

SHORT COMMUNICATION

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A conformational comparison of crystallographically independent molecules in organic crystals with achiral space groups. By N. GAUTHAM, *Department of Crystallography and Biophysics,* University of Madras, Guindy Campus, Madras-600 025, India*

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Abstract

An analysis of conformational similarity between crystallographically independent molecules in 767 structures taken from the Cambridge Structural Database and distributed among the 165 achiral space groups results in an average r.m.s. deviation of 0.84 Å between the coordinates of the respective atoms in the two molecules.

Introduction

A study (Padmaja, Ramakumar & Viswamitra, 1990) of the occurrence of crystallographically non-equivalent molecules in the unit cells of organic crystals using the Cambridge Structural Database (CSD, Allen *et al.*, 1979) revealed that about 8.3% of the crystal structures solved have a *Z* value greater than the crystallographic multiplicity. Some of these (typically 3–12%, Mighell, Himes & Rodgers, 1983) may be due to incorrect space-group assignment. A few others could be due to the presence of pseudosymmetry (Desiraju, Calabrese & Harlow, 1991). In these cases therefore it is to be expected that the conformations of the crystallographically non-equivalent molecules should be identical or at least very similar. In the rest of the structures, the degree of such similarity is not known. General packing principles are silent on this issue except to indicate that in those cases when there are two molecules in the asymmetric unit, the two molecules may exist as dimers in solution and crystallize out in the same configuration (Kitaigorodskii, 1961).

We have previously made a study of the conformations of such non-equivalent molecules (Sona & Gautham, 1992). This study was carried out for the structures in the CSD occurring in one of the 65 chiral space groups and showed that in most cases the two molecules were very similar to each other in conformation. We have now extended this study to cover the 165 achiral space groups. In the present study we compare the conformation of one of the non-equivalent molecules with the other in two different ways. Firstly, with the coordinates as reported, and secondly, after taking the enantiomer of the second molecule.

* Contribution No. 779.

Method

There are a total of 2485 structures in the 1987 release of the CSD with two or more molecules per asymmetric unit in the 165 achiral space groups, *i.e.* space groups which possess an operation of the second kind. (Actually the structures are classified in 170 achiral space groups since five rhombohedral unit cells can also be referred to a hexagonal axial system.) Of these 767 were used in the present analysis. The rest were omitted using the same criteria as we used in the preceding study (Sona & Gautham, 1992). These criteria are: (i) *R* factor to be less than 0.10; (ii) structures to possess exactly two chemically equivalent molecules in the asymmetric unit; (iii) the two molecules to have exactly equal two-dimensional chemical connectivity patterns.

To compare the conformation of one molecule with another and then that of the first again with the mirrored version of the second, we used the program *BMFIT* (Yuen & Nyburg, 1979; Nyburg, 1974). This is a weighted (the weights were unity in the present case) rigid-body matching program which prints out the best fits between one molecule and each of the two enantiomers of a second molecule. The method used is that of Kabsch (1976) extended to ensure that both a proper and improper rotation are obtained. The r.m.s. deviations of the respective atomic coordinates of the two molecules are printed out in Å as a measure of the fit.†

The programs, in Fortran77, were run on a Micro-VAX II computer.

Discussion

As has been remarked earlier (Padmaja, Ramakumar & Viswamitra, 1990; Sona & Gautham, 1992), the percentage of structures which have more than one molecule in the asymmetric unit increases with a decrease in the symmetry of the space group. In the present study 10.6% of the

† A list of CSD reference codes, r.m.s. deviations and full literature references to the 767 structures analysed have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54680 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Central tendencies of the r.m.s. deviations

| Space group | No. of structures | Average r.m.s. deviation | Standard deviation | Median r.m.s. deviation |
|---------------------------------|-------------------|--------------------------|--------------------|-------------------------|
| All | 767 | 0.84 | 0.78 | 0.65 |
| <i>P</i> $\bar{1}$ | 352 | 0.95 | 0.85 | 0.76 |
| <i>P</i> ₂ <i>/c</i> | 292 | 0.70 | 0.65 | 0.55 |
| <i>C</i> ₂ <i>/c</i> | 24 | 0.84 | 0.75 | 0.66 |
| <i>Pca</i> ₂ | 22 | 0.97 | 0.78 | 0.77 |
| <i>Pna</i> ₂ | 20 | 0.99 | 1.02 | 0.41 |
| <i>Pbca</i> | 29 | 0.84 | 0.80 | 0.44 |
| Rest* | 28 | 0.57 | 0.63 | 0.23 |

* *Pc* (8), *P2/c* (2), *Cc* (7), *Cm* (1), *Pba2* (1), *Pbcn* (2), *Pccn* (2), *Iba2* (3), *P4* (1), *R3c* (1).

10 121 structures in the space group *P* $\bar{1}$ have a *Z* value greater than the space-group multiplicity. This proportion is 6.4% of the 12 650 structures in *P*₂*/c* and drops to 3.8% of the 2273 structures in the more symmetrical space group *Pbca*. The higher space groups in the tetragonal and

hexagonal systems show a similar trend though the number of data points is insufficient for true significance. The rhombohedral space group *R* $\bar{3}$ is, however, a strong exception to this rule and 42.4% of the 158 structures in this space group have *Z* > 6.

The results of the conformational comparisons are summarized in Table 1 and Fig. 1.

It can be seen that the two molecules tend to be close to each other in conformation. Such a similarity in the conformation was also seen in the analysis of the structures in the chiral space groups (Sona & Gautham, 1992). In 41.3% of cases the r.m.s. deviation is less when one of the molecules is mirrored. In these cases the two molecules in the asymmetric unit may be enantiomers.

Among the space groups, the highest populated one, *P* $\bar{1}$, has a larger average r.m.s. deviation than the next most populated one, *P*₂*/c*. The data points in the former are also more spread out as indicated by the larger standard deviation of 0.85.

Twenty-six structures have an r.m.s. deviation of less than 0.05 Å. Some of these could possibly be due to incorrect space-group assignment.

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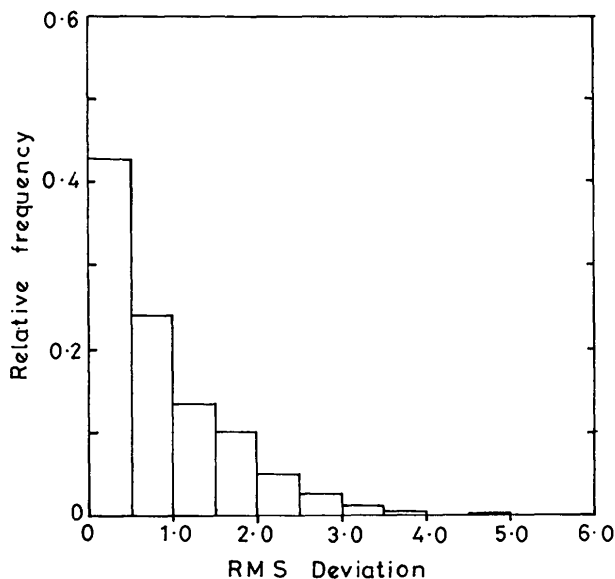


Fig. 1. Histogram of relative frequency of r.m.s. deviations for all data, in all space groups.

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