

- CROWTHER, R. A. & BLOW, D. M. (1967). *Acta Cryst.* **23**, 544–548.
- DICKERSON, R. E. (1987). In *Unusual DNA Structures*, edited by R. D. WELLS & S. C. HARVEY. New York: Springer-Verlag. In the press.
- DREW, H. R., SAMSON, S. & DICKERSON, R. E. (1982). *Proc. Natl Acad. Sci. USA*, **79**, 4040–4044.
- DREW, H. R., WING, R. M., TAKANO, T., BROKA, C., TANAKA, S., ITAKURA, K. & DICKERSON, R. E. (1981). *Proc. Natl Acad. Sci. USA*, **78**, 2179–2183.
- FITZGERALD, P. M. (1988). *J. Appl. Cryst.* **21**, 273–278.
- FRATINI, A. V., KOPKA, M. L., DREW, H. R. & DICKERSON, R. E. (1982). *J. Biol. Chem.* **257**, 14686–14707.
- HO, P. S., FREDERICK, C. A., QUIGLEY, G. J., VAN DER MAREL, G. A., VAN BOOM, J. H., WANG, A. H. J. & RICH, A. (1985). *EMBO J.* **4**, 3617–3623.
- HUNTER, W. N., BROWN, T., ANAND, N. N. & KENNARD, O. (1986). *Nature (London)*, **320**, 552–555.
- HUNTER, W. N., BROWN, T., KNEALE, G., ANAND, N. N., RABINOVICH, D. & KENNARD, O. (1987). *J. Biol. Chem.* Submitted.
- IKUTA, S., CHATTOPADHYAYA, R., ITO, H., DICKERSON, R. E. & KEARNS, D. (1986). *Biochemistry*, **25**, 4840–4849.
- LATTMAN, E. E. & LOVE, W. E. (1970). *Acta Cryst.* **B26**, 1854–1857.
- MCCALL, M., BROWN, T. & KENNARD, O. (1985). *J. Mol. Biol.* **183**, 385–396.
- QUINTANA, J., CHATTOPADHYAYA, R., CONNER, B. & DICKERSON, R. E. (1988). In preparation.
- RABINOVICH, D., HARAN, T., EISENSTEIN, M. & SHAKKED, Z. (1988). *J. Mol. Biol.* **200**, 151–161.
- RABINOVICH, D. & SHAKKED, Z. (1984). *Acta Cryst.* **A40**, 195–200.
- RAO, S. N., JIH, J. & HARTSUCK, J. A. (1980). *Acta Cryst.* **A36**, 878–884.
- SHAKKED, Z., RABINOVICH, D., CRUSE, W. B. T., EGERT, E., KENNARD, O., SALA, G., SALISBURY, S. A. & VISWAMITRA, M. A. (1981). *Proc. Soc. London Ser. B*, **213**, 479–487.
- SUSSMAN, J. L., HOLBROOK, S. R., CHURCH, G. M. & KIM, S.-H. (1977). *Acta Cryst.* **A33**, 800–804.
- WANG, A. H. J., GESSNER, R. V., VAN DER MAREL, G. A., VAN BOOM, J. H. & RICH, A. (1985). *Proc. Natl Acad. Sci. USA*, **82**, 3611–3615.
- WANG, A. H. J., HAKOSHIMA, T., VAN DER MAREL, G., VAN BOOM, J. H. & RICH, A. (1984). *Cell*, **37**, 321–331.
- WANG, A. H. J., QUIGLEY, G. J., KOLPAK, F. L., CRAWFORD, J. L., VAN BOOM, J. H., VAN DER MAREL, G. & RICH, A. (1979). *Nature (London)*, **282**, 680–686.
- WARD, K. B., WISHNER, B. C., LATTMAN, E. E. & LOVE, W. E. (1975). *J. Mol. Biol.* **98**, 161–177.

Acta Cryst. (1988). **B44**, 657–663

Local Structures of Orientationally Disordered Crystals. I. Compatibility Matrices

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Abstract

In this paper, steric criteria have been used to study the orientational relationships of neighbouring molecules in orientationally disordered crystals whose structures have been described in terms of the site model. Compatibility matrices have been defined: they are square matrices of order $N \times N$, where N is the number of distinguishable molecular orientations per crystalline site; these elements, which are either 0 or 1, represent the compatibility between pairs of molecular orientations located at two given neighbouring sites. These elements are determined by studying the contacts of the van der Waals envelopes of the molecules involved, and different characteristics of these envelopes (shape, radius, centre location) have been considered. For the five compounds (seven phases) that were examined, the data resulting from recent compilations [Nyburg & Faerman (1985). *Acta Cryst.* **B41**, 274–279; Nyburg, Faerman & Prasad (1987). *Acta Cryst.* **B43**, 106–110] yield the highest compatibility ratios. The variation of the compatibility ratio τ vs temperature or vs ε (the parameter which defines the way van der Waals

envelopes overlap) gives information on the influence of thermal contraction on orientational freedom. Furthermore, the examination of the compatibility matrices, together with an analysis of the shortest intermolecular distances, indicates the nature of the contacts which entail steric hindrance.

Introduction

A number of molecular crystals can exhibit a plastic phase (Timmermans, 1938) which is characterized by a great orientational freedom of the molecules. These plastic phases can best be described in terms of the site model (often loosely called 'Frenkel model') according to which the molecules reorient between a limited number of potential wells at the bottoms of which they perform damped librations (Brot & Lassier-Govers, 1976). By cooling such a crystal, the reorientational motion may be frozen to yield a glassy crystal (Adachi, Suga & Seki, 1968; Fuchs, Virlet, André & Szwarc, 1985) within which the orientational disorder is retained in the same crystalline structure (André, Ceccaldi & Szwarc, 1984).

The crystalline structures of such orientationally disordered phases can be determined through X-ray measurements, but it must be emphasized that the resulting structural descriptions correspond to time- and space-averaged models. To calculate the structure factors, each lattice site is assumed to be occupied by a 'mean' molecule which is obtained by superimposing N molecules lying at N distinguishable orientations, each one usually being assigned a $1/N$ weight. (In what follows we will use 'orientation' for 'distinguishable orientation'.)

In principle, an X-ray refining process leads to a structural model in which the overlaps of the electronic densities of neighbouring molecules are minimized (*i.e.* a model in which steric hindrance has been accounted for). But in the case of the solids we are interested in, the mean molecule we referred to before is only a mathematical device. To study intermolecular contacts, all components of the mean molecule that are distinguishable molecular orientations have to be considered independently. Thus we have to describe how each orientation of one molecule lying at a given site interacts with each orientation of another molecule lying at a neighbouring site. As the close contacts between molecules in a solid are mainly ruled by repulsive forces, we will consider that the most important parameters are the steric ones. On this basis, it is expected that some of the pairs of orientations that we have just defined will not be compatible because of too important a steric hindrance. Such incompatibilities are intrinsic components of the structural disorder and our purpose is to use them ultimately to build a 'microscope' to view the local configurations of disordered solids.

In the meantime, this preliminary paper is devoted to the definition of the compatibility matrices which are intended to describe the above steric incompatibilities (or compatibilities). It also specifies the choice of pertinent molecular models and of steric parameters, which are the van der Waals envelopes of the involved atoms and molecules. The resulting descriptions will be applied to some orientationally disordered crystals.

Compatibility matrices

In orientationally disordered crystals, the number of atom-atom distances to consider may be large. It is equal to $(N_a N)^2$, where N_a is the number of atoms per molecule and N is the number of molecular orientations per site. This number is $N = N_s N_p$, where N_s is the order of the symmetry group of the crystalline site, which is a subgroup of the crystal point group, and N_p is the number of distinguishable molecular positions which are related to the motion around a symmetry element which has only a statistical existence: for instance, in 1,2,3-trichloro-4,5,6-trimethylbenzene, the molecules perform C_6 , C_3 or C_2 reorientations about the sixfold

axis of the benzene ring which can be considered as a quasi-sixfold axis for the whole molecule from the steric point of view (Fourme, Renaud & André, 1972).

Instead of describing the detailed intermolecular contacts, which would be cumbersome, we will introduce compatibility matrices which we have briefly defined before (André, Ceccaldi & Szwarc, 1984; Ceccaldi, 1985).

A compatibility matrix is a square matrix of order $N \times N$ in which element A_{kl} represents the compatibility between a molecule in orientation k and another molecule lying in the neighbouring site in orientation l .

The value of A_{kl} is determined by calculating all distances D between every pair of atoms i and j ($1 \leq i, j \leq N_a$) and comparing them to a threshold value

$$d_{ij} = \varepsilon(r_i + r_j).$$

If one single distance D is less than the corresponding d_{ij} value, A_{kl} is 0. Otherwise it is equal to 1. The lengths r_i and r_j are the van der Waals radii of atoms i and j respectively; ε is a parameter less than or equal to 1, which is meant to allow some overlap of the van der Waals envelopes: such an overlap may be justified by molecular motions (librations, large-angle jumps, *etc.*). It is also meant to take into account the possibility of individual orientations relaxing from the idealized positions determined from average crystal structure analysis.

A compatibility matrix may contain a large number of elements. In the case of cyclohexanol, it is a 96×96 matrix (André, Ceccaldi & Szwarc, 1984). To get an overall idea of steric hindrance, we have defined a compatibility ratio τ :

$$\tau = N^{-2} \sum_{k=1}^N \sum_{l=1}^N A_{kl}.$$

To describe the environment of a given molecule, a single compatibility matrix is sufficient to obtain the unique τ value of a family of equivalent neighbouring sites. To study the incompatibilities corresponding to orientation pairs, that is to study each A_{kl} element, it is generally necessary to determine all the matrices of the equivalent neighbouring sites.

Program *COMPAT* allows us to build compatibility matrices and to perform some analyses of the results.

Molecular model

Molecules are considered as rigid bodies. H atoms play an important part in intermolecular contacts and require particular care. Calculations of interatomic distances must be made with molecular models in which H-atom positions have been determined through neutron or electron diffraction.

When the structures have been determined by X-ray diffraction studies, it must be kept in mind that the X-H

Table 1. *Van der Waals envelope parameters for some atoms*

(a) Nyburg & Faerman (1985) only studied the S atom of the C=S group, the envelope is an ellipsoid of revolution with $a = 1.60$ and $b = 2.03$ Å; (b) Bondi (1968); (c) this value was proposed by Kitaigorodsky (1973). Bondi gives 1.50 Å and Nyburg gives a sphere of radius 1.54 Å for the O atom of the C=O group; (d) this corresponds to a spherical envelope for the N atom of the C≡N group (Nyburg & Faerman, 1985); (e) Bondi (1968); (f) Kitaigorodsky (1973); (g) this corresponds to a C—H bond in which the C atom is sp^3 hybridized; (h) atom bonded to an sp^2 -hybridized C atom; parameter c indicates that the ellipsoid centre is shifted 0.42 Å nearer the C atom.

Atom	Envelope	Radius (Å)
C	Sphere	1.80
S	Sphere ^a	1.74 ^b
O	Sphere	1.52 ^c
N	Sphere	1.60 ^d or 1.70 ^e
H ^f	Sphere	1.17
H ^g	Ellipsoid	$a = 1.01; b = 1.26$
H ^h	Ellipsoid	$a = 1.35; b = 1.38; c = 0.42$

distances are 'seen' 0.1 Å shorter than they are in neutron-based determinations (Allen, 1986). Therefore it is necessary to lengthen the X-ray-determined X—H distances by 0.1 Å to find the true positions of the H atoms, which are the van der Waals envelope centres. The calculations of intermolecular distances may then be carried out.

Van der Waals envelopes

From structural results it is possible to define characteristic envelopes for different atoms. Such envelopes follow from the interatomic distances that are determined in well resolved structures of a number of ordered molecular solids. After Pauling's (1942) work followed by Kitaigorodsky's (1973) studies using the principle of close packing, the concept of contact sphere, or van der Waals sphere, has been introduced. Bondi (1968) made a systematic compilation taking advantage of the increasing number of available structural data; he calculated more plausible van der Waals radii for a number of atoms and pointed out deviations which suggested that some envelopes could be ellipsoidal.

Recently, Nyburg and his collaborators (Nyburg & Faerman, 1985; Nyburg, Faerman & Prasad, 1987) systematically compiled the structural data file of the University of Cambridge (Cambridge Structural Database, CSD) and obtained a series of new results about the envelopes of a number of atoms bonded to C atoms in molecular crystals.

According to these results, the van der Waals envelope of an atom X is an ellipsoid of revolution which is defined by the lengths of two radii. The ellipsoid is flattened in the C— X direction which thus corresponds to the shorter radius. To characterize the contact between atoms X and Y , the length of the van

Table 2. *Quinuclidine phase I; dependence of compatibility ratio on shape, size and centre position of H-atom envelope*

Envelope	Radius (Å)	Envelope centre—C atom distance (Å)	τ (%)
Sphere	1.17	0.99	61.6
Sphere	1.25	0.99	42.7
Sphere	1.17	1.08	45.1
Ellipsoid	1.26–1.01	1.08	64.8

der Waals radius is a function of the angle between directions C— X and X — Y . If one takes as a reference an atom whose position has been determined by neutron diffraction, it may be necessary to consider an envelope whose centre has been shifted along the C— X bond with respect to the atom position. Finally, the lengths of the radii of the ellipsoid depend on the nature of the C— X bonding or on the natures of the bonds in which the C atom is involved. The most striking example is given by the C—H single bond for which the van der Waals envelopes of the H atoms are not the same for sp^2 -hybridized or sp^3 -hybridized C atoms.

Some of these results are summarized in Table 1 which gives the characteristics of the van der Waals envelopes corresponding to the atoms of the compounds we have studied here.

Results

We analyse results for five compounds: 1-adamantanecarbonitrile, cyclohexanol and thiophene, because they are known to yield glassy crystalline phases, and cyclohexane and quinuclidine, which were chosen arbitrarily. Their structures have all been described in terms of the site model (for 1-adamantanecarbonitrile, see *Appendix 2*).

Unless specified, the compatibility matrices which are referred to correspond to nearest neighbours and the compatibility ratios have been calculated for $\epsilon = 1$, that is for non-overlapping van der Waals envelopes.

We first report the compatibility ratios for phase I of quinuclidine as functions of the positions of the centres and the shapes and sizes of the van der Waals envelopes (Table 2). The structure of this solid has been determined by using a molecular model in which the C—H bond length is 0.99 Å (Fourme, 1979) which is a suitable choice because the experimental data were obtained by means of X-ray diffraction measurements. Use of the above C—H distance together with the standard radius for a spherical-H-atom van der Waals envelope, 1.17 Å, would result in too weak an occupancy volume, so that the corresponding compatibility ratio (61.6%) would appear too high. It may be tempting to compensate for the envelope centre shift by increasing the sphere radius to 1.25 Å: Table 2 shows that this entails a marked decrease of τ to 42.7%, a value which is lower than that (45.1%) which results

Table 3. *Compatibility ratios for some crystals*

τ_1 refers to a spherical envelope for the H atoms and τ_2 to an ellipsoidal envelope: (a) Kahn, Fourme, André & Renaud (1973); (b) Fourme (1979); (c) Amoureux & Bee (1979); (d) Amoureux, Sauvajol & Bee (1981); (e) Foulon, Lefebvre, Amoureux, Muller & Magnier (1985); (f) André, Ceccaldi & Szwarc (1984); (g) André, Figuière, Fourme, Ghelfenstein, Labarre & Szwarc (1984).

	Compatibility matrix order	Compatibility ratio (%)	
		τ_1	τ_2
Cyclohexane I ^a	24 × 24	50.7	61.1
Quinuclidine I ^b	48 × 48	45.1	64.8
Adamantanecarbonitrile I ^{c,d,e}	48 × 48	38.7	57.8
Adamantanecarbonitrile I ^f	48 × 48	20.3	37.2
Cyclohexanol I ^g	96 × 96	53.6	61.2
Cyclohexanol I ^g	96 × 96	44.1	49.4
Thiophene I ^g	20 × 20		
site $\frac{1}{2}, \frac{1}{2}, 0$		72.2	81.2
site $0, \frac{1}{2}, \frac{1}{2}$		23.0	37.5
site $\frac{1}{2}, 0, \frac{1}{2}$		66.8	82.5

from considering an H-atom sphere centred at 1.08 Å from the C atom with a standard radius. All these compatibility ratios are smaller than that which corresponds to the envelopes that Nyburg *et al.* recommend: if ellipsoidal envelopes corresponding to H atoms bonded to sp^3 -hybridized C atoms are used, their flattened shapes lead to a 64.8% τ value.

The influence of the shapes of H-atom van der Waals envelopes on the compatibility ratios has been studied for seven crystalline phases (Table 3). For the first four, which are cubic phases, the calculated differences generally lie between 10 and 20%. Cyclohexanol is an exception, with lower differences (7.6% for phase I and 5.3% for phase I_g) between spherical and ellipsoidal envelopes; but it must be stressed that the corresponding structural models do not take into account the H atom of the OH group that may play an important part in intermolecular contacts, especially by being involved in hydrogen bonds.

Large differences between the spherical and ellipsoidal geometries also exist for phase I of thiophene, for which three kinds of nearest neighbours have to be considered because of its orthorhombic structures (André, Figuière, Fourme, Ghelfenstein, Labarre & Szwarc, 1984) (at $T = 183$ K, $a = 9.721$, $b = 6.610$, $c = 7.090$ Å, $Pnma$, $Z = 4$).

Let us now consider the variation of the compatibility ratio as a function of the overlap parameter ϵ . We will examine phase I of thiophene; Fig. 1 represents the τ variation for the three kinds of nearest neighbours for the cases of spherical and ellipsoidal envelopes respectively. When ϵ is close to 1, that is for weak overlaps, the curves $\tau(\epsilon)$ for both kinds of envelopes behave the same way; the differences between them become very low for $\epsilon = 0.8$, that is for quite unrealistic overlaps ($\epsilon = 0.8$ would mean overlaps equal to 0.40 Å for an H—H contact, 0.56 Å for C—H and 0.72 Å for C—C!).

The compatibility ratios for the three kinds of nearest neighbours of the initial site are quite different. For site $0, \frac{1}{2}, \frac{1}{2}$, which is the closest one, τ is less than one half the

values which correspond to the other two sites. It is very tempting to relate this result to the behaviour that thiophene exhibits when cooled along the metastable phase sequence at temperatures lower than 175 K (André & Szwarc, 1986): superstructures, incommensurate with the enduring orthorhombic lattice, appear with a doubling of the parameter in the b direction and a multiplication by a factor of the order of 20 in the c direction. Furthermore, the thermal expansivity along b is negative, as if the crystal could not accommodate more contraction due to cooling in a direction along which steric incompatibilities are already important. The above low τ value is probably the origin of the existence of a second peak at high second-moment values in the calculated distribution of local NMR second moments for phase I of thiophene (André, Bessada, Fuchs, Rousseau & Szwarc, 1988).

Finally, intermolecular contacts in phases I and I_g of 1-adamantanecarbonitrile have been compared; the time- and space-averaged structures of these phases are similar (Foulon, Lefebvre, Amoureux, Muller & Magnier, 1985). Fig. 2 represents the variation of τ for both

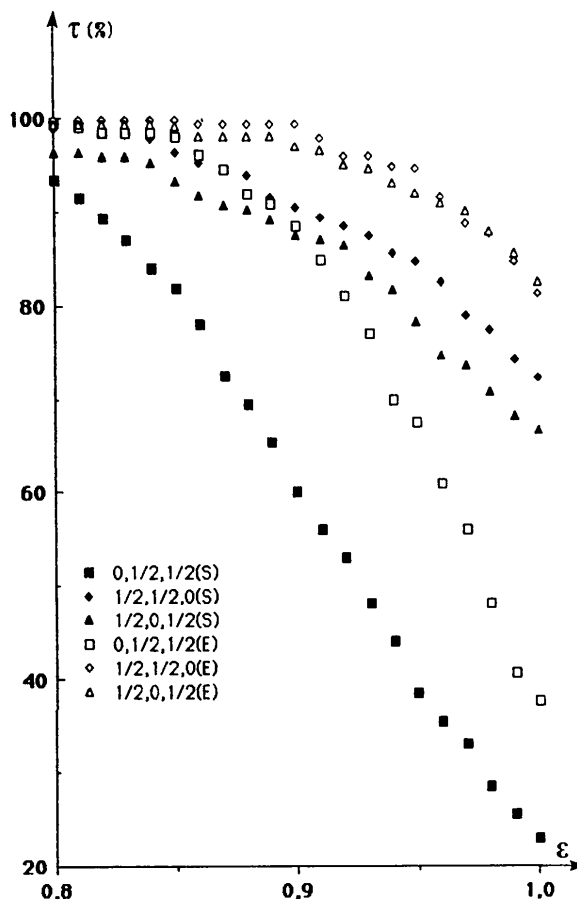


Fig. 1. Variation of the compatibility ratios τ as functions of the overlap parameter ϵ for the three kinds of nearest neighbours in phase I of thiophene: S or E = spherical or ellipsoidal van der Waals envelopes for H atoms.

phases as a function of the overlap parameter ε . The analysis of the atom-atom contact distances for $\varepsilon = 1$ shows that the mutual relationships between nearest neighbours (which are related by translations of the $\frac{1}{2}, \frac{1}{2}, 0$ type) are mainly governed by N-N contacts in both phases: hence, positions like x, y, z and $\frac{1}{2}-y, \frac{1}{2}-x, z$ are not sterically compatible. There are 128 such N-N distances that are equal to or shorter than half the sum of two N-atom van der Waals radii. The difference between the compatibility ratios for phases I and I_g comes from the change of the number of intermolecular distances that are shorter than the threshold values d_{ij} : there are 2728 such distances for phase I and 4584 ones for phase I_g , to be compared with a total of 1679616 interatomic distances to be calculated. Among these short distances, 1744 in phase I and 3268 in phase I_g involve H atoms. As Foulon *et al.* (1985) have already noticed and as may be expected because of the great similarities of the crystalline structures, the thermal contraction of the lattice from phase I to phase I_g is the main cause of the change in steric hindrance through the increase of contacts which involve H atoms.

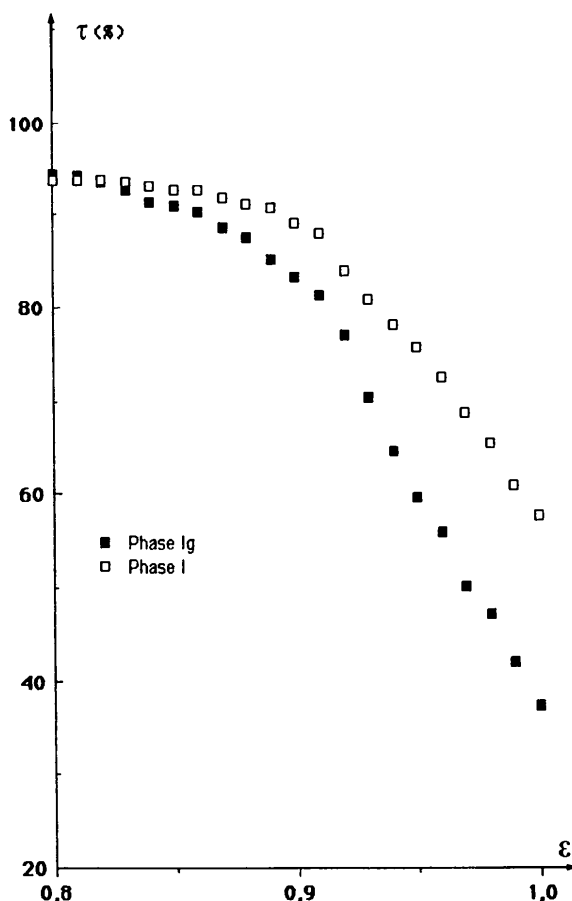


Fig. 2. Variation of the compatibility ratios τ as functions of the overlap parameter ε for phases I and I_g of 1-adamantane-carbonitrile.

In the case of adamantane-carbonitrile there exist contacts between next-nearest neighbours (which are related through translations that are equal to the unit-cell parameter). The corresponding compatibility ratios are the same in both phases, $\tau = 97.2\%$. The incompatibilities involve positions of the x, y, z and $1-x, y, z$ types. Therefore, there is no steric effect resulting from thermal contraction of the unit cell in the directions of the principal axes of the lattice.

Discussion

The analysis of the molecular positions in orientationally disordered crystals that has been made here in terms of steric parameters necessitates that the lattice structural descriptions are established by assuming the validity of the site model. This is not too constraining a hypothesis since this model seems to be the best one for describing the crystals in which we are interested. Nevertheless, the analysis of some disordered crystals may not be amenable to this treatment.

The contacts between neighbouring molecules have been described by means of compatibility matrices in which each element A_{kl} defines the steric compatibility ($A_{kl} = 1$) or incompatibility ($A_{kl} = 0$) between an orientational state at a given site and another orientational state at a given neighbouring site. The compatibility ratio τ , which is the ratio between the sum of all elements and the number of matrix elements, gives an overall estimation of orientational freedom within the studied crystals. For the seven crystalline phases which have been examined, the highest τ values are obtained by using the most recent values for the atomic van der Waals radii from the compilation of Nyburg *et al.* The differences may reach 20% with respect to the compatibility ratios obtained by using former values for these radii (Table 3). If we make the naive assumption that the best steric description is that which leads to easier molecular packings, then the above results for τ mean that the compilation of Nyburg *et al.* gives better van der Waals envelopes than previous descriptions.

Even without allowing for overlaps of the van der Waals envelopes of different molecules, the compatibility ratios are generally higher than 50% for the plastic phases. The only exception we encountered comes from the contacts between the closest nearest neighbours in thiophene for which τ is 37.5% at 183 K. We think this is connected with the existence of the intricate phase sequences in thiophene.

For the glassy crystalline phases of 1-adamantane-carbonitrile and cyclohexanol, the τ values are much lower than the values corresponding to the mother plastic phases. These decreases in τ illustrate the influence of thermal contraction on orientational freedom. This influence is also indicated by the variation of τ as a function of the overlap parameter ε .

Furthermore, when combined with an analysis of the shortest intermolecular distances, examination of the compatibility matrices gives information on the contacts which cause steric hindrance. This should enable us to eliminate a number of intermolecular relationships or to detect the types of interactions which influence these relationships as temperature varies, as we have seen in the case of 1-adamantanecarbonitrile.

Concluding remarks

In this paper, we have defined compatibility matrices which describe how pairs of neighbouring molecules sterically interact in orientationally disordered crystals. We put the stress on compatibility ratios which measure the proportions of neighbouring molecular interactions which do not experience significant steric hindrance. This can be considered as a semi-quantitative criterion of orientational freedom.

But the main use of compatibility matrices will be to build clusters of one hundred molecules or so, within which each molecule will be sterically compatible with *all* neighbouring molecules. Such clusters will be considered as samples extracted from the overall crystal and will be used to study local configurations and orientational correlations. We expect that statistical studies of great numbers of such clusters will help us to obtain a good description of order (or disorder) in these crystals.

Preliminary results have already been obtained in calculations of X-ray diffuse scattering (Ceccaldi, 1985) and of theoretical intermolecular contributions to NMR second moments (André, Bessada, Fuchs, Rousseau & Szwarc, 1988).

Another development has already been tackled: it uses similar matrices in which matrix-element values are related to interaction energies. Monte-Carlo calculations are under way and comparisons will be made between volume- and energy-driven crystal building. These developments will be described in future papers.

APPENDIX I

Program *COMPAT* (Fortran77) allows the calculation of the compatibility matrix for all molecular orientations that may exist in two neighbouring sites of any space group. Two different cases have been distinguished. In one case, the neighbouring site is obtained through a general operation of the space group (R_s, T_s), where R_s and T_s are respectively the rotation matrix and the translation associated with the above operation; then the N^2 elements of the matrix are calculated. In the other case, the site is centrosymmetric and a Bravais translation is sufficient to obtain the nearest neighbour. This produces symmetries in the compatibility matrix and only $N(N +$

$1)/2$ elements have to be calculated, which diminishes the computing time.

This program allows the calculations of the total compatibility ratio τ as a function of the overlap parameter ε . It is also possible to analyse the contacts which cause steric incompatibilities between two orientations and to find the shortest intermolecular distances.

APPENDIX 2

Phases I and I_g of 1-adamantanecarbonitrile correspond to space group $Fm\bar{3}m$. The lattice parameter is 9.822 Å in phase I at 295 K and 9.636 Å in phase I_g at 110 K. There are four molecules per unit cell ($Z = 4$). The asymmetric unit is located at the unit-cell origin. These data together with the corresponding structure factors have been published by Foulon *et al.* (1985), but they are derived assuming a continuous rotation of the molecules around their dipolar axes which are constrained along the fourfold crystalline axes.

The compatibility matrix method can only be applied by using a structural model which has been built in terms of the site model, but this is in any case considered as the best one for orientationally disordered solids. Therefore we have performed a new refinement with the site-model hypothesis using the *ORION* program and assigning a unit weight to each reflexion that Foulon *et al.* measured.

Within both phases, the molecule is supposed to lie in a general position: the dipolar axis has not been constrained along the [100] direction and the centre of gravity has not been forced to stay on a crystalline fourfold axis. Such assumptions agree with the observation of a secondary dielectric absorption which suggests the existence of a precessional motion of the molecular dipolar axis (Pathmanathan & Johari, 1985). Eight parameters have been refined: the scale factor, an overall temperature factor B and six parameters (three angles and the centre-of-gravity coordinates) that define the molecular position.

(a) Phase I: we obtain $B = 5.07(23) \text{ \AA}^2$, $\theta_1 = 0.23(153)$, $\theta_2 = -5.30(44)$, $\theta_3 = -2.03(63)^\circ$, $u_1 = 0.0514(12)$, $u_2 = 0.0028(20)$, $u_3 = 0.0009(31)$, $(\Delta/\sigma)_{\max} \leq 0.006$. The angle between the molecular axis and the crystalline fourfold axis is 5.8° and the centre of gravity is close to this axis. The conventional residual factors are $R = 0.042$ and $wR = 0.027$ (instead of 0.046 and 0.087 respectively for the continuous cylindrical rotation model: however, the two values for wR are not comparable, because they do not correspond to the same weights. This is also the case for phase I_g).

(b) Phase I_g : the refinement started from the structural model we determined for phase I. The refined parameters are $B = 2.90(12) \text{ \AA}^2$, $\theta_1 = 6.36(44)$, $\theta_2 = -2.49(41)$, $\theta_3 = -1.82(35)^\circ$, $u_1 = 0.0482(7)$, u_2

$= 0.0020$ (14) and $u_3 = -0.0006$ (15), $(\Delta/\sigma)_{\max} \leq 0.080$. The angle between the dipolar axis and the [100] direction is less than in phase I, being 3° . The centre of gravity stays near the crystalline axis and its distance to the origin has not changed. The residual factors are $R = 0.068$ and $wR = 0.042$ (instead of 0.075 and 0.102 respectively for the continuous cylindrical rotation model).

References

- ADACHI, K., SUGA, H. & SEKI, S. (1968). *Bull. Chem. Soc. Jpn*, **41**, 1073–1087.
- ALLEN, F. H. (1986). *Acta Cryst.* **B42**, 515–522.
- AMOUREUX, J. P. & BEE, M. (1979). *Acta Cryst.* **B35**, 2957–2962.
- AMOUREUX, J. P., SAUVAJOL, J. L. & BEE, M. (1981). *Acta Cryst.* **A37**, 97–104.
- ANDRÉ, D., BESSADA, C., FUCHS, A. H., ROUSSEAU, B. & SZWARC, H. (1988). *J. Phys. (Paris)*, **49**, 281–288.
- ANDRÉ, D., CECCALDI, D. & SZWARC, H. (1984). *J. Phys. (Paris)*, **45**, 731–737.
- ANDRÉ, D., FIGUIÈRE, P., FOURME, R., GHELLENSTEIN, M., LABARRE, D. & SZWARC, H. (1984). *J. Phys. Chem. Solids*, **45**, 299–309.
- ANDRÉ, D. & SZWARC, H. (1986). *J. Phys. (Paris)*, **47**, 61–70.
- BONDI, A. (1968). *Physical Properties of Molecular Crystals, Liquids and Glasses*, p. 450. New York: John Wiley.
- BROT, C. & LASSIER-GOVERS, B. (1976). *Ber. Bunsenges. Phys. Chem.* **80**, 31–41.
- CECCALDI, D. (1985). *Phys. Rev. B*, **31**, 8221–8225.
- FOULON, M., LEFEBVRE, J., AMOUREUX, J. P., MULLER, M. & MAGNIER, D. (1985). *J. Phys. (Paris)*, **46**, 919–926.
- FOURME, R. (1979). *J. Phys. (Paris)*, **40**, 557–561.
- FOURME, R., RENAUD, M. & ANDRÉ, D. (1972). *Mol. Cryst. Liq. Cryst.* **17**, 209–221.
- FUCHS, A. H., VIRLET, J., ANDRÉ, D. & SZWARC, H. (1985). *J. Chim. Phys.* **82**, 293–303.
- KAHN, R., FOURME, R., ANDRÉ, D. & RENAUD, M. (1973). *Acta Cryst.* **B29**, 131–138.
- KITAIGORODSKY, A. I. (1973). *Molecular Crystals and Molecules*, p. 10. New York: Academic Press.
- NYBURG, S. C. & FAERMAN, C. H. (1985). *Acta Cryst.* **B41**, 274–279.
- NYBURG, S. C., FAERMAN, C. H. & PRASAD, L. (1987). *Acta Cryst.* **B43**, 106–110.
- PATHMANATHAN, K. & JOHARI, G. P. (1985). *J. Phys. C*, **18**, 6535–6545.
- PAULING, L. (1942). *The Nature of the Chemical Bond*, p. 192. Ithaca: Cornell Univ. Press.
- TIMMERMANS, J. (1938). *J. Chim. Phys.* **35**, 331–344.

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Mapping the Conformation of Eight-Membered Rings

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Abstract

It is demonstrated how puckering parameters, calculated from atomic coordinates, map out the various symmetrical conformations of eight-membered rings onto the surface, defined by a set of tori on a unit sphere. The ten classical forms occur on right toroidal surfaces located at positions, fixed by characteristic values of a polar angle, on the sphere. The mapping represents the geometrical interpretation of five parameters in three-dimensional space. The surface projects as a two-dimensional presentation that can be interpreted directly. Some of the tori have minor radii of zero and contract into circles which represent simple pseudorotational cycles. When the major radius is zero a great circle, perpendicular to the equator of the unit sphere, is generated. A logical nomenclature to distinguish all settings of the possible conformations is proposed. There is one-to-one correspondence with all pseudorotational and interconversion pathways determined before by independent methods.

Introduction

The purpose of this work is to establish a direct procedure to obtain a consistent specification of the conformation of eight-membered cyclic fragments from crystallographic or Cartesian atomic coordinates. The conformation is to be specified in terms of a limited number of possible symmetrical forms, not necessarily the low-energy forms. External steric factors can conceivably freeze any flexible unit into a transitional conformation not normally accessible to the isolated entity. An identification scheme should therefore include all symmetrical forms, irrespective of steric strain.

The possible symmetry elements with respect to the mean plane through a puckered eight-membered ring include vertical axes and planes, and horizontal twofold axes. Possible vertical axes are C_4 , S_4 and C_2 . The full symmetry of possible forms should be consistent with the condition of chemical viability, to exclude arrangements with severely interpenetrating non-bonded atoms