The Suggested Role of Partial Dislocations in the Single Crystal $\rightleftharpoons$ Single Crystal Phase Transition of a Cyclo-octane Molecular Cationic Salt

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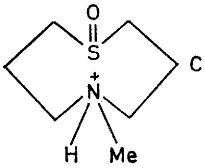
It is suggested that the facile low-temperature solid-state inter-conversion of the α- and β-phases of 5-methyl-1-thia-5-azoniacyclo-octane 1-oxide perchlorate occurs on recurrent (102) type planes. The mechanism, which is likely to be of general validity in organic solid-state chemistry, dispenses with the need to postulate co-operative conformational changes on half of the molecular cations (mol-ions) in each row and in each column, and also explains all the known experimental facts relating to the transition.

DURING the course of the determination of the crystal structure of 5-methyl-1-thia-5-azoniacyclo-octane 1-oxide perchlorate (I), Paul and Go[1] discovered a remarkable process in which the molecular cations (mol-ions) undergo a reversible change in relative orientation within the unit cell when the temperature is varied between 3 and 25 °C. Although the enthalpy and entropy changes, and even the precise temperature of the transition are not yet known, it is nevertheless clear that the conformation of the individual, eight-membered-ring mol-ions is an approximate 'boat-chair,' being effectively unchanged by the crystalline transformation. It is also clear that the phase transition is topotactic (see ref. 2—4 for a definition and discussions of topotactic reactions in organic chemistry), and that there is 'no visible change in the appearance of the crystal'[1] during the transformation. The form stable at 3 °C [α-(I)] belongs to the space group $P2_1/c$ with dimensions[1] $a = 9.87$, $b = 8.78$, $c = 13.26$ Å and $\beta = 97° 54'$, whereas the β-form, stable at 25 °C, has a space group $P2_1/a$ with $a = 20.10$, $b = 8.89$, $c = 6.77$ Å and $\beta = 97° 48'$.



(I)

From an analysis of the crystal and molecular structures of α- and β-(I), Paul and Go[1] suggested that the phase transition may be visualized in terms of one-half of the mol-ions in each row and in each column of one phase undergoing a ring inversion and a rotation as shown in Figure 1. They also argued that, since diffusive motion is unlikely—in view of the facile nature of the interconversion—the actual mechanism of the transformation also entails the co-operative and organized processes of inversion and rotation of half the total number of mol-ions and half the total of perchlorate anions as symbolized in Figure 2 (where the D- and L-notation distinguish the appropriate enantiomeric forms of the mol-ions).

Whilst it is indeed true that lattice sites containing one-half the enantiomeric mol-ions in each row and column become occupied, as a result of the phase transition, by the apposite enantiomers, it does not follow that the actual inversion and rotation are crucial, and may not even be necessary. We should like to propose an alternative mechanism for the transformation, based on the simple idea of co-operative planar shear, the analogical and interpretative value of which has been under-utilized in chemical discussions (see refs. 3 and 5).

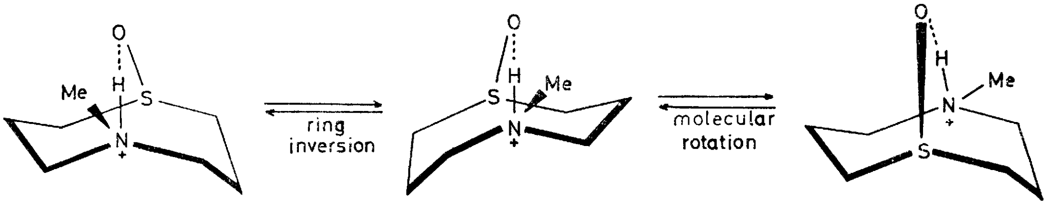


FIGURE 1 Illustration of the conformational change, consisting of ring inversion and molecular rotation, which Paul and Go[1] suggest is necessary for one-half of the mol-ions in each row and each column to undergo during the phase transition

First consider the (102) type planes[*] in the α-form (see Figure 3) and suppose that a partial dislocation of Burgers vector $\frac{1}{2}[\bar{2}01]$ is passed through one of these planes. The net effect is to 'deform' the crystal so as to yield the profile outlined in Figure 3(b). {Note that the net effect of the passage of a partial dislocation on a given (102) type plane is to shift all ions beyond that plane in either the $\frac{1}{2}[201]$ or $\frac{1}{2}[20\bar{1}]$ direction. For

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[*] The Miller indices (102) suggest themselves because it is noted that on going from the α- to the β-form the *a* unit-cell vector approximately doubles, the *b* dimension remains essentially unchanged, and the *c* value approximately halves.

[1] I. C. Paul and K. T. Go, *J. Chem. Soc.* (*B*), 1969, 33.

[2] M. D. Cohen and B. S. Green, *Chem. in Britain*, 1973, **9**, 490.

[3] J. M. Thomas, *Phil. Trans. Roy. Soc.*, 1974, **277**, 251.

[4] I. C. Paul and D. Y. Curtin, *Accounts Chem. Res.*, 1973, **6**, 217.

[5] J. M. Thomas, *Adv. Catalysis*, 1969, **19**, 293; *Chem. in Britain*, 1970, **6**, 60; J. M. Thomas and J. O. Williams, *Progr. Solid-State Chem.*, 1971, **6**, 121.

simplicity only a few curved arrows denoting this shift are shown in Figure 3(a) and (b), *etc.*} If a similar partial dislocation glides in the opposite sense, *i.e.* $\frac{1}{2}[20\bar{1}]$ on the alternate (102) type plane, the new crystalline profile will be that shown in Figure 3(c). Clearly, the recurrent passage of glissile partial dislocations on alternate (102) planes yields ultimately the β-form of the crystal [note the circumscribed unit cells in Figures 3(a) and (e)]. The single-crystal $\rightleftharpoons$ single-crystal transformation may, therefore, be envisaged to take place without postulating the occurrence of rotation and inversion (*i.e.* without the need for conformational changes in mol-ions fixed at lattice sites). Even though 'translation' of the enantiomeric mol-ion is required in this new mechanism, no diffusive motion in the usually accepted sense is demanded. The proposed interpretation, which corresponds to co-operative shear, brings this particular phase-transition closer to phenomena well-known in the realm of metallurgy and mineralogy. The kinship between the mechanism summarized in Figure 3 and the accepted picture for the diffusionless martensitic transformation displayed by, for example, metallic cobalt [6,7] (in going to and from the cubic and hexagonal phases) is to be noted. There is also a marked similarity between our mechanism for (I) and the inter-relationship recently recognized [8,9] to

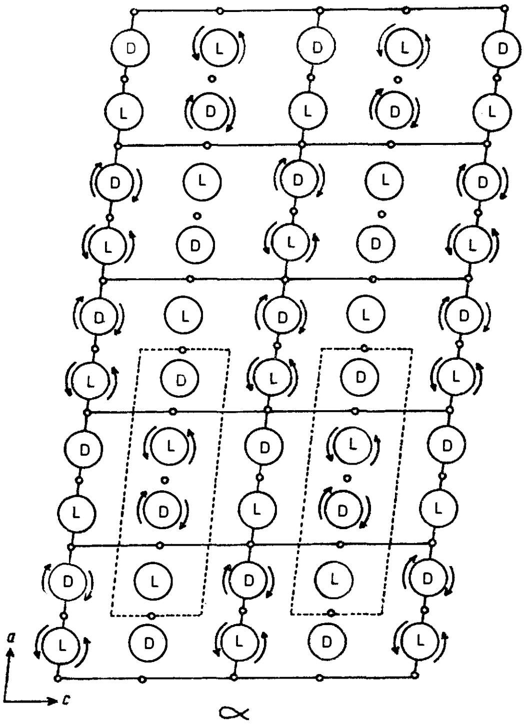

FIGURE 2 Projection along [010] of the α-phase. The large circles represent the molecular cations (the D and L designating the appropriate enantiomorphs) and the small circles the perchlorate. The outline of two cells of the β-form are also superimposed in dotted lines. The particular mol-ions which, according to Paul and Go,[1] are required to rotate and invert during the phase transition are also represented, the direction of the arrows indicating the sense of the rotation.

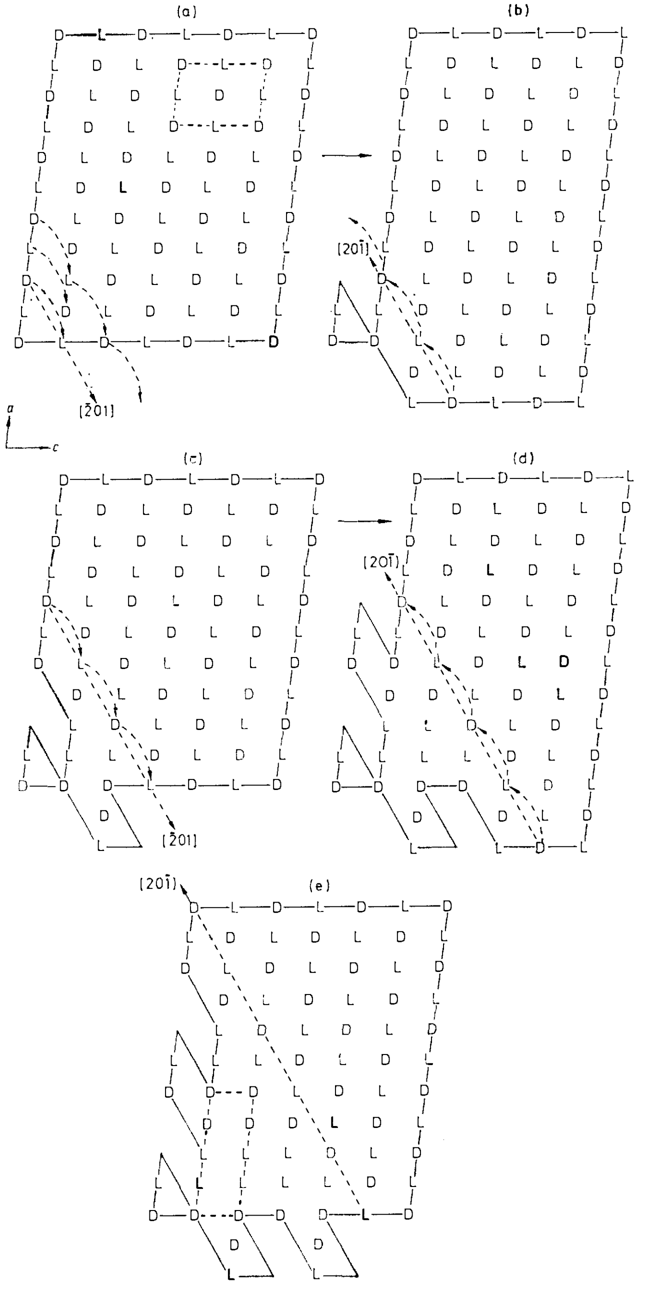

FIGURE 3 Schematic model of the progressive conversion of the α- to the β-form by the passage of partial dislocations. For simplicity only the cations are shown. In (a) the (102) plane on which the shear of $\frac{1}{2}$ $[\bar{2}01]$ leads to (b), is shown. In (b) the (102) plane in which the opposite shear of $\frac{1}{2}$ $[20\bar{1}]$ operates is delineated. The arrows indicate some of the translations which result from the operation of (102) $\frac{1}{2}$ $[\bar{2}01]$ and (102) $\frac{1}{2}$ $[20\bar{1}]$. By progressive opposite shear of $\frac{1}{2}$ $[\bar{2}01]$, $\frac{1}{2}$ $[20\bar{1}]$, $\frac{1}{2}$ $[\bar{2}01]$, *etc.*, on adjacent planes the α- is converted into the β-phase. Note the outlined unit cells in (a) and (e)

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[6] E. Votova, *J. Inst. Metals*, 1961, **90**, 129.

[7] F. R. N. Nabarro, 'Theory of Crystal Dislocations,' Clarendon Press, Oxford, 1967.

[8] J. S. Anderson and R. J. D. Tilley in 'Surface and Defect Properties of Solids,' eds. M. W. Roberts and J. M. Thomas, Chemical Society, London, 1974, vol. 3, p. 33.

[9] I. E. Grey and A. F. Reid, *J. Solid State Chem.*, 1972, **4**, 186.

exist between rutile (TiO_2) on the one hand and its high-pressure polymorph, which has the α-PbO_2 structure, on the other. The α-PbO_2 structure may be generated from the rutile structure as a result of the passage of recurrent partial dislocations again in opposite senses on contiguous (011) planes. A mechanism such as the suggested diffusionless martensitic transformation of the α-(I) $\rightleftharpoons$ β-(I) accounts for all the known experimental facts [including the minor changes in volume (*ca.* 5%) and shape.]*

It need not follow that (102) type planes are the only possible ones which permit shear of the kind needed to interconvert the α- and β-forms of (I) but it does appear likely that any other feasible planes should have a common zone axis, *i.e.* along [010]. There may well be others. It must also be borne in mind that the new interpretation for this single-crystal $\rightleftharpoons$ single-crystal phase transition could also be cast in the language of lattice-dynamic theory.[10] Thus one may envisage the conversion of the α- to the β-form to be effected by the softening of phonon modes along the [102] directions within the α-phase. In this framework also it is again not necessary to picture conformational changes taking place in mol-ions fixed at certain lattice sites.

It is clearly desirable that measurements of the energetic and crystalline parameters associated with the phase transition of (I) (and related materials which display the same phenomenon) as well as refined spectroscopic measurements to detect conformational changes be carried out. In particular it would be of interest from the standpoint of our proposed mechanism to discover whether the transformation can be stress-induced.[11] Unfortunately samples of (I), which are liable to undergo explosive decomposition, are not easy to prepare.[12] Attempts are now underway to prepare mol-ion salts containing the same cyclo-octane derivative as cation but other anions.

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* The mechanism implies, *inter alia*, that the driving force for the conversion is bound up with the stacking-fault energies of extended faults in the solid. These energies in turn devolve upon the intermolecular forces associated with nearest and next-nearest neighbouring species.

[10] G. S. Pawley in ' Transfer and Storage of Energy by Molecules,' ed. G. M. Burnett and A. M. North, 1974, ch. 4.

[11] M. J. Bevis and P. S. Allen, in ' Surface and Defect Properties of Solids,' eds. M. W. Roberts and J. M. Thomas, Chemical Society, London, 1974, vol. 3, p. 93.

[12] A. E. Yethon, Ph.D. Thesis, University of Illinois, 1963.