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SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

Acta Cryst. (1979). B**35**, 1933

Produit de cyclisation: la dihydro-5,6 (oxo-2 propyl)-6 4*H*-pyrrolo[1,2-*a*]thiéno[3,2-*f*][diazépine-1,4] one-4. Errata.

Par NGUYEN-HUY-DUNG, *Laboratoire de Chimie Minérale et Structurale, UER des Sciences Pharmaceutiques de Caen,* 1 *rue Vaubenard,* 14032 *Caen CEDEX, France* et SYLVAIN RAULT et MAX ROBBA, *Laboratoire de Pharmacie Chimique, UER des Sciences Pharmaceutiques de Caen,* 1 *rue Vaubenard,* 14032 *Caen CEDEX, France*

(*Reçu le* 14 *juin* 1979)

Abstract

In the paper by Nguyen-Huy-Dung, Rault & Robba [*Acta Cryst.* (1979), B**35**, 1290–1293] the values given for M_r, D_x and μ are incorrect. The correct values are: $M_r = 260{\cdot}31$, $D_x = 1{\cdot}40$ Mg m^{-3}, $\mu = 0{\cdot}256$ mm^{-1}.

Le résumé contient tous les détails.

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Some comments on refinement in a space group of unnecessarily low symmetry.*

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Abstract

Releasing the constraint of a center of symmetry causes a well known singularity, which, however, often goes unrecognized. Deleting an element of translational symmetry (transition to a supercell) also causes singularity. In contrast, deleting any element other than a center or a pure translation (to give a lower Laue group) is uneventful.

* Contribution No. 5962 from the Arthur Amos Noyes Laboratory.

Lee (1971) has suggested that 'in cases where the space group is not absolutely certain, from a structural point of view it is safest (and cannot be wrong) to assume the lower symmetry'. In rebuttal, Donohue (1971) pointed out that the logical import of Lee's suggestion is that all structures should

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be refined in space group $P1$, and concluded that 'Unfortunately, the least-squares method cannot then be used, for if a set of parameters corresponding to a higher symmetry is refined in $P1$, catastrophic results will ensue (see Ermer & Dunitz, 1970)'. While we agree with Donohue's thesis that 'A crystal structure should not be refined in a space group of unnecessarily low symmetry', and can see neither profit nor point in so doing, his prediction of catastrophic results is not always correct.

In fact, refinement difficulties – that is, singularities or near singularities in the least-squares matrix – will ensue only if the lowering of the symmetry involves the removal of a center of symmetry. If instead of a center some other symmetry element is removed, thereby reducing the Laue symmetry, then no general difficulty results: least-squares refinement can proceed uneventfully, and the derived structure should be entirely normal (except for special cases as, for example, when the increased number of parameters may exceed the number of independent observations). Thus, a structure with the symmetry of space group $P2_1$ can be refined quite normally in space group $P1$, whereas a structure with the symmetry of $P\bar{1}$ cannot.

This conclusion follows intuitively from the very concept of Laue symmetry. Except for anomalous dispersion, the symmetry of the diffraction problem *is* the Laue symmetry, and any deviation, however small, from a given Laue symmetry is reflected in corresponding changes in the symmetry of the diffraction pattern, including the distribution of the intensities. In particular, the derivatives of the intensities with respect to any parameter that describes a lowering of the Laue symmetry will not in general all vanish.

An example of a successful refinement in a space group of unnecessarily low symmetry is bis(tetraethylammonium) tetrachlorodioxouranate(VI) (Bois, Nguyen & Rodier, 1976), where satisfactory refinement and a reasonable structure were obtained in space group $P\bar{1}$; we have demonstrated (Schomaker & Marsh, 1979) that the structure can be more appropriately described in $P2_1/n$. We have also worked out explicit structure factor expressions for unsymmetrical distortions from several simple space groups ($P2$, $P2_1$, Pm, Cc, $P2/m$, $P2_1/n$, and $R3$), retaining any centers but otherwise taking care in each case to consider the most general displacement of a position that included no change in the *average* position corresponding to the original symmetry. For a general starting position and a general reflection hkl, the derivative of $|F(hkl)|$ with respect to any such displacement (or with respect to unsymmetrical changes in an occupation parameter) was always seen not to vanish. On the other hand, these derivatives *are* zero if the lowering of symmetry involves only a small distortion from a centrosymmetric structure, for in this case neither the Laue symmetry nor the diffraction intensities change (ignoring any effect due to anomalous dispersion); the sole change in the structure factor F is to add a small imaginary component to the original, real value, and the derivative of $|F|$ with respect to the distortion vanishes.

Accordingly, deleting a centrosymmetric constraint does cause singularity, and difficulties in refining centrosymmetric structures in non-centrosymmetric space groups have been described many times in the literature. However, in many other instances these difficulties appear to have been hidden, either intentionally or unintentionally, by a blocking of inversion-related atoms into separate refinement matrices; in such instances, the only hints of trouble may be slow convergence and unreasonable results. As Ermer & Dunitz (1970) pointed out, it is not possible to obtain successful refinement to a reasonable non-centrosymmetric structure merely by expanding the parameters of a centrosymmetric model. In this regard, we emphasize that the reflections most crucial to the decision as to whether or not a structure is centrosymmetric are the very weak ones, for it is these reflections that are most sensitive to the small imaginary components arising from non-centrosymmetric distortions. The common practice of deleting weak reflections from the data set may make it difficult or impossible to reach the correct decision. Of course, a strict decision is more difficult to make the more nearly the structure is centrosymmetric – and in the limit impossible by diffraction alone.

It is now natural to ask what conditions will lead to singularity, aside from insufficient data. We note three cases, the third perhaps not previously emphasized: (1) any small distortion asymmetric to a center of symmetry, which only adds a small imaginary component to the original real F, so that the derivative of $|F|$ with respect to the distortion vanishes; (2) any allowed free shift of origin in a polar space group, which only rotates the original complex F, so that again the derivative of $|F|$ vanishes; (3) a transition to a supercell. Here, the derivatives of the supercell intensities with respect to a distortion leading to that supercell vanish, in view of $dI \propto |F|\, d|F|$, because the initial supercell F's are themselves zero. The derivatives of the original subcell intensities also vanish because the contribution F_i of any site, i, in the subcell is just the same, and of just the same phase, for each of the subcells that will make up a supercell. If the generation of the supercell involves atomic displacements, the contributions due to these displacements are at right angles to F_i and the sum over the subcells in a supercell vanishes for any set of displacements that preserves the original subcell average; if ordering of the site occupations is involved, the contributions from the various subcells will all be parallel to F_i but will sum to zero, again for any rearrangement that preserves the subcell averages. As in the centrosymmetric–non-centrosymmetric problem, the nature of the distortions giving rise to supercell reflections cannot be determined by any refinement process that begins with the undistorted, subcell structure.

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