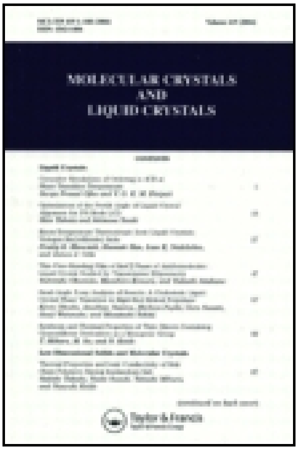

Molecular Crystals and Liquid Crystals

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

Calculation of the Formation and Migration Energies for a Vacancy in the Naphthalene Crystal

Alain Dautant [a] & Louis Bonpunt [a]

[a] Laboratoire de Cristallographie, UA 144 au CNRS, Université de Bordeaux I, 351, Cours de la Libération, 33405, Talence, Cedex, France

Version of record first published: 13 Dec 2006.

To cite this article: Alain Dautant & Louis Bonpunt (1986): Calculation of the Formation and Migration Energies for a Vacancy in the Naphthalene Crystal, Molecular Crystals and Liquid Crystals, 137:1, 221-230

To link to this article: http://dx.doi.org/10.1080/00268948608070925

Mol. Cryst. Liq. Cryst., 1986, Vol. 137, pp. 221-230
0026-8941/86/1374-0221$15.00/0

Printed in the United States of America

CALCULATION OF THE FORMATION AND MIGRATION ENERGIES FOR A VACANCY IN THE NAPHTHALENE CRYSTAL.

ALAIN DAUTANT and LOUIS BONPUNT
Laboratoire de Cristallographie, UA 144 au CNRS,
Université de Bordeaux I, 351, Cours de la Libération
33405 Talence Cedex, France.

Abstract We have determined the formation energy of the molecular vacancy in the crystal of naphthalene using atom-atom potential method. This energy is equal to the difference between the lattice energy, 73.8 kJ.mole^{-1}, and the energy corresponding to the relaxation of the neighbouring molecules. This latter was found to be small (less than 3 kJ.mole^{-1}).
The migration of the naphthalene molecule from one site to another vacant site were also studied for different cases corresponding to different jump directions. For example, the calculated value of the migration energy for the [010] jump is 22 kJ.mole^{-1}, whereas we obtained 30 kJ.mole^{-1} for the [001] jump. These results can be considered as a contribution to the study of the anisotropy of diffusion in low symmetry crystals.

INTRODUCTION

The interpretation of experimental results of diffusion in organic crystals is limited by the deficiency of theoretical data. The development of calculations[1-2-3] of vacancy formation energies and activation energies for molecular migrations would allow us to test the validity of assumptions made to explain diffusion in these crystals. Such a fundamental approach is possible thanks to the work of Kitaïgoroskii[4] and Williams[5] using the atom-atom potentials method. In this paper, we shall present results of calculations related to the molecular mobility at large distances in naphthalene, in order to interpret our diffusion experimental data in this material[6] .

MODEL OF THE POTENTIAL FUNCTION

The functional form chosen for the pairwise-additive atom-atom potentials is the (exp-6) function :

$$V_{ij} = Ar_{ij}^{-6} + B \exp(-Cr_{ij})$$

where V_{ij} is the potential energy between two non-bonded atoms situated at the distance r_{ij}. The A, B and C values are available in the literature. The set of r values results from the X-ray crystal structure of naphthalene. Naphthalene is monoclinic (space group $P2_1/a$, a = 8.235 Å, b = 6.003 Å, c = 8.658 Å and β = 122°55') with two molecules (Z = 2) in the unit cell (A and B) related through the 2_1 axis or through the glide plane. Calculations have been performed on a crystallite consisting of 110 molecules. The Fortran program used is the version number 13[8] or PCK6 that we have adapted to our computer (Mini 6-92 of CII-Honeywell-Bull).

Choice and test of the potential functions

In order to determine the parameters of the potentials, it is necessary to calculate, using different sets of parameters, some physical values measured previously. The potentials (IV) of Williams[9] have been chosen because, as we shall show, they give results in good agreement with the experimental data.

Lattice energy

The experimental values of the sublimation heat available in the literature show a great dispersion (from 66.6 to 81.9 kJ.mole^{-1}). We have measured it ourselves in our laboratory[10] by the Knudsen effusion method. The result, is 72.1 kJ.mole^{-1}, close to the published value in the Handbook of Chemistry and Physics, 61st edition. If we neglect the zero point energy, the lattice energy is equal to the heat of sublimation of the crystal. We have found :

$E_{lat} = 73.8$ kJ.mole^{-1}

Rotational barrier height

N.M.R. experiments, using the variation of T1ρ relaxation time versus temperature, have permitted us to determine the activation enthalpy for the in-plane rotation of the molecule of naphthalene. The values obtained by Schutz[11] and by Mc Guigan[12] are respectively 105±8 kJ.mole^{-1} and 91±7 kJ.mole^{-1} . This reorientational energy has been calculated by the atom-atom potentials method with the Williams IV parameters by Ostertag[13](125 kJ.mole^{-1}) and by Boyd[14](78 kJ.mole^{-1}).

The quantitative agreement between these calculated and observed parameters is clearly poorer than in the case of the lattice energy, although the qualitative trend is well reproduced. We can consider that the parameters of Williams IV permit a satisfactory estimation of such physical values for naphthalene.

VACANCY FORMATION ENERGY

A vacancy is created by removing one molecule from the site (0,0,0), the central position of the crystallite. In order to maintain the symmetry of the vacancy site,the translations of two molecules, occupying symmetrical positions with regard to this site, are equal in amplitude but in opposite directions whereas the rotations are identical. The energy is minimized by displacements of the mass centers or by rotations of the twelve nearest neighbouring molecules. The process starts with the positions of the molecules corresponding to the "energy minimized theoretical" structure. The final coordinates of neighbouring molecules around the vacancy are not very different from their initial ones : any displacement of mass centers is above 0.003 Å and the rotations about the inertial axes are below 3°. The energy variation due to the relaxation of molecules round the defect is $E_{rel} = 3$ kJ.mole^{-1}. The vacancy formation energy is :

$$E_f = E_{lat} - E_{rel} = 71 \text{ kJ.mole}^{-1}$$

ACTIVATION ENERGIES FOR MOLECULAR MIGRATIONS

Due to the anisotropy of the crystalline structure, there are different types of possible jumps. In this work, we shall present the migration energy calculations in two different crystallographic directions: [010] and [001]. The structure is constituted by the packing of (001) molecular sheets. We have chosen to study these two particular jumps because the first, [010], is intrasheet and the second, [001], is intersheet. The study consists in moving the molecule step by step from its initial site to its final one which is the initial position of the vacancy. At each step, the energy minimum of the crystallite is obtained by the relaxation of the environment, i.e., by translation and rotation of the jumping molecule and the four nearest neighbours of the saddle point. The steps are about 0.05 times the jump length. The other molecules of the crystallite are constrained to remain on their site.

Jump [010]

Description (Fig.1) :

The diffusing molecule I, of type A, situated at (0,0,0) should pass between four molecules of type B :

- two situated in the basal plane : II at (-1/2, 1/2, 0) and III at (1/2, 1/2, 0).
- two situated respectively just below and just above the basal plane : IV at (-1/2, 1/2, -1) and V at (-1/2,1/2,1).

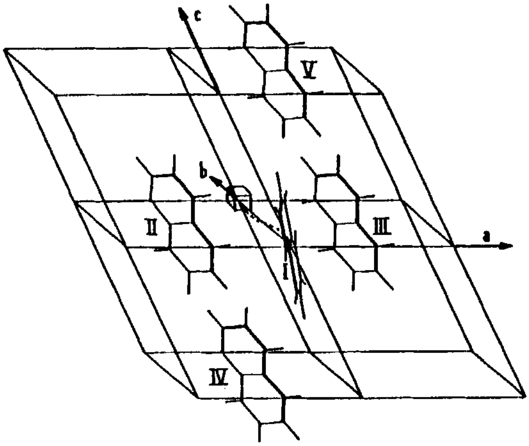

FIGURE 1. The molecule (I) moves towards the vacancy, along the b axis, and passes between its four nearest neigbouring molecules at the saddle point (0,1/2,0).

The vacancy, symbolized by a small parallelepiped, is initially at (0,1,0). The jump length is equal to the b parameter (6.003 Å). When the jump is achieved, the molecule is in the same orientation (A) as in its initial state.

Results:

The path is curved. In a first step, up to about 2 Å, the molecule deviates from the b axis (Δx max = 0.1 Å and Δz max = 0.2Å), towards molecule III to minimize the repulsive interactions with the molecule II. We observe at the same time a large rotation bringing the molecular plane of I almost parallel to the plane of the B molecules. The potential energy (fig.2) reaches a maximum value E_{mig}=22 kJ.mole^{-1}. Beyond 2 Å, the molecule is on the way to the crystallographic inversion center situated at (0, 1/2, 0). For this particular position, this inversion center is regenerated with, as a matter of fact, two "half-vacancies" at (0,0,0) and (0,1,0). The neighboring molecules move in order to restore the inversion center. The energy decreases by about 4 kJ.mole^{-1} with respect to the maximum of 22 kJ.mole^{-1}.Then, the in-plane molecular axes of the diffusing molecule make an angle of 28° with those of the neighboring molecules. Thus the C-C repulsions are minimized. The second half-path is exactly symmetrical to the first half-path.

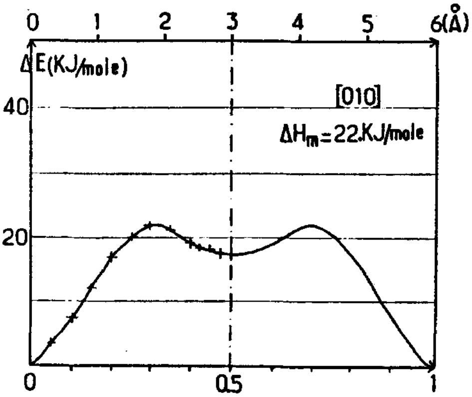

FIGURE 2. Variation of the potential energy versus the displacement of the molecule (I) along the b axis.

If only the jump that we have just studied was efficient, the diffusion observed in this same direction would have for activation energy :

$$E_{dif}^{[\bar{0}10]} = E_{mig}^{[\bar{0}10]} + E_f = 93 \text{ kJ.mole}^{-1}$$

Jump $[\bar{0}01]$:

Description (Fig.3)

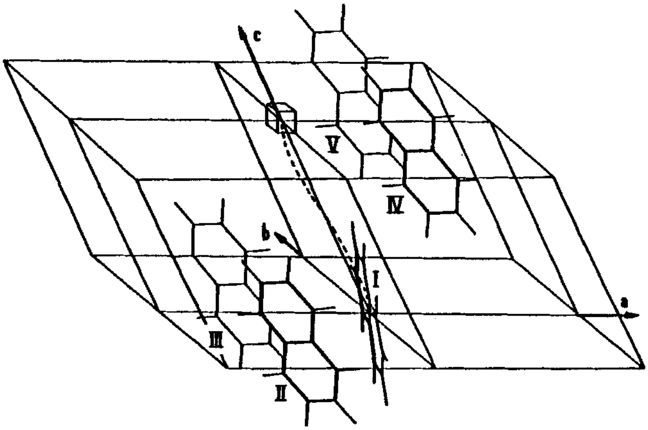

FIGURE 3. The molecule (I) moves towards the vacancy, along the c axis and passes between its four nearest neighbouring molecules at the saddle point (0, 0, 1/2).

It is an intersheet jump. Now, the molecule I of type A situated at (0,0,0) should pass between four molecules of type B :

- two situated in the initial sheet : II at (-1/2, -1/2,0) and III at (-1/2, 1/2, 0).
- two situated in the final sheet : IV at (1/2, -1/2, 1) and V at (1/2, 1/2, 1).

Initially, the vacancy is at (0,0,1), at a distance equal to the c parameter (8.658 Å) of the starting site.

Results :

In this case the path corresponding to the minimum energy deviates from the displacement axis. The potential energy (Fig.4) is also symmetrical with regard to the crystallographic inversion center situated at (0,0,1/2). It passes through a maximum of $E_{mig} = 30$ kJ.mole^{-1} for a value of 3.1 Å for the z coordinate.

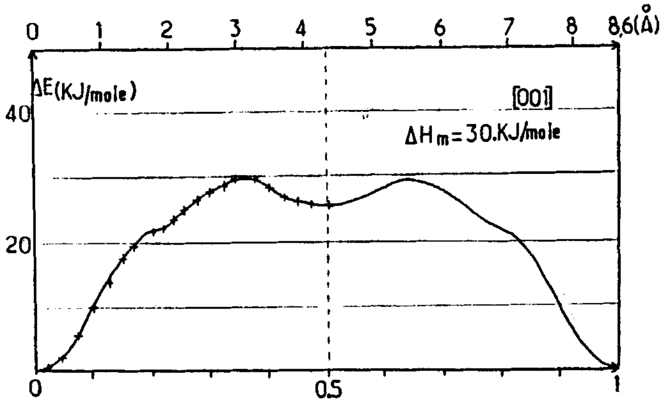

FIGURE 4. Variation of the potential energy versus the displacement of the molecule (I) along the c axis.

If only the [001] jump is taken into account, the observed diffusion in this direction would have an activation energy of :

$$E_{dif}^{[001]} = E_{mig}^{[001]} + E_f = 103 \text{ kJ.mole}^{-1}$$

CONCLUSION :

We have calculated the activation energies corresponding to two different molecular jumps in a low symmetry crystal structure. It appears that these energies are different. These first results confirm that, for naphthalene (as for all crystals of low symmetry), each type of jump should be studied before establishing a theoretical model allowing the interpretation of the experimental results. At this time the only results available in the literature concern the c^* direction (Hampton and Sherwood[15] by tracer diffusion and Corke and Sherwood[16] by creep studies under low stress). Work is in progress in our laboratory to determine completely the self-diffusion tensor. Then we shall be able to compare the theoretical model and experimental data.

ACKNOWLEDGEMENT

We wish to acknowledge Dr Madeleine Meyer, of the Laboratoire de Physique des Matériaux of CNRS-Meudon, for her assistance throughout this study.

REFERENCES

1. C.A.Fyfe and D.Harold-Smith, Chem.J.Elem.,54, 783,(1976).
2. D.P.Craig, B.R.Markey and A.O. Griewank, Chem.Phys. Letters, 62, 223 (1979).
3. M.Meyer, Proceedings of the Daresbury study week-end, DL/SCI/R15, 102 (1981).
4. Kitaïgorodskii, Molecular Crystals and Molecules (Academic Press, New-York, 1973). p.357.
5. D.E. Williams, Acta Cryst. A, 28, 629, (1972).
6. L.Bonpunt, A.Dautant, A.Loumaïd and Y.Haget, this issue.
7. D.W.J. Cruickshank, Acta Cryst., 10, 504 (1957).
8. M. Meyer and S.Ramdas, private communication.
9. D.E. Williams, J.Chem.Phys., 45, 3770 (1966).
10. J.R.Housty and N.B.Chanh, unpublished result.
11. J.U. Von Schütz and H.C.Wolf, Z.Naturforsch, 27a, 42 (1972).
12. S.Mc Guigan, J.H.Strange and J.M.Chezeau, Mol.Phys. 49(2), 275 (1983).

13. R.Ostertag, Ph.D.Thesis, Stuttgart University (1971).

14. R.K.Boyd, C.A. Fyfe and D.A. Wright, J.Phys.Chem.Sol., 35, 1355 (1974).

15. E.M. Hampton and J.N. Sherwood, J.Chem.Soc. Faraday Trans.I, 71, 1392 (1975).

16. N.T.Corke and J.N. Sherwood, J.Mat.Sci., 6, 68 (1971).