

the molecules in the single-well potential. According to the group-theoretical analysis, this means that one of the six phonons described by the general polarization vector defined above would be expected to exhibit a soft-mode behaviour at the zone boundary of the high-temperature phase. This mode becomes a totally symmetric zone-centre phonon in the low-temperature phase; hence some symptoms of the soft-mode behaviour should be observed in the Raman spectra of this phase.

If static disorder is assumed for the high-temperature phase, the orientational motions should be understood as jumps of NIPC molecules between two statistically occupied potential wells. Such a system could be conveniently described by a pseudospin model in which the pseudospin operator takes values ± 1 , defining two possible molecular orientations. Then the phase transition could be interpreted as a freezing of the pseudospin-wave motion which would be described by the same polarization vector as in the case of a soft-phonon induced phase transition. From the experimental point of view, the quasielastic peak should be observed in the high-temperature phase in neutron scattering experiments. The width of this peak should decrease when the temperature of the phase transition is approached.

Usually, it is rather difficult to find examples of phase transitions in molecular crystals which would have such a 'pure' character as described above. Therefore, one should expect that the phase transition

in the NIPC crystal has a more complicated, mixed, order-disorder and displacive, nature.

One of us (AM) would like to thank the University of Lille I for financial support during his stays in France.

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Acta Cryst. (1986). B42, 193-198

Centrosymmetric or Noncentrosymmetric?*

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(Received 24 June 1985; accepted 13 August 1985)

Abstract

In cases where diffraction data do not provide a clear choice between a centrosymmetric and a noncentrosymmetric space group, it is better to opt for the centrosymmetric description even though disorder may result. The disorder model implies that the crystal is a composite of two or more molecular structures that cannot be distinguished from one another. On the other hand, attempts to refine a single, ordered model in the noncentrosymmetric space group (which

should lead to poor convergence because of near singularities) may lead to the erroneous conclusion that a unique structure has been found. Three examples of this latter situation are given.

One of the most troublesome problems in crystal-structure analysis is resolving the ambiguity between a centrosymmetric and a noncentrosymmetric space group when systematic absences are of no help. This ambiguity exists within many pairs of commonly occurring space groups, such as $P1-P\bar{1}$, $P2_1-P2_1/m$, $Cc-C2/c$, $Pna2_1-Pnam$, and many others. If the

* Contribution No. 7215 from the Arthur Amos Noyes Laboratory of Chemical Physics.

structure is very nearly centrosymmetric, the diffraction data are insensitive to the ambiguity: for a particular structure factor F_{hkl} the contribution due to the antisymmetric distortion is small (since the distortion from centrosymmetry is small) and imaginary – at right angles to the real contribution due to the centrosymmetric component; hence it has little effect on the magnitude of F unless F is very small (in which case the reflection is ignored in most laboratories).

A particularly bothersome situation arises when the choice is between a disordered structure in the centrosymmetric space group and an ordered (or a more ordered) structure in the noncentrosymmetric space group. Here, the real component of F provides information concerning the average centrosymmetric structure while all the information concerning the ordering of the structure into two unrelated moieties (if such ordering indeed occurs) is contained in the small, imaginary component. It may well be impossible to recover these details from the diffraction data alone. In such cases, it seems preferable to resort to the disordered, centrosymmetric description, thus admitting that only the average structure is being determined.

I describe here three examples of this situation. In all three the original authors chose to describe closely centrosymmetric structures in noncentrosymmetric space groups. The resulting deformations from centrosymmetry are somewhat unusual and suspect, and it seems preferable to describe all three structures as disordered in the corresponding centrosymmetric space groups.

(I) *Dichloro[1,2-ethanedione bis(dimethylhydrazone)](η-ethylene)platinum(II)*

The structure of this compound, $\text{PtCl}_2(\text{C}_2\text{H}_4)_2(\text{C}_6\text{H}_{14}\text{N}_4)$, was described in space group $P2_1$ [monoclinic; $a = 8.998$ (3), $b = 8.133$ (4), $c = 9.872$ (2) Å, $\beta = 106.72$ (3)°, $Z = 2$] and refined to an R of 0.050 for 1404 reflections (Bavoso, Funicello, Morelli & Pavone, 1984; BFMP). Surprising features of the structure included asymmetry in the bonding about Pt and in the hydrazone ligand, with one dimethylated N atom planar and the other pyramidal; the four N–CH₃ distances ranged from 1.39 (3) to 1.53 (3) Å.

It seems preferable to describe the structure in space group $P2_1/m$. The $P2_1/m$ description can be derived from the coordinates in Table 1 of BFMP by placing the Pt, C, and N atoms on the mirror plane at $y = 0.25$ and the two Cl atoms in equivalent positions above and below this plane. Full-matrix least-squares refinement quickly converged at $R = 0.0505$ for the 1388 reflections coded as 'observed' in Supplementary Publication No. SUP 39649. In this refinement, the Pt, Cl, C, and N atoms were given anisotropic U_{ij} 's and the H atoms were ignored, as in BFMP. (Subsequent difference maps clearly

showed the four H atoms of the coordinated ethylene group, lying on opposite sides of the molecular mirror plane, but the remaining H atoms were unclear.) These $P2_1/m$ coordinates are given in Table 1.

The bond lengths (Fig. 1) obtained from this $P2_1/m$ refinement seem more satisfying than those from the $P2_1$ refinement of BFMP in that the pairs of Pt–Cl, Pt–N and Pt–C distances are statistically equal and the two halves of the hydrazone ligand appear identical. However, the differences among the terminal N–C distances are unrealistic: there is no reason to expect that the *endo* (relative to Pt) distances would be so much shorter than the *exo* distances. Another disturbing feature of the $P2_1/m$ model is the large U_{22} terms (Table 1), particularly for N(2) and N(4). These terms, which represent out-of-plane displacements with r.m.s. values up to 0.4–0.5 Å, suggest that alternative models in $P2_1/m$ can be developed in which some of the atoms are disordered between pairs of sites on opposite sides of the plane. I investigated three such models, with four, six, and all ten hydrazone C and N atoms disordered in this way (and assigned isotropic B 's). All three converged to essentially equal R 's of about 0.051 – the same as reached for the ordered, anisotropic model of Table 1. Each of these models can lead to a variety of bond lengths and angles, depending upon the way in which the disordered atoms are presumed to be connected to one another; essentially any reasonable preconception of the structure can be satisfied. For all such models, however, the out-of-plane coordinate (y) of each atom couples strongly with the U_{22} component of B for that atom, and neither value can be determined with confidence (hence the necessity for assuming an isotropic B).

All that can be said, then, is that the $P2_1/m$ model of Table 1 probably describes an average of a number of structures in which the hydrazone atoms are displaced from the mirror plane in various ways we cannot determine. Hence, we cannot know with confidence the bond lengths and angles in an individual molecule, or whether the external N atoms N(2) and N(4) are planar or pyramidal. [The interior distances involving C(5) and C(6) should be fairly reliable, because the U_{22} terms of N(1), C(5), C(6) and N(3) are moderate; distances and angles involving N(2) and N(4) are especially conjectural.] The four N–CH₃ bond lengths could well be equal; if so, the minimum length would be about 1.45 Å, for models in which the *exo* atoms C(4) and C(7) have nearly the same y values as their neighboring N atoms.

Refinement in $P2_1$, such as carried out by BFMP, must be based on a presumed starting model which is non-planar, since the planar model of Table 1 would lead to singularities (Ermer & Dunitz, 1970) if refinement in $P2_1$ were attempted. (The f'' component of anomalous scattering by Pt would in principle break this singularity, but the effect is too small to

Table 1. $\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{C}_6\text{H}_{14}\text{N}_4)$: coordinates ($\times 10^4$) and U_{ij} 's ($\times 10^3$); space group $P2_1/m$ The U_{ij} 's are of the form: $-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	7580.5 (8)	2500	1695.9 (9)	29.4 (3)	55.5 (4)	45.1 (4)	0	18.2 (3)	0
Cl	7572 (5)	5326 (5)	1706 (5)	56 (2)	58 (2)	97 (3)	0 (2)	28 (2)	-2 (2)
C(1)	5187 (20)	2500	1534 (24)	32 (8)	79 (15)	78 (14)	0	36 (9)	0
C(2)	6142 (23)	2500	3035 (23)	50 (11)	117 (21)	64 (13)	0	43 (10)	0
C(3)	6022 (28)	2500	-1744 (28)	59 (14)	110 (23)	83 (18)	0	1 (13)	0
C(4)	8338 (34)	2500	-2635 (25)	104 (20)	176 (33)	48 (13)	0	41 (14)	0
N(1)	8476 (17)	2500	-212 (17)	34 (8)	126 (18)	53 (10)	0	26 (7)	0
N(2)	7576 (21)	2500	-1510 (20)	44 (10)	265 (34)	42 (10)	0	16 (8)	0
C(5)	10016 (25)	2500	115 (23)	53 (10)	82 (16)	57 (12)	0	29 (9)	0
C(6)	10893 (22)	2500	1502 (25)	40 (10)	88 (17)	75 (15)	0	26 (10)	0
N(3)	10216 (16)	2500	2520 (18)	32 (7)	78 (13)	65 (11)	0	19 (7)	0
N(4)	10986 (20)	2500	3883 (19)	42 (9)	198 (28)	46 (10)	0	7 (8)	0
C(7)	12664 (28)	2500	4258 (32)	43 (13)	219 (41)	97 (21)	0	8 (13)	0
C(8)	10243 (35)	2500	4827 (26)	105 (21)	120 (25)	56 (14)	0	32 (14)	0

be of use.) Many such models can be devised, all leading to essentially equivalent R 's. For example, I attempted further refinement, in $P2_1$, beginning with the coordinates and U_{ij} 's reported by BFMP. Through seven cycles of full-matrix refinement the R stayed at 0.050 but there was no hint of convergence; in the seventh cycle the largest indicated shift was still 0.15 Å. In terms both of R and of the sum of squares of weighted residuals there was essentially nothing to choose between these seven models, yet they covered a relatively wide range of atomic parameters. Thus, it is probably illusory to presume that any 'correct' $P2_1$ model can be found.

Another, perhaps more convincing, argument can be made against the BFMP model - and, by implication, against any $P2_1$ model. Included in SUP 39649 are $F(\text{obs.})$ and $F(\text{calc.})$ values for 219 reflections coded as 'unobserved'; they are the ones most sensitive to the centrosymmetric-noncentrosymmetric ambiguity (Marsh, 1981; Schomaker & Marsh, 1979). Some totals for these reflections are given in Table 2; they clearly favor the centrosymmetric model. For these reflections, the average value of $F(\text{calc.})$ for the $P2_1$ model is appreciably larger than $F(\text{obs.})$, undoubtedly because of the imaginary component of $F(\text{calc.})$; this trend should be evident in any $P2_1$ model. The trend is much less severe for the $P2_1/m$ model, where the imaginary component is absent.

In sum: lacking further evidence, we must be con-

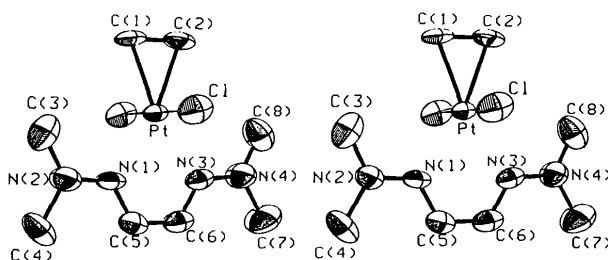


Fig. 1. $\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{C}_6\text{H}_{14}\text{N}_4)$: the $P2_1/m$ representation. [Bond lengths: Pt-C(1) 2.11, Pt-C(2) 2.10, C(1)-C(2) 1.48, N(2)-C(3) 1.35, N(2)-C(4) 1.46, N(1)-N(2) 1.30, N(1)-C(5) 1.33, C(5)-C(6) 1.37, C(6)-N(3) 1.32, N(3)-N(4) 1.32, N(4)-C(7) 1.45, N(4)-C(8) 1.29 Å (e.s.d.'s ~ 0.02-0.03 Å).]

tent with the $P2_1/m$ description and an apparently disordered model which precludes any precise description of the structure of an individual molecule.

(II) $\text{Cu}([\text{12}] \text{janeS}_4)(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

The crystal structure of this compound [(1,4,7,10-tetrathiacyclododecane)copper(II) perchlorate monohydrate] was recently described (Pett, Diadario, Dockal, Corfield, Ceccarelli, Glick, Ochrymowycz & Rorabacher, 1983; PDDCCGOR) in space group $Pbc2_1$ [orthorhombic; $a = 9.010$ (2), $b = 15.775$ (3), $c = 13.380$ (2) Å]. The authors noted a pseudo mirror plane 'perpendicular to the c axis, mimicking what would be the mirror plane in $Pbcm$ ', and further noted that this pseudo plane 'led to problems in refining the heavy-atom positions. Whenever the S atoms were allowed to refine anisotropically, they inevitably moved to positions consistent with $Pbcm$, resulting in unrealistic bond distances'. Accordingly, the refinement was carried out with isotropic B 's, and the residual index R was relatively high at 0.127. While the molecular dimensions were moderately satisfactory, the ranges of Cu-S and S-C distances were quite large at 2.30 (1)–2.37 (1) Å and 1.73 (4)–1.91 (4) Å and the C-C distances were short, at 1.41 (3) Å.

On the basis of the diffraction data at hand, there is no reason not to describe the structure in the centrosymmetric $Pbcm$. Refinement in $Pbcm$, including anisotropic U 's for all atoms (H atoms were excluded, as in PDDCCGOR), led quickly to an R of 0.068 for the 1083 reflections included in the supplementary F table. (The number of 'observed' reflections reported by PDDCCGOR is 1089.) The total number of parameters was 118, compared to 96 parameters for the isotropic refinement in $Pbc2_1$. Coordinates for this $Pbcm$ model are given in Table 3.

Besides a much lower R , the $Pbcm$ refinement leads to statistically equal Cu-S [2.325 (3) Å] and S-C [1.815 (9) Å] bond lengths and to e.s.d.'s about one-half as large as those reported for the $Pbc2_1$ refinement (PDDCCGOR). However, the C-C distances remain unrealistically small, ranging from 1.22 (2) to

Table 2. $\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{C}_6\text{H}_{14}\text{N}_4)$: some sums for the 'unobserved' reflections.

	$F(\text{obs.}) > 0$		$F(\text{obs.}) = 0$	
	$P2_1^{(a)}$	$P2_1/m^{(b)}$	$P2_1^{(a)}$	$P2_1/m^{(b)}$
$\sum F(\text{obs.})$	730	734	0	0
$\sum F(\text{calc.}) $	910	796	297	225
$\sum \Delta F $	326	285	297	225
R	0.45	0.39	—	—
No.	148		71	

(a) Bavoso *et al.* (1984).

(b) This work, Table 1.

1.27 (3) Å. Moreover, the three independent S–C–S groupings are nearly planar whereas, like ethylenediamine (en), they are expected to be puckered. The four independent C atoms show large anisotropies in their U_{ij} 's with implied r.m.s. displacements of 0.5–0.6 Å in directions perpendicular to the S–C–S planes. The two perchlorate groups show similar behavior, with Cl–O distances from 1.25 (2) to 1.36 (2) Å (the expected value is about 1.45 Å) and perpendicular r.m.s. displacements of 0.4–0.6 Å.

Since en-type ligands are notorious for being disordered, the four C atoms were split into eight half-atoms, each with a refinable isotropic B , and additional least-squares refinement led to a further reduction in R to 0.065; the C–C distances became more reasonable, ranging from 1.45 (3) to 1.56 (3) Å. However, the S–C distances now become disparate (1.69–2.06 Å), suggesting that the S atoms participate in the disorder. The major axes of the S U_{ij} 's are oriented nearly perpendicular to the Cu–S directions, and a disordering of the S atoms along these axes could maintain equal Cu–S bond lengths of about 2.34 Å while also equalizing the S–C distances. At this stage, though, a point of no return had been reached: the separations between disordered pairs of S atoms, at about 0.5 Å, were too small to permit meaningful refinement of both coordinates and U_{ij} 's.

We are left, then, with a model in $Pbcm$ in which the three S–C–S groupings are disordered across planar conformations and the two perchlorate ions show more complicated disorder. (A reasonable model for them can be developed by splitting all five independent O atoms into pairs of half-populated sites.) The disorder introduces uncertainty into effectively all the bond lengths and angles except for Cu–O, which remains at 2.117 (11) Å. What advantage does such a model have over the $Pbc2_1$ structure derived by PDDCCGOR? Besides the obvious one of attaining considerably better agreement with the $F(\text{obs.})$ values, there is a less tangible one: the uncertainties in the structure, caused by the disorder in the atom positions, are there for all to see. While the particular model derived by PDDCCGOR appears at first glance to be unique and unambiguous, it is surely but one of an immense family of structures that could be devised in $Pbc2_1$, each differing in

Table 3. $\text{Cu}^{\text{II}}([\text{12}] \text{janeS}_4)(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$: coordinates ($\times 10^4$) and U_{eq} values ($\times 10^3$); space group $Pbcm$

	$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.			$U_{\text{eq}} (\text{Å}^2)$
	x	y	z	
Cu	1265 (2)	1298 (1)	2500	46 (1)
Cl(1)	3397 (5)	4701 (3)	2500	71 (1)
Cl(2)	7928 (6)	2500	0	71 (1)
S(1,4)	814 (3)	252 (2)	1318 (2)	74 (1)
S(2,3)	2716 (4)	1981 (2)	1307 (2)	87 (1)
O	−702 (12)	2031 (7)	2500	77 (4)
O(1,2)	4312 (16)	4659 (12)	1757 (9)	249 (7)
O(3)	2444 (16)	4035 (11)	2500	170 (7)
O(4)	2686 (24)	5384 (13)	2500	323 (16)
O(5,6)	7142 (16)	2779 (9)	782 (10)	239 (6)
O(7,8)	8681 (19)	1829 (8)	249 (10)	240 (6)
C(1,6)	2380 (17)	390 (14)	497 (13)	156 (7)
C(2,5)	2994 (28)	1112 (9)	422 (15)	191 (8)
C(3,4)	4420 (15)	2030 (12)	2032 (13)	193 (9)
C(7,8)	1471 (21)	−644 (8)	2957 (11)	164 (7)

relatively small but distinct ways as to the pattern of deviation from the average, $Pbcm$ structure. Each of these models would undoubtedly show essentially the same agreement index, for the differences between their $F(\text{calc.})$ values would lie almost entirely in the small imaginary components of F which are unimportant when (as in the present case) only the larger F 's are considered. The hopelessness of trying to differentiate between these many models is inherent in the disordered, $Pbcm$ model; indeed, as in the previous example it is probable that the structure itself fails to differentiate but is, rather, a composite (either static or dynamic, or perhaps both) of many structures with differing puckers of the S–C–S groups and differing orientations of the perchlorate ions.

(III) *The 1:1 complex of 1,4-dithiintetracarboxylic N,N'-dimethyldiimide and acridine,*
 $\text{C}_{10}\text{H}_6\text{N}_2\text{O}_4\text{S}_2 \cdot \text{C}_{13}\text{H}_9\text{N}$

The structure of this compound (Yamaguchi & Ueda, 1984; YU) was described in space group Pn [monoclinic; $a = 13.701$ (11), $b = 10.244$ (4), $c = 7.208$ (2) Å, $\beta = 92.20$ (5)°, $Z = 2$] and refined to an R of 0.039 for 1544 reflections with $I > 3\sigma(I)$. Refinement in $P2/n$ seems preferable. After pairs of coordinates from the Pn refinement (Table 1, YU) were averaged across the approximate center of symmetry, full-matrix refinement in $P2/n$ quickly converged at the same $R = 0.039$ – as reported by YU for Pn , but the number of parameters was only 178 (anisotropic U_{ij} 's for S, O, C, and N and isotropic B 's for H, as in YU, plus scale and isotropic extinction parameters) compared with, presumably, 349 for Pn . Final $P2/n$ parameters are given in Table 4. The e.s.d.'s are approximately one-third as large as reported by YU. The $P2/n$ description requires disorder between the N(1) atom and the C(13)–H group in the acridine molecule, whereas they are ordered in the Pn description. Otherwise, there are only small differences from the dimensions reported by UA – the most notable being the N–C(methyl) distance,

Table 4. $C_{10}H_6N_2O_4S_2 \cdot C_{13}H_9N$: *final coordinates* ($\times 10^5$) and U_{eq} values ($\times 10^4$); space group $P2/n$

$$U_{eq} = \frac{1}{3}(U_{11} \csc^2 \beta + U_{22} + U_{33} \csc^2 \beta + 2U_{13} \csc \beta \cot \beta).$$

	x	y	z	U_{eq} (\AA^2)
S(1, 2)A	37839 (4)	7481 (6)	48779 (9)	361 (1)
O(1, 3)A	74002 (11)	17020 (17)	64671 (27)	519 (5)
O(2, 4)A	43774 (12)	35427 (16)	62557 (26)	490 (4)
N(1, 2)A	60050 (13)	29560 (18)	65175 (28)	392 (5)
C(1, 6)A	50214 (16)	27549 (22)	61363 (31)	357 (5)
C(2, 7)A	49290 (15)	13611 (21)	55446 (30)	313 (5)
C(3, 8)A	58110 (14)	8227 (22)	56219 (30)	319 (4)
C(4, 9)A	65327 (16)	18342 (22)	62440 (33)	374 (5)
C(5, 10)A	64340 (23)	42151 (28)	70614 (48)	514 (7)
N(1), C(13)B	40849 (16)	6255 (25)	-886 (31)	454 (5)
C(1, 7)B	41634 (17)	-6464 (26)	-5920 (32)	414 (6)
C(2, 8)B	50895 (18)	-12846 (26)	-5108 (33)	439 (6)
C(3, 9)B	51465 (24)	-26130 (31)	-10727 (41)	588 (8)
C(4, 10)B	43343 (26)	-32542 (31)	-16767 (45)	645 (9)
C(5, 11)B	34192 (24)	-26260 (33)	-17639 (42)	609 (8)
C(6, 12)B	33300 (20)	-13660 (30)	-12332 (38)	509 (7)

which is now 1.456 (4) \AA rather than 1.42 (1) and 1.49 (1) \AA .

YU carried out 'block-diagonal' refinement, which would have masked the near singularities involved in refining the closely centrosymmetric structure in a noncentrosymmetric space group. However, convergence should have been difficult to achieve (the final shift-to-e.s.d. values are not specified). Accordingly, I carried out four cycles of full-matrix refinement of the reported Pn parameters (YU, Table 1 and SUP 38841), with predictable results: no sign of convergence, large and irregular e.s.d.'s (on the average, about four times as large as reported by YU), distorted bond lengths and angles (for instance, the C-O distances ranged from 1.09 to 1.29 \AA), and highly anisotropic U_{ij} 's. Under these circumstances there is little choice but to opt for the $P2/n$ description, bearing in mind that the diffraction data cannot distinguish between this disordered structure and any of a number of ordered structures in Pn and thus despairing of obtaining a reliable differentiation between the bonding around the N and the CH groups in the central ring of the acridine molecule.

Discussion

All three of these examples carry the same message: unless a clear choice can be made in favor of a noncentrosymmetric model, it is better to describe a structure as centrosymmetric even though disorder results. In the first two examples the disorder comes from the molecules or ions apparently assuming a number of different conformations or orientations; in the third example the disorder involves the random interchange of two orientations of an acridine molecule (or, alternatively, the random interchange of an N atom and a CH group).

The overwhelming advantage of the centrosymmetric descriptions is that refinement proceeds normally, without the near-singularities that are inherent

in attempts to refine in a noncentrosymmetric space group (Ermer & Dunitz, 1970). There is also a less tangible advantage: in accepting the disordered, centrosymmetric representation one must also accept that the results are an average of two or more structures, and hence that detailed knowledge of any of these contributing structures may not be available from diffraction data alone. Attempts to refine in the corresponding noncentrosymmetric space group must encounter problems of near-singularity. In addition, if satisfactory convergence somehow seems to be attained in the noncentrosymmetric space group, one may be deluded into believing that a unique solution has been found when in fact many other structures might be - and probably are - equally satisfactory.

This is not to say that *all* nearly centrosymmetric structures should be treated in this way. There are many examples of small but real deviations from centrosymmetry, particularly for compounds with small B 's as in low-temperature phases or in some inorganic systems. But there are many, many *more* examples of the type described here, where a noncentrosymmetric model has been derived without careful consideration as to whether other models - including the centrosymmetric one - would be satisfactory.

Finally, we urge once more that, if a distinction between a centrosymmetric model and a noncentrosymmetric model is to be attempted, the weak reflections be given the most careful scrutiny. They are the ones most sensitive to the ambiguity.

Added comment. A referee asks what is meant by a 'clear choice' of a noncentrosymmetric model. I don't know. Statistical tests, based on whether or not the additional parameters yield meaningful reduction in various residuals, surely are not definitive: unknown errors are invariably present [perhaps in $I(\text{obs.})$, due to absorption, anisotropic mosaicity, beam inhomogeneity, or whatever; perhaps in $I(\text{calc.})$, due to valence electrons, non-ellipsoidal U 's, monochromator effects, or whatever], and one cannot know how the additional parameters may accommodate such errors. Other physical techniques, such as 'second-harmonic' or piezoelectric measurements, when carefully applied, can sometimes be helpful. But when diffraction data alone are available, a sensible course might be to decide, on mainly subjective grounds, whether or not a centrosymmetric model gives satisfactory agreement between $I(\text{obs.})$ and $I(\text{calc.})$; if it does, there can be no profit in worrying about noncentrosymmetry. Thus, the quandary moves from 'clear choice' to 'satisfactory'. The decision remains with the investigator.

Computational details. All least-squares refinements were based on full-matrix minimization of the quantity $\sum w(F_o^2 - F_c^2)^2$. Since none of the F tables included error estimates, weights w were taken equal

to $1/F_o^2$ for $F_o \geq 4F_o$ (min.) and $\frac{1}{4}F_o \times F_o$ (min.) otherwise (Marsh & Schomaker, 1979). Except where indicated, final shifts were less than 0.1 e.s.d. Calculations were carried out on a VAX-750, using the CRYM system of crystallographic programs.

I am grateful to K. Slagle for much assistance in the data processing, to V. Schomaker for many helpfully critical comments, and to the National Institutes of Health for financial support (Grant No. GM 16966).

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SHORT COMMUNICATION

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Acta Cryst. (1986). B42, 198-200

Least-squares refinement of two protein molecules per asymmetric unit with and without non-crystallographic symmetry restrained. By A. TULINSKY and R. A. BLEVINS,* *Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA*

(Received 17 June 1985; accepted 23 October 1985)

Abstract

Monoclinic crystals of α -chymotrypsin (α -CHT) possess two molecules per asymmetric unit related by non-crystallographic twofold symmetry. The structure has been refined as such at 1.67 Å resolution [free refinement: Blevins & Tulinsky (1985). *J. Biol. Chem.* 260, 4264-4275] and, now, with the equivalence imposed. The equivalence was restrained to conform to expected errors in coordinates (moderate refinement) and to a stringent restraint of 0.05 Å (tight refinement). All three refinements led to a highly acceptable geometry and *R* values (0.179-0.198) along with other key indicators. As anticipated, the tight refinement produced a highly twofold-related structure whereas the moderate refinement produced non-equivalence not unlike that observed in the free refinement: main-chain folding was equivalent but side chains on the surface and in the dimer interface were in general not equivalent. The determination of the solvent structure deteriorated spectacularly in going to the tight equivalence restraint. In cases of high resolution and high quality data, imposition of non-crystallographic symmetry appears ill-advised since the data will preserve the equivalence. At lower resolution, and/or with inferior data, restraining symmetry could be advantageous and expedient in obtaining a consensus structure.

The restrained least-squares refinement of α -chymotrypsin (α -CHT) at 1.67 Å resolution as two molecules per asymmetric unit has shown that the side chains are generally nonequivalent around the surface and in the dimer interface region (Blevins & Tulinsky, 1985*a*) (referred to hereafter as free refinement), which is consistent with other crystallographic observations (Mavridis, Tulinsky & Liebman, 1974; Tulinsky, Mavridis & Mann, 1978; Tulinsky, 1980). However, the main-chain folding and certain other important regions of the two molecules, such as the catalytic and specificity sites, are practically identical. Since there are many instances of more than one molecule per asymmetric unit in protein crystals, we have investigated the effect of imposing equivalence as a restraint in refinement. Since the restraint is not exact, a 'tight' and a 'moderate' alternative were pursued and these results are compared with those of the free refinement (Blevins & Tulinsky, 1985*a*).

The refinement of α -CHT dimer was performed using Hendrickson's program *PROLSQ* (Hendrickson & Konert, 1980): (1) by imposing non-crystallographic twofold symmetry restrained to conform to expected errors in coordinates (0.20-0.25 Å)† (moderate) and (2) as in (1) but with a stringent restraint of 0.05 Å (tight). The results of the free refinement have appeared elsewhere (Blevins & Tulinsky, 1985*a, b*) along with a description of the experimental procedures employed to obtain and process the

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† 0.50 Å proved to be equivalent to no restraint.