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Calculation of the Lattice Energies and the Energies of Complexation of Some Paraquinones and Parahydroquinones

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Abstract

The lattice energies and the solid-state energies of complexation of a number of benzo- and naphtho-quinones and -hydroquinones are calculated by methods making use of atom–atom potentials. For the lattice energies, quantitative agreement with experimental data is satisfying. For the much smaller energies of complexation, qualitative agreement, with the right sign and of the right order of magnitude, is obtained.

Introduction

The quinones form molecular complexes with a number of chemical species, *e.g.* hydroquinones. The crystal structures of three of these molecular complexes, 1,4-napthoquinone–1,4-naphthohydroquinone (2/1), 1,4-naphthoquinone–1,4-hydroquinone (1/1) and 1,4-benzoquinone–1,4-hydroquinone (1/1) are known, as well as the crystal structures of the four individual compounds (Table 1). The various enthalpies of com-

Table 1. *Comparison of the observed and calculated lattice energies and energies of complexation.*

Compound or complex	Crystal-structure reference	$\Delta H_{subl}{}^a$ or $\Delta H_{compl}{}^b$ (kJ/mol)[c]	Calculated ΔE, kJ/(mol of monomer)			
			potentials: set III		potentials: Table 2	
			O—H···O linear A	O—H···O non-linear B	O—H···O linear C	O—H···O non-linear D
1,4-hydroquinone (HQ)	(1)	−103·8	−131	−111	−110	−90
1,4-benzoquinone (BQ)	(2)	−62·8	−62	−62	−42	−42
1,4-naphthohydroquinone (NHQ)	(3)	–	−165	−142	−123	−101
1,4-naphthoquinone (NQ)	(4)	−72·4	−107	−107	−77	−77
complex NQ–NHQ (2/1)	(5)	−2·93	−6·9 (−133)^d	−14·3 (−133)^d	−0·3 (−93)^d	−7·3 (−92)^d
complex NQ–HQ (1/1)	(6)	−2·93	+0·0 (−119)	−7·1 (−116)	+6·5 (−87)	−0·1 (−83)
complex BQ–HQ (1/1)	(7)	−10·0	−9·5 (−106)	−19·5 (−106)	−3·9 (−80)	−14·0 (−80)

(a) Observed enthalpy (− sign) (Magnus, 1956). (b) Reported enthalpy per 'molecular entity' (Artiga, Gaultier, Haget & Chanh, 1978) divided by the number of molecules in the complex. (c) 1 kcal/mol = 4·184 kJ/mol. (d) Between parentheses the lattice energy of the complex, per mol of monomer molecules.

References: (1) Maartman-Moe (1966). (2) van Bolhuis & Kiers (1978). (3) Gaultier & Hauw (1967). (4) Gaultier & Hauw (1965). (5) Artiga, Gaultier, Hauw & Chanh (1978). (6) Thozet & Gaultier (1977). (7) Sakurai (1968).

plexation (Artiga, Gaultier, Haget & Chanh, 1978) and three of the heats of sublimation (Magnus, 1956) have also been reported.

In the present investigation it is our aim to calculate the lattice energies of both the four individual compounds and the three complexes in order to compare the calculated values with experimental data. The calculations will serve as a test for the potentials for the calculation of lattice energies for hydrogen-bonded crystals, as recently developed for carboxylic acids (Derissen & Smit, 1978).

Method of calculation and results

Recently, our way of calculating the lattice energy of a hydrogen-bonded molecular crystal, especially for

Table 2. *Set of atom–atom potentials used in the calculations C and D*

Buckingham potentials: $-Ar^{-6} + B\exp(-Cr)$. Hydrogen-bond potential and electrostatic interactions are as in set III.

Interaction	A kJ Å⁶/mol	B kJ/mol	C Å⁻¹	Summation limit^d, Å
C–C^a	2376·5	349907	3·60	6·0
C–H^a	523·0	36677	3·67	5·5
C–O^b	1310·43	238906	3·85	6·0
H–H^a	114·22	11104	3·74	5·0
H–O^c	443·5	205903	4·496	5·5
O–O^b	1085·3	325097	4·18	6·0

(a) Williams (1967).
(b) Kitajgorodsky, Mirskaya & Nauchitel (1970).
(c) Calculated from O–O parameters from Kitajgorodsky *et al.* (1970) and H–H parameters from Kitajgorodsky, Mirskaya & Tobvis (1968) by the procedure of Mirskaya & Nauchitel (1972).
(d) An O–O limit of 6·0 Å is used analogous to the C–C limit. For heteronuclear interactions the average of the homonuclear interaction values were used. Only 80% of the Buckingham-potential contribution is obtained with these limits. The remainder was obtained by application of a scaling factor.

carboxylic acids, was described (Derissen & Smit, 1978). The atom–atom potential method, with Buckingham (exp − 6) potentials, with an atomic point-charge model for the electrostatic energy and a Lippincott–Schroeder potential for the hydrogen bonds, was employed. The point charges were calculated with the CNDO/2 method from Mulliken populations. For the lattice summations the convergence-acceleration method was applied (Williams, 1971).

In the present work we used set III of these potentials, values of 0·7 Å^{-1} and 7 Å for the summation limits and a value of 0·30 for the convergence constant K.

In order to study the influence of the choice of a particular set of atom–atom potentials on the energies to be calculated, we also applied an alternative set of atom–atom potentials, which was derived from data from various authors (Table 2).

The solid-state energy of complexation was defined as the difference between the lattice energy of the complex (per mol of molecular molecules) and the stoichiometric sum of the lattice energies of the individual compounds divided by the number of molecules that form the complex. The energy of complexation is to a good approximation equal to the enthalpy of complexation. We added a contribution of $-2RT$ (~ −5·0 kJ/mol of monomer molecules) (Mirsky, 1976) to the lattice energies calculated *via* set III. In the potentials of Table 2 this correction is already accounted for.

The crystal structures as reported in the literature were used except for the H-atom positions, which were not accurate enough. We placed H atoms as follows. The ring H atoms were placed 1·09 Å from the adjacent C atom, with the C—H bond in the plane of the three nearest C atoms and the C—H bond bisecting the C—C—C bond angle. The hydroxyl H atoms were placed 1·01 Å from the O atoms. There is, however, a large uncertainty with respect to the other parameters

describing the location of the hydroxyl H atoms. We examined two possibilities: in calculations A and C we positioned the H atoms on the lines joining the donor and acceptor hydrogen-bonded O atoms (a linear model), and in calculations B and D we placed the H atoms in the molecular O—C—C plane with H—O—C = 110·5° (a non-linear model).

The results of our calculations are collected in Table 1 which also includes relevant experimental data.

Discussion

The atom—atom potentials that we used were originally derived for carboxylic acids. They yielded lattice energies which agree with experiment within 5–10% (Derissen & Smit, 1978). So we may hope to obtain this degree of agreement also for the quinones and hydroquinones of the present study. We see from Table 1 that for calculation B the lattice energies for HQ and BQ agree well (the experimental uncertainties usually are of the order of four kJ/mol). For NQ our calculated lattice energy is much larger in absolute value than the experimental value. We mistrust the experimental result, as it does not show the expected increase of at least 25–29 kJ/mol when compared with BQ. [Compare the values for naphthalene $\Delta H_{sub}^{298} = 72·8$ and benzene $\Delta H_{sub}^{278·7} = 44·8$ kJ/mol (Miller, 1962, 1963).]

The uncertainties in the H-atom positions introduce additional uncertainty in the calculated lattice energies. This is manifested especially in the hydrogen bonds of HQ and NHQ. For instance, in HQ the H···O distance for calculations A and B is 1·83 and 1·96 Å respectively. This results in a calculated difference of −10·25 kJ/mol for each of the two hydrogen bonds.

The solid-state energies of complexation are calculated as differences between lattice energies. So, the errors in these small differences are expected to be relatively large. (The experimental errors may be up to 1 kJ/mol.) The best we may hope for is to obtain the right sign and the right order of magnitude for the calculated energies of complexation. In Table 1 we see that this is obtained for both calculations A and B.

From calculations C and D we learn that the potentials used here do not reproduce the lattice energy of benzoquinone very well, but that the energies of complexation and the lattice energies of HQ and NQ are equally well calculated as in calculations A and B.

In order to improve our results within the atom—atom potential method, several possibilities arise. Firstly, the potential set III itself could be improved, especially since the point charges which were derived from CNDO/2 wave functions lead to underestimation of the electrostatic interaction energy. The magnitudes of the atom—atom potentials are correlated in a

complicated way with the magnitudes of the point charges. Next, the H atoms have to be located better, and also the differences between the molecular structures in the gas phase and in the crystalline state have to be taken into account when comparisons with the heat of sublimation are made. Finally, additional interactions may arise from the charge transfer from a molecule to its neighbours in a complex or to a different molecule in the asymmetric unit in a pure compound. This leads to a correction of the electrostatic energy. Such a situation is met in the tetrathiafulvalene–tetracyanoquinodimethane complex (Govers, 1978). The charge flow to a neighbouring molecule in a benzoquinone–hydroquinone complex may be of the order of 0·2–0·7 e (Sakurai, 1968). If a point charge of 0·2 e was located at the centres of the molecules, it would lead to an additional lattice-energy contribution of −10·88 kJ/mol for the BQ–HQ complex.

Our final conclusion is that the atom—atom potentials that we have applied yield reasonable values for the lattice energies. The energies of complexation are also reproduced qualitatively correct, but as they are obtained as small differences between the lattice energies, they are not yet very accurate.

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