

CPSNC.pseudocentro.txt

Supplementary text to
Centrosymmetric and pseudo-centrosymmetric structures refined as non-
centrosymmetric
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Spek
Acta Crystallographica B

Cases of pseudo-centrosymmetric structures:

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Only structures 1993 or later.

Source of pseudo-centrosymmetric structures:

- [A] Clemente, D. A. (2004) Inorg. Chim. Acta 358, 1725-1748.
- [B] Herbstein, F. H. and Marsh, R. E. (1998) Acta Cryst. B54, 677-686.
- [C] Marsh, R. E. (1999) Acta Cryst. B55, 931-936.
- [D] Marsh, R. E. and Spek, A. L. (2001) Acta Cryst. B57, 800-805.
- [E] Marsh, R. E., Kapon, M., Hu, S. and Herbstein, F. H. (2002) Acta Cryst. B58, 62-77.
- [F] Herbstein, F. H., Hu, S. and Kapon, M., (2002) Acta Cryst. B58, 884-892.
- [G] Marsh, R. E. (2002) Acta Cryst. B58, 893-899.
- [H] Clemente D. A. and Marzotto, A. (2003) Acta Cryst. B59, 43-50.
- [I] Marsh, R. E. (2004) Acta Cryst. B60, 252-253.
- [J] Clemente D. A. and Marzotto, A. (2004) Acta Cryst. B60, 287-292.
- [K] Marsh, R. E. (2005) Acta Cryst. B61, 359.
- [P] Referee No 2. (2005) of Flack, H. D. and Bernardinelli, G., (2006) Inorg. Chim. Acta 359, 383 - 387.
- [Q] Clemente, D. A. (2005) Private communication - e-mails 04.09.2005, 05.10.2005
- [R] Marsh, R. E. (2005) Private communication - e-mails 10.09.2005
- [S] Bernardinelli, G, and Flack, H. D. (2005) Current work
- [T] Clemente, D. A. (2005/6) Private communication - e-mails 10.10.2005, 18.10.2005, 10.11.2005, 15.12.2005, 20.01.2006, 29.01.2006, 04.02.2006, 01.03.2006, 21.03.2006
- [U] Djukic, J.P. (2006) Private communication - e-mail

Content of Table:

Search terms used where a searchable electronic version of the original publication was available:

<BASF>
<Flack>
<absolute>
<enantio>
<CD>
<optical>
<chiral>
<racem>
<disorder>

As sources of data we used the papers as published and any supplementary material freely available for download from the journal's online site, the CIF archive of the Cambridge Crystallographic Data Centre (CCDC) or perhaps from FIZ. We never contacted authors for supplementary material. Each paper available in searchable digital form was scanned for the strings of characters listed above. Values pertinent to this study are presented in the Table below. A "?" means that the corresponding value was not reported or could not be deduced from the data sources. The columns of this table contain the following data values:

[]: The code gives a pointer to the literature source indicating that the structure is or might be pseudocentrosymmetric.

Refcode: This column identifies each compound by its CSD Refcode. In Categories Z, A and C, the compounds are ordered alphabetically by refcode, whereas in category B they are ordered by increasing value of Rescat (see below) . A "+" after the refcode means that the Notes section should be consulted.

S,P: Two aspects of the symmetry of the pseudocentrosymmetric crystal structure are given in the Table in columns S and P. S indicates one of the three two-letter codes for crystal structures: NC non-centrosymmetric chiral crystal structure; NA non-centrosymmetric achiral crystal structure; CA centrosymmetric achiral crystal structure. P indicates the number of directions in which it is NOT possible to fix the origin of the (non-centrosymmetric) space group with respect to a symmetry element. In the rest of this paper, we will call these origin-free directions. This information is available in tables of the Euclidean normalizers of space groups.

Fit: Platon fit parameter.

Enantioexcess: Non-crystallographic measurements of the enantioexcess (as a %) of (B) the bulk material and (X) the single crystal used for the diffraction measurement. Values vary from 0 (racemic) to 100 (enantiopure). These numerical values come from OA, CD in solution or in the solid state, and enantioselective chromatography. "a" means the molecule is achiral or would racemize rapidly in solution. "rac" means that although there are no measurements of the enantiopurity, it would seem as though the chemical synthesis is not enantioselective and gives a racemate. "je" means that the composition of the single crystal used for the diffraction experiments is judged by us to be enantiopure.

Rescat: A measure of the proportion of the scattering due to resonant scattering at $\theta = 0$. $\text{Rescat} = 10000.0 * \sqrt{2.0 * \sum (f''^2) / \sum (f^2)}$

Friedl Cover: The value gives a measure of the completeness of the diffraction intensity data with regard to inversion in the origin of reciprocal space (Friedel coverage). Reflections $h k l$ and $-h -k -l$ are called Friedel opposites. If for each value of $h k l$, the intensity of the Friedel opposite $-h -k -l$ (or one symmetry-equivalent to it) has not been measured, then the Friedel coverage is 0%. However if for each value of $h k l$, both the reflection $h k l$ and its Friedel opposite $-h -k -l$ (or one symmetry-equivalent to it) have been measured then the Friedel coverage is 100%. A value given as 0/100 means that although the Friedel coverage of the measurements was 100%, Friedel opposites were averaged prior to least-squares refinement to give a Friedel coverage of 0%.

Refinement software - The computer software used for the least-squares refinement. With most software the starting value of the Flack parameter is 0. However with NRCVAX, the starting value is 0.5 .

R NOLFOJ 0.003 (32)	NC	3	88	je	je	317	0	SHELXL-93	
T TIDJAR 0.05 (7)	NC	1	88	je	je	335	0	SHELXL-93	-
R QONCOL 0.02 (3)	NC	3	85	je	je	350	50	SHELXL-97	-
R XIDZIT 0.02 (2)	NC	3	95	je	je	366	50	SHELXL-93	
R ZAMBEU 0.06 (2)	NC	3	100	je	je	396	0	SHELXL93	
R NULCIG 0.04 (4)	NC	3	80	je	je	429	0	SHELXL93	-
RE NAVLIF+ 0.022 (13)	NC	3	97	a	je	621	0	SHELXL93	-
DE NAVLEB+ 0.014 (7)	NC	3	97	a	je	621	0	SHELXL93	
R RIJPEF 0.033 (13)	NC	3	92	je	je	714	0	SHELXTL	-
T LOPTOZ 0.02 (2)	NC	1	89	je	je	1099	0	SHELX-97	
Q GUJSUZ 0.005 (7)	NC	1	96	je	je	1141	0	SHELXL-97	-
R BABNAU+ 0.01 (1)	NC	3	89	je	je	1509	0	SHELXTL	-

Category B2: Pseudo-centrosymmetric structures - definitely not centrosymmetric. Friedel coverage significantly close to 100% (32 structures)

[] Refcode	S	P	Fit	Enantio		Rescat	Friedl	Refinement	
Absolute				excess			Cover	Software	
Structure				B	X				
R OFESAT 0.5 (16)	NC	3	83	je	je	4	100	SHELXL-97	-
R LIPYUE 3 (2)	NC	3	95	je	je	6	100	SHELXL-97	-
R FITNIF 1.0 (10)	NC	3	83	je	je	7	100	SHELXTL	
R MOBYOR 1.9 (6)	NC	3	92	je	je	8	100	SHELXL-97	-
R TEWXUO 1 (2)	NC	3	94	je	je	8	100	SHELXL-93	
R XADVED 0.1 (6)	NC	3	88	je	je	8	100	SHELXTL	
R QIKSIM 0.1 (2)	NC	3	92	je	je	25	100	SHELXL-97	-
R HOFLOD 0.2 (2)	NC	3	90	je	je	34	100	SHELXL93	
T AHEDUM 0.2 (4)	NC	1	87	je	je	36	85	?	
R QOFRUY 0.03 (15)	NC	3	92	je	je	36	100	SHELXL-97	
Q MAZNIK+ 0.21 (9)	NC	3	88	rac	je	38	100	SHELXL-97	

R	SECBUX	NC	3	80	je	je	39	100	SHELXL-97	
	0.1(3)									
R	HOYYEZ	NC	3	89	je	je	115	100	SHELXL-97	
	0.06(3)									
Q	DOJYAC+	NC	3	88	a	a	116	100	SHELXL-97	
	0.50(10)									
R	TECSOJ	NC	3	96	je	je	127	100	SHELXL-93	-
	0.01(3)									
T	MAKDAE+	NA	1	93	a	a	141	100	SHELXL-97	
	0.27(7)									
T	MOHMUR	NC	1	95	je	je	167	100	SHELXL-97	-
	0.06(9)									
T	LUTXAZ	NC	3	100	je	je	183	100	SHELXTL v5.10	-
	0.021(18)									
T	KAMCAD	NC	1	97	je	je	229	100	SHELXL97	
	0.05(4)									
R	JOFPVAV	NC	3	90	je	je	235	100	SHELXL-97	-
	0.012(13)									
R	IBIMUB	NC	3	96	100	100	256	100	SHELXL-97	
	0.00(4)									
R	QULQET+	NC	3	93	je	je	273	100	SHELXL-93	
	0.000(9)									
R	QULQIX+	NC	3	93	je	je	273	100	SHELXL-93	-
	0.014(13)									
R	HAZHOF+	NC	3	82	je	je	315	100	SHELXL-97	-
	0.001(8)									
T	HORNUX	NC	1	80	je	je	338	100	SHELXL-93	-
	0.04(2)									
R	TIBWUW	NC	3	87	je	je	360	100	SHELXL93	-
	0.012(14)									
T	QERRAG	NC	1	93	je	je	395	90	SHELXL-97	
	0.03(3)									
S	HUFQUU	NC	1	96	je	je	608	100	SHELXL97	
	0.04(2)									
R	LIPZEP	NC	3	100	je	je	696	100	SHELXL-97	-
	0.009(11)									
R	DUBQEW	NC	3	91	je	je	1039	100	SHELXTL	
	0.008(5)									
T	QUGQOY	NC	1	100	je	je	1320	70	SHELXTL5.1	
	0.017(10)									
R	OCARAL	NC	3	100	je	je	1391	100	SHELXL97	-
	0.006(12)									

Category C: Centrosymmetric structures - definitely not non-centrosymmetric (14 structures)

THESE STRUCTURES HAVE BEEN COPIED TO CPSNC.centro.txt

[] Refcode	S	P	Fit	Enantio	Rescat	Friedl	Refinement
Absolute				excess		Cover	Software
Structure				B	X		
T APUQEH	NC	3	100	rac	rac	162	0/61
0.31(9)							
T AXIYUB+	NA	2	100	a	a	316	60
0.11(6)							

T BAWKEQ	NC	1	100	a	a	230	51	SHELXL-97	
0.50(11)									
T CAKTUE	NC	1	100	a	a	339	100	SHELXTL v5.0.3	
0.54(6)									
T EWOJAB	NC	1	100	a	a	178	100	SHELXL-97	
0.0(9)									
T FOHYAD	NC	1	100	a	a	1214	0	SHELXTL	-
0.04(7)									
T FOLLOI+	NC	1	100	rac	rac	224	?/100	SHELXTL 5.1	
0.0(3)									
T IHIQUL	NA	3	100	a	a	1329	19	SHELXL-97	
?									
T IMOSIM+	NA	2	100	rac	rac	282	30	SHELXTL v6.10	
0.135(19)									
T MIZPIU	NC	1	89	a	a	1183	100	SHELXL-97	
0.00									
T VAPHUQ+	NA	2	100	a	a	283	0	SHELXL-93	
0.04(3)									
R VODCOG+	NC	3	94	a	a	416	100	SHELXL-97	
0.45(3)									
R XITPUL+	NC	3	92	a	a	215	0	SHELXL-97	
0.31(16)									
T XOMTIC01+	NC	1	100	a	a	301	0?	SHELXL-93	
0.04(5)									

NOTES

AXIYUB: No mention that TWIN/BASF was used in SHELXL. May be unconverged.

BABBUC: The various molecules in the crystal structure are all achiral. Without the nitrobenzene #3, the crystal structure is very nearly centrosymmetric. However there are absolutely no anomalous Uij's on nitrobenzene #3. A centrosymmetric solution would require disorder and hence anomalous Uij's in a non-centrosymmetric solution. Goldberg (principal author) in a private communication justifies the non-centrosymmetric solution by the N(Z) test, the various E statistics and the lack of high correlation parameters between atomic coordinates and adp's of possibly equivalent atoms in the alternative P-1 group. A non-centrosymmetric solution is also in line with the value of $x = 0.45(4)$ obtained with a Friedel coverage of zero (confirmed by Goldberg). With zero Friedel coverage, a centrosymmetric structure would stick at $x = 0.0$ according to our previous and current work. Even with a zero Friedel coverage, there is sufficient resonant scattering ($R_{scat} = 152$) to pull the refinement to value of x of approximately 0.5. Everybody seems hence in agreement that the crystal structure is non-centrosymmetric, and the crystal studied was twinned by inversion in an approximately 50:50 proportion. (It must be happy twist of fate that the authors measured with a Friedel coverage of zero.)

BABNAU: The original paper gives a value of Roger's eta parameter, $\eta = 1.02(2)$ which has here been converted to the corresponding value of the Flack x parameter.

BERNER: "(there are no known crystal structures incorporating two different hydrophobic amino acids with the same chirality at C α)" - Dalhus and Gorbitz's structures are all quasiracemates (i.e. different hydrophobic amino acids of different chirality at C α). According to an e-mail of 18.10.2005 from Gorbitz, the statement is still true although he is trying to find exceptions and to explain why this is the case.

DOJYAC: DOJYAC is achiral but forms a chiral crystal structure. The crystal is twinned by inversion with a 50:50 composition of the two enantiomorphs.

ENEZUS: The authors vague statement "A refinement of 4 in the centrosymmetric space group C2/c was not successful" is not to be trusted. In their list of coordinates for Cc, the Cr atom is not on one of the centres of symmetry C2/c. Moreover the value of the Flack parameter is not of much help, because they have measured with a Friedel coverage of zero.

FOLLOI: There is an incompatibility in the number of reflections reported in the paper (6628) and that in the CIF (12088). A full-sphere of reflections was measured (26940). Consequently 6628 (12088) correspond to Friedel coverages of 0 (100)% where Friedel opposites have (have not) been averaged respectively. What was used in the refinement reported is both mysterious and critical. The standard uncertainty on the Flack parameter reported in the CIF (none is given in the paper) is very high at 0.3 for a compound with a Rescat of 224.

GOGHUF: ", the assignment of the enantiomer was made. The opposite hand yielded both weighted and unweighted R's that were 0.1% higher"

HAZHOF: HAZHOF is a quasi-racemate.

HERKUK: "The absolute configuration of these alcohols was confirmed by X-ray diffraction studies." . The bulk ee refers to the cis 2-methylcyclopentanol. The single crystal study was carried out on a 3,5-dibromobenzoate derivative (radiation not indicated).

IBUJAQ: IBUJAQ is a quasi racemate. The authors state that they used TWIN/BASF. They also used TWIN/BASF on the enantiopure components of IBUJAQ; 156400: x = 0.03(7), P21, FC = 100; 156402: x = 0.00(5), P21, FC = 100.

IMOSIM: "Interestingly, in the X-ray structure of 5a there are two molecules in the asymmetric unit relating to the two optical isomers of the 'windshield wiper' fluxionality and there are no significant differences in bond lengths and angles." The choice of asymmetric unit is arbitrary when Z' = 2 and could be chosen as: A B, A ent-B, ent-A B or ent-A ent-B. No mention of TWIN/BASF. It may be unconverged.

ISOCAU: Full sphere data to 30 degrees MoKa counts 27055 reflections. A unique region of reciprocal space corresponds to 6763 reflections. This does not tie up with the authors values. Moreover the reporting has a discrepancy between the space group given in the paper Pn21a and that in the supplementary CIF from the CCDC which has P212121 in a non-standard setting. Although the number of reflections (ignoring the systematic absences) is the same for these two space groups, the

equivalent reflections are different. It is not possible to know what the authors did.

MAKDAE: No mention of TWIN/BASF so the refinement may not be converged at $x = 0.27(7)$ in which case there will be a polar dispersion error on the z coordinate of the Nb atom (Is there any indication of short or long bonds to Nb along $[001]$?). $Z = 8$ i.e. $Z' = 2$ with the two molecules roughly related by a centre of symmetry. The authors (caption Figure 2) think there are "four crystallographically distinct molecules" in this structure. Looking at the structure, the cyclohexylidene ring does not have a strong orientation along $[001]$ of the crystal structure and the crystal should probably easily twin by inversion. Another possibility that we considered was that the structure solution might be suffering from a partial polar ambiguity. The latter occurs in the structure solution of compounds with one or two heavy atoms in a sea of light atoms. Most of the structure is correct but some of it corresponds to the inverted structure. Least-squares refinement does not correct this sort of error. Our very limited experience with structure solutions suffering a partial polar ambiguity shows that they display values of the Flack parameter of ~ 0.25 . One needs the structure amplitudes and measurements on a few more crystals to know what is going on exactly in MAKDAE.

MARTOO: "The flack parameters have not been refined."

MAZNIK: MAZNIK is chiral and present as a racemate in the bulk. As the structure is clearly enantiopure, the compound must crystallize by spontaneous resolution to give a racemic conglomerate. The particular crystal used for the diffraction studies is twinned by inversion and has an overall composition of 79% of the C(7)R, C(9)S and 21% of the C(7)S, C(9)R configurations.

NAVLIF/NAVLEB: The molecules (6) and (7) are chiral and the bulk is most likely a racemate or a rapidly enantiomerizing mixture of enantiomers. In the non-centrosymmetric structure solutions presented for each compound, the two molecules in the asymmetric unit are of the SAME chirality and hence closely superposable. Modelling shows that molecules of opposite chirality do not superpose readily. We conclude that the crystal structure is enantiopure and non-centrosymmetric. The crystals measured are not twinned by inversion.

NIQHUQ: "nearly identical agreement indices"

NOKYUH/NOKYOB: NOKYUH is ent-NOKYOB, and NOKYOB is ent-NOKYUH. The original paper gives values of Roger's eta parameter, $\eta = 0.9(1)$ and $\eta = 0.8(1)$ which have here been converted to the corresponding values of the Flack x parameter.

PEXNEL: The original paper gives a value of Roger's eta parameter, $\eta = 0.86(7)$ which has here been converted to the corresponding value of the Flack x parameter.

PINFEY: "Owing to the absence of significant anomalous dispersion, the absolute configurations could not be determined reliably" N.B. Rescat = 1583.

QETJEE: "The real parameters of the unit cell are twice higher than the parameters used for the refinement procedure. While molecules in the later unit cell appeared to be disordered, the twinned unit cell contains four independent molecules without disordering. Unfortunately, the correlation between identical central fragments of these four molecules does not allow us to carry out a correct refinement." Moreover the published structure does not seem to respect the chirality of the enantiopure ester side-chain which is heavily disordered in the proposed structure.

QULQET/QULQIX: QULQET is ent-QULQIX and QULQIX is ent-QULQET.

VAPHUQ: All elements lighter than Ar but measured with CuK α

VODCOG: B&F judge this to be a very bad refinement. Of 237 non-H atoms only 6 Fe and 10 Cu were refined anisotropically. 4 molecules of DMSO out of 6 are disordered, and there are 15 molecules of water in the proposed structure. B&F are sure this structure is centrosymmetric. The value obtained for the Flack parameter agrees with the usual behaviour of a centrosymmetric structure refined as non-centrosymmetric with a Friedel coverage of 100%.

XITPUL: Disordering the MeNEt₃ cation (a very frequent phenomenon) makes the structure centrosymmetric.

XOMTIC01: "... with the Flack x parameter = 0.037(47) in accordance with an acentric group. ... Moreover, another refinement with 61 merged Friedel pairs gave fairly similar results: 286 parameters for 2609 unique data (2500 Fo > /4 u(Fo)) gave ... with the Flack x parameter = 0.036(47) .. ."