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Complexes in the Naphthoquinone Series: Crystal Structures, Electronic Structures, Stability

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Complexes in the Naphthoquinone Series: Crystal Structures, Electronic Structures, Stability

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It is shown that the charge transfer is negligible in the ground state for organic charge transfer complexes between phenols and quinones. Our objective is to determine the origin of the stability of the complexes. The geometric, electronic and energetic properties of these complexes were examined by three techniques, crystal structure determination by X-ray diffraction, spectrum and charge transfer calculation by quantum chemical methods, and lattice energy computation.

I CRYSTAL STRUCTURE

The analysis of the crystal structure of three molecular complexes between a phenol and a quinone has allowed us to ascertain a certain amount of information regarding the arrangement of molecules in these crystals.

The equimolecular naphthoquinone-hydroquinone complex crystallises in the orthorhombic system (space group $P2_12_12_1$).[1] Its structure seems to be made of sheets parallel to the planes (010), with internal cohesion ensured by van der Waals forces. In each sheet and in the [001] direction, molecules pile up in an alternating arrangement to build columns in which each donor molecule is superimposed on an acceptor molecule. The ring of each hydroquinone molecule is superimposed on the carbonyl group of the quinone and the quinoid ring of each quinone molecule is superimposed on the phenol hydroxyl group. The columns are bound by hydrogen bonds between phenols and quinones in the [201] direction thereby forming "periodic bond chains".

The 2.3-dichloro-1.4-naphthoquinone-α-naphthol complex[2] crystallises in the monoclinic system (space group $P2_1/c$); it contains two quinone molecules for each α-naphthol molecule. Along the [010] direction we observe stacks having the following sequence: α-naphthol, quinone, quinone, α-naphthol, ... The bonds between α-naphthol and quinone molecules are achieved by superimposition of phenolic and quinoid rings. Both quinone molecules are related by a center of symmetry. Along the **c** direction, the molecules of 2.3-dichloro-1.4-naphthoquinone are bonded by a strong Cl···O bond (2.95 Å) resulting in "periodic bond chains."

The equimolecular complex between 2-methyl-1.4-naphthoquinone and α-naphthol crystallises in the monoclinic system (group $P2_1/c$)(3). An examination of the structure shows a superimposition of both molecules in the **c** direction and in approximately parallel planes. The quinoid ring covers the phenolic ring. The **c** glide plane generates stacking of the molecules. Between two stacks related by a centre of symmetry, there are hydrogen bonds between the quinone molecules and α-naphthol molecules.

The main feature of the crystal structures is the stacking of the molecules brought about by the overlapping bonds. The piles are linked together by hydrogen bonds or oxygen-chlorine bonds ("periodic bond chains") to form sheets. The internal cohesion between sheets is achieved by van der Waals forces.

II ANALYSIS OF CHARGE TRANSFER

The treatment proposed by Mulliken for the so-called "charge transfer complexes" has been questioned for the last few years by a number of authors.[4] The designation of "charge transfer complexes" confuses the part played by the charge transfer in the ground state and the existence of charge transfer in the excited state. We have undertaken the study of charge transfer in the naphthoquinone-hydroquinone complex by the C.N.D.O./S. method.[5]

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Each complex is treated as a "supermolecule," where the donor and acceptor molecules can be found in their relative position just like in the crystal.

The examination of the above-described crystal structure allows us to define four types of hydroquinone molecules surrounding a naphthoquinone molecule and therefore four types of complexes: two complexes of which molecules are bound by hydrogen bond and two complexes which are bound by molecular overlap as shown in Figure 1. The distances between molecules in the complexes 1 and 2 or 3 and 4 are not nearly the same.

The calculated results of the total energies of isolated molecules and complexes, listed in Table I below, show that hydrogen bonded complexes 1 and 2 are stabilized with respect to the isolated molecules, but complexes 3 and 4 bonded by overlap are not.

The calculation of electronic spectra by means of configuration interaction, taking into account the sixty configurations of lowest energy, gives the results shown in Figure 2 for complex 1. This diagram shows the existence

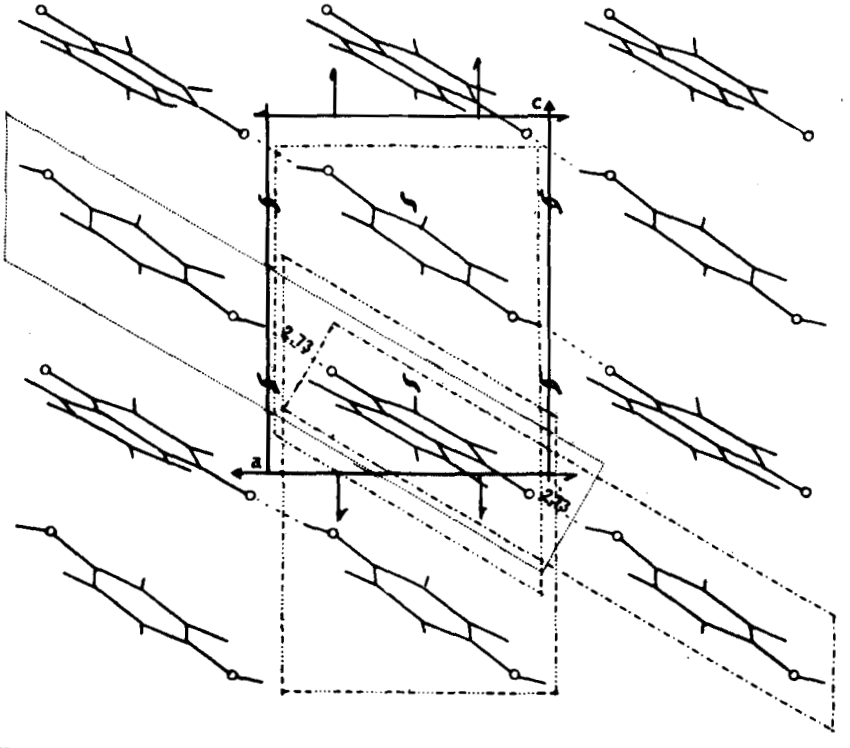

FIGURE 1 Complexes 1, 2, 3, 4 in the naphthoquinone-hydroquinone structure, each complex is separated by various dotted lines.

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TABLE I

Energies of the isolated molecules and the complexes

	Hydro-quinone	Naphtho-quinone	Complex 1	Complex 2	Complex 3	Complex 4
Total energies (eV)	−1881.86	−2488.65	−4371.28	−4370.99	−4369.61	−4369.61
Stabilisation energies (eV)			−0.771	−0.482	+0.91	+0.91
Stabilisation energies (kcal. mole^{-1})			−17.78	−11.49	+20.87	+20.87

of a 304.5 nm band, which is currently designated as a charge transfer band and is not found in the spectra of the isolated molecules. The detailed analysis of the matrix of configuration interactions shows that this band essentially corresponds to an excited state charge transfer between the last highest filled orbital of the hydroquinone donor and the lowest empty orbital of naphthoquinone acceptor. The diagram presented in Figure 3 shows that these conclusions are identical for the four complex types.

Concerning the charge transfer between molecules, it becomes obvious that this transfer is practically non existent in the ground state as shown in the Table II and cannot account for the stability observed in these complexes. However, the excitation results in a transfer of about one electron for all complex types. This excitation transfer corresponds to the band at about 305 nm as we have observed.

This study emphasizes the lack of charge transfer in the ground state. However charge transfer plays an important part in the excited state.

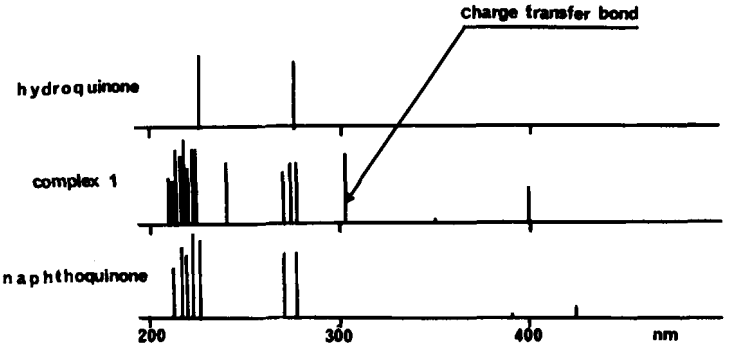

FIGURE 2 Spectra of hydroquinone, naphthoquinone and complex 1.

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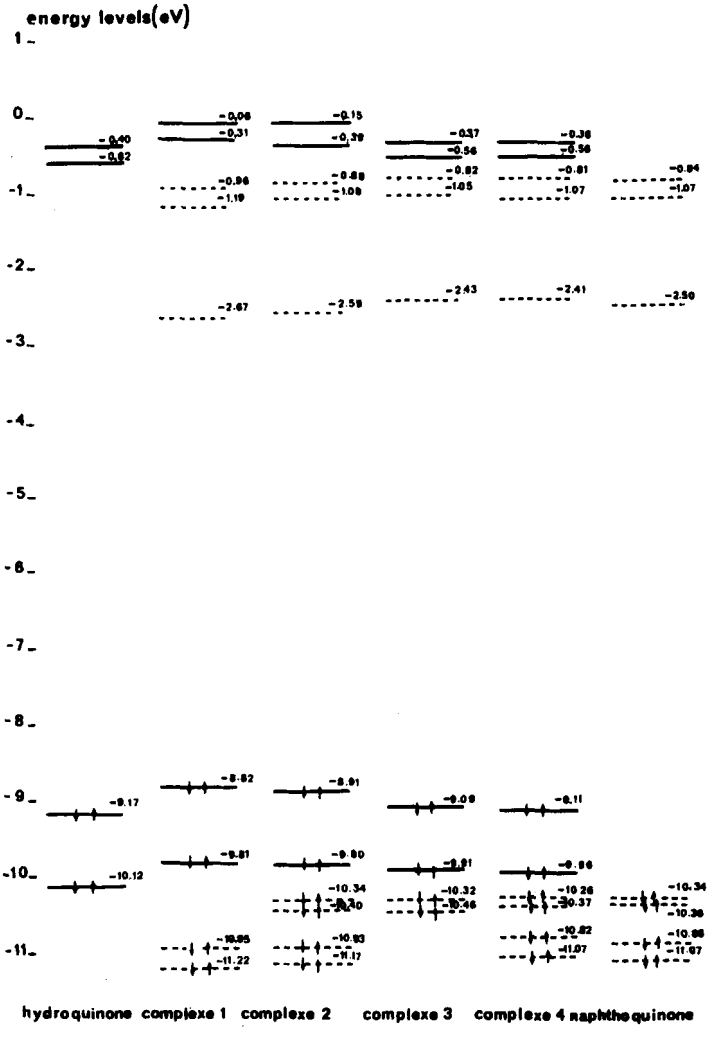

FIGURE 3 Orbital diagram taking into account configuration interaction.

III LATTICE ENERGY COMPUTATION

The energy of intermolecular interaction in crystal has been calculated by means of the method developed by two of us.[6] Starting from experimental crystal structures, we have calculated the various contribution to the energy of interaction in the crystal (electrostatic, polarization, dispersion and repulsive energy). The results are reported in the Table III. It appears from

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TABLE II

Calculated charge-transfer (electrons) in the four complexes between hydroquinone and naphthoquinone

Complexes	1	2	3	4
Ground state	+0.045	+0.029	−0.011	−0.008
Excited state 1	−0.083	−0.032	+0.006	+0.001
2	−0.337	−0.075	+0.008	+0.001
3	−0.999	−0.001	−0.898	−0.949
4	−0.001	−0.991	−0.311	−0.330
5	−0.001	−0.008	−0.117	−0.051
6	−0.001	−0.001	−0.222	−0.284

this table that the dispersion contribution has the greatest stabilizing effect. Considering that the complexes under survey do not all have the same stoichiometry and the same volume, we prefer to compare the results obtained on the basis of experimental values[7] with the calculated one by reducing the value of the energy of interaction in crystal to the unit of volume (1 Å^3). We introduce here an energy density as proposed by Artigua *et al.* in Ref. (7):

$$\varepsilon = \frac{Z\Delta H}{V}$$

Where ε = energy density
Z = number of molecules in the cell
ΔH = enthalpy of crystal cohesion (cal.mole^{-1})
V = volume of the cell (Å^3).

The Table IV lists all the results obtained and shows the satisfactory agreement between the order of magnitude of the experimental values and the calculated values.

CONCLUSIONS

This work shows that the cristalline complexes between phenols and quinones in the napthoquinones series are characterised, from the geometrical point of view, by structures in which hydrogen bonds, molecular overlap, and van der Waals bonds ensure the cohesion in the crystals. In these complexes no charge transfer is observed in the ground state. Calculating the

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TABLE III

Interactions energies in various crystals

	Benzoquinone-hydroquinone		Naphthoquinone-hydroquinone		Naphthoquinone-naphthohydroquinone	
Molecules bonded by hydrogen bonds	E = −1.01		E = 2.06		E = −0.28	
	D = −3.53	−2.84	D = −4.05	4.76	D = −3.49	−2.43
	R = 3.74		R = 6.75		R = 1.34	
	E = −1.01		E = −3.27		E = −0.96	
	D = −3.53	−3.46	D = −4.14	−2.41	D = −2.85	−2.81
	R = 3.72		R = 5.00		R = 1.00	
Molecules bonded by molecular overlap	E = 0.11		E = −0.001		E = 1.88	
	D = −9.77	−0.80	D = −9.57	−4.92	D = −12.56	−5.23
	R = 6.82		R = 4.65		R = 5.45	
	E = −0.25		E = 0.002		E = 0.66	
	D = −9.43	−0.82	D = −9.12	−4.55	D = −13.71	−6.98
	R = 6.22		R = 4.57		R = 6.07	
Total energy of the crystal	E = −5.95		E = −3.89		E = −16.30	
	P = −2.30		P = −2.36		P = −11.20	
	D = −50.72		D = −51.06		D = −93.24	
	R = 29.64		R = 26.28		R = 67.50	
	TE = −29.33		TE = −30.91		TE = −53.25	

E: electrostatic, P: polarisation, D: dispersion, R: repulsion energy, TE:total energy; [ ] total energy without polarisation. All in kcal.mole^{-1}.

TABLE IV

Comparison of calculated and measured density of energy

Complexes	Density of crystal cohesion enthalpy[a] (cal.mole^{-1} Å^{-3})	Density of crystal formation energy (cal.mole^{-1} Å^{-3})
Benzoquinone-hydroquinone	−176	−122.3
1.4-naphthoquinone-hydroquinone	−122	−96.5
1.4-naphthoquinone-naphthohydroquinone	−104	−95.4

[a] Deduced from measurement of complex destruction by dissociation in solution as reported in Ref. (7).

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interaction energy in the crystal we have shown the importance of the dispersion energy in ensuring the stability of the phenol-quinone complexes.

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