S2-O15

Redetermination of Triethyl Phosphine Sulfide: A Commensurately Modulated Structure

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The preliminary work of the structure of triethyl phosphine sulfide, $SP(C_2H_5)_3$ was done by Merrssche, M. V. & Leonard, A. (1959). The parent structure has space group $P6_3mc$ with 1:1 disorder across the mirror plane (Fig. 1). There are two molecules per cell situated on 2_1 screw related sites at 1/3, 2/3, *z* and 2/3, 1/3, *z*+1/2. They considered removal of the disorder by reducing the symmetry to *P31c*, destroying the 2_1 screw operations. Both of their models suffer from high anisotropic atomic displacement parameters in the *c* axis direction.

Data for the compound were recollected on a Kappa CCD area detector diffractometer. Synthetic *hkn*: n=0,1,2 precession photographs show weak reflections that double the *a* and *b* axes (Fig 2), leading to a $Ccm2_1$ orthorhombic space group with $a_o' = 2a_p + b_p$, $b_o' = b_p$, $c_o' = c_p$ with four molecules per cell. It is possible to explain modulation of four molecules per cell in $Ccm2_1$: the primitive orthorhombic subgroups of $Ccm2_1$ are $Pna2_1$, $Pca2_1$, $Pnm2_1$ and $Pcm2_1$. Inspection of the synthetic precession photographs shows the *n* glide absence condition holds (*0k'l'*, *k'+l'*=2n+1) whereas the *c* glide (*0k'l'*, *l'*=2n+1) and *a* glide (*h'0l'*, *h'*=2n+1) absence conditions do not.

Taking account of the anisotropic displacement parameters described in the original determination, we first try to explain the extra reflections using space group $Pnm2_1$ with 3-fold twinning restoring the original hexagonal diffraction symmetry. This mode keeps the disordering of the ethyl chains but allows displacement of the molecules in the *x* and *z* directions. A further modulation is the partial ordering of the ethyl groups with molecules at sites separated by 0 or 1/2 in *z* which occurs for the $Pna2_1$ subgroup. The coexistence of the $Pnm2_1$ and $Pna2_1$ modes produces a local symmetry of *Pn* which with 6-fold twinning also gives the observed hexagonal diffraction symmetry.

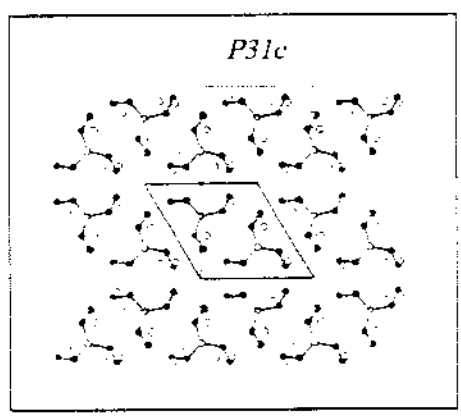

Figure. 1. The 1:1 disorder of $SP(C_2H_5)_3$ of the hexagonal space group *P31c* (● and ○ represent the two orientations).

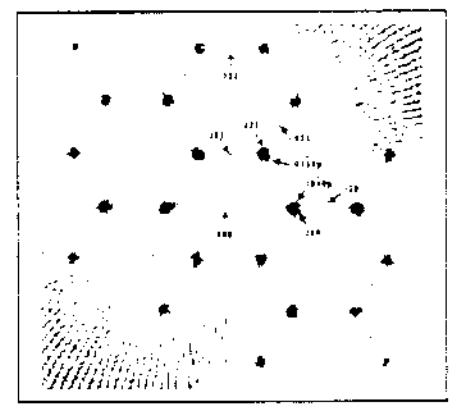

Figure. 2. Synthetic precession *hk*1 photographs that appear to double the *a* and *b* axes.

Keywords: Crystallography, Commensurate modulation structure, Modulated structure, Refinement problem

References

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