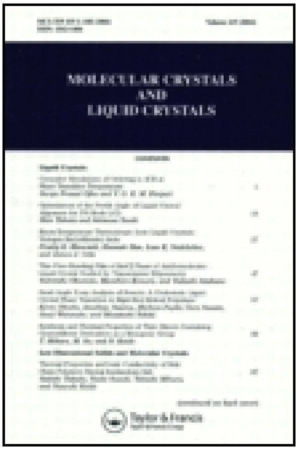

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Anisotropy of Molecular Diffusion in Naphthalene Single Crystals: The Heterodiffusion of β-Naphthol

Louis Bonpunt [a], Alain Dautant [a], Abdellah Loumaid [a] & Yvette Haget [a]

[a] Laboratoire de Cristallographie et de Physique Cristalline - U.A. 144 CNRS - Université de Bordeaux I, 351, Cours de la Libération, 33405, Talence, France

To cite this article: Louis Bonpunt, Alain Dautant, Abdellah Loumaid & Yvette Haget (1986): Anisotropy of Molecular Diffusion in Naphthalene Single Crystals: The Heterodiffusion of β-Naphthol, Molecular Crystals and Liquid Crystals, 137:1, 213-220

To link to this article: http://dx.doi.org/10.1080/00268948608070924

Mol. Cryst. Liq. Cryst., 1986, Vol. 137, pp. 213-220
0026-8941/86/1374-0213$15.00/0

Printed in the United States of America

ANISOTROPY OF MOLECULAR DIFFUSION IN NAPHTHALENE SINGLE CRYSTALS: THE HETERODIFFUSION OF β-NAPHTHOL

LOUIS BONPUNT, ALAIN DAUTANT, ABDELLAH LOUMAID and
YVETTE HAGET
Laboratoire de Cristallographie et de Physique Cristalline - U.A. 144 CNRS - Université de Bordeaux I,
351, Cours de la Libération - 33405 Talence,France.

Abstract Lattice diffusion at 343 K of β-naphthol-8 ^{14}C into naphthalene single crystals has been measured by means of the microtome sectioning technique. Four crystallographic directions of diffusion have been studied, with two to four experiments for each of them to attain exact precision. From these data the diffusion tensor has been determined. It shows a pronounced anisotropy of the mobility of the tracer molecule into the naphthalene lattice.
A geometrical analysis of the different types of jumps into the crystalline structure of naphthalene furnishes first elements for the understanding of this anisotropy.

INTRODUCTION

Most studies of the diffusion process in crystals deal with ionic, metallic and organic crystals of high symmetry (F.C.C., S.C., H.C.P.) whereas rarely are investigations carried out in crystals of lower symmetry. A complete determination of their diffusion tensor would involve passing such obstacles as orientation and cutting of crystals along with measuring the diffusion coefficient along several crystallographic directions.

The organic molecules whose symmetry is not spherical crystallize into low symmetry crystal lattice. It has been recently discovered that some of these organic crystals present such interesting physical properties as high electric conductivity or even superconductivity together with unique spectrographic properties. An acute interpretation of these properties usually requires a perfect knowledge of the structure and properties of all the defects present in each crystal. Therefore studying diffusion would be a good means to solve that type of problem. As a first step, we chose to put under investigation naphthalene which can be considered as a model specimen for molecular physics[1].

The diffusion tensor $\underline{\underline{D}}$ is defined by Fick's first law :

$$\underline{J} = -\underline{\underline{D}}\ \underline{\mathrm{grad}}\ c \qquad (1)$$

Flux and gradient are generally not colinear. $\underline{\underline{D}}$ is a second rank tensor. The equation (1) can be written in tensorial notation[2] :

$$J_i = -D_{ij}\ \mathrm{grad}\ c_j \qquad (2)$$

Matter diffusion is a property described by thermodynamics of irreversible processes. Since Onsager's principle shows that crossed coefficients of linear phenomenological equations equal one another, let us say :

$$D_{ij} = D_{ji} \qquad (3)$$

Therefore the diffusion tensor is symmetrical. Usually to determine a diffusion tensor within a crystal one has to define six parameters, three in order to set the main axes (X_1, X_2, X_3) corresponding to the three axes of the orthonormal system of reference (x_1, x_2, x_3), and three to find its three main coefficients (D_1, D_2 and D_3).

Thanks to symmetry-laws, a lower number of parameters is needed in our case. According to Curie's principle, it is known that the effect's symmetry (a physical property) is either equal or superior to that of the cause (i.e. crystalline structure).For example,in such a monoclinic structure as naphthalene ($P2_1/a$; Z=2, a=8.319, b=5.997, c=8.269 Å, β=116.92° at T=343 K),axis b, a binary axis of symmetry, is necessarily one of the main tensor whereas the two other ones lie in the ac plane of the monoclinic lattice. If one calls X_2 the axis overlaying b, the diagonal coefficients of the tensor for which i=2 or j=2 are of zero value. Therefore the tensor can be read in matrix notation:

$$\begin{pmatrix} D_{11} & 0 & D_{13} \\ 0 & D_{22} & 0 \\ D_{31} & 0 & D_{33} \end{pmatrix}$$

with $D_{13} = D_{31}$ and $D_{22} = D_2$

Since the choice of axes x_1 and x_3 is arbitrary, let us place them respectively end-on to a and c*, two directions which, in the field of the experimental study of diffusion, tend to simplify mathematical treatment of data. c* is the crystallographic direction perpendicular to plane ab. The measurement of diffusion coefficients in directions a, b, and c* will bring us straight to the determination of D_{11}, D_{22} and D_{33}. A 4th series of measurements D_θ , made in direction x_θ within the ac plane, enables us to calculate D_{13} thanks to equations deduced from Mohr's construction[2]. This non-diagonal coefficient allows us to know the relative position of main axes X_1 and X_3 with respect to a and c*.

EXPERIMENTAL

The single crystals of naphthalene was received from Prof. Karl[4] (from the Physics Institute of Stuttgart University). The experimental processes and the method of calculating the vacancy diffusion coefficient have already been described[5]. We now show the precise method adopted for orienting and cutting crystals as well as our choice for the x_Θ direction. The a and b crystallographic axes were found by optical methods of investigation (observation under crossed polarizers, birefrigency). Then the position of c axis was determined by diffraction of a mono- or polychromatic X-ray beam. The x_Θ direction we selected is contained in the $x_1\ x_3$ plane and makes an angle of 52° with x_3.

The crystal was sectioned in order to get samples whose faces were parallel to the four crystallographic planes described above. With the typically classical method we applied, called sectioning-counting, we needed to put a very fine deposit of radioactive naphthol tracer on the face perpendicular to the diffusion direction under consideration. After the diffusion process the crystal is sectioned parallel to the deposit-plane into four µm slices. The activity, A, of each slice is proportional to the concentration, c, of diffusing molecules.

In order to reach a satisfactory degree of precision for the four diffusion coefficients, several experiments (from two to four) had to be carried out with diffusion times from 190 to 473 hours.

RESULTS

When bulk diffusion alone is to be accounted for, a diffusion plot Log c = $f(x^2)$ must be linear since $c = c_o \exp(-\frac{x^2}{4Dt})$ is the solution of Fick's law (Eq.(1)) projected upon any direction. Concretely, we report the Log A = $f(x^2)$ plots which, as we noted previously are equivalent with the exception of one constant.

The tailing instances[5] on linear experimental profiles in x (but not in x^2), due to a faster mobility along dislocation lines, show the necessity of a mathematical correction substracting their contribution. For that purpose we used Le Claire and Rabinovitch's method[6-7-8]. In order to compare the whole series of plots obtained for varying periods of diffusion and previous activities, we resorted to normalisation and eliminated these parameters. Finally from the four average plots corrected once for dislocation influences, and related to the four directions under investigation, we deduced the coefficient values in the four directions

Direction x_1 $Dx_1 = (12.3 \pm 0.4) \, . \, 10^{-17}\ m^2.s^{-1}$
Direction x_2 $Dx_2 = (\ 8.8 \pm 0.3) \, . \, 10^{-17}\ m^2.s^{-1}$
Direction x_3 $Dx_3 = (\ 4.3 \pm 0.3) \, . \, 10^{-17}\ m^2.s^{-1}$
Direction x_θ $Dx_\theta = (\ 7.8 \pm 0.2) \, . \, 10^{-17}\ m^2.s^{-1}$

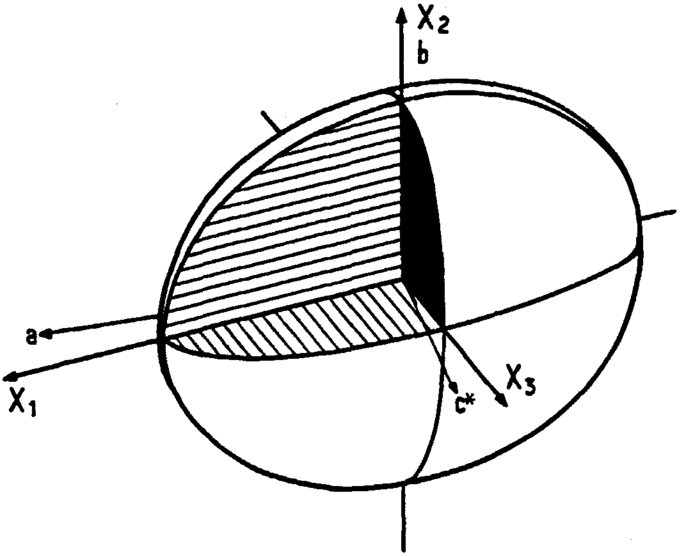

FIGURE 1. Geometrical representation of the diffusion tensor : flux ellipsoid.

$$\begin{pmatrix}12.3 & 0 & 1.5\\ 0 & 8.8 & 0\\ 1.5 & 0 & 4.3\end{pmatrix} \rightarrow \left(\begin{array}{ccc} & & \\ 0 & 8.8 & 0\\ 0 & 0 & 4.0\end{array}\right| \text{in } 10^{-17}\ \text{m}^2.\text{s}^{-1}$$

Diffusion tensor within the (a,b,c*) frame of reference	Tensor brought back to its main axes (X_1, X_2, X_3)

DISCUSSION-CONCLUSION

One of our results in heterodiffusion might be compared to Hampton and Sherwood's study[9] concerning naphthalene self-diffusion in c* direction. The numerical evaluation by these authors of $15.10^{-17}\ m^2 s^{-1}$ calculated at 343 K, has a similiar order of magnitude. Comparison should not be drawn further for two reasons. First they did not apply Le Claire and Rabinovitch's method as we did for correcting dislocation influences; second it would be daring in the present state of knowledge to compare hetero - and self - diffusion data.

However, as a first interpretation we can already try to analyze our results in terms of the structural environment. Naphthalene structure is usually described as a heap of compacted molecular sheets parallel to the (001) plane. The sheet-like aspect may be seen very easily through a projection of the structure upon the (010) plane (Fig.2). When comparing the above projection to the flux ellipsoid section of this plane, it appears also quite clearly that inter-sheet mobility is much lower than mobility within each sheet (about three times lower). As for diffusion within each sheet, it is broadly homogenous ($\frac{D_1}{D_2}$ close to 1.4).

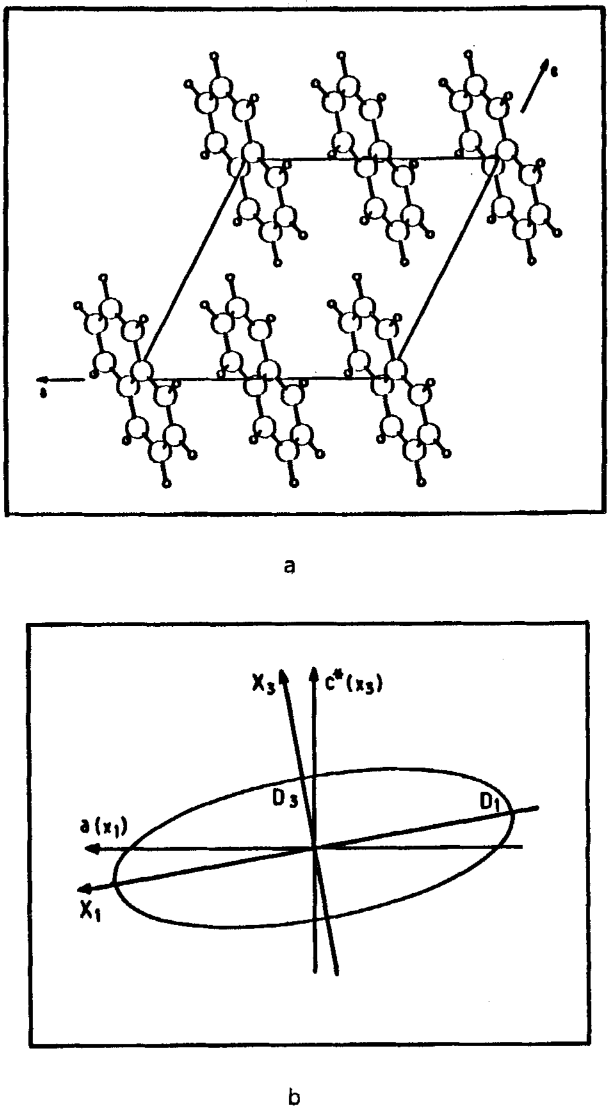

FIGURE 2. a) Naphthalene structure projection along b axis (upon the plane (010)).

b) Section parallel to plane (010) of the flux ellipsoid.

The first complete determination of an heterodiffusion tensor in a low-symmetry structure allows us to confirm the existence of a strong diffusion anisotropy. Now we shall extend our studies to find out whether this anisotropy process exists in the case of naphthalene selfdiffusion. Thus we shall be able to compare the whole of our results with those of Hampton and Sherwood[9] and Sherwood and White[10]. We will also be able to find out the respective roles played by the diffusing molecule (naphthol or naphthalene) and the part played by the host lattice and its own defects.

We wish to express our thanks to Prof. N. Karl for preparing naphthalene crystals for us.

REFERENCES

1. A.I. Kitaigorodskii, Molecular crystals and molecules (Academic Press, New York 1972), p.357
2. J.F.Nye, Propriétés physiques des cristaux (Dunod, Paris 1961).
3. A.Meresse, N.B.Chanh, J.R.Housty and Y.Haget, J.Phys. Chem. Solids, to be published.
4. N.Karl, Crystals : Growth, Properties and Applications (Springer-Verlag,Berlin, Heidelberg, New York, 1980). p. 1-100.
5. A.Dautant, L.Bonpunt, B. Fakhari and Y. Haget, J.Physique Lett. 46, L 117 (1985).
6. A.D.Le Claire, A. Rabinovitch, J.Phys.C 14, 3863 (1981).
7. A.D.Le Claire, A. Rabinovitch, J.Phys.C 15, 3455 (1982).
8. A.D.Le Claire, A. Rabinovitch, J.Phys.C 16, 2087 (1983).
9. E.M. Hampton, J.N. Sherwood, J.Chem.Soc. Faraday Trans. I, 71, 1392 (1975).
10. J.N. Sherwood, D.J. White, Phil.Mag. 15, 745 (1967).