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## Conformational similarities between crystallographically independent molecules in organic crystals.

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### Abstract

The extent of conformational similarity between crystallographically independent molecules in organic crystals was quantified using the r.m.s. deviation of the atoms from a least-squares superposition. This analysis was carried out for a total of 399 structures taken from the Cambridge Structural Database. The structures are distributed among 65 chiral space groups. The analysis shows that in most cases the conformations of the crystallographically independent molecules are very similar.

### Introduction

The availability of the vast amount of crystallographic data in an easily accessible form *viz*., the Cambridge Structural Database (CSD, Allen *et al*., 1979; Allen, Kennard & Taylor, 1983), has given a new impetus to the statistical study of the conformation and packing of organic molecules in crystals. Many of these studies, old (Kitaigorodskii, 1961, 1973) and new (Wilson, 1988, 1990) have been aimed at rationalizing the distribution of reported structures among the various space groups (Mighell, Himes & Rodgers, 1983). Others have sought to exploit the database to obtain new insights into molecular conformation and energetics (Allen, Kennard & Taylor, 1983; Bürgi & Dunitz, 1983; Allen, 1986) and to analyse intermolecular environments (Gavezzotti & Desiraju, 1988; Ramasubbu, Parthasarathy & Murray-Rust, 1986). We have been interested in the packing of organic molecules from the point of view of intermolecular interactions. A specific type of crystallographic arrangement of molecules which lends itself to such a study is that in which there is more than one molecule in the asymmetric unit. A recent systematic study of such crystallographic non-equivalence in the unit cell using the CSD (Padmaja, Ramakumar & Viswamitra, 1990) has shown that about 8·3% of crystal structures solved have a $Z$ value greater than the crystallographic multiplicity. Some of these [typically 3–12% according to Mighell, Himes & Rodgers (1983)], however, may be attributed to an incorrect choice of space group.

We undertook a comparison of the conformations of the crystallographically independent molecules in 399 structures distributed over 65 space groups. The results are presented here.

### Method

Out of a total of 1576 structures in the 1987 release of the CSD with two or more molecules per asymmetric unit in the 65 chiral space groups, all but 399 have been eliminated according to the following criteria: (*a*) Structures with $R$ factors greater than 0·10 were removed. (*b*) Structures with more than two molecules in the asymmetric unit were eliminated. (*c*) A computer program was used to separate the coordinates of each entry into covalently bound clusters. The maximum bonding distance was taken to be 2·2 Å in order to include coordination bonds. When more than two such clusters or clusters with unequal numbers of atoms emerged, that structure was eliminated. (*d*) The order of arrangement of the atoms in the two molecules was checked by comparing the two-dimensional connectivity pattern of each atom in the two molecules. If the order was not the same or the atom list could not be

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rearranged manually to make it the same, the structure was not included for further computations.

In order to compare the conformations of two chemically identical molecules we used the program of Mackay (1984) in which the algorithm fixes the origin at the centre of gravity of each molecule and uses a linear least-squares procedure to arrive at the best axis and angle about which to rotate one molecule so as to superpose it on the other with the minimum r.m.s. deviation between the respective atoms.* The programs were written in Fortran77 and run on a MicroVAX II computer.

Table 1. *Statistical indicators of central tendencies in the data*

| Space group | Percentage of structures with $Z > M$ | No. of structures used | Average r.m.s. deviation | SD | Median |
|---|---|---|---|---|---|
| All data | 12·0 | 399 | 0·326 | 0·40 | 0·15 |
| $P1$ | 52·0 | 55 | 0·608 | 0·60 | 0·46 |
| $P2_1$ | 17·6 | 194 | 0·311 | 0·35 | 0·18 |
| $P2_12_12_1$ | 5·8 | 130 | 0·234 | 0·30 | 0·09 |
| Rest | 6·7 | 20* | 0·289 | 0·42 | 0·07 |

* These are: $C2$ (10), $P2_12_12$ (5), $P4_3$ (2), $P4_1$ (1), $I4_1$ (1).

## Discussion

The proportion of structures in which $Z$ is greater than the multiplicity bears an inverse relationship to the amount of symmetry present. This is in accordance with the results of the more extensive study of Padmaja, Ramakumar & Viswamitra (1990). Thus, while about half the structures belonging to $P1$ have more than one molecule in the asymmetric unit, this proportion drops to one twentieth for $P2_12_12_1$. (Space groups with higher symmetries do not have enough data points to be statistically significant.)

The results of the comparison of the conformations of the crystallographically non-equivalent molecules in the 399 structures is shown as a histogram (Fig. 1). The r.m.s. values range between 0·0 and 2·0 Å, with a significant portion of the structures having a very low value.

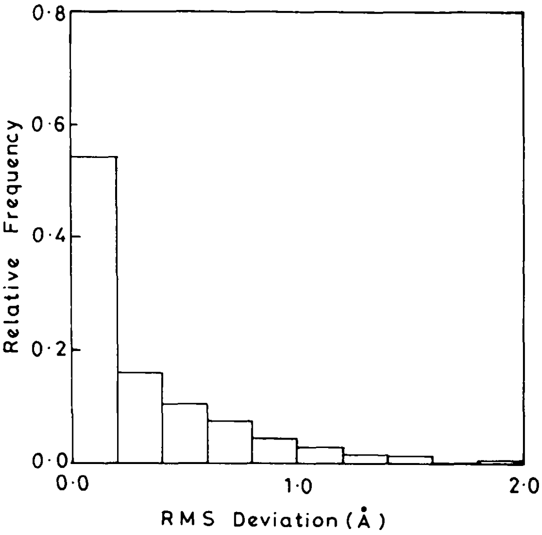

Fig. 1. R.m.s. deviation in the atomic coordinates between pairs of crystallographically independent molecules.

It is apparent that in a substantial number of cases the crystallographically independent molecules are nearly identical to each other in structure. Table 1 gives some numerical indicators. It is quite clear both from the average and the median values of the r.m.s. deviations that in most cases the two molecules are close to congruence. Indeed, for the space group $P2_12_12_1$, in 50% of the structures the two molecules are different from each other by less than 0·09 Å.

The structures belonging to the space group $P1$, however, show greater differences between the conformations of the two molecules, with an average r.m.s. deviation of 0·608 Å and a median value of 0·46 Å. There is also a wider distribution in this space group than in the others as indicated by a $\sigma$ value of 0·60 Å.

A closer examination of the data shows that of the 24 structures with an r.m.s. deviation between the two molecules of less than 0·01 Å, 13 belong to $P2_12_12_1$, 9 to $P2_1$ and one each to $C2$ and $I4_1$. Some of these near congruences could be a consequence of an improper space-group assignment. Thus one molecule in the structure given by the reference code DEXMET10,* in the space group $P2_12_12_1$ (Rohrer & Duax, 1977), requires a rotation of 178·11° about an axis defined by the direction cosines (1·0000, 0·0058, −0·0071) to make it coincide with the other molecule to within an r.m.s. deviation of 0·005 Å. Similarly, in the structure PSCLOV10 in the space group $P2_1$ (Hawley, Ferguson, McKillop & Robertson, 1969), one molecule, when rotated by 89·86° about (0·0001, 1·0000, −0·0027) coincides with the other within an r.m.s. deviation of 0·003 Å.

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* A list of the CSD reference codes, r.m.s. deviations and full literature references to the 399 structures analysed has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54420 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

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## Changes in published type structures.

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### Abstract

The structure of $KSbSe_2$ was first determined [Kaniščeva, Palkina, Kuznecov, Lazarev & Tarasova (1976). *Izv. Akad. Nauk SSSR Neorg. Mater.* **12**, 537–538] in $P1$. Later it was independently determined in $P\overline{1}$ [Dittmar & Schäfer (1977). *Z. Naturforsch. Teil B*, **32**, 1346–1348]. The $P1$ description can be made equivalent to the $P\overline{1}$ structure within reasonable limits and it is concluded that there is only one form with space group $P\overline{1}$. The structure of $OsGe_2$ was determined [Weitz, Born & Hellner (1960). *Z. Metallkd.* **51**, 238–243] in $C2/m$. Later the structures of $NbAs_2$ and $NbSb_2$ were determined in $C2$ [Furuseth & Kjekshus (1964). *Nature* (*London*), **203**, 512] and were regarded as a new structure type. Structures assigned to this type can be described within reasonable experimental error limits as being of the $OsGe_2$ type. Thus the $OsGe_2$ structure in $C2/m$ is to be preferred for classification purposes.

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While preparing the structural indices for a new edition of the Metals and Alloys subfile (Powder Diffraction File, 1991) it was found that some type structures for intermetallic phases could be described with higher symmetry. The structure of $KSbSe_2$ was determined by Kaniščeva, Palkina, Kuznecov, Lazarev & Tarasova (1976) in $P1$ and refined to $R = 0{\cdot}149$ for 1400 independent reflections based on diffractometer measurements with Mo radiation. Later Dittmar & Schäfer (1977) independently determined a structure for $KSbSe_2$ in $P\overline{1}$ and refined it to $R = 0{\cdot}049$ for 1721 reflections based on diffractometer measurements with monochromatized Mo radiation. The descriptions of these two structures are very similar (*Structure Reports*, 1976, Vol. 42A, pp. 20–21; 1978, Vol. 44A, pp. 14–15) and furthermore the powder patterns calculated (Powder Diffraction File, 1990) from the coordinates given (Villars & Calvert, 1985) are virtually identical. Therefore these two reports were compared by running the program *CREDUC* (Le Page, 1982). This revealed the possibility of monoclinic symmetry for both unit cells (Table 1). However when the program *MISSYM* (Le Page, 1987, 1988) was run on the coordinates, triclinic solutions for both structures were calculated but for the $P1$ set an inversion centre was revealed at $-0{\cdot}242$, $-0{\cdot}389$, $-0{\cdot}186$ (referred to the original cell). The discrepancies between the coordinates of pairs of related atoms in the $P1$ set, before averaging, had a range of 0 to 0·194 Å, with $\sigma = 0{\cdot}065$ Å. The $P1$ coordinates, after averaging, are compared in Table 2 to the $P\overline{1}$ set. The differences have a range of 0·001 to 0·034 Å with $\sigma = 0{\cdot}009$ Å and mean of 0·015 Å. It seems reasonable to conclude that $KSbSe_2$ has only one triclinic form and that the correct space group is $P\overline{1}$.

Table 1. *Possible monoclinic unit cells derived from the reduced cells*

| Ref. | Formula | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) |
|---|---|---|---|---|---|---|---|
| D* | $KSbSe_2$ | 8·0132 | 10·1029 | 12·4810 | 89·898 | 105·164 | 89·954 |
| K† | $KSbSe_2$ | 8·0132 | 10·1119 | 12·4820 | 90·138 | 105·197 | 90·0 |

* Dittmar & Schäfer (1977).
† Kaniščeva, Palkina, Kuznecov, Lazarev & Tarasova (1976).

The structure of $OsGe_2$ was determined in $C2/m$ (Weitz, Born & Hellner, 1960; *Structure Reports*, 1960, Vol. 24, pp. 144–145) and refined to $R = 0{\cdot}19$ for 540 reflections based on densitometer measurements of photographic data corrected for absorption. In 1964 the structures of $NbSb_2$ and $NbAs_2$ were determined in $C2$ (Furuseth & Kjekshus, 1964; *Structure Reports*, 1964, Vol. 29, pp. 18–21; Furuseth & Kjekshus, 1965; *Structure Reports*, 1965, Vol. 30A, pp. 14–16) based on photographic data corrected for absorption and taken with Cu radiation; for $NbAs_2$, $R = 0{\cdot}11$ but for $NbSb_2$ refinement could not be taken beyond $R = 0{\cdot}20$. As has been emphasized (Schomaker & Marsh, 1979), refinement difficulties can arise when symmetry elements have been neglected or overlooked. For $NbSb_2$ the coordinates reported had strict $C2/m$ symmetry while for $NbAs_2$ the deviations from $C2/m$ symmetry were 0·04 and 0·23 Å for the As atoms. Another $NbAs_2$ type structure, $MoAs_2$, was refined on the basis of photographic intensities for Mo radiation but no $R$ factor was recorded. (Brown, 1965; *Structure Reports*, 1965, Vol. 30A, p. 21). The deviations from $C2/m$ symmetry were 0·10 and 0·003 Å respectively

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