

Disorder and not Incipient Reaction is the Cause of the Anomalies in the Crystal Structure of *trans*-4-Chloro-2,4,6-tris(trichloromethyl)-1-oxa-3,5-dithiane

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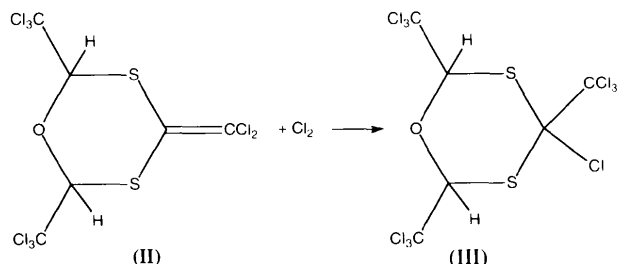
(Received 11 February 1994; accepted 19 September 1994)

Abstract

trans-4-Chloro-2,4,6-tris(trichloromethyl)-1-oxa-3,5-dithiane is orthorhombic at 295 K, $a = 12.236(2)$, $b = 43.051(4)$, $c = 13.010(5)$ Å, *Pbca*, $Z = 16$ [Irving & Irving (1988). *J. Crystallogr. Spectrosc. Res.* **18**, 439–446]. These authors refined the structure to $R_F = 0.042$ using 3725 diffractometer-measured reflections. The results were unusual in that one (*A*) of the two independent molecules in the asymmetric unit was well defined, whereas the other (*B*) showed C—Cl bond lengths significantly longer than normal. The anomalies were interpreted as providing 'a unique demonstration of the reaction path preceding 1,2-*trans*-elimination of a molecule of chlorine from the >CCl—CCl₃ group at position 4'. We propose an alternative explanation in which the second site is occupied at random by molecules mutually rotated by 180° about the (partial and approximate) molecular twofold axis. This model could be refined to $R_F = 0.0395$ and provides a more reasonable explanation of the experimental results than that originally offered. Analysis of the thermal motion of molecule *A* shows that the ring system has considerable flexibility.

1. Introduction

The crystal structure of *trans*-4-chloro-2,4,6-tris(trichloromethyl)-1-oxa-3,5-dithiane [C₆H₂Cl₁₀OS₂; (III) in the reaction scheme below] was reported as orthorhombic with two crystallographically independent molecules in the asymmetric unit (Irving & Irving, 1988).



Solution of the structure by direct methods and subsequent refinement to $R = 0.042$ showed that one

of the independent molecules (*A*) was well defined, but the other (*B*) had unusual values for one C—C and two C—Cl bond lengths [for the latter, C(4A)—Cl(4) = 2.114(9), C(41A)—Cl(C4) = 2.075(10) Å]. These anomalous values were interpreted as showing that the 'title compound represents the first case in which a single structure has provided, albeit serendipitously, a clear indication of the reaction pathway that would be followed in the *trans*-elimination of chlorine from the grouping >CCl—CCl₃'. Such an interpretation immediately poses a number of chemical questions and has led us to explore alternative explanations for the experimental results. We propose a model in which the unusual *apparent* interatomic distances are explained by having the site of the second crystallographically independent molecule occupied in a disordered fashion by two molecules mutually rotated by 180° about their (partial and approximate) twofold axis through opposing O and C atoms of the oxadithiane ring.

Analysis of the thermal motion of molecule *A* shows that it does not behave as a rigid body and that there is appreciable intramolecular libration of the —CCl₃ groups.

All the crystals considered in this paper are racemates. However, reactions and structures are generally discussed in terms of one enantiomer only, maintaining where possible constant optical configuration; extension to the second enantiomer is assumed.

2. Chemical and crystallographic background

2.1. Synthesis of (III)

The title compound (III) was prepared by Irving & Irving (1988), following Chattaway & Kellett (1929), by passing dry chlorine gas into a suspension of β -2,6-bis(trichloromethyl)-4-dichloromethylene-1-oxa-3,5-dithiane [C₆H₂Cl₈OS₂; (II)]; Cl₂ adds to the double bond of (II) to give C₆H₂Cl₁₀OS₂ (III) (Fig. 1). Chemical analysis (C, H, S) of the product gave excellent agreement with the formula C₆H₂Cl₁₀OS₂.

The crystal structure of the precursor (II) has been determined (Irving & Irving, 1986; CSD refcode FUT-POZ); space group $P\bar{1}$ with $Z = 4$. The two molecules in the asymmetric unit chosen for structure analysis [*A* and *B* in the nomenclature of Irving & Irving (1986)]

have opposite optical configurations. The flexibility of the oxadithiane rings is shown by one molecule (*B*) having approximate twofold symmetry, while the other (*A*) deviates appreciably (torsion angles given in Fig. 1). The average conformation in solution undoubtedly has twofold symmetry.

Chlorination of double bonds proceeds through an ionic mechanism (*e.g.* Streitwieser & Heathcock, 1985). A cyclic chloronium cation is first formed, which is then attacked by chloride ions from the opposite side of the double bond to give the *anti*-dichlorinated product. Because of the twofold symmetry of (II), one would expect only one isomer to be produced; this agrees with Chattaway & Kellett [(1929) their scheme and remarks on p. 2912].

2.2. Some details of the published crystallographic analysis

Although it was noted that 'very few of the well formed crystals (colourless square platelets) gave a diffraction pattern at all', the sample used for intensity measurements gave reflections with Mo $K\alpha$ up to (at least) $2\theta = 50^\circ$. Measured intensities were corrected for absorption by the empirical method of North, Phillips & Mathews (1968), and also for decline of three standard reflections with time. 6729 reflections were measured, 5085 were unique and 3725 [$F_o > 4\sigma(F_o)$] were used in the refinement (on F). All atoms except hydrogen were given anisotropic displacement factors. The final R_F factor was 0.042, which was also the value of wR ; $S = 2.3$.

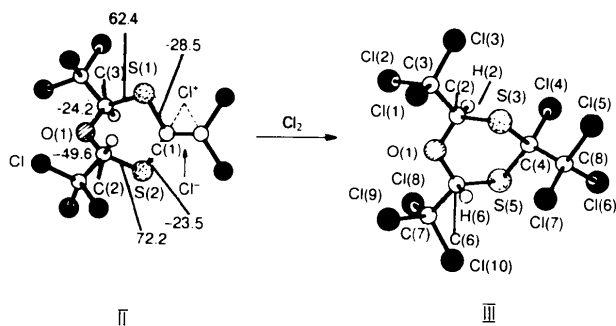


Fig. 1. The conventional reaction scheme, and a diagram showing the schematic molecular shapes (from crystal structure analyses) with the numbering of atoms of (II) and (III), as well as the accepted mode of attack of Cl(2) on the C=C double bond. The configuration shown for (II) is that of molecule *A*, as given by Irving & Irving (1986), and has the *S* configuration at the Csp^3 atoms. The numbering is that of Irving & Irving (1986). The approximate twofold axis runs along the double bond through O. The ring has a boat conformation, while the atoms of the double bond and substituents are coplanar to within 0.05 Å, and the diagram has been oriented with these atoms in the plane of the page. The torsion angles of molecule *B*, as given by Irving & Irving (1986) (reading clockwise from oxygen), are 37.8, -69.7, 28.4, 24.2, -72.2 and 36.6; the configuration at the Csp^3 carbon atoms is *R*. The configuration shown for (III) is that of molecule *A*, as given by Irving & Irving (1988), and has the *S* configuration at the Csp^3 atoms; the corrected torsion angles are given in Table 2.

3. Further crystallographic analysis

F_{obs} , F_{calc} and U_{ij} values were retrieved from Supplementary Publication No. 63075 deposited at the British Library. These had been listed in the non-standard space group $Pcab$, although the structure was described by Irving & Irving (1988) in the standard setting $Pbca$. We have transformed U_{ij} and F_{obs} to $Pbca$, which is used throughout this paper. Structure factors were calculated with *SHELX76* (Sheldrick, 1976) for the listed reflections, using the atomic coordinates given in Table 1 of Irving & Irving (1988) and the transformed U_{ij} values. R_F was 0.042 and spot checks of F_{calc} confirmed that we had indeed reproduced the Irving & Irving (1988) results. The *ORTEP* stereodiagram (Johnson, 1965) of molecule *A* was entirely normal (Fig. 2). That of molecule *B* (Fig. 3) showed the endocyclic and exocyclic C atoms of the >C(Cl)—CCl₃ group to be appreciably disordered, and possibly other atoms to a lesser extent.

Difference ($\Delta\rho$) electron-density maps were calculated by *SHELX76* using $F_{calc}^\#$ values obtained by omitting the contributions of endocyclic and exocyclic carbons of the >C(4)(Cl)—C(8)Cl₃ group of molecule *B*; R_F based on $F_{calc}^\#$ was 0.070. C(4) and C(8) were found

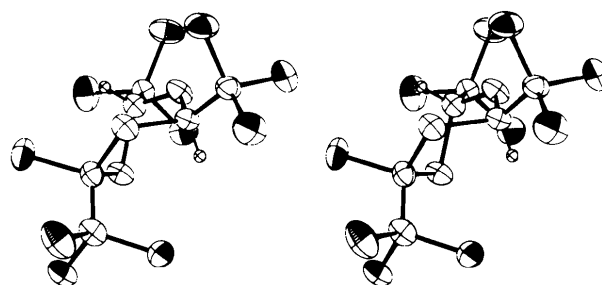


Fig. 2. *ORTEP* stereodiagram (Johnson, 1965) of molecule *A* in site 1. The ellipsoids represent 50% probabilities. The C(4)—C(8) bond is vertical at the bottom of the diagram.

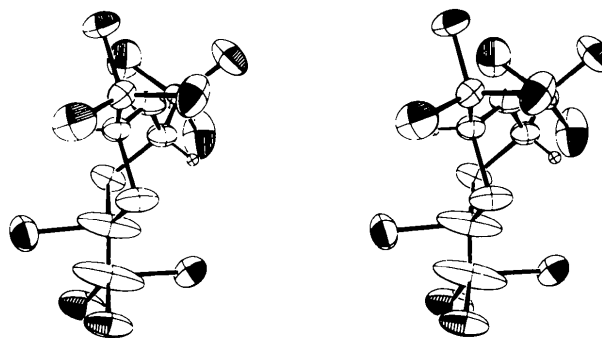


Fig. 3. *ORTEP* stereodiagram (Johnson, 1965) of the molecule designated as *B* by Irving & Irving (1988); the ellipsoid centres are at the coordinates given by Irving & Irving (1988) for their molecule *B*. The ellipsoids represent 50% probabilities. This is site 2 in our nomenclature. The C(4)—C(8) bond is vertical at the bottom of the diagram.

to be located on elongated ellipsoidal peaks analogous to those in Fig. 3, C(4) being poorly resolved into two peaks separated by 0.4 Å while C(8) was clearly resolved into two peaks separated by 0.95 Å, with peak heights in the ratio 60:40. The split atoms were then reintroduced into the structure-factor calculation (isotropic displacement factors, 60:40 ratio) and R_F dropped to 0.040.

Thus, at this stage, we have reproduced R_F as given by the Irving & Irving (1988) model, thereby confirming the validity of their procedures. In addition, we have shown that the difference map calculated from their data, and U_{ij} stereodiagrams, indicate partial disorder in the structure at the site of molecule *B*. This disorder, ignored by Irving & Irving (1988), must be taken into account in any alternative explanation of the experimental measurements. Preliminary structure-factor calculations for a disordered model give a slightly improved value for R_F . Three remarks concerning Irving & Irving (1988) are in order:

(i) The torsion angles given in Table 2 of Irving & Irving (1988) are the *inverse* of those corresponding to the coordinates given in their Table 1 and our Table A.* As the crystal is unequivocally racemic, this remark has only formal significance.

(ii) The torsion angles given in Table 2 of Irving & Irving (1988) for molecules *A* and *B* have similar values but opposite signs. Thus, molecule *B* is a somewhat distorted version of the *enantiomer* of molecule *A*.

(iii) The atomic numbering used here (Fig. 1) is a simplified version of that used by Irving & Irving (1988). The relationship of the numbering schemes is shown in (deposited) Table A.*

We now wish to find a molecular-level model which will explain the difference density maps and stereodiagrams found for molecule *B*.

4. Testing possible models

We distinguish between the two crystallographically independent sites (1, 2) and the molecules that occupy these sites. Site 1 is occupied, in a usual manner, by molecule *A*. The two sites were assumed to be occupied by the enantiomer of *A* in two orientations (denoted by *B* and *C*) in a disordered array and 60:40 ratio. The oxadithiane ring is rather flexible and so the geometries of *B* and *C* differ somewhat from that of *A*. As a starting point we assume that the atoms of molecules *B* and *C* in site 2 superimpose as follows: Cl(1*B*) on Cl(8*C*), Cl(2*B*) on Cl(9*C*), Cl(3*B*) on Cl(10*C*), Cl(4*B*) on Cl(7*C*), Cl(5*B*) on Cl(6*C*), and then conversely [*e.g.* Cl(6*B*) on Cl(5*C*)]

* Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU0315). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

for the remaining Cl pairs; also C(2*B*) on C(6*C*), S(3*B*) on S(5*C*), and H(2) on H(6). However, C(4) and C(8) are appreciably displaced from one another in *B* and *C*, as shown by the rugby balls of Figs. 3 and 4.

4.1. Further refinement of the model

The coordinates and isotropic displacement factors of the H and C(4) and C(8) atoms, and the coordinates and anisotropic displacement factors of the remaining atoms were refined (unit weights) in three blocks, for molecules *A*, *B* (fixed occupation factor 0.6) and *C* (fixed occupation factor 0.4; these occupation factors were inferred from the peak heights in the difference density map). Convergence was reached after three cycles, with $R_F (= R_W) = 0.0395$. The superimposed atoms referred to above were not resolved. Further refinement, or use of more elaborate models, was not considered justified.

4.2. Molecular dimensions

Partial ring geometries for molecules *A*, *B* and *C* are given in Tables 1 and 2, with full details for *A* deposited (Table *G*). There is good agreement between the dimensions of molecules *B* and *C* and those of *A*, except for the >C(Cl)—CCl₃ group, where discrepancies of *ca* 0.1 Å are found in bond lengths, due to the difficulty of accurately locating C(4) (especially) and C(8). Two reasons are proposed: (i) the $\Delta\rho$ map does not show clear resolution of the two C(4) positions, and (ii) the contribution of the C atoms to the structure factors is appreciably less than those of the Cl and S atoms. The dimensions of molecules *B* and *C* have not been deposited because of their systematic errors.

The interatomic distances of molecule *A* have been corrected for thermal motion (see §5); there are only minor differences from the Irving & Irving (1988) values. Within the ring, the thermal motion corrections

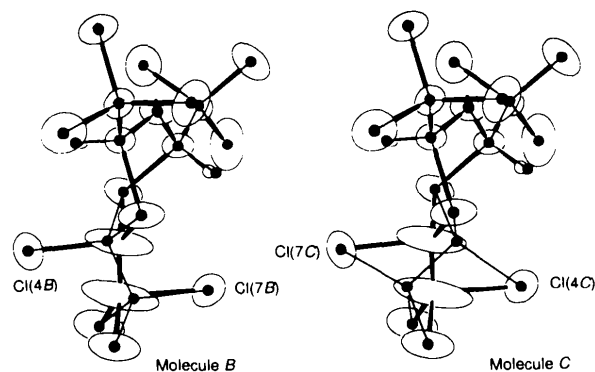


Fig. 4. ORTEP diagram (Johnson, 1965) showing the outlines of the 50% probability ellipsoids of Fig. 3. The heavy lines join the coordinates of molecule *B* according to Irving & Irving (1988). This is site 2 in our nomenclature. The atomic positions of our molecule *B* are shown by small circles linked by lighter lines. A similar superposition is shown for molecule *C*, which is *B* rotated through 180° about the C(4)—O(1) axis. This is not a stereopair.

Table 1. Interatomic distances (Å) in the rings of the three molecules

The e.s.d.'s are those obtained from the refinement; the values for molecules *B* and *C* are subject to additional systematic errors of unknown size because of the superposition of the atoms.

	Molecule A	Molecule B	Molecule C
O(1)—C(2)	1.409 (6)	1.401 (11)	1.402 (17)
C(2)—S(3)	1.817 (5)	1.812 (10)	1.816 (15)
S(3)—C(4)	1.823 (5)	1.849 (9)	1.865 (14)
C(4)—S(5)	1.819 (5)	1.829 (9)	1.825 (14)
S(5)—C(6)	1.822 (5)	1.817 (10)	1.810 (15)
C(6)—O(1)	1.415 (6)	1.403 (11)	1.402 (17)

Table 2. Ring torsion angles (°)

The e.s.d.'s of the torsion angles for molecule *A* have been taken from Irving & Irving (1988), while those for molecules *B* and *C* have not been calculated because of the unknown systematic errors in these values.

	A	B	C
S(5)—C(6)—O(1)—C(2)	-41.4 (5)	39.3	39.1
C(6)—O(1)—C(2)—S(3)	-37.9 (5)	39.6	39.6
O(1)—C(2)—S(3)—C(4)	77.6 (4)	-82.6	-85.5
C(2)—S(3)—C(4)—S(5)	-35.7 (3)	44.7	51.3
S(3)—C(4)—S(5)—C(6)	-19.2 (3)	9.0	1.3
C(4)—S(5)—C(6)—O(1)	70.3 (4)	-62.7	-58.2

are *ca* 0.004 Å and similar to the e.s.d.'s. The mean value of $d(\text{C—S})$ (within the ring) is 1.825 (4) Å (sample e.s.d. bracketed), which agrees well with the mean value of 1.823 (14) Å given for substituted tetrahydrothiopyran rings by Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987); the agreement for $d(\text{C—O})$ [1.415 (2) here and 1.441 (15) Å from Allen *et al.*] is not as good. The mean extra-ring $d(\text{C—C})$ is 1.538 Å, with $d[\text{C}(4)—\text{C}(8)]$ significantly longer at 1.560 Å. The thermal motion corrections to C—Cl distances in CCl₃ groups are 0.007–0.013 Å, and the mean $d(\text{C—Cl})$ is 1.776 (7) Å. The value of $d[\text{C}(4)—\text{Cl}(4)]$ is significantly longer at 1.799 Å (thermal motion correction 0.004 Å). Our mean value for $d(\text{C—Cl})$ agrees well with that given for CCl₄ at 195 K (1.773 Å, after correction for thermal motion; Cohen, Powers & Rudman, 1979) and values of 1.788 (26) and 1.779 (15) Å given by Kaftory (1983) and Allen *et al.* (1987).

4.3. Stereochemical details

The ring conformations (Table 3) have been analysed following Cremer & Pople (1975) and Cremer (1979). Using Fig. 1 of Boeyens (1978) and the Cremer–Pople parameters, the ring of molecule *A* approximates quite closely to the twist-boat conformation, while those of *B* and especially *C* have appreciable admixtures of boat and screw-boat conformations. These conclusions can be translated into a more quantitative form using the analysis of Evans & Boeyens (1989), which expresses the experimental ring conformation as a linear combination of the three classical forms of the six-membered ring – boat, twist and crown. The numerical results obtained from their CONFOR program

are in Table 3, from which the increasing contributions of the boat conformation (and, to a lesser extent, the crown) can be discerned as one proceeds from *A* to *B* to *C*.

5. Thermal motion analysis for molecule A

The basic theory has been described by Dunitz (1979) and more recent developments by Dunitz, Maverick & Trueblood (1988) and Dunitz, Schomaker & Trueblood (1988); the program THMA11 (version of 15 April 1987) was used. Firstly, molecule *A* was treated as an entire rigid body, and then libration of the three trichloromethyl groups was introduced. The $R(U_{ij})^*$ values obtained for observed and calculated values of U_{ij} for all non-H atoms were as follows (using unit weights): (i) rigid body, $R = 0.174$; (ii) librations of CCl₃ groups about C—C bonds included, $R = 0.121$. Only the second set of results is reported here. The r.m.s. value of ΔU_{ij}^2 is 0.0047 Å², while the e.s.d. of ΔU_{ij} is *ca* 0.0058 Å² (both in the crystal system). We start by proceeding as if the molecule were a rigid body. The translational motion of the molecule in the inertial system is fairly isotropic, with the r.m.s. of the eigenvalues of the T -tensor at 0.20, 0.19 and 0.16 Å, respectively. The librational motion is more anisotropic with the corresponding values 3.6, 2.4 and 1.6 Å, respectively. The r.m.s. libration amplitudes of the three CCl₃ groups are in the range 2.8–3.0°. We next consider the $\Delta_{A,B} [= (z_{A,B})^2 - (z_{B,A})^2]$ values, where $(z_{A,B})^2$ is the mean square displacement amplitude (m.s.d.a.) of atom *A* in the direction of *B*. For a rigid body, $\Delta_{A,B} = 0$ and Hirshfeld (1976) has suggested that for pairs of bonded atoms as heavy as C, $\Delta_{A,B}$ should be less than 10 pm² for intensity measurements of adequate quality. We find that within the ring the C atoms are translating about 50 pm² with respect to their bonding partners, suggesting a breathing vibration mode. Two of the CCl₃ groups [those linked to C(2) and C(6)] are internally rigid, but in the third C(8) has a large $\Delta_{A,B}$ value (162 pm²) with respect to Cl(7). The molecule as a whole has 171 pairs of atoms and 11 of the $\Delta_{A,B}$ values are greater than 150 pm². Thus, the molecule can hardly be considered to behave as a rigid body.

6. Other examples?

Similar situations have been encountered in the past. Above 198 K (T_c), monoclinic sulfur (S₈) crystallizes in space group $P2_1/c$ with six molecules in the unit cell, four ordered at general positions and two disordered about centres of symmetry (Goldsmith & Strouse, 1977). The degree of disorder is temperature dependent in monoclinic S₈ [space group $P2_1$ ($Z = 6$) below T_c],

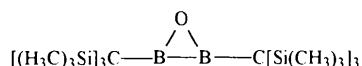
* $\Delta U_{ij} = U_{ij}(\text{obs}) - U_{ij}(\text{calc})$; $R(U_{ij}) = \{\sum(\Delta U_{ij}^2) / \sum[U_{ij}(\text{obs})^2]\}^{1/2}$.

Table 3. Puckering analysis of the rings

The gross ring conformation is given in terms of the φ , θ diagram (see Fig. 1 of Boeyens, 1978)

Molecule	Ring conformation	Q (Å)	φ (°)	θ (°)	Coefficients and angular values of primitive forms		
					Boat	Twist	Crown
A	⁶ T ₂	1.016	95.2	87.3	0.169	0.786	0.044
					8.0	6.0	1.0
B	² T ₆	1.024	280.5	97.2	0.314	0.577	0.108
					20.0	18.0	1.0
C	² T ₆	1.042	284.5	100.3	0.412	0.439	0.149
					20.0	18.0	1.0

whereas it is not clear whether the disorder is frozen in or temperature dependent in the present situation. Bis[(trimethylsilyl)methyl]oxadiborane



(C₂/c, Z = 4) is an example of a molecule where only a small portion is disordered; the central three-membered ring is disordered across a centre of symmetry, while the (trimethylsilyl)methyl groups on both sides are ordered (Paetzold, Geret-Baumgarten & Boese, 1992). Use of a more sophisticated model led to significant improvement in the agreement between computed and diffraction measurements of the bond lengths involving boron (Bühl, Schaefer, von Schleyer & Boese, 1993). A similar example is tri(mesityl)borirene, where the central ring is disordered, but the outer framework of the bulky aromatic groups is ordered (Eisch, Shafii & Rheingold, 1987). Another is tetra-*tert*-butylcyclobutadiene at 123 K, where the central ring is disordered within the framework established by the bulky perimetral *tert*-butyl groups (Dunitz, Krüger, Irgartinger, Maverick, Wang & Nixdorf, 1988). An example involving conformational isomerism is cyclodecene-*cis*-1,6-diol, which crystallizes in space group P₂₁/c with six molecules in the unit cell, four at general positions and two at centres of symmetry (cf. monoclinic S₈). The formally centrosymmetrical sites must contain a disordered arrangement of *cis* molecules, which were found to have a different conformation from those in the general positions (Ermer, Vincent & Dunitz, 1989; cf. Dunitz, 1979). An example involving configurational isomerism is provided by 2,5-dimethyl-3-hexene-2,5-diol, which crystallizes in space group P₁ with two *cis* isomers at general positions and a third moiety at the centre. This third moiety is predominantly the *trans* isomer, although there may be a small admixture of the hexane derivative (Ruysink & Vos, 1972). The present situation is closely akin to the first group of examples, where a small region of a larger molecule is disordered within the ordered framework provided by the larger portion, abetted by fortuitous superposition of many analogous atoms of the two molecules.

Finally, in what sense does the diffraction evidence discriminate between the disorder and incipient reaction

models? Clearly not through the *R* factors, which are nearly equal. The crucial evidence is provided by the resolution of C(8) into two peaks in the $\Delta\rho$ map [and the partial resolution of C(4)]. The separations of 0.9 (and 0.5 Å) are an order of magnitude larger than those encountered in benzene when diffraction is required (unsuccessfully) to differentiate between Kekulé and regular hexagonal structures (Ermer, 1987).

We are grateful to the Technion Fund for the Encouragement of Research and the Vice President for Research for financial support, to Professor J. C. A. Boeyens for a copy of *CONFOR* and helpful advice, and to Dr Alexander Zolotoy for his help with Chemical Design calculations.

Notes added in proof. Another example of one disordered and one ordered molecule in the asymmetric unit has recently come to our attention; it has also been discussed by Burdett (1992, see pp. 503–506). The structure of a purported 1:1 molecular compound of Cr(CO)₅.pyridine (*A*) and Cr(CO)₅.piperidine (*B*) was reported by Cotton, Darensbourg, Fang, Kolthammer, Reed & Thompson [1981; *a* = 13.851 (2), *b* = 11.026 (1), *c* = 17.693 (2) Å, β = 109.93°, space group P₂₁/c, Z = 4 (*A* + *B*)]. The bond lengths in the purported pyridine ring were (moving around the ring from N) 1.403 (6), 1.491 (7), 1.391 (9), 1.407 (9), 1.478 (7) and 1.369 (6) Å, and the ADP's were higher than those in the piperidine ring. Attempts to prepare the molecular compound by recrystallization of a 1:1 mixture of *A* and *B* were unsuccessful. It was suggested by Ries, Bernal, Quest & Albright (1984) that the purported molecular compound was in fact Cr(CO)₅.piperidine, with two molecules of *B* in the asymmetric unit, one of which was entirely normal, while in the second there was a disordered arrangement of 'two piperidine rings rotated by 180° about the N—C(4) axis, each with 50% occupancy'. A quantitative study was not made.

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