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SHORT COMMUNICATIONS

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Acta Cryst. (1987). B**43**, 405-406

An alternative approach to a revision of van der Waals radii for molecular crystals.

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(*Received* 4 *November* 1986; *accepted* 28 *January* 1987)

Abstract

Recently Nyburg & Faerman [*Acta Cryst.* (1985), B41, 274-279] made a revision of non-bonding (van der Waals) radii of atoms in molecular crystals. It was shown that the effective shape of atoms in crystals is spheroidal (elliptical) with two radii, major r_a and minor r_b. In the present paper an alternative approach to the interpretation of their data is proposed. As a result, atoms in crystals still have spherical shape but the centre of the sphere is displaced from the nuclear site along the chemical bond. The implications of the model for the formulation of empirical atom-atom intermolecular potentials are briefly discussed.

Recently Nyburg & Faerman (1985; henceforth NF) published an extensive study of the non-bonded contacts in molecular crystals with N, O, F, S, Se, Cl, Br and I atoms attached to a carbon atom. The study, based on the Cambridge Structural Database, enabled them to conclude that the effective shape of atoms (as described by the van der Waals radius) in molecular crystals is not spherical but spheroidal (elliptical), with shorter radius along the atom-to-carbon vector ('polar flattening').

This conclusion was derived from the analysis of a large number of intermolecular distances d_{XX} (X being one of the previously mentioned atoms). The analysis of the contact scatterplots (polar diagram of d_{XX} distances *versus* angle μ between d_{XX} and the C–X bond) led to the definition of a boundary for the region where there are intermolecular contacts (Fig. 1 in NF). The authors concluded that this boundary is generally ellipsoidal with two radii, major r_a and minor r_b. The exact placing of the boundary was subjective and was not obtained from some fitting procedure. Thus, while some atoms are spherical (N and O) with both radii equal, some others are spheroidal with a significant difference between the two radii r_a and r_b (Table 1 in NF).

The purpose of the present note is to propose an alternative model for the description of the data presented by NF. The boundary line could equally well be a *circle*, whose centre is displaced from the atom position along the C–X bond toward the carbon atom. The value of the shift, Δ, is related to the difference between the NF major and minor radii, r_a and r_b. The proposed model is illustrated in Fig. 1 where the data for iodine are plotted (taken from NF). The full line is the NF ellipse with major radius $2r_a = 4{\cdot}26$ Å and minor radius $2r_b = 3{\cdot}52$ Å. The dashed circle is our proposed boundary with $R = 2r_a$. In order to get a satisfactory agreement with the scatterplot, the centre was shifted by 0·6 Å from the origin. It can be seen that such a boundary fits the data equally well. A similar analysis could be performed for other atoms (Cl, Br, S, Se).

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The interpretation of such a model is that the effective shape of atoms in the crystal can be considered spherical, but the centre of the sphere is displaced along the C–*X* bond. The magnitude of the shift is a parameter close to $2(r_a - r_b)$. Our model lends support to the use of isotropic atom-atom potentials for the description of the physical properties of molecular crystals, but the centre of interaction should be shifted along the C–*X* bond. The effects of bond foreshortening were noted in the calculations of intermolecular potential for the hydrogen dimer (Williams, 1965; Starr & Williams, 1977). The calculations indicated a bond foreshortening of the order of 0·10–0·16 Å, which reflects the shift of electron density into the bonding region. Similar effects were recently noted in the calculations of static and dynamic properties of solid chlorine (Burgos, Murthy & Righini, 1982) and fluorine (Kirin & Etters, 1986). In those systems it was possible to obtain a reasonable fit for the static properties of the crystal lattice (within the famework of a simple isotropic atom-atom model) by shifting the centre of interaction along the bond by 0·186 and 0·055 Å, respectively. The effective 'bond length' was 1·618 Å for chlorine and 1·30 Å for fluorine. Of course, our interpretation is approximate and it is quite likely that anisotropy plays an important role in intermolecular interactions. Especially in the calculations of the physical properties of halogen solids (Cl_2, Br_2 and I_2) it was noted that very accurate static properties of crystal lattices could not be obtained without assuming intermolecular bonding of a special type or an angular-dependent potential (Nyburg & Wong-Ng, 1979; Williams & Hsu, 1985; Burgos *et al.*, 1982; Price & Stone, 1982). There is no doubt that for higher accuracy the anisotropic-potential model is needed, but it remains an open question whether all physical properties can be reproduced with reasonable accuracy even within the framework of such a model. Most of the sophisticated anisotropic intermolecular potentials are fitted only to a small number of physical quantities; it would be useful to examine if such potentials are transferable and if they can reproduce with reasonable accuracy such physical quantities as lattice-vibrational frequencies, high-pressure structural data, pressure dependence of vibrational frequencies *etc.*

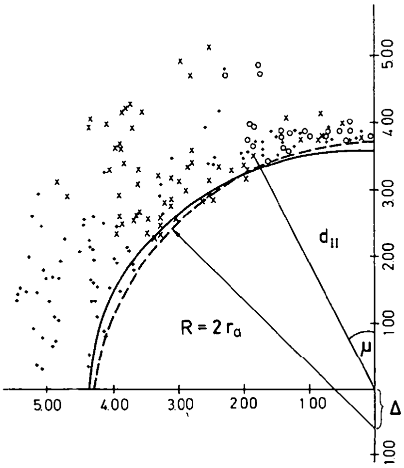

Fig. 1. Polar scatterplot of intermolecular iodine–iodine distance d_{II} (Å) *versus* polar angle μ (μ is the smaller of the two angles μ_1 and μ_2 defined by C–I bonds and intermolecular distance d_{II}). The larger μ value is designated according to its magnitude, 0–30° circles, 30–60° crosses, 60–90° arrows. The data are taken from Fig. 1 of Nyburg & Faerman (1985) and were obtained by examining the large number of crystal structures containing iodine attached to a carbon atom. The full curve is the NF ellipse and the dashed one is the proposed circle.

Since the ultimate goal is to produce a simple and transferable potential for the description of the physical properties of molecular solids, it would be interesting to see if the shift of centre of interaction could lead to satisfactory atom-atom potentials for a broader class of molecular crystals.

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Acta Cryst. (1987). B43, 406

Optical, pyroelectric and X-ray topographic studies of twin domains and twin boundaries in $KLiSO_4$. Erratum.

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(*Received* 22 *May* 1987)

Abstract

In the paper by Klapper, Hahn & Chung [*Acta Cryst.* (1987), **B43**, 147–159] figures have been transposed in two cases. In Fig. 2 on page 150, (*b*) is labeled (*c*) and (*c*) is labeled (*b*). In Fig. 5 on page 153, (*a*) is labeled (*b*) and (*b*) is labeled (*a*). In both cases the labels in the figure captions are correct.

All information is given in the *Abstract.*

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