

THOMAS, D. J. (1990*b*). Calibrating an area-detector diffractometer: integral response. *Proc. R. Soc. London Ser. A*, **428**, 181–214.  
 THOMAS, D. J. (1992*a*). Manuscript on further diffraction geometry. In preparation.  
 THOMAS, D. J. (1992*b*). Manuscript on profile analysis. In preparation.

WESTFALL, R. S. (1980). *Never at Rest: a Biography of Isaac Newton*, p. 12. Cambridge Univ. Press.  
 WONACOTT, A. J. (1977). Geometry of the rotation method. In *The Rotation Method in Crystallography*, edited by U. W. ARNDT & A. J. WONACOTT, ch. 7, pp. 75–103. Amsterdam: North-Holland.

*Acta Cryst.* (1992). **A48**, 158–172

## An Analytical Treatment of Disorder and Resolution of Atomic Electron-Density Functions for Carbon

BY THOMAS LAUBE

*Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule Zürich, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich, Switzerland*

(Received 26 April 1991; accepted 8 August 1991)

### Abstract

Unresolved disorder can lead to structural distortions because of averaged atomic positions. The influence of the isotropic probability density function (p.d.f.), the distance between the disordered positions and the site occupation factors of a disordered C atom on the apparent position and anisotropic p.d.f. of the adjusted atom is studied with a simple model for the centrosymmetrical case. The electron density is derived from the STO-3G wave functions and convoluted analytically with the corresponding p.d.f. The optimal positional and displacement parameters are obtained by minimization of the integral of the square of the difference electron density. Several electron- and difference-density plots are shown in order to demonstrate the goodness of the adjustment and several correlations between the parameters of the disordered and adjusted atoms are discussed. The results are applied to some examples where unresolved disorder may be possible.

### 1. Introduction

Disorder occurs in the crystalline phases of many kinds of organic and inorganic compounds and may be the result of dynamic processes in a molecule or a crystal (dynamic disorder) or of two or more different orientations of a molecule in a crystal with similar energies (static disorder). If the different positions of an atom are resolved in an electron-density or difference-density map, it is in many cases possible to refine these positions with partial populations [assuming isotropic or anisotropic harmonic potentials (see *e.g.* Altona & Sundaralingam, 1972; Siegel, Gutiérrez, Schweizer, Ermer & Mislow, 1986)] or to describe this atom with an anharmonic potential (see

*e.g.* Kuhs, 1983; Bachmann & Schulz, 1984). But if the disordered positions cannot be resolved due to a too small data set or due to the small distance between the positions, then the only hint of the presence of disorder is an unexpected shape or orientation of the displacement ellipsoid (Dunitz, Maverick & Trueblood, 1988; Dunitz, Schomaker & Trueblood, 1988). Some of the most persistent problems of physical organic chemistry are related to unresolved disorder because the different molecules or orientations of molecules are so similar that the distances between the disordered atomic positions are in the range of a few tenths of an ångström or even smaller. Well known examples are the structure of benzene (Ermer, 1987; Janoschek, 1987), antiaromatic systems (Dunitz, Krüger, Irngartinger, Maverick, Wang & Nixdorf, 1988), methanoannulenes (Bianchi, Pilati & Simonetta, 1981; Gatti, Barzagli & Simonetta, 1985) and semibullvalenes (Jackman, Benesi, Mayer, Quast, Peters, Peters & von Schnering, 1989). Some inorganic examples were discussed by Chandrasekhar & Bürgi (1984). A similar problem occurs in the interpretation of the X-ray structures of substituted 8,9,10-trinorborn-2-yl and 8,9,10-trinorborn-2-en-7-yl cations (Laube, 1987, 1989), which could in principle also be described as superpositions of classical ions, if the anisotropic displacement parameters (ADPs) are ignored [for the problem of bridged and equilibrating carbocations, see *e.g.* Brown (1977); Olah, Prakash & Sommer (1985)]. In order to estimate the *maximal possible* distance between disordered positions hidden in ADPs, we analyse in this work with a simple model the influence of the distance between two disordered positions of a C atom, their site occupation factors and their isotropic displacement parameters on the *apparent* position and ADPs of this atom.

## 2. Theoretical part

For the description of the static electron density  $\rho_C$  of a free C atom in direct space, several possibilities are available:

(a) the Fourier transform of the X-ray scattering factor or

(b) *ab initio* wave functions expressed by Slater-type functions or

(c) *ab initio* wave functions expressed by Gaussian-type functions can be computed. Possibility (a) gives very unsatisfactory results, because the X-ray scattering factor is computed by a Fourier transformation from numerical Hartree-Fock wave functions and expressed for convenience by an adjusted sum of Gaussians with nine parameters (Cromer & Mann, 1967, 1968; Doyle & Turner, 1968; Cromer & Waber, 1974). These functions are only a good approximation within a sphere of radius  $(\sin \Theta)/\lambda = 1.5$  or  $2 \text{ \AA}^{-1}$  in the reciprocal space, and the back transformation to direct space results in wavy functions without the sharp and high maximum (a cusp) of electron density at the nucleus because of the series truncation error, *i.e.* integration over only a sphere instead of the whole reciprocal space (Ibers, 1961; Allmann, 1967). Possibility (b) should give the best results for the static electron density, but the convolution products with the atomic p.d.f.s are difficult to compute analytically. Therefore, possibility (c) was chosen because the convolution product between Gaussian functions (or, more generally, Hermite-type functions) is much easier to compute and the error of the static electron density at the nucleus due to the Gaussian approximation should be further reduced by the convolution with the p.d.f., which smears the static electron density.

The STO-3G atomic orbitals (Hahn, Stewart & Pople, 1969) are as follows. If the nucleus lies on the origin of an orthonormal coordinate system with a unit length of 1 Bohr radius [ $a_0 = 0.5291771 \text{ \AA}$ ];  $\Phi'_{1s}(\zeta_1, \mathbf{r})$  is a modified wave function obtained by orientational averaging, see below]:

$$\Phi'_{1s}(\zeta_1, \mathbf{r}) = \zeta_1^{3/2} \sum_{k=1}^3 d_{1s,k} g_{1s}(\alpha_{1,k}, \zeta_1 \mathbf{r}),$$

$$\Phi'_{2s}(\zeta_2, \mathbf{r}) = \zeta_2^{3/2} \sum_{k=1}^3 d_{2s,k} g_{1s}(\alpha_{2,k}, \zeta_2 \mathbf{r}),$$

$$\tilde{\Phi}'_{2p}(\zeta_2, \mathbf{r}) = \zeta_2^{3/2} \sum_{k=1}^3 d_{2p,k} \tilde{g}_{2p}(\alpha_{2,k}, \zeta_2 \mathbf{r}),$$

where

$$g_{1s}(\alpha, \mathbf{r}) = (2\alpha/\pi)^{3/4} \exp(-\alpha r^2),$$

$$g_{2p}(\alpha, \mathbf{r}) = (2^7 \alpha^5 / \pi^3)^{1/4} r \exp(-\alpha r^2) \cos \theta,$$

$$\tilde{g}_{2p}(\alpha, \mathbf{r}) = 3^{-1/2} (2^7 \alpha^5 / \pi^3)^{1/4} r \exp(-\alpha r^2)$$

and  $\zeta_1 = 5.67$ ,  $\zeta_2 = 1.60$  for a free C atom.

We obtained the function  $\tilde{g}_{2p}$  by orientational averaging of  $g_{2p}^2$ , *i.e.*

$$\tilde{g}_{2p}^2 = \int_0^{2\pi} \int_0^\pi g_{2p}^2 r^2 \sin \vartheta d\theta d\varphi / \int_0^{2\pi} \int_0^\pi r^2 \sin \theta d\theta d\varphi$$

and  $g_{1s}$  and  $\tilde{g}_{2p}$  are normalized, *i.e.*

$$\int g_{1s}^2 d\mathbf{r} = 1 \quad \text{and} \quad \int \tilde{g}_{2p}^2 d\mathbf{r} = 1.$$

[Integrals without integration limits are improper integrals over the whole space of the integration variable; for the use of spherical C atoms, see also Kunze & Hall (1987).] The static electron density is obtained (in the real case) by squaring the orbitals, multiplying with the number of electrons, and summing over the orbitals. For carbon in the  $^3P$  state ( $1s^2 2s^2 2p^2$ ), one thus obtains (with orientational averaging)

$$\rho_C = \sum_{i=1}^6 C_{i,1} \exp(-F_{i,1} r^2) + \sum_{i=1}^6 C_{i,2} \exp(-F_{i,2} r^2) + \sum_{i=1}^6 C_{i,3} r^2 \exp(-F_{i,3} r^2).$$

For the coefficients  $C_{ij}$  and  $F_{ij}$  in this expression and the scattering factor corresponding to  $\rho_C$  see the supplementary material.\*

The dynamic electron density  $\rho_{C,\text{dyn}}$  of a C atom, whose nucleus motion follows a Gaussian probability density function p.d.f., can be approximately described as a convolution product [Born-Oppenheimer approximation (see *e.g.* Coulson & Thomas, 1971; Stewart, 1968; Scheringer & Reitz, 1976; Stevens, Rys & Coppens, 1977; Hirshfeld, 1977)]:

$$\rho_{C,\text{dyn}} = \rho_C * \text{p.d.f.}$$

For the evaluation of  $\rho_{C,\text{dyn}}$ , the following convolution products (c.p.s) must be known ( $A_1$  corresponds to an  $F_{ij}$  from  $\rho_C$ ,  $A_{ii}$  to  $1/(2U_{ii})$  from  $U^{-1}/2$  in the p.d.f.):

$$\text{c.p.}_s = \exp\{-A_1[(x-x_1)^2 + (y-y_1)^2 + (z-z_1)^2]\}$$

$$* \exp(-A_{11}x^2 - A_{22}y^2 - A_{33}z^2)$$

$$\text{c.p.}_p = \{[(x-x_1)^2 + (y-y_1)^2 + (z-z_1)^2]\}$$

$$\times \exp\{-A_1[(x-x_1)^2 + (y-y_1)^2 + (z-z_1)^2]\}$$

$$* \exp(-A_{11}x^2 - A_{22}y^2 - A_{33}z^2).$$

Using the definition for the convolution product of two functions of three variables, the analytical formulas were obtained with the computer algebra

\* Diagrams of the static C-atom electron density and the scattering factor, lists of the scattering factors, lists of the results of the optimizations with *DISORFIT*, additional electron-density and difference-density maps and details of the mathematical derivations in the theoretical part have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54613 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

program *MACSYMA* (1988, 1989) (see supplementary material\*). In order to obtain  $\rho_{C,\text{dyn}}$  from  $\rho_C$ , the first 12 terms of  $\rho_C$  (1s and 2s electrons) must be convoluted by using the expression for c.p.<sub>s</sub>, the other six (2p electrons) by using c.p.<sub>p</sub>.

In this study we assume that the disordered C atom may occupy only two positions [nucleus at  $\mathbf{R}_1 = (X_1, 0, 0)^T$  with isotropic displacement parameters  $U_{ii,1}$  or at  $\mathbf{R}_2 = (X_2, 0, 0)^T$  with isotropic displacement parameters  $U_{ii,2}$ ] with the site occupation factors  $p_1$  and  $p_2$  ( $p_1 + p_2 = 1$ ) and that it has the same isotropic p.d.f. in both positions (i.e.  $U_{11,1} = U_{22,1} = U_{33,1} = U_{11,2} = U_{22,2} = U_{33,2}$ ). In order to have centrosymmetry, a disordered atom is also located at  $-\mathbf{R}_1$  and at  $-\mathbf{R}_2$  with identical site occupation factors and p.d.f.s. The adjusted C atom [at  $\mathbf{R}_3 = (X_3, 0, 0)^T$  and at  $-\mathbf{R}_3$ ] must have an anisotropic p.d.f. Therefore, the dynamic electron density of the disordered C-atom  $\rho_{\text{obs}}$  and the dynamic electron density of the adjusted C-atom  $\rho_{\text{calc}}$  are as follows:

$$\begin{aligned} \rho_{\text{obs}}(\mathbf{r}) &= p_1 \rho_{C,\text{dyn}}(\mathbf{r} - \mathbf{R}_1) + p_2 \rho_{C,\text{dyn}}(\mathbf{r} - \mathbf{R}_2) \\ &\quad + p_1 \rho_{C,\text{dyn}}(\mathbf{r} + \mathbf{R}_1) + p_2 \rho_{C,\text{dyn}}(\mathbf{r} + \mathbf{R}_2) \\ \rho_{\text{calc}}(\mathbf{r}) &= \rho_{C,\text{dyn}}(\mathbf{r} - \mathbf{R}_3) + \rho_{C,\text{dyn}}(\mathbf{r} + \mathbf{R}_3). \end{aligned}$$

In the case of unresolved (or unresolvable) disorder, one normally treats this atom first as if it has an anisotropic p.d.f. The best adjustment in the least-squares sense is obtained by minimizing the integral over the square of the difference electron density,

$$I_{\Delta\rho} = \int (\rho_{\text{obs}} - \rho_{\text{calc}})^2 \text{d}\mathbf{r}.$$

The variables are the parameters of the adjusted atom:  $X_3$ ,  $U_{11}$  and  $U_{22} = U_{33}$ . The result of the minimization of  $I_{\Delta\rho}$  in the direct space need not necessarily be identical with the result of the minimization of one of the following functions (in the reciprocal space) usually used in X-ray crystallography, i.e.

$$\begin{aligned} I_{\Delta F} &= \int (|F_{\text{obs}}| - |F_{\text{calc}}|)^2 \text{d}\mathbf{h} \\ I_{\Delta I} &= \int (|F_{\text{obs}}|^2 - |F_{\text{calc}}|^2)^2 \text{d}\mathbf{h} \end{aligned}$$

where  $F_{\text{obs}}$  and  $F_{\text{calc}}$  are the Fourier transforms of  $\rho_{\text{obs}}$  and  $\rho_{\text{calc}}$  (see also Wilson, 1976; Coppens & Hansen, 1977). The weights have been omitted, the neglect of the periodicity in the direct space leads to improper integrals in either space instead of proper integrals in the direct space or sums in the reciprocal space, and infinite resolution is assumed. The reason for these simplifications is that the absolute values in  $I_{\Delta F}$  make a simple evaluation (i.e. no separate integrations over intervals or regions) impossible (but  $I_{\Delta I}$  could be evaluated in the centrosymmetrical case). Because  $(\rho_{\text{obs}} - \rho_{\text{calc}})^2 = |\rho_{\text{obs}} - \rho_{\text{calc}}|^2$ , it follows that

$$I_{\Delta\rho} = \int |F_{\text{obs}} - F_{\text{calc}}|^2 \text{d}\mathbf{h} = \int (F_{\text{obs}} - F_{\text{calc}})^2 \text{d}\mathbf{h}$$

in the centrosymmetrical case applying Plancherel's theorem or Parseval's theorem (Zygmund, 1988; Champeney, 1989) ( $\rho_{\text{obs}}$  and  $\rho_{\text{calc}}$  are absolutely and square integrable, because they are expressed as sums of squares of Hermite-type functions, i.e. good functions).

Because  $\rho_{\text{obs}} - \rho_{\text{calc}}$  is in our approximation a sum of  $6 \times 18 = 108$  convolution products of the type c.p.<sub>s</sub> or c.p.<sub>p</sub>,  $I_{\Delta\rho}$  is a sum of  $108 \times 109/2 = 5886$  different integrals  $I_{pp}$  (the indices  $p$  for the two factors, each in braces, stand for 'convoluted  $p$  density';  $s$  would stand for 'convoluted  $s$  density', see below), where

$$\begin{aligned} I_{pp} &= \int \{ [f_0 + f_1(x - x_1)^2 + f_2y^2 + f_3z^2] \\ &\quad \times \exp[-a_{11}(x - x_1)^2 - a_{22}y^2 - a_{33}z^2] \} \\ &\quad \times \{ [g_0 + g_1(x - x_2)^2 + g_2y^2 + g_3z^2] \\ &\quad \times \exp[-b_{11}(x - x_2)^2 - b_{22}y^2 - b_{33}z^2] \} \text{d}\mathbf{r} \end{aligned}$$

with the nucleus of the first atom at  $\mathbf{r}_1 = (x_1, 0, 0)^T$  and the nucleus of the second atom at  $\mathbf{r}_2 = (x_2, 0, 0)^T$ . The vectors  $\mathbf{r}_1$  and  $\mathbf{r}_2$  can each be one of the vectors:  $\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, -\mathbf{R}_1, -\mathbf{R}_2, -\mathbf{R}_3$ ; all coefficients  $f_i$  and  $g_i$  ( $i = 0, \dots, 3$ ) are nonnegative and all  $a_{ii}$  and  $b_{ii}$  ( $i = 1, \dots, 3$ ) are positive. All special cases ( $I_{ss}$ ;  $I_{sp}$ ;  $\mathbf{r}_1 = \mathbf{r}_2$ ) are contained in the formula for  $I_{pp}$ , which was computed with *MACSYMA* (1988, 1989) (see supplementary material\*).

Because the disordered atom is smeared isotropically and all atoms lie on the  $x$  axis, the electron density of the adjusted C atom is determined by three parameters: its  $x$  coordinate  $X_{3,\text{opt}}$  and the two displacement parameters  $U_{11,\text{opt}}$  and  $U_{22,\text{opt}} = U_{33,\text{opt}}$ . Although we know the closed solution for  $I_{pp}$ , the optimal values of  $X_3$ ,  $U_{11}$  and  $U_{22}$  can only be determined numerically by minimization of  $I_{\Delta\rho}$ . Therefore, a Fortran77 program *DISORFIT* was written in order to perform these computations. The minimization itself was performed by the subroutine *DBCONF* from the IMSL *MATH/LIBRARY* (1989) using simple constraints in order to keep  $X_3$  in the region around  $X_1$  and  $X_2$  and to keep  $U_{11}$  and  $U_{22}$  positive. An additional option allows the search for local minima of  $I_{\Delta\rho}$ . The result in the form of a solution vector  $\mathbf{v}_{\text{min}} = (X_{3,\text{opt}}, U_{11,\text{opt}}, U_{22,\text{opt}})^T$  is checked in the usual way:  $\text{grad } I_{\Delta\rho}$  at  $\mathbf{v} = \mathbf{v}_{\text{min}}$  must be sufficiently near to  $(0, 0, 0)^T$ , and all eigenvalues of the Hessian of  $I_{\Delta\rho}$  at  $\mathbf{v} = \mathbf{v}_{\text{min}}$  must be greater than zero (i.e. solutions on the constraints are not considered). The final  $R$  value is given as

$$R = \left[ \int (\rho_{\text{obs}} - \rho_{\text{calc}})^2 \text{d}\mathbf{r} / \int \rho_{\text{obs}}^2 \text{d}\mathbf{r} \right]^{1/2}.$$

The program searches also for extremal points of  $\rho_{\text{obs}}$  and of the final  $\rho_{\text{obs}} - \rho_{\text{calc}}$  on the positive  $x$  axis and writes all results in a data file, which can be read

\* See deposition footnote.

\* See deposition footnote.

by the plotting program *DISORPLT* [which uses several routines from the IMSL *MATH/LIBRARY* (1989), the IMSL *SFUN/LIBRARY* (1989) and the graphics subroutine package Erlanger Grafik System, (1989)] in order to generate contour-line diagrams of  $\rho_{\text{obs}}$ ,  $\rho_{\text{calc}}$  or  $\rho_{\text{obs}} - \rho_{\text{calc}}$  in the  $xy$  plane. Furthermore, a contour line of p.d.f.<sub>obs</sub> (i.e. the 'true' joint p.d.f. of both disordered partial C atoms) or p.d.f.<sub>calc</sub> [corresponding to a cut through an *ORTEP* ellipsoid of the adjusted atom (Johnson, 1976)] or both of them may be drawn in the same diagram for a given probability  $p$  to find the atom inside the surface generated by a rotation of the contour line around the  $x$  axis (for details see the supplementary material\*). For all following examples,  $p = 0.5$  is chosen as in most *ORTEP* diagrams in the literature.

### 3. Examples

The following examples have been computed with *DISORFIT* [in all cases,  $X_1 = 10 \text{ \AA}$  and  $U_{11,1} = U_{22,1} = U_{33,1} = U_{11,2} = U_{22,2} = U_{33,2}$ ;  $x = a(b)c$  means  $x$  goes from  $a$  to  $c$  in increments of  $b$ ]:

$$\begin{aligned} X_2 - X_1 &= 0.25 \text{ (0.25) } 2.00 \text{ \AA} \\ U_{ii,j} &= 0.01 \text{ (0.01) } 0.05 \text{ \AA}^2 \\ p_1/p_2 &= 1 \text{ and } 3. \end{aligned}$$

The chemically relevant values of  $X_2 - X_1$  lie in the range up to about  $1 \text{ \AA}$ , but the larger values were included to show the asymptotic behaviour (see below). The isotropic displacement parameters  $U_{ii,j}$  cover the most frequent range;  $p_1/p_2 = 1$  refers to the discussion of the 8,9,10-trinorborn-2-en-7-yl cation (Laube, 1989) and  $p_1/p_2 = 3$  refers to the 8,9,10-trinorborn-2-yl cation (Laube, 1987, 1989). Contour-line diagrams of some electron densities and difference densities in the  $xy$  plane (computed with *DISORPLT*) are shown in Figs. 1-6.

The 50% probability contour lines of p.d.f.<sub>calc</sub> (a cut through the *ORTEP* ellipsoid) and p.d.f.<sub>obs</sub> are plotted with thick lines. It must be emphasized that  $\rho_{\text{obs}}$  and  $\rho_{\text{obs}} - \rho_{\text{calc}}$  are the *exact density functions* and not the density and difference-density functions obtained in X-ray crystallography, where the Fourier transform of  $F_{\text{obs}}$  is computed with the absolute values of  $F_{\text{obs}}$  and the phase angles of  $F_{\text{calc}}$ . This difference, however, becomes negligible if  $\rho_{\text{obs}}$  and  $\rho_{\text{calc}}$  are very similar (i.e. small values of  $X_2 - X_1$ , large displacement parameters). The 'X-ray electron densities' have been computed for simple examples, where all atomic electron-density functions are described by one simple Gaussian function (see also Laube, 1989, reference 41). The unusually high electron density especially for the small displacement parameters is

due to the fact that these computations correspond to an *infinite resolution* (Allmann, 1967; see also Scheringer, 1977). Because the two centrosymmetrically related split atoms have in our examples a distance of  $20 \text{ \AA}$ , the results are valid also for non-centrosymmetrical structures.

### 4. Discussion

In order to discuss the results of the 80 *DISORFIT* jobs, the auxiliary plot program *DISORSTA* was written, which reads all data files generated by *DISORFIT* and draws plots which show the relations between parameters using the Erlanger Grafik System (1989) (see Figs. 7-10).

In the case  $p_1/p_2 = 1$  the adjusted atom lies in most cases, as expected, centred between the two disordered positions (Fig. 7, left column). For small displacement parameters ( $U_{ii,j} = 0.01 \text{ \AA}^2$ ), however, local minima of  $I_{\Delta\rho}$  occur for  $X_2 - X_1 \approx 1 \text{ \AA}$  and  $X_3$  around  $X_1$  or  $X_2$  (thin markers) and they become global (degenerate) minima for  $X_2 - X_1 \approx 1.5 \text{ \AA}$ . This bifurcation is not observed for larger displacement parameters  $U_{ii,j}$ . Because  $\rho_{\text{calc}}$  must try to fit the density of both disordered positions equally well,  $U_{11,\text{opt}}$  becomes very large. It seems that  $U_{11,\text{opt}}$  approaches asymptotically the empirical function  $U_{11,\text{opt}}^{1/2} \approx 0.68(X_2 - X_1)$  for large  $(X_2 - X_1)$ , essentially independent of  $U_{22,\text{opt}}$  or  $U_{ii,j}$  (see Fig. 7, middle)!  $U_{22,\text{opt}}$  has approximately the value of  $U_{ii,j}$ . The agreement becomes worse with larger  $(X_2 - X_1)$  and better with larger  $U_{ii,j}$ , i.e. when  $\rho_{\text{obs}}$  is more smeared (Fig. 7, right column).

The behaviour of the adjusted atom is quite different for  $p_1/p_2 = 3$  (Fig. 8):  $X_{3,\text{opt}}$  is shifted for small values of  $(X_2 - X_1)$  towards the weighted average of the disordered positions, but returns to the atomic position with the larger weight ( $X_1$ ), as depicted in Fig. 8, left column. The maximal distance of  $X_{3,\text{opt}}$  from  $X_1$  is about  $0.1 \text{ \AA}$ . The difference between the adjusted displacement parameters  $U_{11,\text{opt}}$  and  $U_{22,\text{opt}}$  is most pronounced when  $X_{3,\text{opt}}$  is most distant from  $X_1$ : see Fig. 8, middle column. Nevertheless, the displacement parameters never show the dramatic anisotropy observed in Fig. 7. The  $R$  factors (Fig. 8, right column) show a similar trend to that in Fig. 7.

In order to analyse qualitatively the behaviour of the displacement parameters upon cooling, we plot  $U_{11,\text{opt}}$  and  $U_{22,\text{opt}}$  vs  $U_{ii,j}$  (on logarithmic scales, see Figs. 9 and 10, left columns; smaller values of  $U_{ii,j}$  correspond to a lower temperature). In the case  $p_1/p_2 = 1$ ,  $U_{11,\text{opt}}$  is practically temperature invariant for  $X_2 - X_1 \geq 0.5 \text{ \AA}$ , whereas  $U_{22,\text{opt}}$  is approximately equal to  $U_{ii,j}$  (Fig. 9, left column)! In these cases, the two disordered positions are resolved, i.e. one finds a saddle point for  $\rho_{\text{obs}}$  (Fig. 9, right column; for a discussion of resolution, see e.g. Wilson, 1979;

\* See deposition footnote.

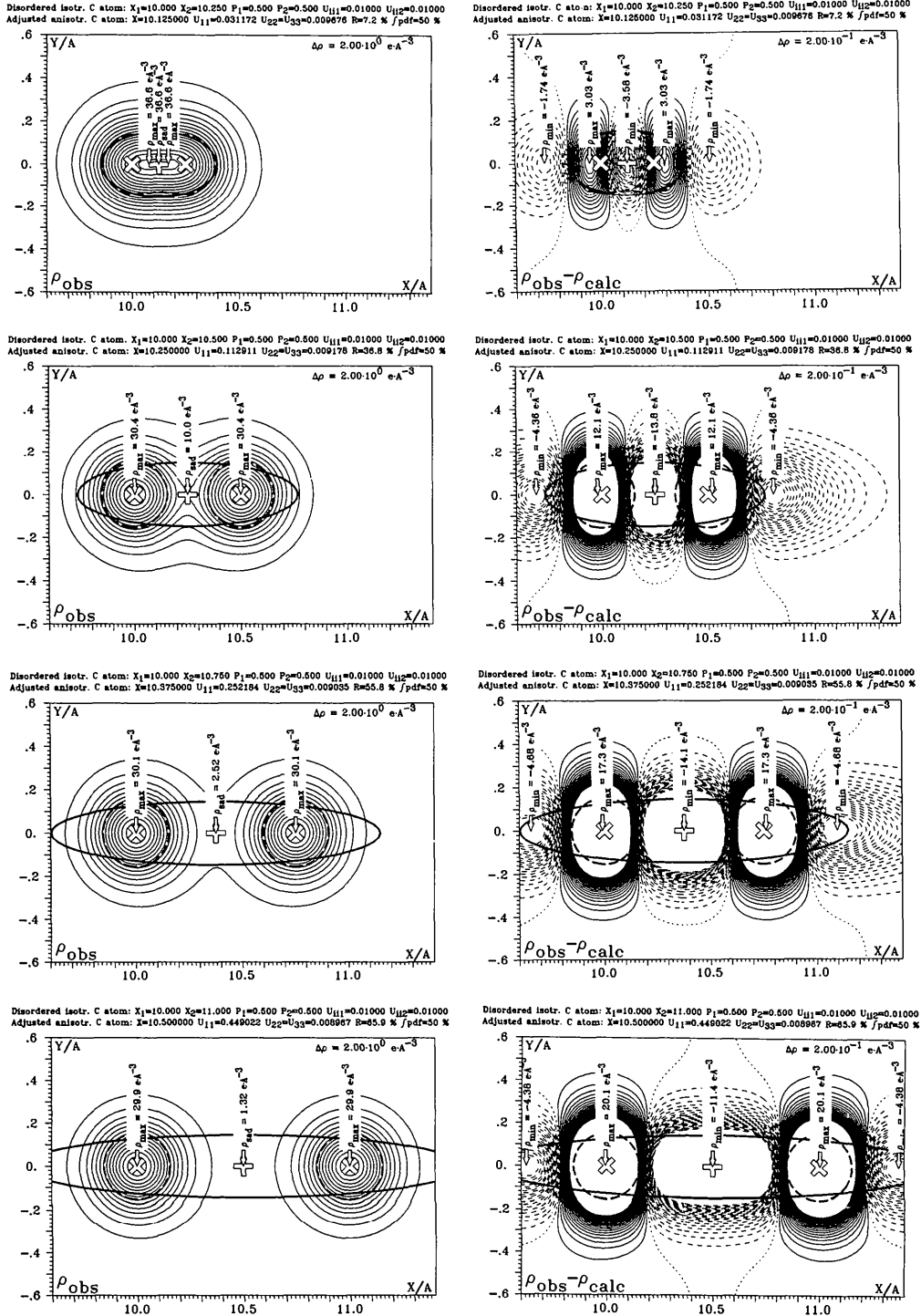


Fig. 1. Adjustment of an anisotropically smeared C atom (nucleus marked by +) on a disordered and isotropically smeared C atom (nuclei marked by x; all  $U_{ij}=0.01 \text{ \AA}^2$ ; site occupation factors  $p_1=0.5$  and  $p_2=0.5$ ) with the distances  $X_2 - X_1 = 0.25, 0.50, 0.75, 1.00 \text{ \AA}$  (from top to bottom) between the disordered positions. Solid contour lines: positive density; dashed: negative; dotted: zero; the extremal points are marked by arrows. The thick solid ellipse is the 50% contour line of  $p.d.f._{calc}$ , the dashed curve is the 50% contour of  $p.d.f._{obs}$ . Left column:  $\rho_{obs}$  with  $\Delta\rho = 2 \text{ e}\cdot\text{\AA}^{-3}$ ; right column:  $\rho_{obs} - \rho_{calc}$  with  $\Delta\rho = 0.2 \text{ e}\cdot\text{\AA}^{-3}$ .

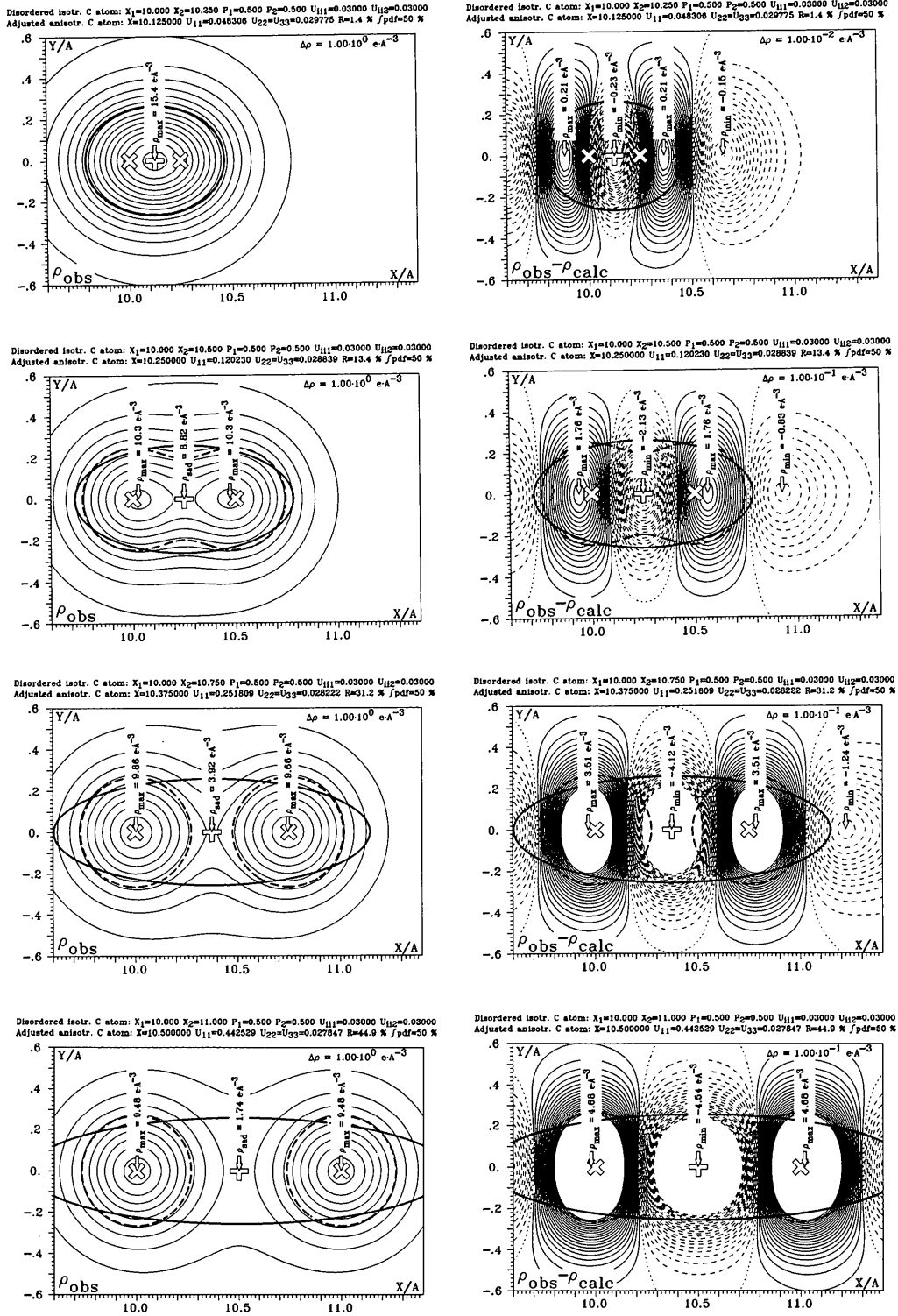


Fig. 2. Adjustment of an anisotropically smeared C atom (nucleus marked by +) on a disordered and isotropically smeared C atom (nuclei marked by x; all  $U_{i,j} = 0.03 \text{ \AA}^2$ ; site occupation factors  $p_1 = 0.5$  and  $p_2 = 0.5$ ) with the distances  $X_2 - X_1 = 0.25, 0.50, 0.75, 1.00 \text{ \AA}$  (from top to bottom) between the disordered positions. Solid contour lines: positive density; dashed: negative; dotted: zero; the extremal points are marked by arrows. The thick solid ellipse is the 50% contour line of  $\rho_{\text{calc}}$ , the dashed curve is the 50% contour of  $\rho_{\text{obs}}$ . Left column:  $\rho_{\text{obs}}$  with  $\Delta\rho = 1 \text{ e}\cdot\text{\AA}^{-3}$ ; right column:  $\rho_{\text{obs}} - \rho_{\text{calc}}$  with  $\Delta\rho = 0.01$  (top),  $0.1$  (others)  $\text{e}\cdot\text{\AA}^{-3}$ .

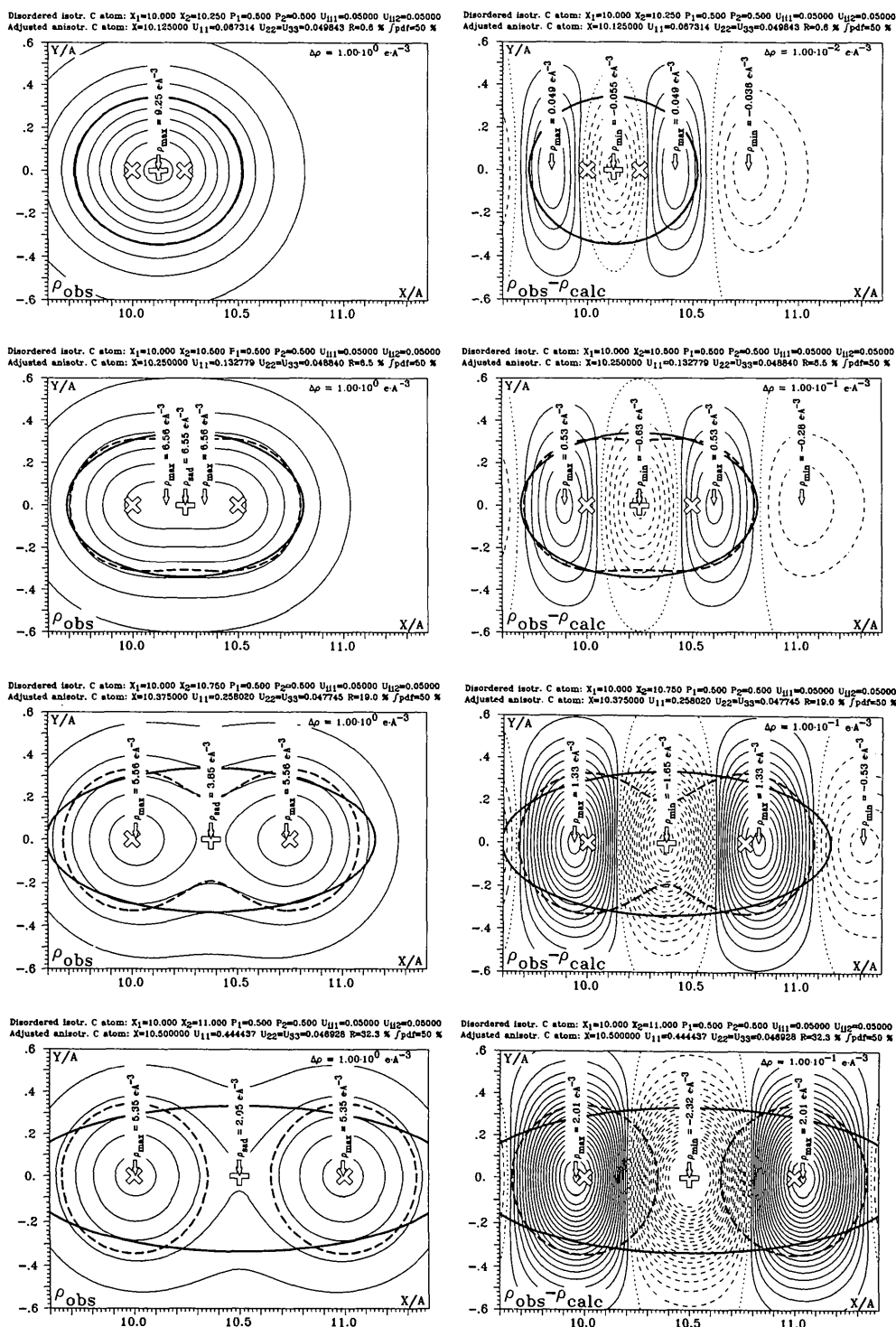


Fig. 3. Adjustment of an anisotropically smeared C atom (nucleus marked by +) on a disordered and isotropically smeared C atom (nuclei marked by x; all  $U_{ij} = 0.05 \text{ \AA}^2$ ; site occupation factors  $p_1 = 0.5$  and  $p_2 = 0.5$ ) with the distances  $X_2 - X_1 = 0.25, 0.50, 0.75, 1.00 \text{ \AA}$  (from top to bottom) between the disordered positions. Solid contour lines: positive density; dashed: negative; dotted: zero; the extremal points are marked by arrows. The thick solid ellipse is the 50% contour line of p.d.f.<sub>calc</sub>, the dashed curve is the 50% contour of p.d.f.<sub>obs</sub>. Left column:  $\rho_{\text{obs}}$  with  $\Delta\rho = 1 \text{ e}\text{\AA}^{-3}$ , right column:  $\rho_{\text{obs}} - \rho_{\text{calc}}$  with  $\Delta\rho = 0.01$  (top), 0.1 (others)  $\text{e}\text{\AA}^{-3}$ .

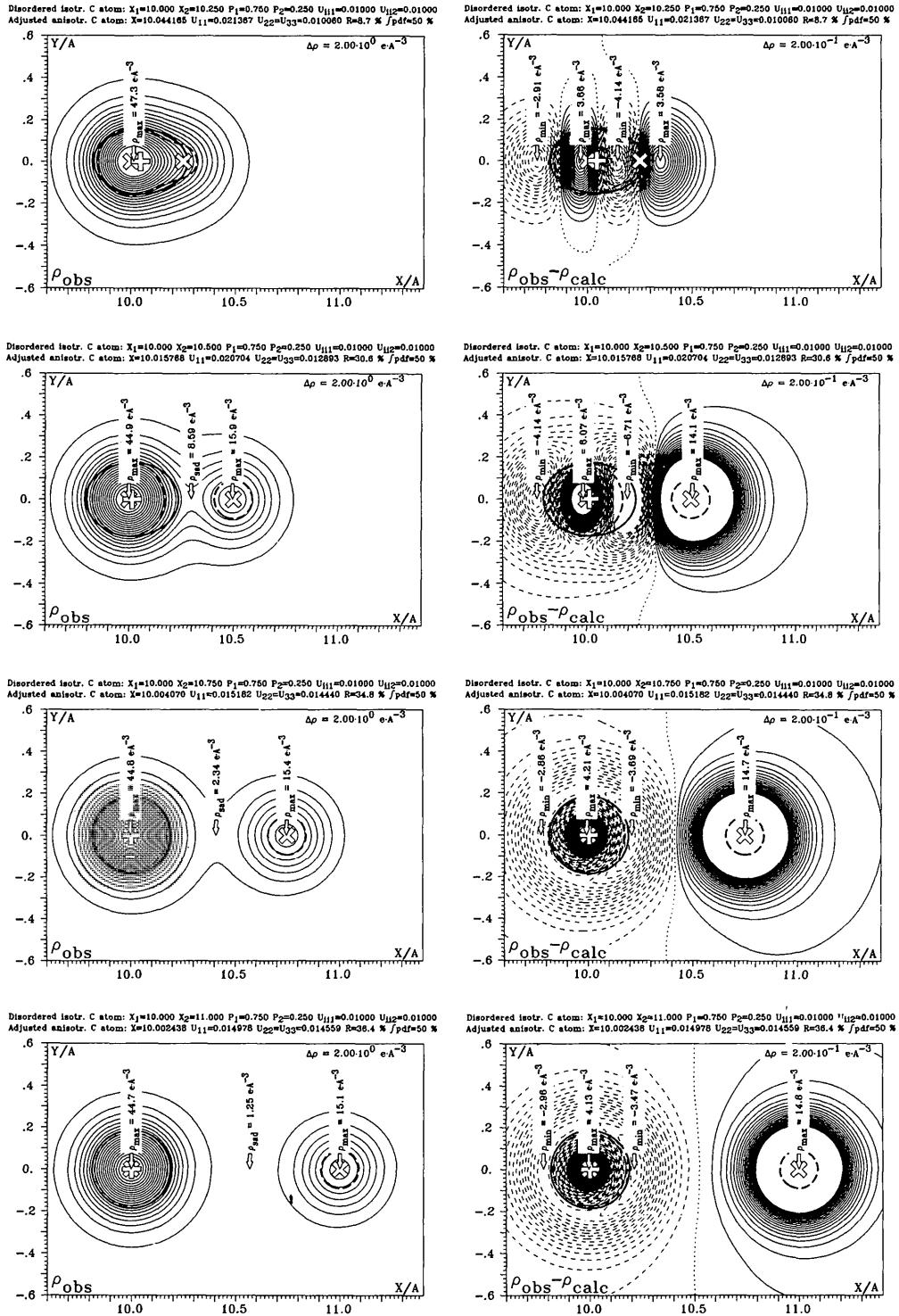


Fig. 4. Adjustment of an anisotropically smeared C atom (nuclei marked by +) on a disordered and isotropically smeared C atom (nuclei marked by x; all  $U_{i,j} = 0.01 \text{\AA}^2$ ; site occupation factors  $p_1 = 0.75$  and  $p_2 = 0.25$ ) with the distances  $X_2 - X_1 = 0.25, 0.50, 0.75, 1.00 \text{\AA}$  (from top to bottom) between the disordered positions. Solid contour lines: positive density; dashed: negative; dotted: zero; the extremal points are marked by arrows. The thick solid ellipse is the 50% contour line of  $p.d.f._{calc}$ , the dashed curve is the 50% contour of  $p.d.f._{obs}$ . Left column:  $\rho_{obs}$  with  $\Delta\rho = 2 e\text{\AA}^{-3}$ ; right column:  $\rho_{obs} - \rho_{calc}$  with  $\Delta\rho = 0.2 e\text{\AA}^{-3}$ .



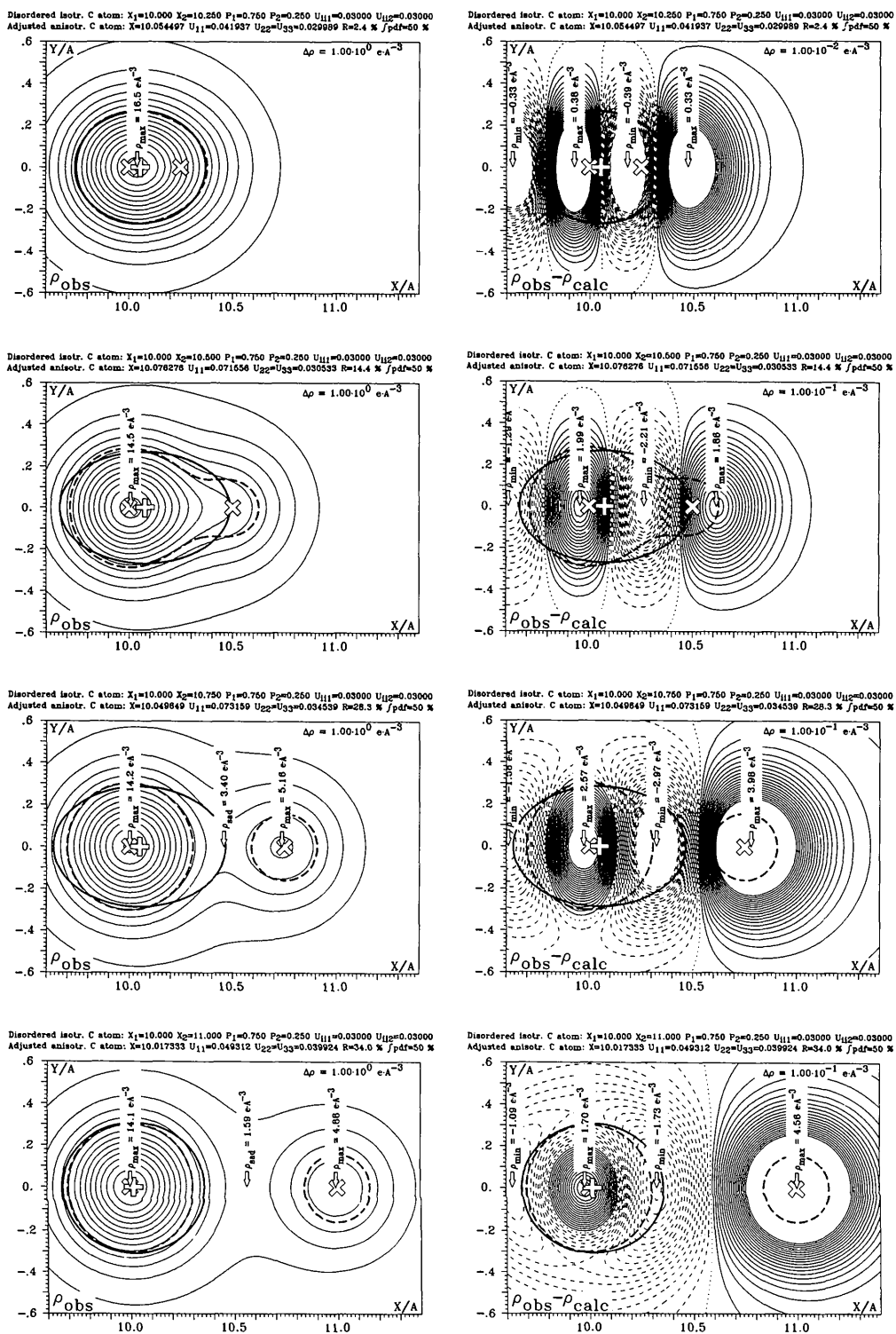


Fig. 5. Adjustment of an anisotropically smeared C atom (nucleus marked by +) on a disordered and isotropically smeared C atom (nuclei marked by x; all  $U_{i,j} = 0.03 \text{ \AA}^2$ ; site occupation factors  $p_1 = 0.75$  and  $p_2 = 0.25$ ) with the distances  $X_2 - X_1 = 0.25, 0.50, 0.75, 1.00 \text{ \AA}$  (from top to bottom) between the disordered positions. Solid contour lines: positive density; dashed: negative; dotted: zero; the extremal points are marked by arrows. The thick solid ellipse is the 50% contour line of p.d.f.<sub>calc.</sub>, the dashed curve is the 50% contour of p.d.f.<sub>obs.</sub>. Left column:  $\rho_{\text{obs}}$  with  $\Delta\rho = 1 \text{ e\AA}^{-3}$ ; right column:  $\rho_{\text{obs}} - \rho_{\text{calc}}$  with  $\Delta\rho = 0.01$  (top), 0.1 (others)  $\text{e\AA}^{-3}$ .

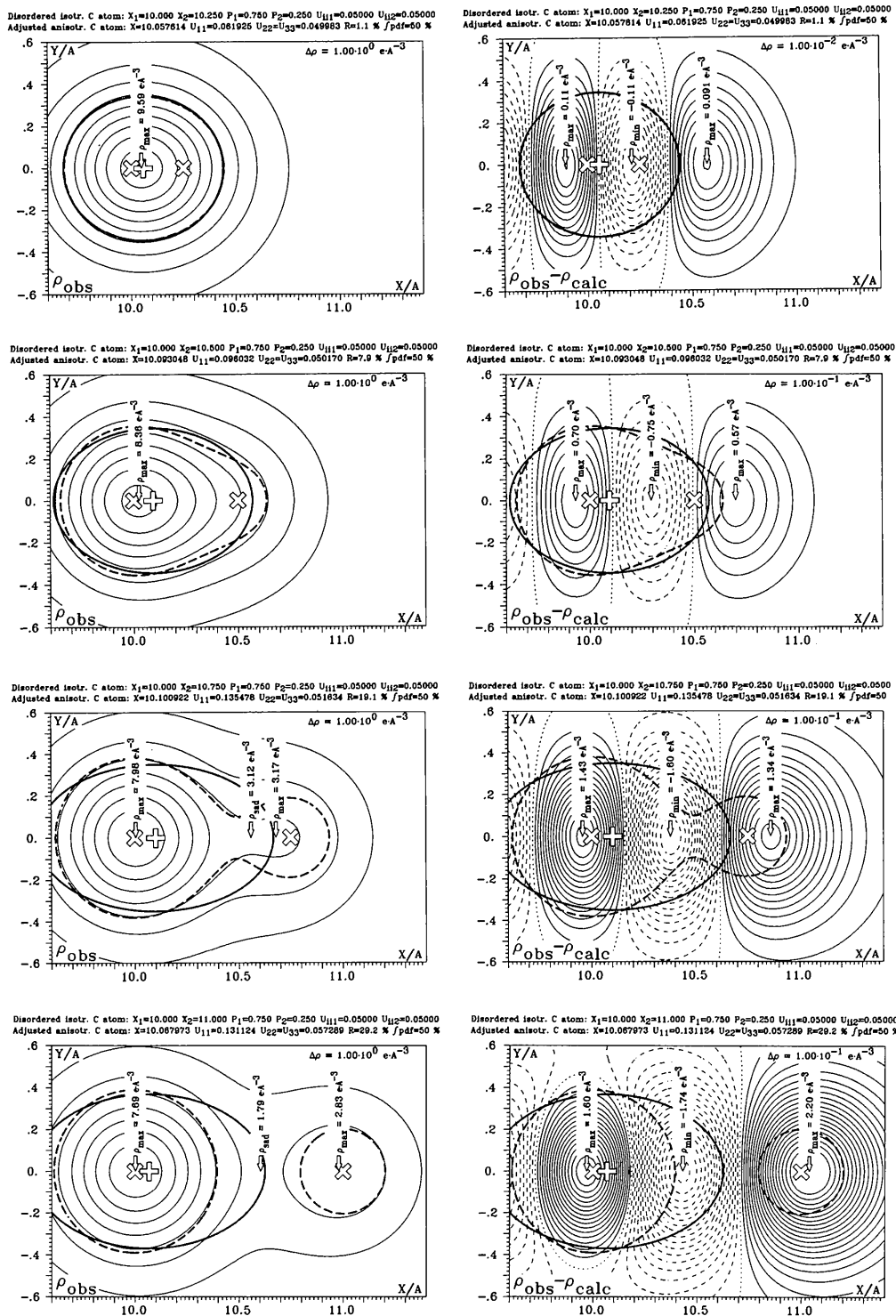


Fig. 6. Adjustment of an anisotropically smeared C atom (nucleus marked by +) on a disordered and isotropically smeared C atom (nuclei marked by x; all  $U_{i,j} = 0.05 \text{ \AA}^2$ ; site occupation factors  $p_1 = 0.75$  and  $p_2 = 0.25$ ) with the distances  $X_2 - X_1 = 0.25, 0.50, 0.75, 1.00 \text{ \AA}$  (from top to bottom) between the disordered positions. Solid contour lines: positive density; dashed: negative; dotted: zero; the extremal points are marked by arrows. The thick solid ellipse is the 50% contour line of  $p.d.f._{calc}$ , the dashed curve is the 50% contour of  $p.d.f._{obs}$ . Left column:  $\rho_{obs}$  with  $\Delta\rho = 1 \text{ e\AA}^{-3}$ ; right column:  $\rho_{obs} - \rho_{calc}$  with  $\Delta\rho = 0.01$  (top),  $0.1$  (others)  $\text{e\AA}^{-3}$ .

Stenkamp & Jensen, 1984). Only for small values of  $X_2 - X_1$  (about  $0.25 \text{ \AA}$ ) does  $U_{11,\text{opt}}$  decrease with falling temperature, but less than  $U_{22,\text{opt}}$  and  $U_{ii}$ . In the case  $p_1/p_2 = 3$ ,  $U_{11,\text{opt}}$  and  $U_{22,\text{opt}}$  always decrease upon lowering the temperature (Fig. 10, left column). Although  $U_{11,\text{opt}}$  is always larger than  $U_{22,\text{opt}}$ , it may be difficult to distinguish between a disorder case and a normal ADP by measuring at different temperatures. The behaviour does not depend on the resolution of the disordered positions (Fig. 10, right column).

### 5. Applications

Benzene (Bacon, Curry & Wilson, 1964; Cox, Cruickshank & Smith, 1958) may be one of the most difficult cases because, if one assumes that the crystal consists of statically disordered  $D_{3h}$  molecules, then the distance between two disordered positions is about  $0.058 \text{ \AA}$  (Ermer, 1987). If we set all  $U_{ii,j} = 0.01 \text{ \AA}^2$  (corresponding to a good measurement at liquid-nitrogen temperature), the adjusted ADPs  $U_{11,\text{opt}} = 0.0109 \text{ \AA}^2$  and  $U_{22,\text{opt}} = 0.0100 \text{ \AA}^2$  ( $R = 0.029\%$ ,

maximal absolute value of the final  $\rho_{\text{obs}} - \rho_{\text{calc}} = 0.023 \text{ e\AA}^{-3}$ ) are very similar, and libration or rotation of  $D_{3h}$  or  $D_{6h}$  molecules would result in a smearing of the electron density in the same direction as caused by the assumed disorder. Therefore, a diffraction experiment at liquid-nitrogen temperature would not give the point group of benzene.

Our previously published simple and qualitative analysis of the ADPs of the 8,9,10-trinorborn-2-yl and 8,9,10-trinorborn-2-en-7-yl cations (Laube, 1987, 1989) in terms of possible hidden disorder due to 'classical' ions can now be quantified. The atom with the largest distance between possible disordered positions (C6 with  $0.95 \text{ \AA}$ ) in the 8,9,10-trinorborn-2-yl cation has experimentally determined U eigenvalues of  $0.071$ ,  $0.033$  and  $0.017 \text{ \AA}^2$ , *i.e.* if these values are assumed to be due to disorder (neglecting rigid-body motion, which explains the displacement ellipsoids), the maximal possible distance between unresolved disordered positions of this atom would be about  $0.4 \text{ \AA}$  according to Fig. 8 (and also Fig. 7), and the deviation in its position would be about  $0.07 \text{ \AA}$  along

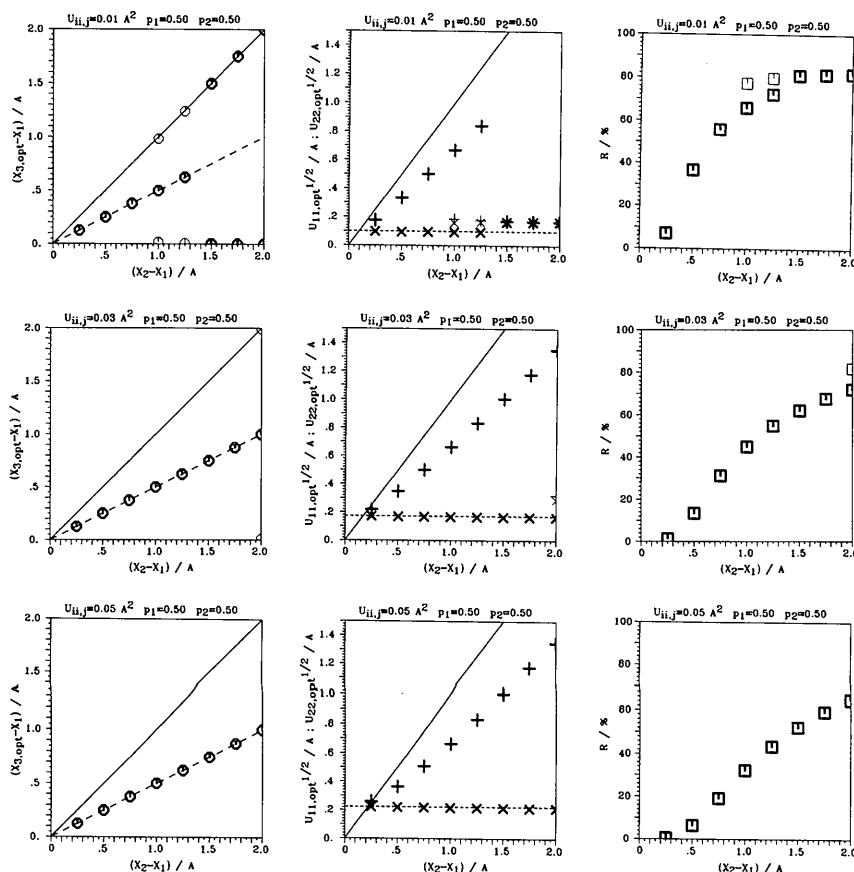


Fig. 7. Dependence of  $X_{3,\text{opt}} - X_1$  (left column),  $U_{11,\text{opt}}^{1/2}$  and  $U_{22,\text{opt}}^{1/2}$  (marked by + and x; middle column) and  $R$  (right column) on  $X_2 - X_1$  for the adjustment on a disordered C atom with the site occupation factors  $p_1 = 0.5$  and  $p_2 = 0.5$ . Thin markers indicate the results of local minima. In the left column, the solid line indicates the position of  $X_2$  (*i.e.*  $X_2 - X_1$ ) and the dashed line the weighted average between  $X_1$  and  $X_2$ . In the middle column, the solid line indicates  $X_2 - X_1$  and the dashed horizontal line  $U_{ii,j}^{1/2}$ . The isotropic displacement parameters are:  $0.01 \text{ \AA}^2$  (top row),  $0.03 \text{ \AA}^2$  (middle),  $0.05 \text{ \AA}^2$  (bottom).

the principal axis of the largest eigenvalue. Fig. 11 shows qualitatively the C2–C1–C6 fragment of the 8,9,10-trinorborn-2-yl cation with the *ORTEP* ellipsoids.

The thick solid lines connect the experimentally determined atoms, the thin lines show the 'true' structure for the assumed disorder with the weight about 0.75 and the dashed line the minor Wagner–Meerwein isomer (C2'–C1'–C6') with a similar structure and a weight of about 0.25. Because the orientation of the displacement ellipsoids of C1 and C2 contradicts such a case of disorder (the experimentally determined and the calculated directions of the axes of the largest displacement differ by 60 to 90°), our estimation for the 'true' positions of C1, C1', C2 and C2' is uncertain. The orientations of the displacement ellipsoids of the methyl C11 and C21 atoms (not shown in Fig. 11) also contradict the disorder and, for all other C atoms of this cation, the disorder model does not predict very significant displacement parameters because the computed distances between the disordered positions are small (0.28 Å for C71, less than 0.2 Å for all other

C atoms). The shift of C6 by 0.07 Å enlarges the angle C2–C1–C6 by about 2.3°, and if we double this value in order to account for the positional changes of C1 and C2, we get in the *worst case* an angle C2–C1–C6 of  $81.6^\circ + 2 \times 2.3^\circ = 86.2^\circ$ , and this angle is still a sufficient proof for the strong deviation of the structure of our 8,9,10-trinorborn-2-yl cation from the structure of 8,9,10-trinorbornane or a 'classical' ion. It must be emphasized that the thermal parameters of the 8,9,10-trinorborn-2-yl cation are sufficiently well explained by a rigid-body motion (Laube, 1989).

The largest eigenvalues of  $U$  for C2, C3, C21 and C31 in the 8,9,10-trinorborn-2-en-7-yl cation are 0.055, 0.046, 0.079 and 0.069 Å<sup>2</sup>. According to Fig. 3, top row, and Fig. 7, bottom row, and neglecting the direction of the principal axis of the largest elongation of the p.d.f. (because of the nearly isotropic displacements), we must in the *worst case* assume that these atoms are disordered with maximal distances of about 0.3 Å between the disordered positions due to the presence of two Wagner–Meerwein isomers. This is much less than the expected values of 0.57 and 1.93 Å

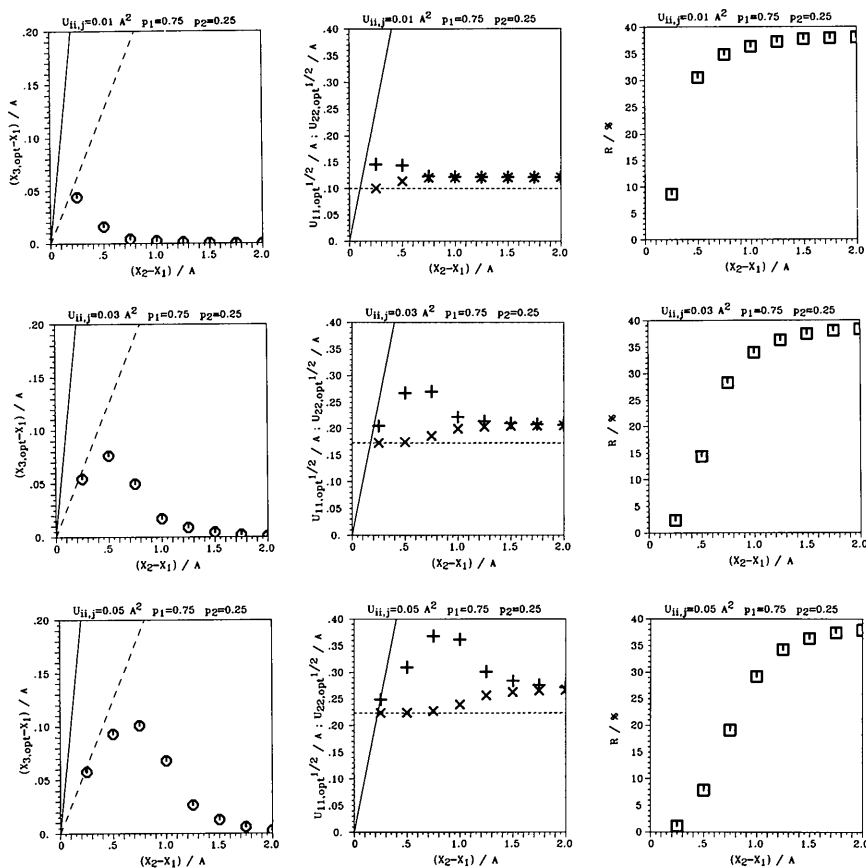


Fig. 8. Dependence of  $X_{3,\text{opt}} - X_1$  (left column),  $U_{11,\text{opt}}^{1/2}$  and  $U_{22,\text{opt}}^{1/2}$  (marked by + and ×; middle column) and  $R$  (right column) on  $X_2 - X_1$  for the adjustment on a disordered C atom with the site occupation factors  $p_1 = 0.75$  and  $p_2 = 0.25$ . In the left column, the solid line indicates the position of  $X_2$  (i.e.  $X_2 - X_1$ ) and the dashed line the weighted average between  $X_1$  and  $X_2$ . In the middle column, the solid line indicates  $X_2 - X_1$  and the dashed horizontal line  $U_{ii,j}^{1/2}$ . The isotropic displacement parameters are: 0.01 Å<sup>2</sup> (top row), 0.03 Å<sup>2</sup> (middle), 0.05 Å<sup>2</sup> (bottom).

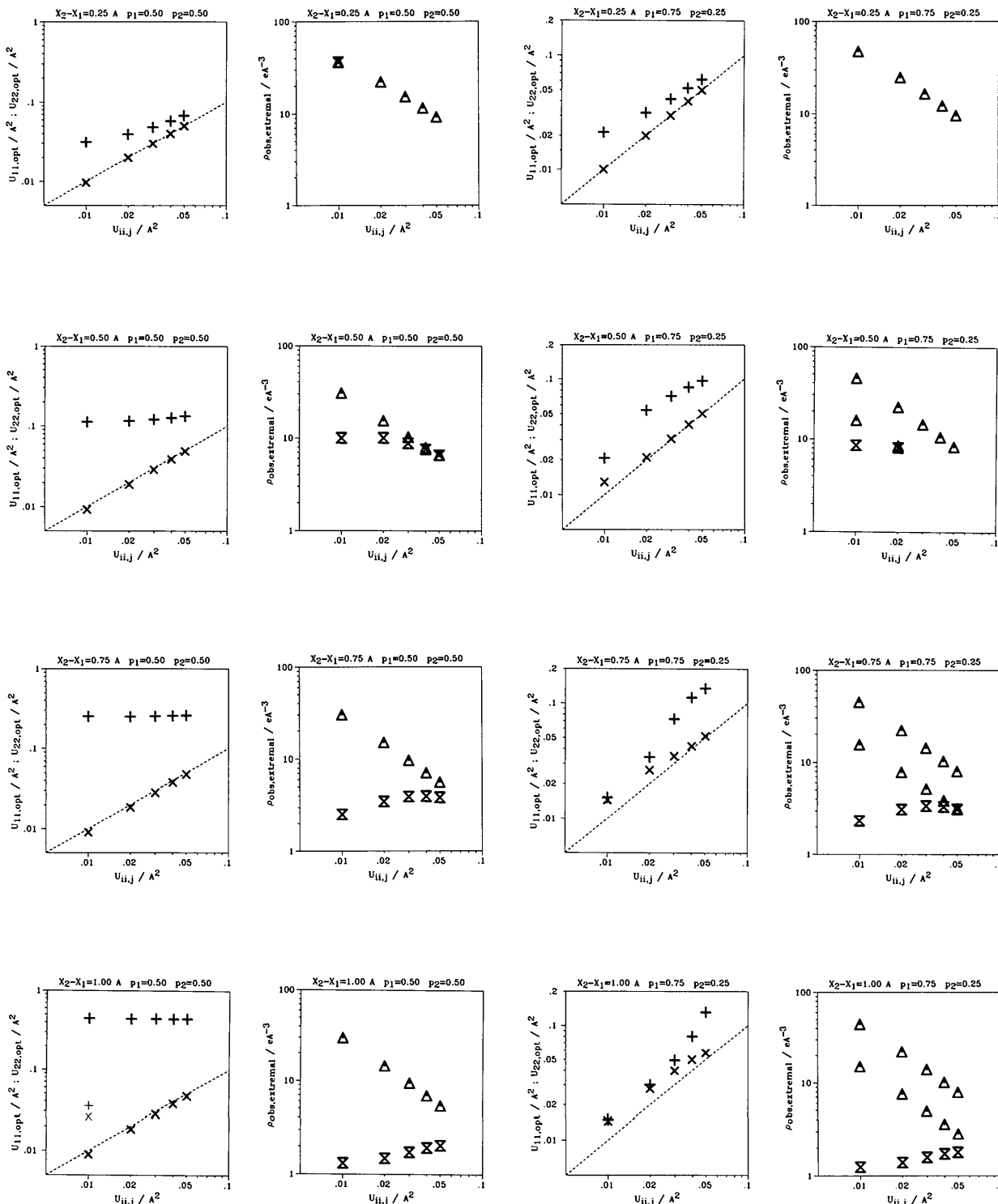


Fig. 9. Dependence of  $U_{11,opt}^{1/2}$  and  $U_{22,opt}^{1/2}$  (marked by + and x; left column) and of the extremal values of  $\rho_{obs}$  (maxima marked by  $\Delta$ , saddle points by  $\bar{X}$ ; right column) on the isotropic displacement parameters  $U_{ii,j}$  of the disordered C atom (site occupation factors:  $p_1=0.5$  and  $p_2=0.5$ ). Thin markers indicate the results of local minima. All axes are logarithmic. The dashed line in the left diagrams indicates  $U_{ii,j}$ . Distance  $X_2 - X_1$  between the disordered C atoms from top to bottom: 0.25, 0.50, 0.75, 1.00 Å.

Fig. 10. Dependence of  $U_{11,opt}^{1/2}$  and  $U_{22,opt}^{1/2}$  (marked by + and x; left column) and of the extremal values of  $\rho_{obs}$  (maxima marked by  $\Delta$ , saddle points by  $\bar{X}$ ; right column) on the isotropic displacement parameters  $U_{ii,j}$  of the disordered C atom (site occupation factors:  $p_1=0.75$  and  $p_2=0.25$ ). All axes are logarithmic. The dashed line in the left diagrams indicates  $U_{ii,j}$ . Distance  $X_2 - X_1$  between the disordered C atoms from top to bottom: 0.25, 0.50, 0.75, 1.00 Å.

for a disorder between 'classical' cations. It shows at the same time that equilibrating ions with distances between corresponding positions of about  $0.3 \text{ \AA}$  could be present in the crystal, but they would still be essentially as 'nonclassical' as the observed structure (Laube, 1989).

The programs *DISORFIT* (1899 lines) and *DISORPLT* (1743 lines) are written in Fortran77 and were compiled with the Microsoft Fortran compiler 5.0 (for an IBM PS/2 70-A21 with 80387) or the NOS/VE Fortran compiler 1.7 (for a CDC Cyber 180-855). Most of the computations are done in double precision (*i.e.* 8 byte for a real variable on the PS/2, 16 byte on the Cyber). Typical run times for one *DISORFIT* job (four optimizations with different constraints) are about 2 h, a few extreme cases need up to 1 d of CPU time on either machine. *DISORPLT* needs about 0.5 h for one contour-line plot. *DISORSTA* (639 lines) is also written in Fortran77, but was used only on a PS/2 (run time about 1 s per diagram). The programs are available from the author upon request.

The original idea to perform these calculations came from Professor Dr Hans Georg von Schnering (Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany). I thank Dr Engelbert Zass for several CAS ONLINE literature searches. The present work would have been impossible without the 386 PC version of *MACSYMA*, which was bought from a Dozentenstipendium from the Fonds der Chemischen Industrie (Germany), for which I am very grateful. A generous gift of CPU time by Mr Markus Elsener on the VAX 8700 'CUMULI' is acknowledged.

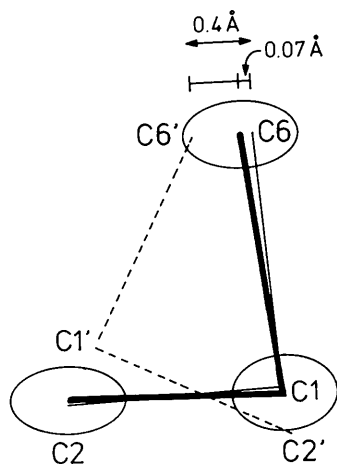


Fig. 11. The atoms C1, C2 and C6 (thick bonds) and approximate projections of their ORTEP ellipsoids of the 2,4-dimethyl-9-norborn-2-yl cation (Laube, 1987, 1989). The worst case of unresolved disorder is indicated by the two thin structures (one with solid, one with dashed lines).

## References

- ALLMANN, A. (1967). *Acta Cryst.* **22**, 434-435.
- ALTONA, C. & SUNDARALINGAM, M. (1972). *Acta Cryst.* **B28**, 1806-1816.
- BACHMANN, R. & SCHULZ, H. (1984). *Acta Cryst.* **A40**, 668-675.
- BACON, G. E., CURRY, N. A. & WILSON, S. A. (1964). *Proc. R. Soc. London Ser. A*, **279**, 98-110.
- BIANCHI, R., PILATI, T. & SIMONETTA, M. (1981). *J. Am. Chem. Soc.* **103**, 6426-6431.
- BROWN, H. C. (1977). *The Nonclassical Ion Problem*, with comments by P. v. R. SCHLEYER. New York, London: Plenum Press.
- CHAMPENEY, D. C. (1989). *A Handbook of Fourier Theorems*, p. 54. Cambridge Univ. Press.
- CHANDRASEKHAR, K. & BÜRGI, H. B. (1984). *Acta Cryst.* **B40**, 387-397.
- COPPENS, P. & HANSEN, N. K. (1977). *Isr. J. Chem.* **16**, 163-167.
- COULSON, C. A. & THOMAS, M. W. (1971). *Acta Cryst.* **B27**, 1354-1359.
- COX, E. G., CRUICKSHANK, D. W. J. & SMITH, J. A. S. (1958). *Proc. R. Soc. London Ser. A*, **247**, 1-21.
- CROMER, D. T. & MANN, J. B. (1967). *X-ray Scattering Factors Computed from Numerical Hartree-Fock Wave Functions*. Report LA-3816. Los Alamos Scientific Laboratory, Univ. of California, Los Alamos, NM, USA.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321-324.
- CROMER, D. T. & WABER, T. J. (1974). In *International Tables for X-ray Crystallography*, Vol. IV, pp. 71-147. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390-397.
- DUNITZ, J. D., KRÜGER, C., IRNGARTINGER, H., MAVERICK, E. F., WANG, Y. & NIXDORF, M. (1988). *Angew. Chem. Int. Ed. Engl.* **27**, 387.
- DUNITZ, J. D., MAVERICK, E. F. & TRUEBLOOD, K. N. (1988). *Angew. Chem. Int. Ed. Engl.* **27**, 880-895.
- DUNITZ, J. D., SCHOMAKER, V. & TRUEBLOOD, K. N. (1988). *J. Phys. Chem.* **92**, 856-867.
- Erlanger Grafik System (1989). Version 2.10M. A Fortran graphics subroutine library. Regionales Rechenzentrum Erlangen, Germany.
- ERMER, O. (1987). *Angew. Chem. Int. Ed. Engl.* **26**, 782.
- GATTI, C., BARZAGHI, M. & SIMONETTA, M. (1985). *J. Am. Chem. Soc.* **107**, 878-887.
- HEHRE, W. J., STEWART, R. F. & POPLE, J. A. (1969). *J. Chem. Phys.* **51**, 2657-2664.
- HIRSHFELD, F. L. (1977). *Isr. J. Chem.* **16**, 168-174.
- IBERS, J. A. (1961). *Acta Cryst.* **14**, 538-539.
- JACKMAN, L. M., BENESI, A., MAYER, A., QUAST, H., PETERS, E.-M., PETERS, K. & VON SCHNERING, H. G. (1989). *J. Am. Chem. Soc.* **111**, 1512-1513.
- JANOSCHEK, R. (1987). *Angew. Chem. Int. Ed. Engl.* **26**, 1298.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- KUHS, W. F. (1983). *Acta Cryst.* **A39**, 148-158.
- KUNZE, K. L. & HALL, M. B. (1987). *J. Am. Chem. Soc.* **109**, 7617-7623.
- LAUBE, T. (1987). *Angew. Chem. Int. Ed. Engl.* **26**, 560-562.
- LAUBE, T. (1989). *J. Am. Chem. Soc.* **111**, 9224-9232.
- MACSYMA* (1988). Version 412.61. Copyright: Symbolics, Inc., Cambridge, Massachusetts, USA; portions copyright: Massachusetts Institute of Technology and Univ. of California, USA.
- MACSYMA* (1989). Version 415.25. Copyright: Symbolics, Inc., Cambridge, Massachusetts, USA; portions copyright: Massachusetts Institute of Technology and Univ. of California, USA.
- MATH/LIBRARY* (1989). Version 1.1. *Fortran Subroutines for Mathematical Applications*. Houston, Texas: IMSL.
- OLAH, G. A., PRAKASH, G. K. S. & SOMMER, J. (1985). *Superacids*, pp. 124-162. New York: Wiley.

- SCHERINGER, C. (1977). *Acta Cryst.* **A44**, 588–592.  
 SCHERINGER, C. & REITZ, H. (1976). *Acta Cryst.* **A32**, 271–273.  
 SFUN/LIBRARY (1989). Version 2.1. *Fortran Subroutines for Evaluating Special Functions*. Houston, Texas: IMSL.  
 SIEGEL, J., GUTIÉRREZ, A., SCHWEIZER, W. B., ERMER, O. & MISLOW, K. (1986). *J. Am. Chem. Soc.* **108**, 1569–1575.  
 STENKAMP, R. E. & JENSEN, L. H. (1984). *Acta Cryst.* **A40**, 251–254.  
 STEVENS, E. D., RYS, J. & COPPENS, P. (1977). *Acta Cryst.* **A33**, 333–338.  
 STEWART, R. F. (1968). *Acta Cryst.* **A24**, 497–505.  
 WILSON, A. J. C. (1976). *Acta Cryst.* **A32**, 781–783.  
 WILSON, A. J. C. (1979). *Acta Cryst.* **A35**, 122–130.  
 ZYGMUND, A. (1988). *Trigonometric Series*, 2nd ed., Vols. I & II Combined, Vol. II, pp. 248–250. Cambridge Univ. Press.

*Acta Cryst.* (1992). **A48**, 172–174

## An Efficient Molecular-Replacement Translation Function Based on the Evaluation of Direct-Methods Phase Invariants

BY DAVID A. LANGS

*Medical Foundation of Buffalo, Inc., Buffalo, New York 14203, USA*

(Received 13 May 1991; accepted 12 August 1991)

### Abstract

Traditional molecular-replacement translation functions are based on direct- or reciprocal-space correlations between the observed diffraction amplitudes and the calculated amplitudes and phases of the symmetry-related molecular transforms of the search fragment as a function of the displacement vector. An alternative method that has been described is based on evaluating a list of phase invariants as a function of the position of the search model in the unit cell and seeking those regions which satisfy the expectation value of these invariants as predicted by probability theory. As originally formulated, this procedure required the iterative computation of the phases and the evaluation of the list of invariants as the search model was stepped over the grid points defining the asymmetric portion of the unit cell. A new computational procedure is described whereby the values of the invariants are expressed solely as a function of the displacement vector  $\mathbf{r}$  as a Fourier series that can be evaluated by a standard fast Fourier transform (FFT) without having to compute and insert the values of the phases based on the search model at each grid point.

### Introduction

Translation functions are computational algorithms by which the true unit-cell location of a correctly oriented molecule or fragment, whose absolute position is unknown, may be determined. Various techniques to determine translation solutions exist and include vector search methods (Nordman & Schilling, 1970), electron-density convolutions (Rossmann & Blow, 1962), Patterson correlation functions (Vand & Pepinsky, 1956) and computing the crystallo-

graphic residual on a grid encompassing the searched space (Booth, 1945; Bhuiya & Stanley, 1964). An up-to-date and thorough review of the literature by Beurskens and co-workers is highly recommended to those who wish to become more familiar with these established methods (Beurskens, Gould, Bruins Slot & Bosman, 1987).

An alternative method that has been proposed and tested involves the evaluation of direct-methods phase invariants as a function of the position of the fragment in the unit cell (Fortier & Langs, 1979). These grid search procedures produced encouraging results for a number of different phase-invariant types, including both negative and positive quartets (Hauptman, 1974) as well as the three-phase seminvariants (Hauptman & Green, 1978). A figure of merit is computed at each grid point, based on an  $E$ -weighted sum of the cosine values of a particular invariant type, and the translation solution is expected to produce either a positive maximum or a negative minimum, depending on whether the group of invariants is expected to be positive or negative. For example, NQUEST (DeTitta, Edmonds, Langs & Hauptman, 1975) is a figure of merit that is based on the expected negative value of quartets,  $E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{m}}$ , for which the magnitudes of the four main terms  $E_{\mathbf{h}}$ ,  $E_{\mathbf{k}}$ ,  $E_{\mathbf{l}}$  and  $E_{\mathbf{m}}$  are large, and the magnitudes of the three cross terms  $E_{\mathbf{h}+\mathbf{k}}$ ,  $E_{\mathbf{h}+\mathbf{l}}$  and  $E_{\mathbf{h}+\mathbf{m}}$  are small, e.g. less than 0.70, where  $\mathbf{h}+\mathbf{k}+\mathbf{l}+\mathbf{m}=\mathbf{0}$ ,  $B=2|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{m}}|/N$  and  $N$  is the number of equivalent atoms in the primitive unit cell.

$$\text{NQUEST} = \sum_{\mathbf{h},\mathbf{k},\mathbf{l}} B \cos(\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} + \varphi_{\mathbf{m}}) / \sum_{\mathbf{h},\mathbf{k},\mathbf{l}} B \quad (1)$$

NQUEST is evaluated from the phases computed from the search model at each point in the grid search and