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.

References


Centrosymmetric or Noncentrosymmetric?*

BY RICHARD E. MARSH

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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—P1, P21—P21/m, Cc—C2/c, Pna21—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 $F_{\text{ BACKUP}}$, 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.

(1) Dichloro[1,2-ethanedione bis(dimethylhydrazone)]($\eta$-ethylene)platinum(II)

The structure of this compound, PtCl$_2$(C$_2$H$_4$)$_2$-(C$_6$H$_4$N$_4$)$_2$, was described in space group $P2_1/m$ [monoclinic; $a = 8.998$ (3), $b = 8.133$ (4), $c = 9.872$ (2) Å, $\beta = 106.72$ (3)$^\circ$, $Z = 2$] 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–CH$_3$ bond lengths could well be equal; if so, the minimum length would be about 1.45 Å, for four N–CH$_3$ bond lengths 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 C(5) and C(6) should 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–CH$_3$ 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
be of use.) Many such models can be devised, all leading to essentially equivalent R's. For example, I attempted further refinement, in P2₁, beginning with the coordinates and Uₜ'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' P₂₁ model can be found.

Another, perhaps more convincing, argument can be made against the BFMP model - and, by implication, against any P₂₁ model. Included in SUP 39649 are F(obs.) and F(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 3; they clearly favor the centrosymmetric model. For these reflections, the average value of F(calc.) for the P₂₁ model is appreciably larger than F(obs.), undoubtedly because of the imaginary component of F(calc.); this trend should be evident in any P₂₁ model. The trend is much less severe for the P₂₁/m model, where the imaginary component is absent.

In sum: lacking further evidence, we must be content with the P₂₁/m description and an apparently disordered model which precludes any precise description of the structure of an individual molecule.

(II) Cu([12]aneS₄)(ClO₄)₂·H₂O

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 Pbc2₁ [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 Pbc2₁. 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 Pbc2₁ refinement (PDDCCGOR). However, the C–C distances remain unrealistically small, ranging from 1.22 (2) to...
that could be devised in surely but one of an immense family of structures at first glance to be unique and unambiguous, it is uncertainties in the structure, caused by the disorder in the particular model derived by PDDCCGOR appears atom positions, are there for all to see. While the advantage does such a model have over the derived by PDDCCGOR? Besides the obvious one of attaining considerably better agreement with the F(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–C–S groups and differing orientations of the perchlorate ions.

Table 2. PtCl₂(C₆H₄,N₄): some sums for the unobserved reflections.  

<table>
<thead>
<tr>
<th>No.</th>
<th>F(obs.) &gt; 0</th>
<th>F(obs.) = 0</th>
</tr>
</thead>
<tbody>
<tr>
<td>P₂₁⁺</td>
<td>P₂₁⁻</td>
<td>P₂₁⁻</td>
</tr>
<tr>
<td>Σ F(obs.)</td>
<td>730</td>
<td>734</td>
</tr>
<tr>
<td>Σ F(calc.)</td>
<td>910</td>
<td>796</td>
</tr>
<tr>
<td>Σ ΔF</td>
<td>326</td>
<td>285</td>
</tr>
<tr>
<td>R</td>
<td>0.45</td>
<td>0.39</td>
</tr>
<tr>
<td>(a) Bavoso et al. (1984).</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) This work, Table 1.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.27 (3) Å. Moreover, the three independent S–C–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 Uᵦ’s with implied r.m.s. displacements of 0.5–0.6 Å in directions perpendicular to the S–C–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 anisotropic, ranging from 1.45 (3) to 1.56 (3) Å. 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 Uᵦ’s.

We are left, then, with a model in Pbcm in which the three S–C–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 Pbc₂₁ structure derived by PDDCCGOR? Besides the obvious one of attaining considerably better agreement with the F(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 Pbc₂₁, each differing in 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(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–C–S groups and differing orientations of the perchlorate ions.

(III) The 1:1 complex of 1,4-dithiintetracarboxylic N,N'-dimethylimidamide and acridine, C₁₀H₆N₂O₄S₂C₁₃H₉N

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Uₑq (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1265 (2)</td>
<td>1298 (1)</td>
<td>2500</td>
</tr>
<tr>
<td>Cl(1)</td>
<td>3397 (5)</td>
<td>4705 (3)</td>
<td>2500</td>
</tr>
<tr>
<td>Cl(2)</td>
<td>7928 (6)</td>
<td>2500</td>
<td>0</td>
</tr>
<tr>
<td>S(1,4)</td>
<td>814 (3)</td>
<td>252 (2)</td>
<td>1318 (2)</td>
</tr>
<tr>
<td>S(2,3)</td>
<td>2716 (4)</td>
<td>1981 (2)</td>
<td>1307 (2)</td>
</tr>
<tr>
<td>O</td>
<td>-702 (12)</td>
<td>2037 (7)</td>
<td>2500</td>
</tr>
<tr>
<td>O(1,2)</td>
<td>4312 (16)</td>
<td>4639 (12)</td>
<td>1757 (9)</td>
</tr>
<tr>
<td>O(3)</td>
<td>2444 (16)</td>
<td>4035 (11)</td>
<td>2500</td>
</tr>
<tr>
<td>O(4)</td>
<td>2686 (24)</td>
<td>5384 (13)</td>
<td>2500</td>
</tr>
<tr>
<td>O(5,6)</td>
<td>7142 (16)</td>
<td>2779 (9)</td>
<td>782 (10)</td>
</tr>
<tr>
<td>O(7,8)</td>
<td>8681 (19)</td>
<td>1829 (8)</td>
<td>249 (10)</td>
</tr>
<tr>
<td>Cl(1,6)</td>
<td>2380 (17)</td>
<td>390 (14)</td>
<td>497 (13)</td>
</tr>
<tr>
<td>Cl(2,5)</td>
<td>2994 (28)</td>
<td>1112 (9)</td>
<td>422 (15)</td>
</tr>
<tr>
<td>Cl(3,4)</td>
<td>4420 (15)</td>
<td>2030 (12)</td>
<td>2032 (13)</td>
</tr>
<tr>
<td>Cl(7,8)</td>
<td>1471 (21)</td>
<td>-544 (8)</td>
<td>2957 (11)</td>
</tr>
</tbody>
</table>

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, β = 92.20 (5)°, Z = 2] and refined to an R of 0.039 for 1544 reflections with I > 3σ(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 Uᵦ’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,
which is now 1.456 (4) Å rather than 1.42 (1) and 1.49 (1) Å.

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 noncentrosymmetric space group. However, converging to the closely centrosymmetric structure in a noncentrosymmetric model has been derived without careful consideration of obtaining a reliable differentiation between the centrosymmetric and noncentrosymmetric representations. 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(obs.), due to absorption, anisotropic mosaicity, beam inhomogeneity, or whatever; perhaps in I(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(obs.) and I(calc.); if it does, there can be no profit in worrying about noncentrosymmetry. Thus, the quinary of 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 for all observations.
to $1/F_o^2$ for $F_o \geq 4F_o$ (min.) and $1/4F_o \times F_o$ (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).

References


SHORT COMMUNICATION

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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 $\alpha$-chymotrypsin ($\alpha$-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.

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