Topological Description of Pseudosymmetries in *trans*-2,3,4,5,5a,6,7,8,9,9a-Decahydro-2-methyl-4-phenylaminocarbonylbenzo[*f*][1,4]oxazepin-3-one and Other Structures which Crystallize in Space Group $P\bar{1}$ with $Z = 8$

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Abstract

The pseudosymmetries of the title compound resemble a monoclinic unit cell with space group $P112_1/a$. However, the structure of $C_{17}H_{22}N_2O_3$ was determined in a triclinic unit cell [$a = 10.500$ (4), $b = 11.617$ (3), $c = 28.622$ (3) Å, $\alpha = 83.15$ (2), $\beta = 83.41$ (4), $\gamma = 68.48$ (2)°; $V = 3215$ (2) Å^3, $Z = 8$: four molecules in the asymmetric unit] by direct methods and refined on F^2 values in space group $P\bar{1}$ to final $R[F^2 > 2\sigma(F^2)] = 0.0457$ and $wR(F^2) = 0.114$. The conformation of molecule $M1$ basically agrees with that of $M4$, whereas molecules $M2$ and $M3$ form a second group of conformers. $M1$–$M2$ and $M4$–$M3$ dimers are related by a pseudoscrew axis along the c axis and complemented by a pseudoglide plane located at $z \simeq \frac{1}{4}$ or $\frac{3}{4}$, respectively. The analysis of pseudosymmetries in the title crystal was then extended to other structures selected from 66 Cambridge Structural Database entries with $P\bar{1}$ and $Z = 8$. A topological survey of the pseudosymmetries reveals a rich variety of the *2$_1$/*c pair. In the unit cells of several crystals one or two coordinates of these types of pseudosymmetries are bound to $(2n - 1)\frac{1}{8}$ values or in their vicinity. Such operators (termed *secondary* pseudosymmetries) are accompanied by their respective complementary symmetries with translation(s) of *ca* $(2n - 1)\frac{1}{4}$. Their cooperation with *primary* pseudosymmetries (possessing standard position and translation) and with themselves seems to shed light on the origin of symmetries in crystals. These observations are also valid for a few monoclinic crystals.

1. Introduction

The X-ray analyses of the title compound (hereinafter referred to as SZ55C) together with its 4-(2-chloro- and 4-(4-chlorobenzoyl) derivatives served as a routine check of molecular geometries inferred from ^{1}H and ^{13}C NMR spectra for a series of *trans*-perhydro-1,4-benzoxazepin-3-one derivatives (Simon *et al.*, 1995). The conformation of the benzoxazepine moiety was characterized by the structure analysis of *trans*-2,3,4,5,-5a,6,7,8,9,9a-decahydro-4-(4-chlorobenzoyl)-2-methyl-

benzo[*f*][1,4]oxazepin-3-one (Simon *et al.*, 1995), while the crystal structure of its 4-(2-chlorobenzoyl) analog is reported elsewhere (Kálmán & Argay, 1996). The occurrence of space group $P\bar{1}$ (No. 2) and $Z = 8$ for the title compound prompted us to analyze the relationship between the four symmetry-independent molecules in detail along the lines of a paper by Desiraju *et al.* (1991) on pseudoinversion centers in space group $P\bar{1}$, $Z = 4$. A look at the unit cell in Fig. 1 reveals noncrystallographic symmetries between the eight molecules. In the oblique triclinic system there are rectangular symmetry relationships along and nearly perpendicular to the c axis. The molecules form two distinct groups characterized by conformers $M1$ and $M2$, respectively. Pairs are linked by a hydrogen bond of NH···O type to form four dimers. This molecular array can be regarded as pseudomonoclinic. The recognized noncrystallographic relationships are decipherable as pseudosymmetries by the use of program *BUNYIP* (Hester & Hall, 1995) and in detail by a combined coordinate midpoint and translation analysis (hereinafter referred to as CMTA).

2. Experimental

2.1. *X-ray structure determination*

The preparation of the title compound (SZ55C) has been described previously (Simon *et al.*, 1995). Data were collected on a CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation. The struc-
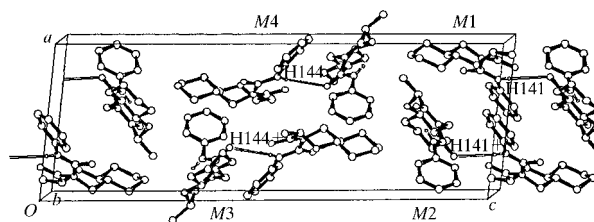

Fig. 1. A view of the full unit cell of SZ55C, showing eight molecules which form four dimers *via* hydrogen bonds of the type NH···O (the hydrogen-bond connections are labeled). The pseudosymmetries can easily be recognized along with and perpendicular to the c axis.

Table 1. *Experimental details*

Crystal data

Chemical formula	$C_{17}H_{22}N_2O_3$
Chemical formula weight	302.37
Cell setting	Triclinic
Space group	$P\bar{1}$
a (Å)	10.500 (4)
b (Å)	11.617 (3)
c (Å)	28.622 (3)
α (°)	83.15 (2)
β (°)	83.41 (2)
γ (°)	68.48 (2)
V (Å^3)	3215.0 (15)
Z	8
D_x (Mg m^{-3})	1.249
Radiation type	Cu $K\alpha$
Wavelength (Å)	1.5418
No. of reflections for cell parameters	25
θ range (°)	14.71–18.64
μ (mm^{-1})	0.697
Temperature (K)	293 (2)
Crystal form	Block
Crystal size (mm)	$0.4 \times 0.12 \times 0.07$
Crystal color	Colorless

Data collection

Diffractometer	Enraf–Nonius CAD-4
Data collection method	ω–θ scans
Absorption correction	ψ scans (Reibenspies, 1989)
T_{min}	0.854
T_{max}	1.000
No. of measured reflections	14504
No. of independent reflections	13406
No. of observed reflections	8097
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.0115
θ_{max} (°)	75.87
Range of h, k, l	$0 \rightarrow h \rightarrow 13$
	$-13 \rightarrow k \rightarrow 14$
	$-35 \rightarrow l \rightarrow 35$
No. of standard reflections	3
Frequency of standard reflections	Every 60 min
Intensity decay (%)	1

Refinement

Refinement on	F^2
$R[F^2>2\sigma(F^2)]$	0.0457
$wR(F^2)$	0.1137
S	0.978
No. of reflections used in refinement	13 402
No. of parameters used	799
H-atom treatment	Riding
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0662P)^2 + 0.8632P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	-0.004
$\Delta\rho_{max}$ (e Å^{-3})	0.188
$\Delta\rho_{min}$ (e Å^{-3})	-0.184
Extinction method	$SHELXL$93 (Sheldrick, 1993)
Extinction coefficient	0.00188 (13)
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Computer programs

Data collection	*CAD*-4 *EXPRESS* (Enraf–Nonius, 1994)

Table 1 (*cont.*)

Cell refinement	*CAD*-4 *EXPRESS*
Data reduction	*XCAD*4 (Harms, 1996)
Structure solution	*SHELXS*86 (Sheldrick, 1990)
Structure refinement	*SHELXL*93 (Sheldrick, 1993)

ture was solved with the program *SHELXS*86 (Sheldrick, 1990) in a triclinic unit cell (Table 1). A careful check of the intensity distribution in reciprocal space excluded any successful unit-cell transformation into higher symmetry systems. The structure was then refined on F^2 values with the program *SHELXL*93 (Sheldrick, 1993). Further details of the refinement are summarized in Table 1. Fig. 1 shows a packing diagram, while the atomic coordinates are listed in Table 2.

2.2. *Symmetry analysis using BUNYIP (Hester & Hall, 1995)*

The eight molecules in the triclinic unit cell of SZ55C (Fig. 1) form two subgroups distinguished by a similar conformation between molecules $M1$ and $M4$, and between $M2$ and $M3$, respectively. Their conformational difference is depicted in Fig. 2 by the $M1/M2$ pair. The molecules form dimers, *via* NH$\cdots$O$=$C hydrogen bonds, in which $M1$ and $M4$ are the donors, while $M2$ and $M3$ act exclusively as acceptors.

Between molecules $M4$ and $M1$ (the latter taken automatically with the coordinates $x, y, z-1$), the program *BUNYIP* (Hester & Hall, 1995) found a twofold screw axis approximately parallel to the crystallographic c axis, as described by equation (i) listed in Table 3 and displaced from the origin by $0.77a$ and $0.53b$. Its mean midpoint deviation is $\nabla_1 = 0.020$ (15), while the mean translation of 14.010 (17) Å is close to $c/2 = 14.311$ (3) Å. In the next step $M\bar{4}$ and $M1$ (the latter taken automatically with the coordinates $x-1, y, z$) were found to be related by a glide plane described by equation (ii) in Table 3. The corresponding midpoint deviation is $\nabla_2 = 0.0026$ (23), but is accompanied by a mean translation of 4.051 (61) Å, which differs from half of the shortest crystal axis $a/2 = 5.250$ (4) Å. Application of *BUNYIP* (Hester & Hall, 1995) for molecules $M2$ and $M\bar{3}$ also revealed a glide plane, but its mean translation along axis a was found to be only 3.965 (33) Å (76% of $a/2$).

3. Discussion

3.1. *Study of symmetry displacements in the title crystal SZ55C*

At the outset it should be noted that in space group $P\bar{1}$ any new point $p(x'y'z')$ generated by a pseudosymmetry† *S_j to $p(xyz)$ automatically implies a second

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† The pseudosymmety operators are distinguished by the label * preceeding the operator symbol.

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for SZ55C*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O11	0.8176 (2)	0.77392 (15)	0.92455 (6)	0.0507 (4)
C21	0.9026 (2)	0.7012 (2)	0.96115 (8)	0.0444 (5)
C31	0.8609 (2)	0.5882 (2)	0.97590 (8)	0.0424 (5)
N41	0.8756 (2)	0.5106 (2)	0.94121 (6)	0.0426 (4)
C51	0.9604 (2)	0.5194 (2)	0.89648 (8)	0.0490 (6)
C5a1	0.8898 (2)	0.6280 (2)	0.86234 (8)	0.0503 (6)
C61	0.9638 (3)	0.6137 (3)	0.81290 (9)	0.0658 (7)
C71	0.8843 (4)	0.7165 (3)	0.77826 (10)	0.0800 (9)
C81	0.8576 (4)	0.8436 (3)	0.79417 (10)	0.0852 (10)
C91	0.7941 (3)	0.8574 (3)	0.84478 (10)	0.0718 (8)
C9a1	0.8794 (2)	0.7520 (2)	0.87726 (8)	0.0506 (6)
C101	0.8799 (3)	0.7810 (2)	1.00142 (9)	0.0580 (6)
O111	0.8127 (2)	0.5724 (2)	1.01605 (5)	0.0547 (4)
C121	0.8065 (2)	0.4244 (2)	0.94311 (8)	0.0452 (5)
O131	0.8048 (2)	0.3784 (2)	0.90729 (6)	0.0669 (5)
N141	0.7463 (2)	0.4005 (2)	0.98536 (7)	0.0465 (4)
C151	0.6750 (2)	0.3164 (2)	0.99438 (8)	0.0441 (5)
C161	0.7141 (3)	0.2076 (2)	0.97226 (10)	0.0579 (6)
C171	0.6445 (3)	0.1260 (3)	0.98500 (12)	0.0758 (9)
C181	0.5381 (3)	0.1525 (3)	1.01931 (13)	0.0785 (9)
C191	0.4985 (3)	0.2605 (3)	1.04094 (11)	0.0675 (8)
C201	0.5656 (2)	0.3435 (2)	1.02849 (9)	0.0509 (6)
O12	0.5719 (2)	0.3438 (2)	0.79064 (6)	0.0555 (4)
C22	0.6461 (2)	0.4059 (2)	0.81032 (9)	0.0535 (6)
C32	0.5458 (2)	0.5321 (2)	0.82393 (9)	0.0505 (6)
N42	0.4438 (2)	0.5320 (2)	0.85913 (6)	0.0441 (4)
C52	0.4459 (3)	0.4135 (2)	0.88578 (8)	0.0479 (5)
C5a2	0.4078 (2)	0.3308 (2)	0.85720 (8)	0.0466 (5)
C62	0.3588 (3)	0.2382 (3)	0.88945 (10)	0.0655 (7)
C72	0.3157 (3)	0.1583 (3)	0.86114 (12)	0.0792 (9)
C82	0.4290 (4)	0.0930 (3)	0.82559 (13)	0.0873 (10)
C92	0.4819 (3)	0.1827 (3)	0.79377 (11)	0.0767 (9)
C9a2	0.5246 (3)	0.2617 (2)	0.82280 (9)	0.0526 (6)
C102	0.7540 (3)	0.4196 (3)	0.77229 (12)	0.0782 (9)
O112	0.5547 (2)	0.6276 (2)	0.80326 (7)	0.0723 (6)
C122	0.3254 (2)	0.6380 (2)	0.87008 (8)	0.0441 (5)
O132	0.2351 (2)	0.62561 (15)	0.89867 (6)	0.0551 (4)
N142	0.3220 (2)	0.7474 (2)	0.84747 (7)	0.0525 (5)
C152	0.2112 (2)	0.8619 (2)	0.85322 (8)	0.0472 (5)
C162	0.1482 (3)	0.8951 (2)	0.89701 (9)	0.0578 (6)
C172	0.0425 (3)	1.0077 (3)	0.90129 (11)	0.0694 (8)
C182	−0.0012 (3)	1.0871 (3)	0.86192 (12)	0.0727 (8)
C192	0.0621 (3)	1.0552 (3)	0.81836 (11)	0.0679 (8)
C202	0.1683 (3)	0.9426 (2)	0.81382 (9)	0.0583 (6)
O13	0.0058 (2)	0.78798 (14)	0.30074 (5)	0.0458 (4)
C23	−0.0735 (2)	0.7135 (2)	0.31902 (8)	0.0450 (5)
C33	0.0222 (2)	0.5790 (2)	0.32890 (8)	0.0437 (5)
N43	0.1132 (2)	0.5570 (2)	0.36320 (6)	0.0413 (4)
C53	0.1036 (2)	0.6571 (2)	0.39221 (7)	0.0448 (5)
C5a3	0.1515 (2)	0.7568 (2)	0.36567 (8)	0.0452 (5)
C63	0.1916 (3)	0.8279 (2)	0.39941 (10)	0.0639 (7)
C73	0.2423 (4)	0.9252 (3)	0.37335 (13)	0.0853 (10)
C83	0.1370 (4)	1.0144 (3)	0.34170 (12)	0.0887 (11)
C93	0.0937 (3)	0.9457 (3)	0.30812 (10)	0.0712 (8)
C9a3	0.0439 (3)	0.8477 (2)	0.33477 (8)	0.0466 (5)
C103	−0.1697 (2)	0.7232 (2)	0.28254 (11)	0.0676 (8)
O113	0.0188 (2)	0.4974 (2)	0.30654 (7)	0.0627 (5)
C123	0.2285 (2)	0.4443 (2)	0.37064 (8)	0.0425 (5)
O133	0.3075 (2)	0.43836 (15)	0.39961 (6)	0.0551 (4)
N143	0.2421 (2)	0.3514 (2)	0.34450 (7)	0.0501 (5)
C153	0.3519 (2)	0.2349 (2)	0.34758 (9)	0.0477 (5)
C163	0.3937 (3)	0.1723 (2)	0.39032 (10)	0.0597 (7)
C173	0.4977 (3)	0.0582 (3)	0.39187 (12)	0.0722 (8)

Table 2 (*cont.*)

	x	y	z	U_{eq}
C183	0.5611 (3)	0.0053 (3)	0.35123 (13)	0.0810 (9)
C193	0.5201 (3)	0.0667 (3)	0.30841 (13)	0.0848 (10)
C203	0.4163 (3)	0.1827 (3)	0.30625 (10)	0.0658 (7)
O14	0.7161 (2)	0.28366 (15)	0.41286 (5)	0.0510 (4)
C24	0.6152 (2)	0.3299 (2)	0.45090 (8)	0.0455 (5)
C34	0.6458 (2)	0.4339 (2)	0.47003 (8)	0.0424 (5)
N44	0.6412 (2)	0.5345 (2)	0.43820 (6)	0.0435 (4)
C54	0.5745 (2)	0.5528 (2)	0.39369 (8)	0.0478 (5)
C5a4	0.6622 (2)	0.4690 (2)	0.35621 (8)	0.0481 (6)
C64	0.6080 (3)	0.5153 (3)	0.30745 (8)	0.0620 (7)
C74	0.7052 (3)	0.4384 (3)	0.27011 (9)	0.0743 (9)
C84	0.7290 (3)	0.3021 (3)	0.28080 (10)	0.0790 (9)
C94	0.7721 (3)	0.2544 (3)	0.33097 (10)	0.0673 (7)
C9a4	0.6722 (2)	0.3355 (2)	0.36657 (8)	0.0507 (6)
C104	0.6257 (3)	0.2240 (2)	0.48815 (9)	0.0584 (6)
O114	0.6779 (2)	0.4240 (2)	0.51035 (5)	0.0539 (4)
C124	0.7059 (2)	0.6207 (2)	0.44329 (8)	0.0467 (5)
O134	0.7145 (2)	0.6936 (2)	0.40998 (6)	0.0717 (6)
N144	0.7531 (2)	0.6148 (2)	0.48560 (7)	0.0479 (5)
C154	0.8227 (2)	0.6899 (2)	0.49733 (8)	0.0468 (5)
C164	0.7933 (3)	0.8121 (2)	0.47936 (11)	0.0649 (7)
C174	0.8622 (4)	0.8807 (3)	0.49464 (14)	0.0862 (10)
C184	0.9565 (4)	0.8311 (3)	0.52734 (14)	0.0865 (10)
C194	0.9860 (3)	0.7096 (3)	0.54531 (11)	0.0706 (8)
C204	0.9203 (2)	0.6391 (2)	0.53013 (9)	0.0518 (6)

operation (*S_k), which then brings this point perfectly into $p(\bar{x}y\bar{z})$. If a full molecule is generated in such a way then the mismatching of *S_j for the individual atomic pairs as a whole is perfectly matched by the second operation *S_k generated by

$$^*S_j \leftrightarrow \bar{1}(0, 0, 0) \equiv {}^*S_k, \qquad (1)$$

where $\leftrightarrow$ indicates that the operators in the symmetry triplet are commutative. Since *BUNYIP* (Hester & Hall, 1995) found the pseudosymmetries with translations substantially shorter than $\frac{1}{2}$, the results have been complemented by the calculation of coordinate midpoints $\{\mu_x = [x(\mathbf{a}) + x(\mathbf{b})]/2 \ etc.\}$ and the corresponding coordinate differences $[\tau_x = x(\mathbf{a}) - x(\mathbf{b}) \ etc.]$. These manual calculations have been developed into a combined coordinate midpoint and translation analysis (CMTA). They have shown strong correlations between the positions of pseudosymmetries (*S_j) and the translations of the complementary operators (*S_k), as defined by (1) above. Distributions of the midpoint coordinates reveal the mismatches created by *S_j and together with the corresponding coordinate differences help to recognize the complementary *S_k. Their displacements from the standard positions $(0, \pm\frac{1}{4}, \pm\frac{1}{4})$ are denoted by δ^x, δ^y and δ^z, whereas Δ^x, Δ^y and Δ^z refer to deviations from the crystallographic translations, either $\pm\frac{1}{2}$ and/or zero.

As shown by Fig. 1 molecules of SZ55C are scattered on two separate orbits of noncrystallographic symmetries. Molecular pairs *M1/M4* and *M2/M3* are ostensibly related by a twofold screw axis (*S_j) taken at $(\frac{1}{4}, \frac{1}{2}, z)$ or $(\frac{3}{4}, \frac{1}{2}, z)$. They are complemented by glide planes (*S_k)

between $M1/M\bar{4}$ and $M\bar{2}/M3$ at $(x, y, \frac{1}{4})$ and $(x, y, \frac{3}{4})$, respectively. A scattergram of the coordinate midpoints μ_x/μ_y (Fig. 3) for the 44 non-H atoms of the $M1/M4$ and $M\bar{2}/M\bar{3}$ pairs gives $y = 0.5885x + 0.4535$, with a high regression coefficient (0.995). Separately, the μ_x/μ_y plots give somewhat lower regression coefficients [$R = 0.980$ ($M1/M4$) and 0.968 ($M\bar{2}/M\bar{3}$)], which suggests that the molecules (donor and acceptor) bound together in dimers are related by the same symmetry axis ($*S_j$). The mean differences in the z coordinates [$\langle \tau_z \rangle = 0.503$ (7) for $M1/M4$ and 0.497 (8) for $M\bar{2}/M\bar{3}$] definitely refer to a screw axis. This makes an angle of ca 11° with axis c at $\sim (\frac{3}{4}, \frac{1}{2}, 0)$ and the N14—H14 donor group (from $M1/M4$) is located quite close to this crossing point. However, several μ_x/μ_y pairs, in particular for O13 ($M1/M4$), show substantial displacements (δ^x and δ^y) from the line shown in Fig. 3, indicating an imperfect symmetry rela-

Table 3. *Least-squares equations generated by BUNYIP (Hester & Hall, 1995) for the noncrystallographic symmetries revealed in SZ55C*

Equation (i): $-0.2066x - 0.3318y + z = 0$
Equation (ii): $-0.1727x - 0.3405y + z = 20.949$
Equation (iii): $-0.1762x - 0.3304y + z = 0$
Equation (iv): $-0.1671x - 0.3118y + z = 21.012$

tionship between the related molecules. This can be attributed to small, but visible conformational differences between these molecules, *e.g.* C5—N4–C12—O13 −7.3 (3)° for $M1$ *versus* −10.1 (3)° for $M4$.

The complementary glide plane ($*S_k$) bisects the c axis at $z \simeq \frac{1}{4}$ or $\frac{3}{4}$ (Fig. 1). The orientation of this symmetry plane to axes a and b may be calculated from the coordinate midpoints μ_x/μ_y for $M2/M\bar{3}$ and $M1/M\bar{4}$ molecular pairs. As required by (1), each δ^z displacement along axis c is perfectly matched by the shift of the related atom along the screw axis. The deviation from $\frac{1}{2}$ is measured by $\Delta^z = -2\delta^z$. This observation is also valid for the mean $\langle \delta^z \rangle$ of the total 44 non-H atomic pairs and it is equal to half of the mean $\langle \Delta^z \rangle$. Similarly, each displacement (δ^x and δ^y) of the screw axis ($*S_j$) from $x = \frac{3}{4}$, $y = \frac{1}{2}$ is also perfectly compensated in the x and y coordinates of $M\bar{4}$ by the complementary operation $*S_k$. Rather than $\tau_x = \frac{1}{2}$ and $\tau_y = 0$, the related atoms are separated by $\tau_x = \frac{1}{2} + \Delta^x$ and $\tau_y = \Delta^y$.

To summarize, in the triclinic unit cell of SZ55C there are eight molecules which form four dimers. These dimers are generated by the same pseudosymmetry, $*2_1/*a$. The imperfectness of these symmetries is summarized in Table 4(a). The mean displacements $\langle \delta^i \rangle$ ($i = x$, y or z) of the $*2_1$ and $*a$ operators can be calculated directly for the molecular pairs $M1/M4$ or $M2/M3$ by using (2a)–(2c), where N is the number (44) of the atomic pairs (excluding H atoms)
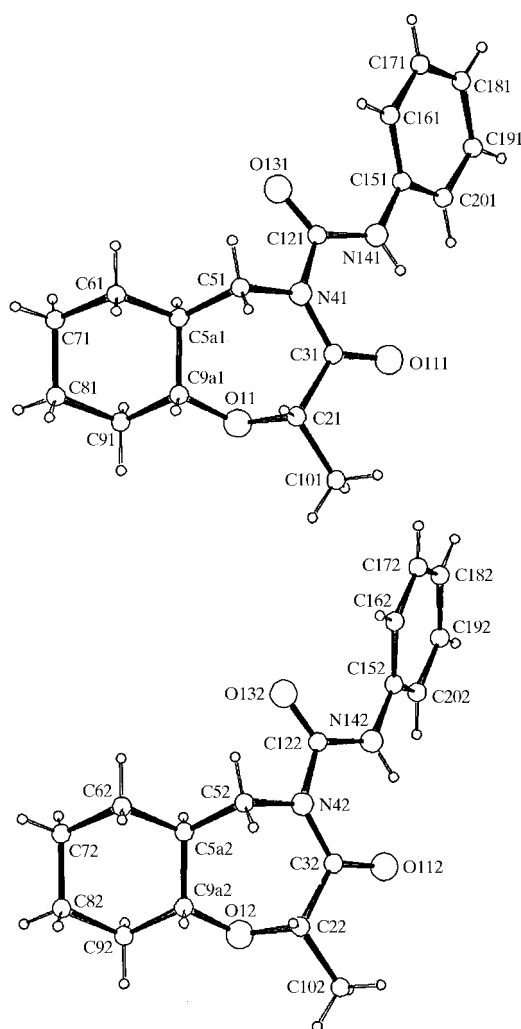

Fig. 2. Perspective view of SZ55C molecules, showing their conformational differences. They are represented by $M1$ and $M2$ differing visibly from each other.
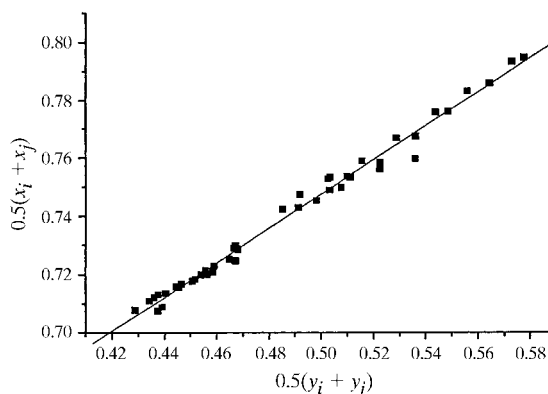

Fig. 3. A plot of the midpoint coordinates $\mu_x = \frac{1}{2}(x_i + x_j)$ against $\mu_y = \frac{1}{2}(y_i + y_j)$ values for the 44 non-H atoms with a regression coefficient of 0.995. The two molecular pairs $M1/M4$ and $M2/M3$ form two separate groups. The lower cluster belongs to $M2/M3$.

Table 4. *Coordinate midpoint and translation analysis of SZ55C crystals and the closely related BOKXII*

For both structures only the two related atomic pairs (1:4 and 2:3) are listed. Each related pair is represented by five rows of data. The mean midpoint values $\langle\mu_i\rangle$ and mean translations $\langle\tau_i\rangle$ are listed in colums 2–4 and 5–7, respectively. Their σ_{n-1} values are given in the subsequent rows. The idealized symmetry operators $*S_j$ and $*S_k$ are listed in colums 8 and 9. The fifth row of each pair gives the δ^i displacements (columns 2–4) from the idealized positions and Δ^i deviations (columns 5–7) from the canonical translations. The effective translations are in bold.

	$\langle\mu_x\rangle$	$\langle\mu_y\rangle$	$\langle\mu_z\rangle$	$\langle\tau_x\rangle$	$\langle\tau_y\rangle$	$\langle\tau_z\rangle$	$*S_j$	$*S_k$
(a) SZ55C								
1:4	0.762	0.524	—	—	—	**0.503**		$*2_1(\frac{3}{4},\frac{1}{2},z)$
σ_{n-1}	0.016	0.027	—	—	—	0.007		
$1:\bar{4}$	—	—	0.752	**0.524**	0.048	—	$*a(x,y,\frac{3}{4})$	
σ_{n-1}	—	—	0.004	0.032	0.054	—		
$\delta^i\|\Delta^i$	0.012	0.024	0.002	0.024	0.048	0.003		
2:3	0.282	0.550	—	—	—	**0.497**		$*2_1(\frac{1}{4},\frac{1}{2},z)$
σ_{n-1}	0.007	0.012	—	—	—	0.009		
$2:\bar{3}$	—	—	0.248	**0.563**	1.099	—	$*a(x,y,\frac{1}{4})$	
σ_{n-1}	—	—	0.004	0.014	0.024	—		
	0.032	0.050	0.002	0.063	0.099	0.003		
(b) BOKXII								
1:4	—	0.276	—	**0.505**	—	0.002	$*a(x,\frac{1}{4},z)$	
σ_{n-1}	—	0.020	—	0.004	—	0.002		
$1:\bar{4}$	0.248	—	0.499	—	**0.552**	—		$*2_1(\frac{1}{4},y,\frac{1}{2})$
σ_{n-1}	0.002	—	0.001	—	0.039	—		
$\delta^i\|\Delta^i$	0.002	0.026	0.001	0.005	0.052	0.002		
2:3	—	0.337	—	**0.513**	—	0.003	$*a(x,\frac{1}{3},z)$	
σ_{n-1}	—	0.018	—	0.012	—	0.004		
$2:\bar{3}$	0.757	—	0.502	—	**0.674**	—	$\tau=\frac{2}{3}$	$*2_\tau(\frac{3}{4},y,\frac{1}{2})$
σ_{n-1}	0.006	—	0.002	—	0.007	—		
$\delta^i\|\Delta^i$	0.007	0.004	0.002	0.013	0.007	0.031		

$$\langle\delta^x\rangle = -\Sigma[x(M1) + x(M4) - 1.5]/2N \quad (2a)$$

$$\langle\delta^y\rangle = -\Sigma[y(M1) + y(M4) - 1.0]/2N \quad (2b)$$

$$\langle\delta^z\rangle = -\Sigma[z(M1) + z(M\bar{4}) - 1.0]/2N. \quad (2c)$$

Thus, the triclinic unit cell of SZ55C incorporating four dimers can be regarded as pseudomonoclinic with space group $P112_1/a$.

This result has raised the following questions:

(a) Are there other structures in space group $P\bar{1}$ with $Z = 8$ possessing similar imperfect noncrystallographic symmetries?

(b) If yes, are such structures characterized by similarly imperfect pseudosymmetries?

3.2. Database investigation

These questions have been answered using the Cambridge Structural Database (CSD, April 1996 release; Allen & Kennard, 1993). A data search, apart from 19 structures solved in nonstandard forms of the centered triclinic space group ($A\bar{1}$, $C\bar{1}$, $F\bar{1}$ and $I\bar{1}$), revealed 66 entries with four molecules in the asymmetric unit. Seven entries, BOKXII, CIJSAP, DIYMED, EXCHLN, FURACL, JIFZUT and KUGWUE, were reported with some reference to the presence of pseudosymmetries. Six structures, owing to the lack of atomic coordinates, were unsuitable for further consideration; five crystals were formed by dimers and tetramers, whereas six structures were built up by substantially different conformers. Six structures, BIZVEL,

CMABOX10, DENDAB, DEPRIZ, GEGDOL10 and ZZZEIG01, are characterized as possessing 'hypersymmetries' (Zorky & Dashevskaya, 1993). In connection with such phenomena, Zorky & Dashevskaya (1993) and recently Zorky (1996) emphasized that the recognition of 'hypersymmetries' needs special skill. According to them, hypersymmetry in general is not identical to pseudosymmetry and 'the detection of HS operations in a crystal of known structure demands special calculations'. To avoid confusion, the structures labeled by 'hypersymmetry' were omitted from our present work. Similarly, the 22 metal complexes have also been ignored, for the present.

Finally, there are 14 crystal structures (BUDTEZ, DILFEJ, FAPXAV, FOBJUB01, GAFBUK, HAVGAM, HEFCAW, JAHGOO, KUJZOE, TAPDOD, VARCOG, VEWBII, YIHHOM and ZEPCEC) which were reported without any note on noncrystallographic symmetries. They were also subjected to CMTA. Of course, each structure was also checked for the possibility of a transformation into a unit cell of higher (e.g. monoclinic) symmetry, using the program *LePage* (Spek, 1988). Only four crystal structures could be transformed into centered monoclinic unit cells (*vide infra*).

3.3. Principles of coordinate midpoint and translation analysis (CMTA)

First the seven structures BOKXII, CIJSAP, DIYMED, EXCHLN, FURACL, JIFZUT and

Table 5. *Full coordinate midpoint and translation analysis of crystal EXCHLN*

Two times six pairs formed from the eight molecules in the triclinic unit cell are listed. The effective translations are in bold.

EXCHLN	$\langle\mu_x\rangle$	$\langle\mu_y\rangle$	$\langle\mu_z\rangle$	$\langle\tau_x\rangle$	$\langle\tau_y\rangle$	$\langle\tau_z\rangle$	$*S_j$	$*S_k$
1:2	—	—	—	**0.107**	**0.226**	**0.724**		$\Delta t(0,\frac{1}{4},\frac{3}{4})$
σ_{n-1}	—			0.032	0.054	0.086		
1:$\bar{2}$	0.054	0.113	0.362	—	—	—	$*\bar{1}(0,\frac{1}{8},\frac{3}{8})$	
σ_{n-1}	0.028	0.024	0.043	—	—	—		
$\delta^i|\Delta^i$	0.054	0.012	0.013	0.107	0.024	0.026		
1:3	0.284	—	—	—	**0.248**	**0.169**	$*d(\frac{1}{4},y,z)$	$\tau=\frac{1}{4},\frac{1}{4}$
σ_{n-1}	0.037	—	—	—	0.024	0.096		
1:$\bar{3}$	—	0.124	0.084	**0.568**	—	—		$*2_1(x,\frac{1}{8},\frac{1}{8})$
σ_{n-1}	—	0.029	0.048	0.074	—	—		
$\delta^i|\Delta^i$	0.034	0.001	0.041	0.068	0.002	0.081		
1:4	0.286	—	—	—	0.020	**0.489**	$*c(\frac{1}{4},y,z)$	
σ_{n-1}	0.024	—	—	—	0.003	0.002		
1:$\bar{4}$	—	0.010	0.245	**0.571**	—	—		$*2_1(x,0,\frac{1}{4})$
σ_{n-1}	—	0.002	0.001	0.049	—	—		
$\delta^i|\Delta^i$	0.036	0.010	0.005	0.071	0.020	0.011		
2:3	0.338	—	—	—	0.023	**0.555**	$*c(\frac{1}{3},y,z)$	
σ_{n-1}	0.019	—	—	—	0.015	0.098		
2:$\bar{3}$	—	0.011	0.278	**0.675**	—	—	$\tau=\frac{2}{3}$	$*2_\tau(x,0,\frac{1}{4})$
σ_{n-1}	—	0.007	0.049	0.038	—	—		
$\delta^i|\Delta^i$	0.005	0.011	0.028	0.008	0.023	0.055		
2:4	0.339	—	—	—	**0.206**	**0.234**	$*d(\frac{1}{3},y,z)$	$\tau=\frac{1}{4},\frac{1}{4}$
σ_{n-1}	0.014	—	—	—	0.048	0.087		
2:$\bar{4}$	—	0.103	0.117	**0.678**	—	—	$\tau=\frac{2}{3}$	$*2_\tau(x,\frac{1}{8},\frac{1}{8})$
σ_{n-1}	—	0.024	0.044	0.028	—	—		
$\delta^i|\Delta^i$	0.006	0.022	0.008	0.011	0.044	0.016		
3:4	—	—	—	**0.003**	**0.229**	**0.321**		$\Delta t(0,\frac{1}{4},\frac{1}{4})$
σ_{n-1}	—	—	—	0.038	0.056	0.096		
3:$\bar{4}$	0.002	0.114	0.161	—	—	—	$*\bar{1}(0,\frac{1}{8},\frac{1}{8})$	
σ_{n-1}	0.019	0.028	0.048	—	—	—		
$\delta^i|\Delta^i$	0.002	0.011	0.036	0.003	0.021	0.071		

KUGWUE, then the 14 listed above, were carefully checked by a comparative analysis of the coordinate midpoints (μ_x, μ_y, μ_z) and by the differences (τ_x, τ_y, τ_z), calculating their mean values for 12 genuine pairs of the eight molecules. Namely, the eight molecules are bound by 56 relationships (like Patterson vectors), 44 of which are redundant. The remaining 12 can be listed in two subgroups: (*a*) 1:2, 1:3, 1:4, 2:3, 2:4, 3:4 and (*b*) 1:$\bar{2}$, 1:$\bar{3}$, 1:$\bar{4}$, 2:$\bar{3}$, 2:$\bar{4}$, 3:$\bar{4}$. Accordingly, if we let 1:2 in subgroup (*a*) reveal the symmetry $*S_j$, then its complementary set 1:$\bar{2}$ in subgroup (*b*) must give information on $*S_k$. The presence of $*S_j$ or $*S_k$ is well indicated by the low σ_{n-1} of the mean values† calculated for each column of the coordinate midpoints and differences of the related atoms. In subgroup (*a*) for the midpoint columns:

(*A*) three low σ_{n-1} values suggest a center of symmetry,

(*B*) two low σ_{n-1} values indicate a twofold rotor, and

(*C*) one low σ_{n-1} value, in general, can be attributed to the presence of a mirror.

If one of these conclusions is correct then the corresponding pair in subgroup (*b*) exhibits the complementary relationships:

(*A*′) all three mean $\langle\tau_x\rangle$, $\langle\tau_y\rangle$, $\langle\tau_z\rangle$ translations have low σ_{n-1} values,

† $\sigma_{n-1} = [\Sigma\Delta^2/(n-1)]^{1/2}$, where $\Delta = [(\Sigma x^2/n)^{1/2} - x]$.

(*B*′) two columns of translations with low σ_{n-1} values are accompanied by one midpoint column possessing a low σ_{n-1} value, and

(*C*′) one column of translations with low σ_{n-1} value is accompanied by two midpoint columns possessing low σ_{n-1} values.

Within the A/A', B/B' and C/C' cases the $\langle\Delta^x\rangle = \langle-2\delta^x\rangle$, $\langle\Delta^y\rangle = \langle-2\delta^y\rangle$ and $\langle\Delta^z\rangle = \langle-2\delta^z\rangle$ conditions are perfectly satisfied.

The results of CMTA calculations are listed in Tables 4–6 for SZ55C, BOKXII, EXCHLN and KUGWUE only. The $\langle\tau_x\rangle$, $\langle\tau_y\rangle$ and $\langle\tau_z\rangle$ translations in columns 4–6 are the mean coordinates of the 'satellite' Patterson vectors, which describe the character of the symmetry operators formed between two more or less perfectly related molecules. To reveal the topological relationship between the eight molecules a *cube* can be drawn, each corner of which represents one molecule. On such a sketch each edge or plane diagonal represents a pseudosymmetry, while the body diagonals are equal to the crystallographic inversion center taken in the Wyckoff positions (*a*)–(*h*). From this it follows that each of the six {110} body diagonal planes is an orbit of four molecules, *e.g.* 1, 2, $\bar{1}$ and $\bar{2}$, denoted hereinafter by {1:2}, and bordered either by two pairs of pseudorotors and mirrors or pseudoinversion centers and their doubled translations from the closest Wyckoff position. Triangles,

Table 6. *Full coordinate midpoint and translation analysis of crystal KUGWUE*

Two times six pairs formed from the eight molecules in the triclinic unit cell are listed. The effective translations are in bold.

KUGWUE	$\langle\mu_x\rangle$	$\langle\mu_y\rangle$	$\langle\mu_z\rangle$	$\langle\tau_x\rangle$	$\langle\tau_y\rangle$	$\langle\tau_z\rangle$	$*S_j$	$*S_k$
1:2	0.238	0.124	0.121	—	—	—	$*\bar{1}(\frac{1}{4},\frac{1}{8},\frac{1}{8})$	
σ_{n-1}	0.009	0.002	0.005	—	—	—		
1:$\bar{2}$	—	—	—	**0.475**	**0.247**	**0.242**		$\Delta t(\frac{1}{2},\frac{1}{4},\frac{1}{4})$
σ_{n-1}	—	—	—	0.018	0.005	0.010		
$\delta^i\vert\Delta^i$	0.012	0.001	0.004	0.025	0.003	0.008		
1:3	0.252	—	0.372	—	**0.497**	—		$*2_1(\frac{1}{4},y,\frac{3}{8})$
σ_{n-1}	0.002	—	0.001	—	0.016	—		
1:$\bar{3}$	—	0.248	—	**0.504**	—	**0.746**	$*n_q(x,\frac{1}{4},z)$	$q=\frac{3}{4}$
σ_{n-1}	—	0.008	—	0.004	—	0.003		
$\delta^i\vert\Delta^i$	0.002	0.002	0.002	0.004	0.003	0.004		
1:4	—	0.374	—	0.019	—	**0.504**	$*c(x,\frac{3}{8},z)$	
σ_{n-1}	—	0.010	—	0.014	—	0.006		
1:$\bar{4}$	0.009	—	0.252	—	**0.749**	—	$q=\frac{3}{4}$	$*2_q(0,y,\frac{1}{4})$
σ_{n-1}	0.007	—	0.003	—	0.019	—		
$\delta^i\vert\Delta^i$	0.009	0.001	0.002	0.019	0.001	0.004		
2:3	—	0.372	—	0.029	—	**0.504**	$*c(x,\frac{3}{8},z)$	
σ_{n-1}	—	0.006	—	0.015	—	0.010		
2:$\bar{3}$	0.015	—	0.252	—	**0.744**	—	$q=\frac{3}{4}$	$*2_q(0,y,\frac{1}{4})$
σ_{n-1}	0.007	—	0.005	—	0.012	—		
$\delta^i\vert\Delta^i$	0.015	0.003	0.002	0.029	0.006	0.004		
2:4	0.247	—	0.373	—	**0.501**	—		$*2_1(\frac{1}{4},y,\frac{3}{8})$
σ_{n-1}	0.003	—	0.003	—	0.015	—		
2:$\bar{4}$	—	0.251	—	**0.494**	—	**0.746**	$*n_q(x,\frac{1}{4},z)$	$q=\frac{3}{4}$
σ_{n-1}	—	0.008	—	0.005	—	0.007		
$\delta^i\vert\Delta^i$	0.003	0.001	0.002	0.006	0.001	0.004		
3:4	0.262	0.622	0.625	—	—	—	$*\bar{1}(\frac{1}{4},\frac{5}{8},\frac{5}{8})$	
σ_{n-1}	0.005	0.018	0.028	—	—	—		
3:$\bar{4}$	—	—	—	**0.523**	**0.245**	**0.250**		$\Delta t(\frac{1}{2},\frac{1}{4},\frac{1}{4})$
σ_{n-1}	—	—	—	0.010	0.004	0.005		
$\delta^i\vert\Delta^i$	0.012	0.003	0.000	0.023	0.005	0.000		

assigned to any of the six (practically three) {100} planes, represent a *triplet* of three related pseudosymmetries. Further triplets of pseudosymmetries can also be assigned to the four {111} planes. Sketches of a cube of pseudosymmetries (hereinafter referred to as CPS) can be drawn quickly. In general, pseudoinversion centers are represented by plane diagonals on the top of the CPS. The CPS sketches drawn from the symmetry operators listed in Tables 4–6 and other CMTA calculations (*e.g.* YIHHOM *etc.*) helped to visualize all the relationships between the discovered forms of the pseudosymmetries.

3.4. *Selected examples*

If molecules assume substantially different conformations in the asymmetric unit then no pseudosymmetries can be assigned to them (*cf.* FIMJUG, FODYEC, KEPKOF, PADCEC, VOLFOR and YABWEB). However, when molecules retain some conformational
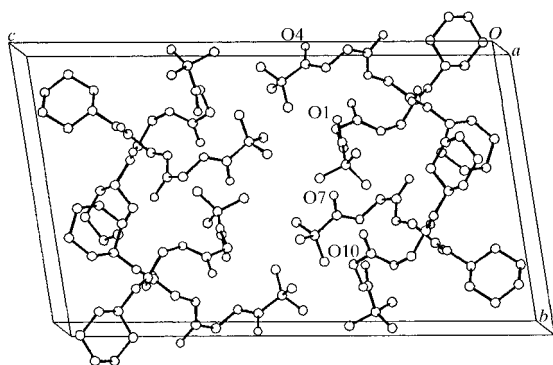

Fig. 4. A perspective view of the packing of pivaloyl-glycyl-glycine-cyclohexylamide (KUJZOE). The hydrogen positions have been deliberately omitted.
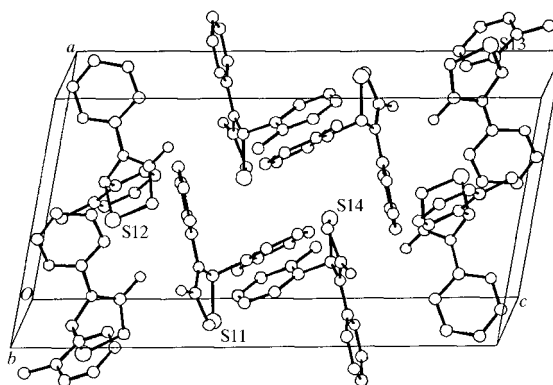

Fig. 5. Packing of 3-(2-pyridyl)-2-(2-tolyl)-1,3-thiazolidin-4-one (BOKXII).

similarities in the crystals, they may give rise to the formation of pseudosymmetries. Since these unit cells belong to an oblique system, the simplest way is to develop pseudoinversion centers as shown by numerous triclinic structures with $Z = 4$ (Desiraju *et al.*, 1991). Interestingly, with the use of CMTA we found only three triclinic structures with $Z = 8$ possessing only pseudoinversion centers. In FOBJUB01 (Valle *et al.*, 1989) 1-aminocyclopropanecarboxylic acid hemihydrate molecules generate a pair of $*\bar{1}$ at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ and $(\frac{3}{4}, \frac{1}{4}, \frac{1}{2})$, whereas in TAPDOD (Peters *et al.*, 1992) 3-methoxypyrazine-1-oxide molecules are located around them at $(\frac{1}{2}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{1}{4}, \frac{5}{8})$, respectively. In FURACL (5-fluorouracil; Fallon, 1973) a pseudoinversion center splits into two positions: 0.228 (21), −0.110 (2), 0.278 (11) for molecules {1:3} and 0.272 (5), −0.108 (1), 0.243 (3) for molecules {2:4} around $(\frac{1}{4}, -\frac{1}{8}, \frac{1}{4})$. This suggests that a molecular packing formed exclusively by a cluster of inversion centers (hypercentric structures) is less stable than structures in which the most common pair of symmetries $2_1/c$ (Kitaigorodskii, 1961; Brock & Dunitz, 1994) is also present. This conclusion is substantiated by the known prevalence of $P2_1/c$ (35%) over the triclinic $P\bar{1}$ (19%) in the CSD.

The obvious presence of $*2_1/*a$ pseudosymmetry in the title compound has attracted our attention to this phenomenon. However, in SZ55C there are only four dimers, which occupy a single orbit. In general, the triclinic crystals with $Z = 8$ should possess two $*2_1/*c$ orbits which are able to locate four molecules on each. The question is how independent are these orbits or are they automatically interdependent? Well, in KUJZOE the two orbits are superimposed; in BOKXII, owing to visible conformational differences among the molecules, they are independent, while EXCHLN represents a transitional state. In KUGWUE and YIHHOM, where the conformational differences are meaningless, these orbits are interdependent. Finally, VARCOG, which is one of the four triclinic unit cells, can be transformed into the monoclinic system, which represents a novel
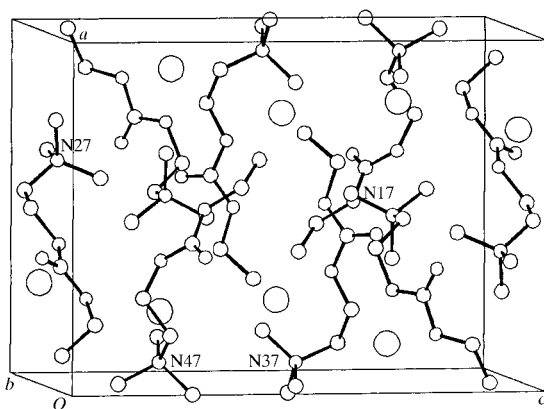

Fig. 6. Packing of ethoxycarbonylcholine iodine (EXCHLN).

case. Apart from the centered relationship between the molecules, it exhibits only two unusual pairs of pseudosymmetries labeled as $*2_q/*n_q$.

KUJZOE (Gellman *et al.*, 1992) can be regarded as an incipient stage of the symmetry formations. The four pivaloyl-glycyl-glycine-cyclohexylamide molecules, in terms of conformational differences, can be sorted into two pairs (Fig. 4). Within the {1:4} pair there are only small differences in the internal rotations, whereas in the {2:3} pair the cyclohexane ring exhibits different orientations. Accordingly, with similar mean displacements but different standard deviations [$\langle\delta^i\rangle$: 0.001 (42), 0.001 (15), 0.001 (15) for {1:4} and 0.002 (53), 0.004 (23), 0.000 (9) for {2:3}] they generate two pairs of $*2_1/*b$ pseudosymmetries in a simple superposition. The glide plane is shifted, however, from $x = \frac{1}{4}$ to an unusual position of $\frac{3}{16}$, to which the screw axis responds with an irregular translation of ca $\tau = \frac{3}{8}$. A standard topological description of their relationship can be given as

$$*2_\tau(x, \tfrac{1}{4}, 0) \leftrightarrow *b(\tfrac{3}{16}, y, z) \equiv \bar{1}(0, 0, 0), \qquad (3)$$

where τ indicates noncrystallographic translations of $\frac{3}{8}$ and $\frac{5}{8}$, which are inseparable. However, the $*2_\tau$ rotor coordinates y and z remain close to the standard $\frac{1}{4}$ and 0.

BOKXII (Hickel *et al.*, 1983), 3-(2-pyridyl)-2-(2-tolyl)-1,3-thiazolidin-4-one [Table 4(*b*), Fig. 5], topologically exhibits a transitional state between SZ55C and KUJZOE. Here the molecules are located on two partly separated orbits. Molecules {1:4} are located on a $*2_1/*a$ orbit with a displacement of 0.026 (20) shown by the glide plane $*a$ from the standard $\frac{1}{4}$ position. The screw axis responds to this by a mean translation $\langle\tau_y\rangle = 0.552$ (40) along the b axis, thus the helicity of this rotor is slightly violated. The screw axis itself is almost perfectly located at $x = \frac{1}{4}$ and $z = \frac{1}{2}$, therefore, $*a$ has a regular translation of $\langle\tau_x\rangle = \frac{1}{2}$. The corresponding symmetry triplet

$$*2_1(\tfrac{1}{4}, y, 0) \leftrightarrow *a(x, \tfrac{1}{4}, z) \equiv \bar{1}(0, 0, 0) \qquad (4a)$$

is similar to that found in SZ55C. The second orbit {2:3} is generated by the glide plane a, similar to KUJZOE which bisects axis b at $y = 0.337$ (17). Therefore, it is complemented by a screw axis with an irregular translation of $\langle\tau_y\rangle = 0.674$ (34). The symmetry triplet

$$*2_\tau(\tfrac{1}{4}, y, 0) \leftrightarrow *a(x, \tfrac{1}{3}, z) \equiv \bar{1}(0, 0, 0), \qquad (4b)$$

together with (4a), shows that $*2_1$ and $*2_\tau$, apart from their slightly different δ^x and δ^z displacements, are located almost at the same position: $\frac{1}{4}, y, 0$. In a first approximation their coincidence may be described as a twin screw axis {$*2_1 + *2_\tau$} with two types of translations: almost regular ($\frac{1}{2}$) and irregular ($\frac{2}{3}$), respectively. These separate orbits {1:4} and {2:3} are in accordance with the conformational differences exhibited by the five-membered hetero ring in 3-(2-pyridyl)-2-(2-tolyl)-1,3-thiazolidin-4-one. In molecules 1 and 4 the conformation

is half chair, whereas molecules 2 and 3 are envelope shaped with somewhat different puckering amplitudes. The other internal rotations about the exocyclic C2—C1′ and N3—C12 bonds are fairly similar.

Further development in the noncrystallographic symmetries is shown by the structure (Fig. 6) of ethoxycarbonylcholine iodine, EXCHLN (Jensen, 1981). Molecules {1:4} located on the first orbit (Table 5) are related by a standard triplet

$$*2_1(x, 0, \tfrac{1}{4}) \leftrightarrow {}^*c(\tfrac{1}{4}, y, z) \equiv \bar{1}(0, 0, 0), \qquad (5a)$$

where the translation of the glide plane is almost perfectly $\tfrac{1}{2}$, while that of the screw axis has a deviation of $\Delta^x = 0.071\,(49)$ from $\tfrac{1}{2}$. On the second orbit, however, similar to KUJZOE and BOKXII, molecules {2:3} are held together by a glide plane at $x = 0.338\,(19)$ and a screw axis with the irregular translation $\langle \tau_x \rangle = 0.675\,(38)$,

$$*2_\tau(x, 0, \tfrac{1}{4}) \leftrightarrow {}^*c(\tfrac{1}{3}, y, z) \equiv \bar{1}(0, 0, 0). \qquad (5b)$$

From (5a) and (5b) it follows that in the $(x, 0, \tfrac{1}{4})$ position there is again a twin screw axis marked with $\{*2_1 + *2_\tau\}$. To distinguish the operators located on 'standard' orbits [(5a)] from the new forms sitting either in unusual positions or generating irregular translations, or both [(5b)], the latter will be hereinafter termed *secondary* and the former as *primary* pseudosymmetries.

Despite the visible dissimilarities between the EXCHLN conformations, the four molecules with their bent shapes are related by several weak pseudosymmetries (*cf.* CPS sketches). For example, molecules [1:2̄] and [3̄:4] are linked by pseudoinversion centers with high standard deviations. These pseudoinversion centers are located at $(0, \tfrac{1}{8}, \tfrac{3}{8})$ and $(0, \tfrac{1}{8}, \tfrac{1}{8})$, and they generate more pseudosymmetries with the operators in (5a). One formed *e.g.* between molecules [4:2̄] is given as

$$*c(\tfrac{1}{4}, y, z) \leftrightarrow {}^*\bar{1}(0, \tfrac{1}{8}, \tfrac{3}{8}) = *2_\tau(x, \tfrac{1}{8}, \tfrac{1}{8}). \qquad (5c)$$

Part of these secondary pseudosymmetries (among them there are also inversion centers) is located on a unit mesh formed parallel to the *bc* plane, with one or two
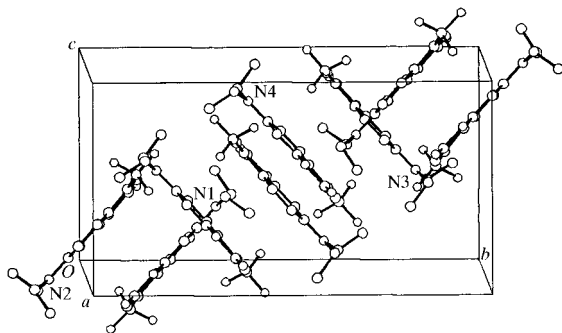
fractional coordinates of $(2n - 1)\tfrac{1}{8}$ (*i.e.* midpoints between the positions $0, \tfrac{1}{4}, \tfrac{1}{2}$ *etc.* of the oblique unit cells). Naturally, operators possessing $(2n - 1)\tfrac{1}{8}$ coordinates are complemented by translation(s) of $(2n - 1)\tfrac{1}{4}$ type, respectively.

A vast pile of variably imperfect primary and secondary pseudosymmetries seem to match the conformational dissimilarities assumed by EXCHLN molecules. In contrast, the conformations of the molecules in KUGWUE (Chinnakali *et al.*, 1992) are the same, at least within experimental error. Thus, the close packing of KUGWUE is hardly dependent on conformational dissimilarities. In addition, all pseudosymmetries listed in Table 6 for 7-diethylamino-4-trifluoromethylcoumarin molecules (Fig. 7) are secondary; thus one element of each pair is also located on a unit mesh formed with one or two $(2n - 1)\tfrac{1}{8}$ fractional coordinates. The {1:3} and {2:4} orbits are equally described by (6a), whereas {1:4} and {2:3} orbits are determined by a screw axis located in a regular position with its glide plane shifted by $\Delta y = \tfrac{1}{8}$ from $\tfrac{1}{4}$ as given by (6b),

$$*2_1(\tfrac{1}{4}, y, \tfrac{3}{8}) \leftrightarrow {}^*n_q(x, \tfrac{1}{4}, z_q) \equiv \bar{1}(0, 0, 0) \qquad (6a)$$

$$*2_q(0, y, \tfrac{1}{4}) \leftrightarrow {}^*c(x, \tfrac{3}{8}, z) \equiv \bar{1}(0, 0, 0). \qquad (6b)$$

In both triplets the translations close to $\tfrac{1}{4}$ or $\tfrac{3}{4}$ are marked hereinafter by a q (quarter) index. Similar to EXCHLN, interconnections between these four secondary pseudosymmetries are pseudoinversion centers

$$*2_q(0, y, \tfrac{1}{4}) \leftrightarrow {}^*n_q(x, \tfrac{1}{4}, z_q) = {}^*\bar{1}(\tfrac{1}{4}, \tfrac{1}{8}, \tfrac{1}{8}) \qquad (6c)$$

$$*2_1(\tfrac{1}{4}, y, \tfrac{3}{8}) \leftrightarrow {}^*c(x, \tfrac{3}{8}, z) = {}^*\bar{1}(\tfrac{1}{4}, \tfrac{5}{8}, \tfrac{5}{8}) \qquad (6d)$$

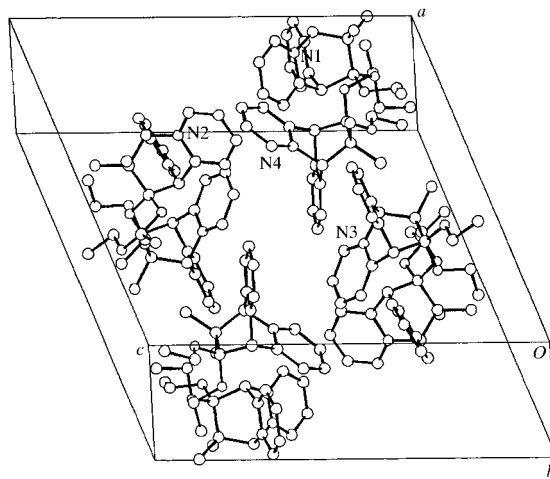Fig. 7. Packing of 7-diethylamino-4-trifluoromethylcoumarin (KUGWUE).

Fig. 8. Packing of (+)-12,12-diethoxy-13,13-dimethyl-6,11-ethano-6,11-dihydrobenzo[*b*]quinolizinium chloride monohydrate (YIHHOM). CMTA was only extended to the 24 atoms of the eight organic cations, omitting the Cl⁻ cations and water molecules shown in the center of the unit cell.

formed between molecules 1:2 and 3:4, respectively, also with rather low standard deviations.

The crystals of YIHHOM (Mallamo *et al.*, 1994) are built up from bulky and rigid molecules. Consequently, their close packing is not affected by conformational differences. In addition, YIHHOM exhibits a novel array of pseudosymmetries: along each of the three crystal axes there is a twofold rotor accompanied by its own glide plane, which suggests a pseudo-orthorhombic array ($a = 15.910$, $b = 16.771$, $c = 17.108$ Å, $\alpha = 89.12$, $\beta = 67.89$, $\gamma = 87.52°$). A survey of the symmetries revealed between molecules of (+)-12,12-diethoxy-13,13-dimethyl-6,11-ethano-6,11-dihydrobenzo[*b*]quinolizinium chloride monohydrate (Fig. 8) has shown a new phenomenon. While the first {1:3} orbit has the glide plane *a located at $y = 0.125$ (18) with $\langle \delta^y \rangle = 0$, which generates a rotor translation of $q = 0.250$ (36) described by (7a), the second orbit {2:4} can be described by a similar triplet, (7b),

$$*2_q(\tfrac{1}{4}, y, 0) \leftrightarrow *a(x, \tfrac{1}{8}, z) \equiv \overline{1}(0, 0, 0) \qquad (7a)$$

$$*2_q(\tfrac{1}{4}, y, \tfrac{1}{2}) \leftrightarrow *a(x, \tfrac{3}{8}, z) \equiv \overline{1}(\tfrac{1}{2}, 0, \tfrac{1}{2}), \qquad (7b)$$

in which the glide plane *a is sitting at $\sim \tfrac{3}{8}$ with a displacement of $\langle \delta^y \rangle = 0.012$ (16). These two glide planes split from a common position at $y = \tfrac{1}{4}$. Those separated from each other by $\Delta y \simeq \tfrac{1}{4}$ possess only divided (halved) functions between the molecules.

The rotors along axes *a* and *c* establish further interconnections. Molecules {1:4} with substantially higher σ_{n-1} values for the observed displacements are related by a *2_τ rotor along axis *a* and its complementary glide *b is located at $x = 0.147$ (32) with $\langle \delta^x \rangle = 0.022$. Consequently, translation along axis *a* $\langle \tau_x \rangle = 0.294$ (64) deviates somewhat from $\tfrac{1}{4}$. A similar triplet is valid for the molecules located on the {2:3} orbit with a $\Delta z = \tfrac{1}{2}$ shift of *2_τ. (The corresponding σ_{n-1} values are also high.) Furthermore, both {1:2} and {3:4} orbits are generated by an unusual pair of operators, which also take two positions. A twofold *2 axis located at $x = 0.113$ (50) and $y = 0.127$ (57) with low displacements of $\langle \delta^x \rangle = 0.012$ and $\langle \delta^y \rangle = 0.002$ from the special position at ($\tfrac{1}{8}, \tfrac{1}{8}, z$), together with a crystallographic inversion center, generates a diamond glide plane [(7c)]. A CPS sketch clearly reveals that beyond this triplet embedded in a {110} plane, there are a further two triplets located in planes {111} and {100}, respectively, which incorporate the same diamond glide plane,

$$*2(\tfrac{1}{8}, \tfrac{1}{8}, z) \leftrightarrow \overline{1}(0, 0, 0) \equiv *d(x, y, 0) \qquad (7c)$$

$$*2_q(\tfrac{1}{4}, y, 0) \leftrightarrow *b(\tfrac{1}{8}, y, z) = *d(x, y, 0) \qquad (7d)$$

$$*2_q(x, \tfrac{1}{4}, 0) \leftrightarrow *a(x, \tfrac{1}{8}, z) = *d(x, y, 0). \qquad (7e)$$

Mutatis mutandis, the interconnection between the pseudoscrew axes $*2_q(x, \tfrac{1}{4}, 0)$ and $*2_q(\tfrac{1}{4}, y, 0)$ is the twofold axis $*2(\tfrac{1}{8}, \tfrac{1}{8}, z)$. Summing up, the pseudosymmetries of YIHHOM, which possesses relatively

large and rigid molecules with differing degrees of imperfectness, are formed in each main direction using such symmetry pairs as *2/*d, which can be found first (among the 230 space groups) only in orthorhombic *Fdd*2 (No. 43) and *Fddd* (No. 70).

Finally, the use of the program *LePage* (Spek, 1988) revealed four centered monoclinic unit cells, DIYMED (Hutton *et al.*, 1986), DILFEY (Lin *et al.*, 1985), CIJSAP (Lanfranchi *et al.*, 1984) and VARCOG (Koft *et al.*, 1989), with different figures of merit: 0.025, 0.114, 0.267 and 0.490, respectively. Apart from DIYMED, where the space group *C*2/*c* [the third most popular (7%) centrosymmetric space group in the CSD] with $Z = 16$ could be identified, in the other three centered unit cells only the secondary pseudosymmetries described above were found. Since all of them are (pseudo)monoclinic unit cells with $Z = 16$, they will be discussed elsewhere (Kálmán, 1998). In any case, a short comment on VARCOG (Koft *et al.*, 1989) should be given. The molecules of VARCOG with a similar conformation were transformed into a centered monoclinic unit cell, which has only two triplets of secondary pseudosymmetries,

$$*2_q(\tfrac{5}{8}, y, \tfrac{1}{4}) \leftrightarrow *n_q(x_q, \tfrac{1}{8}, z) \equiv \overline{1}(0, 0, 0) \qquad (8a)$$

$$*2_q(\tfrac{3}{8}, y, \tfrac{3}{4}) \leftrightarrow *n_q(x_q, \tfrac{7}{8}, z) \equiv \overline{1}(0, 0, 0). \qquad (8b)$$

These screw axes are parallel to the rectangular *b* axis and thus the pseudosymmetry $*2_q/*n_q$ can be regarded
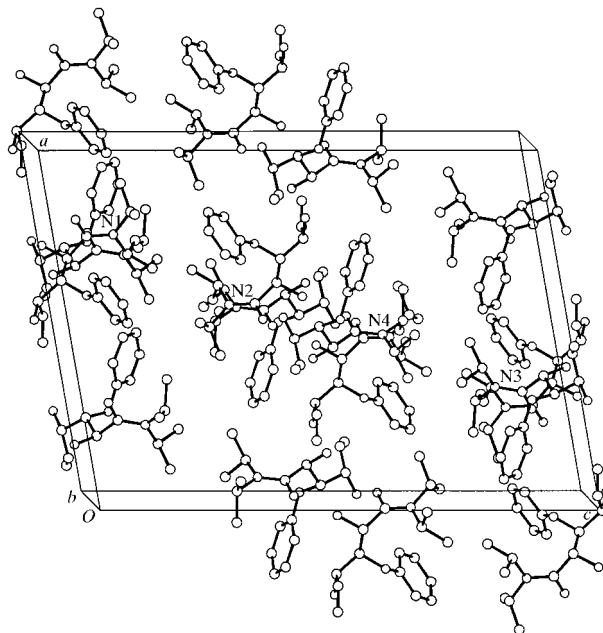

Fig. 9. Packing of *N*,*N*′-diisopropyl-2,4-dihydroxy-3-phenoxyhex-5-enamide (VARCOG) in the transformed (Spek, 1988) pseudo-monoclinic unit cell with $Z = 16$.

as one of the topological alternatives of the standard $2_1/n$ pair in the centered monoclinic unit cells.

4. Conclusions

The examples discussed here have shown a great variety of the most common symmetry pairs $2_1/c$, taking various forms of secondary pseudosymmetries. First, the symmetry migration from the standard positions occupied by the primary forms $*2_1(0, y, \frac{1}{4})$ and $*c(x, \frac{1}{4}, z)$ is to be described. In KUJZOE, BOKXII and EXCHLN, where the molecules exhibit various degrees of conformational dissimilarities, the symmetry shift has a transitional state (labeled as $\tau/2$) from $\frac{1}{4}$ towards the symmetrically equidistant positions at $\frac{1}{4} \pm \frac{1}{8}$. When the best form of close packing is no longer disturbed by conformational differences (KUGWUE, YIHHOM etc.), then the symmetry migration reaches a symmetric equilibrium in the $(2n - 1)\frac{1}{8}$ positions on a diperiodic unit mesh. The migration (shift) has three archetypes. The notations refer to the standard form of space group $P2_1/c$ (No. 14):

(a) the screw axis is displaced by $\pm\frac{1}{8}$: $*2_1(0, y, \frac{3}{8})$, complemented by $*c_q(x, \frac{1}{4}, z)$;

(b) the glide plane is displaced by $\pm\frac{1}{8}$: $*c(x, \frac{3}{8}, z)$, complemented by $*2_q(0, y, \frac{1}{4})$;

(c) both the operators are displaced by $\pm\frac{1}{8}$: $*2_q(0, y, \frac{1}{8})$, $*c_q(x, \frac{1}{8}, z)$, they complement each other. Each symmetry migration is automatically complemented by an irregular translation which in an ideal case amounts to $q = \frac{1}{4}/\frac{3}{4}$ as depicted by the motif

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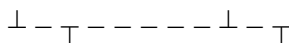
In addition, as can be seen above, primary and secondary pseudosymmetries may jointly generate pseudoinversion centers with coordinates $(\frac{1}{4}, \frac{1}{8}, \frac{1}{4})$, $(0, \frac{1}{8}, \frac{3}{8})$ etc. They also participate in the stabilization of structures crystallized in the triclinic system with $\bar{1}$ and $Z = 8$.

The advantage of *secondary* pseudosymmetries in the structures investigated can be attributed to their duplication in the diperiodic unit cell with one or two coordinates of $(2n - 1)\frac{1}{8}$. They simultaneously give rise to the loss of half of their function within and around the unit cell. In other words, the function of a glide plane g at $\frac{1}{4}$ is divided symmetrically by its twin form located at $\frac{1}{4} \pm \frac{1}{8}$, respectively. This seems to help the rigid and bulky molecules (*e.g.* KUGWUE, VARCOG and YIHHOM) against their diminished self-complementarity to reach an optimum of close packing. However, irregularities of *secondary* pseudosymmetries (except *d* in EXCHLN) cannot be interpreted in the domain of the 230 space groups. Nevertheless, owing to their special functions, they recurrently exist within the boundaries of both oblique and partly rectangular unit cells. The transfor-

mation of DIYMED, DILFEY, CIJSAP and VARCOG from an oblique to a centered monoclinic unit cell enabled us to regard the above-defined three irregular topologies of $2_1/c$ as three independent, but *transitional*, space groups. Similarly, space groups $P2_1/m$ (No. 11) and $P2/c$ (No. 13) with their populations 0.7 and 0.5% (CSD) are also topological alternatives of the most common (35%) space group $P2_1/c$ (No. 14). Of course, we must bear in mind that they do not occur in perfect form. This would violate the laws of nature represented by the 230 rational space groups. However, they may occur with some imperfectness as parts of a centered unit cell. Indeed, since the space group $C2/c$ (No. 15) is the centered form of $P2_1/c$, the symmetry exhibited by VARCOG, DILFEY and CIJSAP can be regarded as the centered forms of the third *transitional* space group $P2_q/n_q$, described by the triplet given by (8a). In contrast, DIYMED, with the lowest figure of merit (0.025) being quite close to $C2/c$ with $Z = 16$, possesses a $2_1/c_q$ triplet also along with a rectangular b axis.

A detailed description of the unusual topologies of $P2_1/n$, termed *transitional* space groups following the rules of *International Tables for Crystallography* (1983, Vol. A), is to be published (Kálmán, 1998). Attention should also be paid to the structures with 'hypersymmetry' (Zorky & Dashevskaya, 1993). After highlighting the similarities and dissimilarities between the forms of noncrystallographic symmetries revealed in this paper and those claimed by Zorky & Dashevskaya (1993), a revision of the nomenclature of such symmetries is strongly called for.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Brock, C. P. & Dunitz, J. D. (1994). *Chem. Mater.* **6**, 1118–1127.
Chinnakali, K., Sivakumar, K. & Natarajan, S. (1992). *Acta Cryst.* C**48**, 1859–1862.
Desiraju, G. R., Calabrese, J. C. & Harlow, R. L (1991). *Acta Cryst.* B**47**, 77–86.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.

Fallon, L. III (1973). *Acta Cryst.* B**29**, 2549–2556.

Gellman, S. H., Powell, D. R. & Desper, J. M. (1992). *Tetrahedron Lett.* **33**, 1963–1964.

Harms (1996). *XCAD*4. *Data Reduction Program for CAD*-4 *Diffractometers*. Enraf–Nonius, Delft, The Netherlands.

Hester, J. & Hall, S. R. (1995). *BUNYIP in Xtal_GX*, edited by S. R. Hall & D. du Boulay. University of Western Australia, Australia.

Hickel, D., Leger, J. M., Carpy, A., Vigorita, M. G., Chimirri, A. & Grasso, S. (1983). *Acta Cryst.* C**39**, 240–245.

Hutton, A. T., Modro, T. A., Niven, M. L. & Scaillet, S. (1986). *J. Chem. Soc. Perkin Trans.* 2, pp. 17–24.

Jensen, B. (1981). *Acta Cryst.* B**37**, 881–885.

Kálmán, A. (1998). *Acta Cryst.* In preparation.

Kálmán, A. & Argay, Gy. (1996). *Z. Kristallogr.* **211**, 719–720.

Kitaigorodskii, A. I. (1961). *Organic Chemical Crystallography*. New York: Consultant's Bureau.

Koft, E. R., Dorff, P. & Kullnig, R. (1989). *J. Org. Chem.* **54**, 2936–2940.

Lanfranchi, M., Manotti Lanfredi, A. M., Pellinghelli, M. A. & Tiripicchio, A. (1984). *Acta Cryst.* C**40**, 1239–1242.

Lin, X., Pan, Z., Guo, R. & Huang, Q. (1985). *Acta Chim. Sin.* **43**, 5–9.

Mallamo, J. P., Earley, W. G., Kumar, V., Subramanyam, C., Dority, J. A. Jr, Miller, M. S., DeHaven-Hudkins, D. L., Ault, B., Herrmann, J. L. Jr, Dung, J.-S., McMullen, L. A., Jaeger, E., Kullnig, R. & Magee, L. J. (1994). *J. Med. Chem.* **37**, 4438–4448.

Peters, D. A., Beddoes, R. L. & Joule, J. A. (1992). *Acta Cryst.* C**48**, 307–311.

Reibenspies, J. (1989). *DATCOR. Program for Empirical Absorption Correction.* Texas A&M University, College Station, Texas, USA.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Simon, L., Talpas, S. G., Fülöp, F., Bernáth, G., Argay, Gy., Kálmán, A. & Sohár, P. (1995). *J. Heterocycl. Chem.* **32**, 161–167.

Spek, A. L. (1988). *J. Appl. Cryst.* **21**, 578–579.

Valle, G., Crisma, M., Toniolo, C., Holt, E. M., Tamura, M., Bland, J. & Stammer, C. H. (1989). *Int. J. Pept. Protein Res.* **34**, 56–65.

Zorky, P. M. (1996). *J. Mol. Struct.* **374**, 9–28.

Zorky, P. M. & Dashevskaya, E. E. (1993). *Acta Chim. Hung.* **130**, 247–259.