increases. The latter category would deserve special attention, but the number of observed cases is still insufficient for a detailed analysis.

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Valence Defects in Ice

RECENTLY, Dunitz[1] proposed a new model for the valence (orientational) defects in ice, the X defect, which he considers to be energetically more favourable than the model we proposed in 1962 (ref. 2), namely, a modified D defect with both molecules rotated. He has also pointed out that the present state of the theory is such that only rough orders of magnitude can be estimated for all the quantities involved. It is in view of this situation that we believe that both models should be considered energetically equivalent, and more elaborate calculations are necessary for a definite answer to the problem. To support this comment we have performed some new calculations, based on our point charge model[2], for both Dunitz's X and our modified D defect. The results are given in Table 1.

Table 1

Rotated D defect		X defect	
r	1·33 Å	r	1·5 Å
E_N	− 7	E_N	− 7
E_L	3	E_L	3
$E_{D_1}-E_N$	5	$E_{X_1}, 2-E_N$	10
E_D	4	E_X	1
E_{DL}	19	E_{XL}	21

r is the distance between the two non-bonded hydrogen atoms. All energies are in kcal mole⁻¹.

It must be noted that the value of E_{DL} for the rotated D defect is lower than that given in ref. 2, the reason being as follows. The previous E_D was obtained starting from Bjerrum's D defect[3] and rotating both molecules involved in the defect independently as rigid bodies in the particular case in which the defect bond, O–H H–O, and two neighbouring hydrogen bonds remain in the same plane through rotation. We have now tried more favourable rotations of both molecules, each one rotating again independently as a rigid body but around its other, normal, hydrogen bond. As in the previous paper[2] we consider only interactions between pairs of nearest neighbour molecules. Apart from the simplifying assumption that all configurations are *trans*, all possible orientations of the molecules are considered and averaged. The calculations were programmed by the Ferranti *Mercury* computer of the University of Buenos Aires.

The difference in energy between the group of molecules involved in the D defect (the two molecules that have the defect bond and its six first neighbours) and the same group in a perfect lattice shows a minimum for 30°. This difference is $E_D - E_N$, as there is only one defect bond, the rest being slightly deformed hydrogen bonds, contributing ΔE_D to the energy. Therefore $E_D - E_N = (E_{D_1} - E_N) + \Delta E_D$. To compute $E_{DL} = (E_D - E_N) + (E_L - E_N)$ we use our previous[2], calculated values of E_N and E_L (Table 1). It should be noted that the value of E_L is not negligible.

The difference in energy between the molecules involved in the X defect (one molecule rotated 60° and its four neighbours) and the same group in a perfect lattice is

$E_X − 2E_N$, as in this case two bonds form the defect, the two others being slightly deformed hydrogen bonds contributing ΔE_X to the energy. Again $E_X − 2 E_N = (E_{X_1} − 2 E_N) + \Delta E_X$. Therefore $E_{XL} = (E_X − 2E_N) + (E_L − E_N)$, where the previous values for E_X and E_N should be used to compare E_{XL} with E_{DL}. Further rotations of the two adequate neighbour molecules for the X defect decrease the difference between E_{XL} and E_{DL} from 2 to ½ kcal mole⁻¹, this being a minimum for angles of 10°. Therefore E_{XL} and E_{DL}, both calculated with the same model, compared reasonably well with the experimental value of 15·7 ± 0·9 kcal mole⁻¹.

It is worth noting that there are important contributions to the energy of the D defect, E_D, apart from the repulsions between the two non-bonded hydrogen atoms. This repulsion, as calculated with the formula for $E(r)$ given in Dunitz's paper, gives for the rotated D defect about 18 kcal mole⁻¹. The interactions between the complete molecules, as calculated with our point charge model, gives 1·7 kcal mole⁻¹. A similar difference is found for the X defect.

With respect to the activation energies for diffusion of the defects, we have calculated that of the L defect, the activated state corresponding to a rotation of one molecule half-way between the initial and final position of the defect. This rotation is around one O–H bond and the activation energy obtained is of 5·3 kcal mole⁻¹. This value compares well with the experimental one[4] and is in agreement with the intuitive idea of one hydrogen bond being broken in the process of the transport of the L defect. The problem of the activation energy of the other defect is more difficult. In fact, there are several models proposed for the defect[5,6], apart from the two mentioned here, all of them energetically similar. There is no simple way of deciding among them and also the experimental results of ice doped with ammonia[7] are scarce and difficult to interpret.

Our main conclusion is that there is no difference from an energetical point of view between X and a rotated D defect and that the results show, once again, what we had already said: "that the general idea of a rotation is adequate", but more elaborate calculations are needed to decide the particular form of the rotation.

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Palladium-catalysed Olefine Isomerization

UNDER the influence of palladium II halides it has been shown[1] that olefines undergo isomerization involving movement of the double bond to successive positions along the carbon chain. Information concerning the mechanism of this reaction has been elucidated on one hand by the use of deuterated acetic acid as solvent and by utilizing deuterated *n*-oct-1-ene on the other. Thus it was shown from the infra-red spectrum that no deuterium entered the hydrocarbon when *n*-oct-1-ene isomerized in the presence of sodium tetrachloro µµ′-dichloro–dipalladate II dissolved in CH_3CO_2D, proving that at no stage in the mechanism is hydrogen lost from the hydrocarbon either as proton or hydride ion.

In view of the ability of palladium to form olefine complexes[2] and, further, the tendency of these to give π-allylic complexes[3] implying the labilization of one of the hydrogens on the olefine: