axis, the orthorhombic SG=$P2_12_12_1$ can be obtained. The angle α' appears to differ significantly (0.43°) from 90°, but similar errors are reported by Marsh[50] and by Herbstein.[51] Moreover, the atomic coordinates leave no doubt that the orthorhombic description is correct, and it seems clear that the accuracies in the β angle of the monoclinic cell are appreciably worse than represented by the reported s.u. The necessary shifts for achieving the higher symmetry range from 0.0006 Å for Cl4–Cl5 pair to 0.027 Å for C31–C47 pair. Since the shifts are so low there are no significant changes in bond lengths.

3.3.3.4. RISYOH[52]—(2*S*)-(1*S*,2*R*,4*R*)-10-(dicyclo-hexylsulfamoyl)isobornyl 2-cyano-2-methyl-4-pentenoate. The original authors have described this compound in the monoclinic SG=$P2_1$, with β=90.550(5)°. However, considering that the two molecules in the asymmetric unit are related by a 2_1 screw-axis, the orthorhombic SG=$P2_12_12_1$ can be obtained. We note that there is a substantial error (0.55°) in α', but similar errors are reported by Marsh[50] and by Herbstein.[51] The x' and z' coordinates are compatible, well within the reported s.u., with the symmetry of SG=$P2_12_12_1$, while the y' coordinates present deviations (0.03–0.05 Å) that are six to eight times the reported s.u. for all the atom pairs with the exception of the four atomic pairs: C3–C40, C9–C32, C22–C50, C29–C58, that present instead normal deviations also for the y' coordinate. Although also the R_{laue} is slightly higher than 5.0%, we are sure that the correct space group is $P2_12_12_1$ because of the low R_{shelx}=2.54% and the low shifts necessary to achieve the higher symmetry, in fact they range from 0.015 Å for the C21–C51 pair to 0.061 Å for the C18–C45 pair. Since the shifts are low there are no significant changes in bond lengths, however, a refinement in the new space group should be carried out to achieve a better structure.

3.3.3.5. WAQZAP[53]—(+)-(*S*)-2-(1-hydroxyphenyl-methyl)-chromen-4-one monohydrate. The structure of this optically active alcohol was described as monoclinic, SG=$P2_1$ with β=89.96(3)°. However, the two independent organic molecules in the asymmetric unit are related by a 2_1 screw-axis along *c*, and the four water molecules are related by a 2_1 screw-axis along *a*. Thus the orthorhombic SG=$P2_12_12_1$ can be obtained. The angle α' does not differ significantly from 90° (cell parameters were refined from 2000 reflections collected with a diffractometer equipped with a 2D area detector[41]). The mean shift necessary to achieve the higher symmetry within the organic molecule is 0.033 Å, while the four water molecules show larger shifts (0.153–0.164). However, the water molecules are misplaced, in fact they would be hydrogen bonded with unrealistically short distances: 1.75(5) Å, 2.03(5) Å, 1.91(5) Å and 1.86(5) Å. Also CSD suggests: “There appears to be a disordered water molecule present.”

3.3.3.6. WIPJAG[54]—*trans*-5,7-dicyano-6,7-dihydro-5*H*-dibenz(*c*,*e*)azepine. This compound was described as monoclinic, SG=$P2_1$, *Z*=4. The transformation vectors define an orthorhombic cell and reveals that the two purportedly independent molecules are related by an unrecognised 2_1 screw axis along *b* of the new cell, that is the *a* axis of the monoclinic cell. However, the definition of the new space group has been very difficult because the original structure presents many short intermolecular contacts, four are less than 0.90 Å. However, Dr Greg Shields (CCDC staff) has solved the puzzle, suggesting to us that probably the original authors have used a non-standard setting of $P2_1$, with operators $(+x,+y,+z)$; $(-x,1/2+y,1/2-z)$. This suggestion leads to normal intermolecular contacts and also reveals that the true space group is $P2_12_12_1$ (No. 19) with *Z*=4. We note that the earlier authors say “the two symmetry-independent molecules in the unit cell are almost identical in their geometry.”

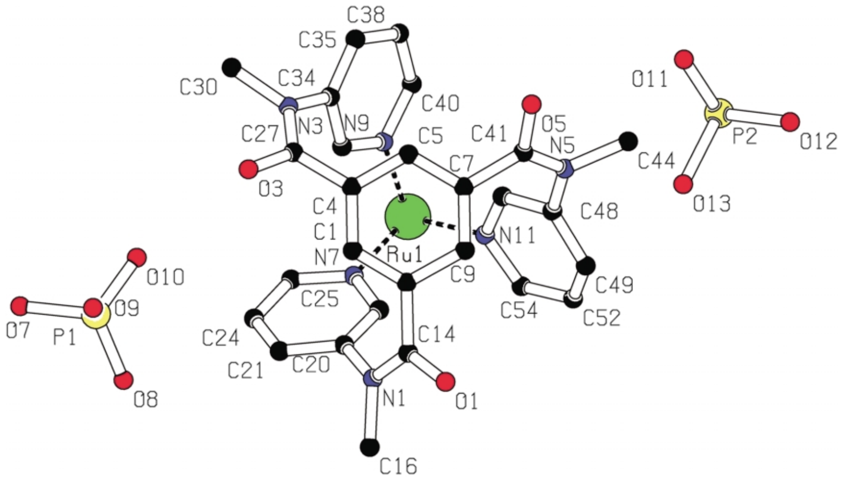

Figure 1. View of $[\mathrm{RuL2}]^{2+}$ cation and PO_4 groups along the $\bar{3}$ axis in UBUFIG compound (L=tripodant ligand, $C_{27}H_{24}N_6O_3$), for clarity only one L ligand is shown, the other L ligand can be built up through the centre of symmetry coincident with the Ru atom.

The orthorhombic description yields no significant different bond lengths or angles.

3.3.4. From $P2_1$ (No. 4) to $C222_1$ (No. 20).

3.3.4.1. ZECPOM[55]—tetraferrocenylethene. Considering that the two independent tetraferrocenylethene molecules are related by a twofold axis, one can define the new space group as $C222_1$ (No. 20). The shifts are small, they range from 0.002 for Fe5–Fe8 pair to 0.052 Å for the C55–C78 pair. Since the shifts are so low no remarkable variation of bond lengths and angles was observed, for example the central double bonds that are 1.34 and 1.37 in $P2_1$ become 1.354 Å in $C222_1$.

3.3.5. From $P2_1$ (No. 4) to $P4_3$ (No. 78). The structure of APLSOL has already been corrected by us.[1]

3.4. Category 4: add a center of symmetry and change the Laue group

3.4.1. From $P1$ (No. 1) to $R\bar{3}$ (No. 148).

3.4.1.1. UBUFIG[56]—bis(*N*,*N*′,*N*″-trimethyl-*N*,*N*′,*N*″-tris-(3-pyridyl)-1,3,5-benzenetricarboxamide-*N*,*N*′,*N*″)-ruthenium(ii) phosphate phosphite tetradecahydrate. This compound was described in a non-reduced triclinic cell, SG=$P1$ (No. 1), with Z=1. The transformation vectors defines a triply primitive hexagonal cell with Z=3 and places the Ru(ii) ion at the site symmetry $\bar{3}$ in space group $R\bar{3}$ (No. 148). The $\bar{3}$ axis being normal to the phenyl ring of the tripodant ligand (L) and passing through its centre produces a $[\mathrm{RuL}_2]^{2+}$cation with point group $\bar{3}$ (see Fig. 1). We note that the free ligand L (L=UBUDEA,[56] SG = $Pa\bar{3}$ (No. 205)) also presents a ternary axis perpendicular to the phenyl ring and passing through its centre. The shifts necessary to achieve the higher symmetry for the $[\mathrm{RuL}_2]^{2+}$ cation range from 0.003 to 0.061 Å. Moreover the improvement in molecular geometry is noteworthy, for example the six disparate C═O double bond distances become 1.23 Å, and the 12 C–C distances of the two phenyl rings perpendicular to the $\bar{3}$ axis became 1.3905 Å, the same values found in the free ligand.[56] A particular discussion is necessary for the phosphate and H_3O_3P groups, in fact they show unusual P–O distances ranging from 1.28 to 2.15 Å, these feature can be explained by a substitutional disorder and by the omission of the centre of symmetry. The phosphate group lies on a threefold axis passing along the P1–O9 bond, also the P2 atom of the H_3O_3P residue lies on a threefold axis. Moreover, the PO_4 tetrahedra and the H_3O_3P group are only roughly related by the centre of symmetry coincident with the Ru(ii) ion (see Fig. 1), in fact the shifts are high, in particular for the atomic pair P1–P2 (0.574 Å).

3.5. Category 5: structures with non-space-group translation

Non-space-group translation means that the unit cell does not correspond to the smallest possible one and consequently the description of the structure must be changed. Since a superstructure, refined on the basis of weak superlattice reflections, leads to high correlations and near-singularities in the refinement procedure,[7] we obtain in real space unrealistic bond lengths and angles and consequently, in our language, large shifts. The revised structures of this type are very few,[3,57] a well documented example is COJJAM that was revised to COJJAM01.[3] In this compound the shifts are very high, in fact they range from 0.024 Å for the pair C12–C65 to 0.251 Å the pair C31–C46, while the mean shift is 0.118 Å.

The ADDSYM function in PLATON[3] has given three possible candidates, JECREO,[58] GOMKAU,[60] and PENLUP,[61] however, since it is difficult to decide on the correctness of this change without the structure factor tables, we have analysed the distances and angles before and after the change. This analysis has suggested that only JECREO must be changed, while the other two require the structure factor tables to achieve a definitive result and thus are reported as borderline compounds.

3.5.1. JECREO[58]—5-(2,4,6-trimethylbenzenesulfonylamido)-6-phenylhexa-2,3-diene. This compound was described as monoclinic, SG=$P2_1$, with Z=4. However, the two independent organic molecules in the asymmetric unit are nearly related by a non crystallographic translation of $a/2$, this means that the first molecule can be obtained by the second one through the symmetry operation, not contained in $P2_1$, $(-1/2+x,y,z)$. When the a axis is reduced by one half it appears evident that the cell is not reduced, the reduction procedure leads to the monoclinic cell reported in Table 1. The shifts range from 0.029 to 0.439 Å (mean shift is 0.130 Å). Although the shifts are relatively high there is a distinct improvement in the molecular geometry that has convinced us that the change in cell dimension is appropriate.

3.6. Category 6: structures at a borderline situation

We report four compounds for which the evidence favouring possible higher symmetry is equivocal. We have not deposited such examples at the CSD because it is difficult to reach convincing conclusions in the absence of the primary intensity data.

3.6.1. DAQSUJ[59]—(2*R*,3*R*)-3-hydroxy-2-(*n*-propyl)-2,3-dihydro-5*H*-1,5-benzoxazepin-4-one, $C_{12}H_{15}NO_3$; $R_{shelx}=28.26\%$, maximum shift=0.450 Å. This compound was described as monoclinic, SG=$P2_1$, with $Z=4$. However, the fractional coordinates of the two molecules in the asymmetric unit are related by apparently fortuitous relations: $x_1+x_2=0.5099(20)$, $y_1+y_2=1.1788(20)$, $z_1+z_2=0.9709(10)$. This means that there is a nearly exact centre of symmetry at $(-0.2550,0.5894,0.4855)$, in fact the shifts range from 0.04 Å for the C5–C17 pair to 0.10 Å for the C12–C14 pair. This is an unexpected result because the original authors reported that the crystal contain only the (2*R*,3*R*) enantiomer. A detailed analysis of the two molecules reveal that the first molecule contains the C1 and C2 atoms in the *R* configuration, while the second molecule contains the chemically equivalent C13 and C14 atoms in the *S* configuration. We may ask now if this centre of symmetry is only local or crystallographic. The presence of a crystallographic centre of symmetry produces in this crystal a glide plane of type *a*, however, the shifts introduced by this glide plane are as high as ~0.40 Å. The mismatch is due principally to Δz, in fact the z coordinate of the centre of symmetry should be 0.5000 and not 0.4855, a difference of ~0.20 Å. Although these high shifts are usually found when the centre of symmetry goes unrecognised, we cannot deposit this compound with CSD in the absence of the primary intensity data and because the molecular geometry is (unexpectedly) normal, namely the refinement in $P2_1$ has not produced any molecular distortion.

3.6.2. GOMKAU[60]—(*t*-butoxy)carbonyl-phenylalanine-thioisoleucyl-a-aminoisobutyryl-phenylalanine ethyl ether, $C_{35}H_{50}N_4O_6S$; $R_{shelx}=9.66\%$, maximum shift=0.348 Å (excluding the C26–C61 pair). This compound was described as monoclinic, SG=$P2_1$, with $Z=4$. The second molecule is obtained by translating the first one nearly by $c/2$. The shifts range from 0.077 to 0.348 Å, but the shift for the pair C26–C61 is very high, namely 0.81 Å. This occurrence is explained by the original authors who state: “there are two independent molecules A and B in the asymmetric unit. They have the same configuration and very similar conformations, with the exception of the ethyl arm of the isoleucine, where the torsion angles about the C23–C24 bond in the molecule A differ by about 95° from those about the corresponding C58–C60 bond in molecule B.” The different torsion angle changes the position of C61 in respect of C26. One can debate if the breakdown of non-space group translation by the pair C26–C61 is sufficient for supporting the c axis choice made by the original authors, but we suggest that the refinement with a shorter c axis and occupancy factors 0.50 for C26 and C61 should be preferred, i.e. a disordered model. However, we cannot deposit the GOMKAU.CIF file in the absence of the primary intensity data and also because the distances in the original description are normal, (apart for the two chemically equivalent benzene rings C30–C35 and C65–C70, that present very short C–C aromatic distances, but this may be due to thermal motion) and because the distances in the new description are not substantially improved.

3.6.3. PENLUP[61]—*N*-*p*-tosyl-L-valine-1-phenyl-prop-2-yn-1-yl ester, $C_{21}H_{23}NO_4S$; $R_{shelx}=8.09\%$, maximum shift=0.48 Å. This compound was described as monoclinic, SG=$P2_1$, with $Z=4$. However, the first molecule in the asymmetric unit can be roughly obtained by applying to the second molecule the symmetry operation, not contained in $P2_1$,: $(-1/2-x,1/2+y,-1-z)$. This non-conventional operation, produces overlap of many atoms with shifts ranging from 0.07 to 0.20 Å. However, few atoms contained in benzene, toluene, or in $-CH(CH_3)_2$ moieties show larger shifts (0.22–0.48 Å). Such large shifts are due to the different torsion angles of these groups around the C–C bond that links them to the rest of the molecule. Although the bond lengths in the original publication are not satisfactory, we cannot deposit the PENLUP.CIF file in the absence of the primary intensity data, also because the distances in the new description are not substantially improved.

3.6.4. NOBWAC[62]—(1*S*,2*S*,5*R*)-1-((3*R*)-3-hydroxy-4,4-dimethylpentyl)-2-isopropyl-5-methylcyclohexano, $C_{17}H_{34}O_2$; $R_{shelx}=8.94\%$, $R_{laue}=12.5\%$, maximum shift=0.33 Å. The crystal structure of this chiral compound has been described as monoclinic, SG=$P2_1$, with $a=10.645(11)$ Å, $b=18.040(6)$ Å, $c=10.737(10)$ Å, $\beta=119.53(7)°$, $Z=4$, the s.u. on a and c axes and on β angle are unusually high. Moreover, the bond lengths between analogous atoms are unsatisfactory and the final R factor is high (12.36%), so the original authors tested a twin model with an hypothetical threefold twin axis along [010]. However, the lattice vectors $[\bar{1}\ 0\ \bar{1}]$, $[1\ 0\ \bar{1}]$ and $[0\ \bar{1}\ 0]$ define an orthorhombic cell, SG=$C222_1$ (No. 20), with $a'=10.767(14)$ Å, $b'=18.473(14)$ Å, $c'=18.040(6)$ Å, $\alpha'=90.00°$, $\beta'=90.00°$, $\gamma'=89.43°$, $Z=8$. The revised angle γ' differ 0.57° from 90°, a very high value. The corresponding coordinate transformations are: $x'=-1/2(x+z)+1/4$, $y'=1/2(x-z)+1/4$, $z'=-y+0.7210$. The new space group reveals that the two independent molecules (in $P2_1$) are nearly related by a twofold axis along b of the new cell. However, the matching of the two molecules is not satisfactory, in fact the shifts range from 0.05 to 0.33 Å (mean shift=0.16 Å). Since this space-group change is between two non-centrosymmetric space groups such great shifts are not justified, some other problems must be present, probably twinning, as suspected by the original authors. In fact we note that in the lattice, in addition to the original monoclinic cell, that is metrically near hexagonal, there are three other primitive cells that are nearly metrically hexagonal, moreover there is also a nearly metrically rhombohedral cell with parameters $a'=21.009$ Å, $b'=20.993$ Å, $c'=20.947$ Å, $\alpha'=52.27°$, $\beta'=52.41°$, $\gamma'=52.83°$, $Z=12$.

3.7. Category 7: structures with misprints or other mistakes

3.7.1. FAKBIC[63]—4-(5″-dimethylamino-2′,2″-bithienyl-5′-yl)-1-methylpyridinium *p*-toluenesulfonate. $[C_{16}H_{17}N_2S_2]^+$ $[C_7H_7O_3S]^-$. This compound was reported as triclinic, SG=$P1$ (No. 1) and $Z=2$. Considering that CSD file reports the atomic coordinates of only one formula unit and that the calculated density is 1.361 g cm^{-3} the SG should be $P\bar{1}$ (No. 2) with $Z=2$. This is nothing more than a simple misprint.

3.7.2. WORSEB[64]—4,5-bis(2-iodoferrocenyl)-2,2-dimethyl-1,3-dioxolane, $[C_{25}H_{24}Fe_2I_2O_2]$. This compound was described as monoclinic SG=$P2_1$ (No. 4) and $Z=8$. However, the original authors have deposited with CSD the atomic coordinates for only one of (four?) independent molecules in the unit cell. Thus the crystallographic analysis must be stopped here, but it must be considered that this chiral compound has a C_2 axis of molecular symmetry passing through the dioxolane ring.

4. Discussion and conclusion

Even if the structures are described in space groups of unnecessarily low symmetry the atom connectivity and the chemical identity of the compound are not in question, however, crystal structure analysis can give much more, namely the exact situation of the chemical bonds inside the molecule. As we have demonstrated this is greatly affected when the centre of symmetry goes unrecognised or when non-space groups translations are introduced.

We have noted a great number of chiral compounds with an approximate center of inversion, they try to reach a centrosymmetric SG even if it is forbidden by their molecular structure, but also in this case near singularity in the normal equation matrix led to incorrect distances if special precautions are not taken, e.g. by using constraints.[3]

The great number of chiral structures contained in Tetrahedron journals have revealed six interesting space-group changes from $P2_1$ (No. 4) to $P2_12_12_1$ (No. 19). RIGCUF and RISYOH present high errors on β angle of 0.43 and 0.550°, respectively, which seems unlikely although there are precedents.[50,51] The low shifts (max. shifts=0.027 and 0.061 Å) required to achieve the higher symmetry convinced us that these two space group changes are necessary. Although Tetrahedron journals contain a great number of chiral structures, 17 examples of SG change from non-centrosymmetric to centrosymmetric have been found. The near singularity of the normal equation matrix produces large shifts in the position of crystallographic equivalent atoms and consequently unusual bond distances. In such cases the first test on the correctness of the crystal and molecular structure resides on the correctness of the chemistry of the molecular structure, i.e. of bond lengths and angles. One certain (JECREO) and two borderline examples (GOMRAU and PENLUP) of non-space group translations are reported. Also in this case the near singularity of the normal equation matrix causes very high shifts, so high that in two cases the cell change is questionable. Two other borderline examples (DAQSUJ, NOBWAC) are reported, but their SG cannot be ascertained with precision because the lack of the structure factor tables. As already suggested[65] these tables must be stored as electronic files by the journals that publish crystal structures or by the CCDC system together with the fractional coordinates. We remember that the F tables contain, stored in reciprocal space, not only the crystal and molecular structure but also any other experimental information (included the experimental electron density on the chemical bonds !). Thus the lack of F tables produces a serious limitation on the scientific information.

The total number of revised crystal structures is 30 on 1291 analysed structures (121 in $P1$ and 1170 in $P2_1$), 26 are presented here and 4 (INDRA, PADWOG, VEMSAH, APLSOL) were corrected in other journals. Thus the percentage of incorrect structures is 2.32%, a little lower than 3% evaluated by Baur and Tillmans[66] for all the published structures (~272000) corresponding to a total of nearly 8000 structures. However, the percentage of incorrect assignments strongly depends on the starting SG, for instance the per-centage of C2 is higher than 3.00%[3] and is very high 15%[67] for the space groups of point-group C3 ($P3$,$P3_1$,$P3_2$,$R3$).

Acknowledgements

I am very grateful to my wife and my two sons for the moral support given to me during this work. I thank also the staff of the CCDC for providing many helpful information, particular thanks are due to Dr Greg Shields (CCDC) who has solved the puzzle regarding the WIPJAG compound.

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