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OPEN-SHELL SCF–CI CALCULATIONS FOR RADICAL CATIONS OF DIHYDROXYNAPHTHALENES WITH C_{2v} AND C_{2h} SYMMETRY

Z.H. Khan

Department of Physics, Jamia Millia Islamia, Jamia Nagar, New Delhi-110025, India

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Electronic spectra of radical cations of dihydroxynaphthalenes with C_{2v} and C_{2h} symmetry are calculated using an open-shell SCF method with configuration interaction (CI). The characteristic behaviour of electronic transitions depending on the positions of the hydroxyl substituents is discussed. An interesting aspect of this work is the estimation of the first ionization potentials (IP's) of neutral dihydroxynaphthalenes from the energy of the lowest non-Koopmans state for their radical cations. This method for the prediction of IP's is found to be at least as good as that of the Koopmans' theorem with energy correction due to bond perturbation.

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1. Introduction

Long since the spectroscopy of hydroxy-substituted aromatics has received considerable attention, both theoretically as well as experimentally [1–9]. The reason for the special interest in such systems lies in the fact that they provide good candidates for studying the behaviour of electronic transitions by varying the number and positions of substituent groups, hydrogen bonding within the system and with solvent molecules and, apart from the above, the usefulness of some of these systems in the pharmaceutical industry. Radical cations of such hydrocarbons have, however, received little attention so far. The first comprehensive study on ionic species of 1- and 2-naphthols in boric acid glass was made by Khan et al. [10]. Unfortunately, the technique used in this work for producing radical cations proved to be unsuccessful for dihydroxynaphthalenes (henceforth to be abbreviated as DHN's) due to some complex formation between the hydrocarbons and the boric acid (BA) glass. This is not surprising since Broadbent et al. [11] long back reported the formation of chelated esters of BA and 1.2-DHN. In such circumstances, the recently reported fluorescence spectra of radical cations of some DHN's in BA glass by Baharvand et al. [12] are highly doubtful. This view is further supported from the present results of open-shell SCF–CI calculations on the electronic spectra of DHN cations which do not show any logical correspondence with the author's measurement of optical absorption bands of the species (not given in this paper) that were produced by UV irradiated samples of the neutral hydrocarbons. Another difficulty with such molecular systems is their possible decomposition on heating which is perhaps the reason that UV photoelectron spectra (PES) for such molecular systems are not readily available in the literature.

In view of the above limitations, the main thrust of this paper is the following:
(a) To carry out a detailed theoretical study of the ionic species and thus to provide a reliable source of data on electronic states of radical cations of DHN's.
(b) Study of the characteristic behaviour of electronic transitions depending on the positions of the hydroxyl substituents.
(c) To investigate as to how the electronic states of cations can furnish information about PES data of their neutral precursors.

To achieve the above objectives, open-shell SCF–CI calculations are made on radical cations of DHN's using the procedure initially given by Wasilewski [13] and extended in the present work to substituted systems. Calculations were also made using the Longuet-Higgins and Pople method [14]; but only the former one has been used for the purpose of discussions as the results obtained from the two methods are almost identical.

2. Computational details

The Wasilewski's formalism adopted in this work has its origin in the open-shell SCF method of Roothaan [15]. The beauty of the approach lies in its simplicity where closed-shell SCF orbitals are chosen as the orbital basis and subsequently modified with the help of certain formulas to construct open-shell SCF orbitals.

The ground state configuration of an open-shell system with an odd number of π electrons can be written in the form:

$$^2\Psi_g = \left|\Phi_1\overline{\Phi_1}\ldots\Phi_k\overline{\Phi_k}\ldots\Phi_m\right|, \tag{1}$$

where the subscripts k and m correspond to the doubly-occupied and singly-occupied MO's, respectively. If vacant MO's are represented by the letter x, then the different types of excited state doublet configurations constructed from the π one-electron excitations can be classified as follows:
a) $\mathrm{I} : k \longrightarrow m$,
b) $\mathrm{A} : m \longrightarrow m+1$,
c) $\mathrm{B}_1 : m \longrightarrow x \quad (x > m+1)$,

d) $B_2, B_3 : k \rightarrow x$.
Here, the I-type configurations are characteristic of the ions only, while the remaining configurations are present in neutral systems as well. The A-type configurations arise from HOMO → LUMO excitation and show an interesting property as discussed in Section 3.5. The classifications B_2 and B_3 in the last type of excitation, $\Phi_k \rightarrow \Phi_x$, arise from two different orientations of the spins α and β, i.e. $1/(2)^{1/2} \times (\alpha\beta\alpha - \beta\alpha\alpha)$ and $1/(6)^{1/2} \times (2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)$, respectively.

For CI calculations, the CI matrix formulas given by Wasilewski [13] were used and a scheme was adopted where, apart from the ground state configuration, all the 71 π one-electron excited doublet configurations were considered. For this, a computer software package "IONSP1" was written by the author [16].

The program starts with the construction of the input Hückel matrix for a molecular system from its atomic coordinates initially assuming carbon atoms in place of substituted atoms. For dihydroxynaphthalenes, this matrix was modified using empirical values for Coulomb integrals (α) and resonance integrals (β) for oxygen atoms calculated from the expressions:

$$\alpha_O = \alpha_C + h_O\beta_{CC}, \tag{2}$$

$$\beta_{CO} = k_{CO}\beta_{CC}, \tag{3}$$

where α_C and β_{CC} are the Coulomb and resonance integrals for the unsubstituted system, and the parameters h_O and k_{CO} were chosen as 2.0 and 0.8, respectively. For calculations, β_{CC} was taken as -2.27 eV and β_{CO} as -2.30 eV for neighbouring atoms and was neglected when the atoms were not bonded. Also, the molecules were assumed to have hexagonal structure and planar geometry and their C–C and C–O bondlengths were chosen as 1.40 and 1.37 Å, respectively.

The Hückel eigenvalues and eigenvectors $c_{k\mu}$ were obtained by diagonalizing the input Hückel matrix. This followed the computation of the density matrix $P_{\mu\nu}$ for the closed-shell given by the expression:

$$P_{\mu\nu} = 2\sum_k c_{k\mu}c_{k\nu}, \tag{4}$$

where the summation extends over the doubly-occupied orbitals only. The one-centre Coulomb repulsion integrals $\Gamma_{\mu\mu}$ were taken as the difference of the ionization potential I_μ and electron affinity A_μ for the respective atoms,

$$\Gamma_{\mu\mu} = I_\mu - A_\mu. \tag{5}$$

The following parameters were adopted for ionization potentials and electron affinities: $I_C = 11.16$ eV, $I_O = 32.9$ eV, $A_C = 0.03$ eV, and $A_O = 11.7$ eV. The above parameters are found to give good results for radical ions of 1- and 2-naphthols [10]. The two-centre integrals $\Gamma_{\mu\nu}$ were evaluated using the Mataga–Nishimoto approximation [17]:

$$\Gamma_{\mu\nu} = 14.3986/\{R_{\mu\nu} + 14.3986/[0.5(\Gamma_{\mu\mu} + \Gamma_{\nu\nu})]\}. \tag{6}$$

The next step involves the construction of the F matrix over AO's whose diagonalization leads to a new set of eigenvalues and eigenvectors. From this, the density matrix and the F matrix over AO's are reconstructed and the process is repeated until self-consistency is achieved. This is followed by the computation of F matrix over MO's for closed-shell which is then transformed using certain formulas given by Wasilewski [13] thereby introducing the concept of the open-shell. The CI matrix for ion is then evaluated which on diagonalization yields the state eigenvalues and eigenvectors. Finally, energies of the electronic transitions, their transition moments and oscillator strengths are computed.

The computer program was originally written on a Cyber 170 computer at the National Informatics Centre, New Delhi. It was later adopted for the WIPRO Series 386 computer in the Department of Physics of the University where the present calculations were also made.

3. Results and discussion

The results of open-shell SCF–CI calculations for radical cations of DHN's with C_{2v} and C_{2h} symmetry are given in Tables I–VI.

TABLE I

Results of open-shell SCF–CI calculations for 1.4-Dihydroxynaphthalene cation.

	E(eV)	f[†]	Class	Character[‡]		
a	1.50	0.00;y	I	0.87(6→7)I	−0.32(4→7)I	
b	2.02	0.06;x	I	0.93(5→7)I		
c	2.31	0.00;y	AI	−0.68(7→8)A	0.62(4→7)I	
d	2.46	0.14;y	IA	0.54(7→8)A	0.49(4→7)I	−0.41(6→9)B3
e	3.44	0.01;y	BI	0.56(7→10)B1	−0.50(3→7)I	0.45(5→8)B3
f	3.98	0.01;x	B	0.87(7→9)B1	0.42(6→8)B2	
g	4.42	0.12;y	IB	−0.63(3→7)I	−0.49(7→10)B1	
h	4.56	0.34;x	B	−0.66(6→8)B3	−0.45(6→8)B2	
i	4.83	0.05;x	IB	−0.63(2→7)I	−0.46(7→11)B1	−0.35(4→8)B3
j	5.08	0.20;x	IB	0.61(2→7)I	−0.50(7→11)B1	
k	5.22	0.12;y	IB	−0.55(1→7)I	0.44(6→9)B3	
l	5.65	0.12;x	B	−0.62(5→9)B2	−0.47(6→10)B2	
m	5.65	0.00;y	B	0.89(5→8)B2		
n	5.69	0.02;y	BI	−0.52(6→9)B3	−0.47(1→7)I	0.35(5→8)B2
o	5.92	0.38;x	B	−0.49(6→8)B2	−0.44(6→10)B3	0.40(6→8)B3

[†] f: Oscillator strength. The letters x and y followed by f-values show the polarizations of electronic transitions along the longer and shorter axes of napthalene, respectively.

[‡] The quantities within parentheses represent the major one-electron configurations whose coefficient to the total wave function exceeds 0.3. The one- and two-letter symbols following the configurations indicate the class to which they belong.

TABLE II

Results of open-shell SCF–CI calculations for 2.3-Dihydroxynaphthalene cation.

	E(eV)	$f^{\dagger}$	Class	Character‡		
a	0.57	0.00;y	I	0.95(6→7)I		
b	1.79	0.09;x	I	0.94(5→7)I		
c	2.06	0.03;y	IA	0.85(4→7)I	−0.35(7→8)A	
d	2.64	0.06;y	AI	0.77(7→8)A	−0.38(6→9)B3	
e	3.40	0.00;y	BI	−0.59(7→10)B1	0.56(2→7)I	−0.46(5→8)B3
f	3.89	0.39;x	B	−0.64(6→8)B3	−0.63(6→8)B2	
g	4.38	0.00;x	B	0.66(7→9)B1	−0.44(6→8)B3	0.39(6→8)B2
h	4.68	0.00;y	IB	−0.64(2→7)I	−0.46(7→10)B1	−0.35(6→11)B3
i	4.87	0.19;x	IB	0.62(3→7)I	−0.39(4→8)B3	
j	5.11	0.09;x	IB	−0.51(3→7)I	−0.46(7→11)B1	
k	5.13	0.05;y	BA	0.74(6→9)B3	0.35(7→8)A	0.32(4→7)I
l	5.49	0.06;x	B	0.57(6→10)B2	0.42(5→9)B2	0.41(6→10)B3
m	5.85	0.31;y	B	−0.69(6→9)B2	0.63(5→8)B2	
n	5.88	0.10;y	B	0.64(5→8)B2	0.62(6→9)B2	−0.35(1→7)I
o	5.89	0.80;x	B	−0.54(6→8)B2	0.49(7→9)B1	0.33(6→8)B3

†,‡ See caption to Table I.

TABLE III

Results of open-shell SCF–CI calculations for 1.8-Dihydroxynaphthalene cation.

	E(eV)	$f^{\dagger}$	Class	Character‡		
a	1.38	0.01;x	I	0.92(6→7)I		
b	1.61	0.07;x	I	−0.94(5→7)I		
c	2.39	0.00;y	AI	0.72(7→8)A	−0.61(4→7)I	
d	2.66	0.13;y	IA	0.60(4→7)I	0.50(7→8)A	−0.43(6→9)B3
e	3.24	0.00;x	IB	−0.62(3→7)I	0.57(7→10)B1	0.44(5→8)B3
f	4.04	0.00;x	B	−0.82(7→9)B1	−0.43(6→8)B2	
g	4.59	0.01;x	IB	−0.62(3→7)I	−0.53(7→10)B1	
h	4.75	0.60;x	B	−0.61(6→8)B3	0.40(5→8)B2	−0.39(6→8)B2
i	4.90	0.05;y	IB	−0.62(2→7)I	−0.51(7→11)B1	−0.35(4→8)B3
j	5.09	0.07;y	BI	−0.50(7→11)B1	0.45(2→7)I	0.41(5→9)B3
k	5.46	0.01;x	B	0.80(5→8)B2	0.55(6→8)B2	
l	5.48	0.03;y	B	0.50(5→9)B2	−0.37(5→9)B3	0.34(6→10)B2
m	5.62	0.02;y	B	−0.54(6→9)B3	0.42(5→9)B2	−0.38(2→7)I
n	5.63	0.00;x	I	0.76(1→7)I		

†,‡ See caption to Table I.

TABLE IV

Results of open-shell SCF–CI calculations for 2.7-Dihydroxynaphthalene cation.

	E(eV)	$f^{\dagger}$	Class	Character‡		
a	0.75	0.02;x	I	−0.95(6→7)I		
b	1.90	0.08;x	I	0.93(4→7)I		
c	2.08	0.03;y	IA	0.85(5→7)I	−0.35(7→8)A	
d	2.69	0.06;y	AB	−0.76(7→8)A	0.37(6→9)B3	
e	3.38	0.00;x	IB	0.54(3→7)I	−0.51(7→10)B1	−0.45(4→8)B3
f	3.97	0.45;x	B	0.69(6→8)B2	0.60(6→8)B3	
g	4.48	0.00;x	B	0.63(7→9)B1	−0.52(6→8)B3	0.34(6→8)B2
h	4.52	0.01;x	IB	0.67(3→7)I	0.46(7→10)B1	0.32(6→11)B3
i	4.79	0.02;y	B	−0.44(6→9)B3	−0.43(5→8)B3	0.41(2→7)I
j	5.16	0.02;y	B	−0.55(6→10)B3	0.42(6→9)B3	−0.35(7→11)B1
k	5.40	0.00;y	BI	0.47(6→9)B2	−0.41(2→7)I	0.37(6→10)B2
l	5.52	0.18;x	BI	0.55(4→8)B2	−0.49(1→7)I	0.37(6→8)B2
m	5.58	0.63;x	IB	0.52(1→7)I	−0.39(7→9)B1	0.36(6→11)B3
n	5.63	0.05;y	IB	0.59(2→7)I	0.42(6→9)B3	

†,‡ See caption to Table I.

TABLE V

Results of open-shell SCF–CI calculations for 1.5-Dihydroxynaphthalene cation.

	E(eV)	$f^{\dagger}$	Class	Character‡		
a	1.39	0.00	I	0.93(6→7)I		
b	1.50	0.10	I	0.94(5→7)I		
c	2.34	0.02	AI	−0.85(7→8)A	0.38(4→7)I	
d	2.72	0.10	IB	−0.77(4→7)I	0.46(6→9)B3	
e	3.12	0.00	IB	0.66(3→7)I	−0.53(7→10)B1	−0.45(5→8)B3
f	3.97	0.01	B	−0.86(7→9)B1	−0.43(6→8)B2	
g	4.33	0.00	BI	0.60(7→10)B1	0.59(3→7)I	
h	4.65	0.52	B	−0.61(6→8)B3	−0.54(6→8)B2	−0.33(2→7)I
i	4.90	0.00	B	−0.75(7→11)B1	−0.37(4→8)B3	
j	5.00	0.24	IB	0.71(2→7)I	−0.33(6→9)B3	
k	5.34	0.00	BI	−0.69(5→8)B2	0.47(1→7)I	
l	5.41	0.00	IB	−0.59(1→7)I	−0.51(5→8)B2	
m	5.53	0.00	B	0.65(5→9)B2	−0.45(5→8)B2	0.38(6→10)B2
n	5.56	0.05	BI	−0.65(6→9)B3	−0.37(2→7)I	

†,‡ See caption to Table I.

TABLE VI

Results of open-shell SCF–CI calculations for 2.6-Dihydroxynaphthalene cation.

	E(eV)	$f^{\dagger}$	Class	Character‡		
a	1.01	0.00	I	0.95(6→7)I		
b	1.57	0.14	I	0.89(5→7)I		
c	2.19	0.00	IA	−0.77(4→7)I	−0.44(7→8)A	−0.32(6→8)B3
d	2.70	0.10	AI	0.68(7→8)A	−0.42(4→7)I	0.34(6→9)B3
e	3.21	0.00	IB	−0.61(3→7)I	0.44(4→8)B3	0.43(7→10)B1
f	4.03	0.12	B	0.58(7→9)B1	−0.54(6→8)B2	−0.38(6→8)B3
g	4.30	0.00	BI	0.58(7→10)B1	0.57(3→7)I	0.32(5→8)B3
h	4.60	0.11	B	−0.50(6→8)B3	−0.49(7→9)B1	−0.45(6→9)B3
i	4.96	0.43	IB	−0.63(2→7)I	−0.40(6→9)B3	0.37(6→8)B2
j	5.04	0.00	IB	−0.39(1→7)I	−0.38(7→11)B1	0.32(5→8)B2
k	5.36	0.00	IB	0.59(1→7)I	−0.34(6→11)B3	
l	5.47	0.50	IB	−0.57(2→7)I	−0.47(6→8)B2	−0.38(7→9)B1
m	5.61	0.00	B	−0.73(5→8)B2		
n	5.82	0.00	B	0.58(7→11)B1	0.36(4→8)B2	
o	5.95	0.82	B	0.60(6→9)B2	0.42(6→8)B2	−0.41(6→8)B3

†,‡ See caption to Table I.

In each of these tables, the first column represents the alphabetical enumeration of the electronic transitions followed by their energies and oscillator strengths (f). Wherever applicable, calculated directions of polarizations for electronic transitions are indicated by the letters x and y which correspond to the longer and shorter axes of naphthalene, respectively. This is followed by the classifications of electronic transition for which one- and two-letter symbols are adopted indicating whether a particular transition is "pure" or "mixed". Pure transitions are considered as those for which the contribution from the second major configuration is less than 0.3. Transitions for which the configurations, other than the first one, have an appreciable contribution (≥ 0.3), are defined as mixed. For the sake of brevity, however, only two-letter symbols are adopted for the mixed transitions. The character of each transition is given in the last few columns with the major configurations followed by their classes. The figure preceding a configuration gives its contribution to the total wave function. The first several transitions listed in the tables are illustrated in Figs. 1–6 depicting the SCF MO diagrams for the ions.

In the following discussion, the systems under investigation are divided into two different groups on the basis of their symmetry. The first group with the C_{2v} symmetry is further subdivided into two classes depending upon whether the symmetry axis lies along the longer or shorter axis of naphthalene.

3.1. Cations of 1.4- and 2.3-DHN's

These molecular systems belong to the C_{2v} point group and have, therefore, two sets of transitions having polarizations perpendicular to each other, but none of them is dipole-forbidden. The symmetry axis lies along the longer axis of naphthalene (cf. Figs. 1 and 2). A look at Tables I and II reveals that for both the ions, the first electronic transition a is a pure I-type one-electron excitation $\Phi_6 \rightarrow \Phi_7$. It is y-polarized and its oscillator strength is negligibly small. The second transition b is x-polarized and, like its predecessor, it is a pure I-type excitation arising from $\Phi_5 \rightarrow \Phi_7$ and has got relatively large oscillator strength.

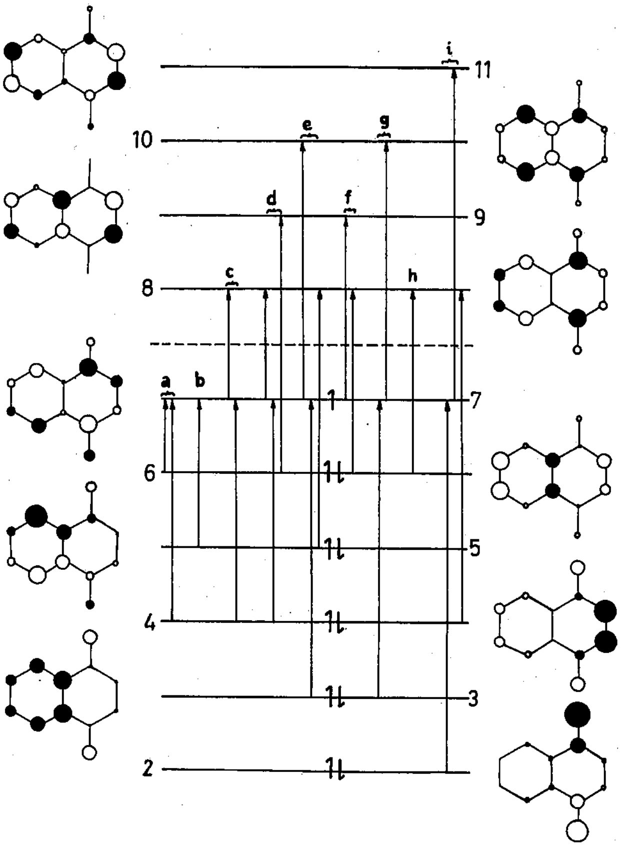

Fig. 1. MO diagram for 1.4-dihydroxynaphthalene cation and different modes of excitation. The horizontal broken line separates the singly-occupied orbital from the lowest vacant orbital. The vertical arrows indicate major configurations whose coefficient in the total wave function exceeds 0.3. The letters (a, b, c, etc.) correspond to the transitions in Table I.

The strong mixing between the configurations $\Phi_7 \rightarrow \Phi_8$ and $\Phi_4 \rightarrow \Phi_7$ gives rise to the c transition. In 1.4-DHN$^+$, the contribution to this transition from the former configuration is the dominant one, whereas for 2.3-DHN$^+$ the latter configuration is the major contributor. In the light of this, the c transition in 1.4- and 2.3-DHN cations is assigned as AI and IA, respectively. The above mixing also results in the **d** transition where the contribution from $\Phi_6 \rightarrow \Phi_9$ also becomes significant. It might however be mentioned that the major contribution to 1.4-DHN$^+$ again comes from the $\Phi_7 \rightarrow \Phi_8$ configuration which amounts to $(0.54)^2$ or 29% of the total wave function. This transition is, therefore, assigned as IA in 1.4-DHN$^+$ and AI in 2.3-DHN$^+$. Both of these transitions are y-polarized.

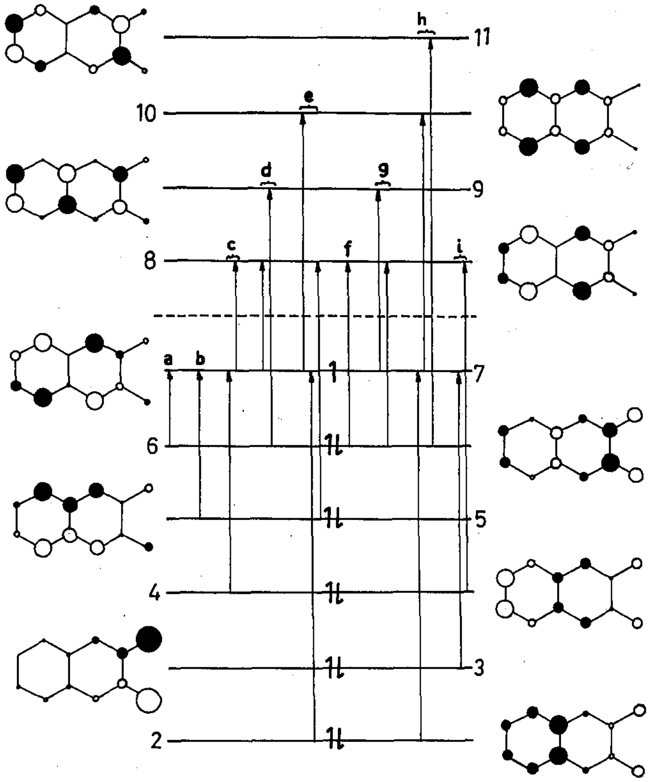

Fig. 2. MO diagram for 2.3-dihydroxynaphthalene cation and different modes of excitation. The letters (a, b, c, etc.) correspond to the transitions in Table II. Also see caption to Fig. 1.

For the remaining transitions, the mixing is of a more complex nature. The transition e, for instance, arises from the interaction between the configurations $\Phi_7 \rightarrow \Phi_{10}$ and $\Phi_5 \rightarrow \Phi_8$ in addition to an appreciable contribution from $\Phi_3 \rightarrow \Phi_7$ in 1.4-DHN$^+$ and $\Phi_2 \rightarrow \Phi_7$ in 2.3-DHN$^+$. This transition is very weak in intensity and is polarized along the y-axis of the molecular ions. The above mixing also gives rise to the g transition (IB-type) in 1.4-DHN$^+$ and the **h** transition in 2.3-DHN$^+$. Similarly, the interaction between the configurations $\Phi_7 \rightarrow \Phi_9$ and $\Phi_6 \rightarrow \Phi_8$ results in the states **f** and **h** in 1.4-DHN$^+$ and **f** and **g** in 2.3-DHN$^+$. Both of these transitions are x-polarized and are classified as B. In 1.4-DHN$^+$, most of the intensity is confined in the second B transition, while the pattern is reversed for 2.3-DHN$^+$. The **i** transition is predominantly of IB type with the major contributions coming from I and B configurations.

3.2. Cations of 1.8- and 2.7-DHN's

From the structure of these molecular systems shown in Figs. 3 and 4, it is clear that they also belong to the C_{2v} point group, but with the symmetry axis lying along the y-direction. As a result of this, polarizations for some of the transitions are reversed as compared to those found for their predecessors. As obvious from Tables III and IV, the first transition **a** for 1.8- and 2.7-DHN cations is x-polarized. The origin of the second I-type transition **b** is however different for the two systems; it arises from the configuration $\Phi_5 \rightarrow \Phi_7$ in 1.8-DHN$^+$, while in 2.7-DHN$^+$ it originates from $\Phi_4 \rightarrow \Phi_7$. The pattern of the remaining transitions is

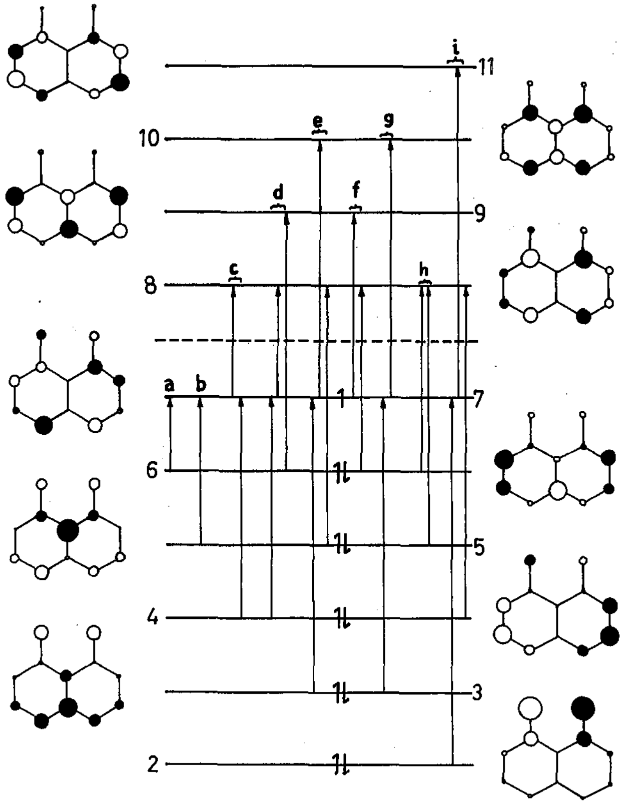

Fig. 3. MO diagram for 1.8-dihydroxynaphthalene cation and different modes of excitation. The letters (a, b, c, etc.) correspond to the transitions in Table III. Also see caption to Fig. 1.

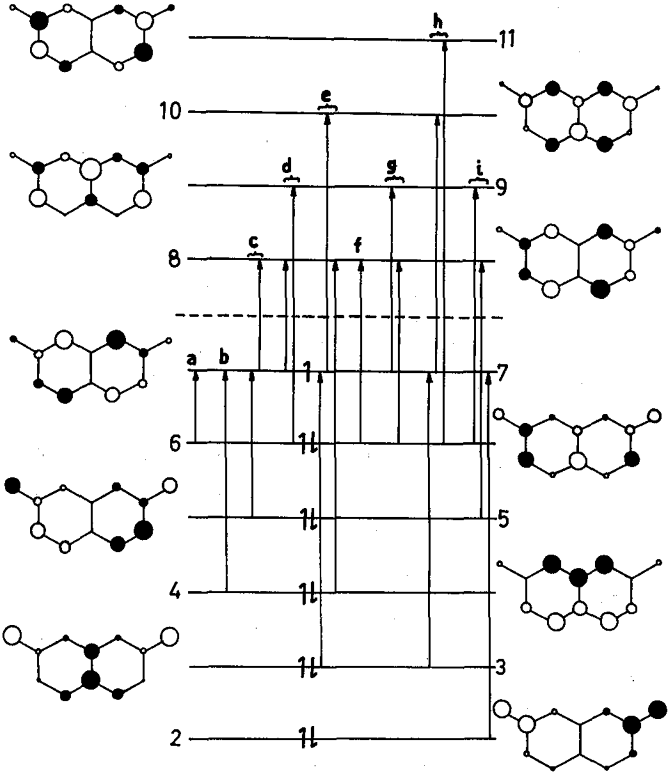

Fig. 4. MO diagram for 2.7-dihydroxynaphthalene cation and different modes of excitation. The letters (a, b, c, etc.) correspond to the transitions in Table IV. Also see caption to Fig. 1.

almost similar to that found for 1.4- and 2.3-DHN cations, with the only difference that the polarizations of the IB transitions get reversed in the present case.

3.3. Cations of 1.5- and 2.6-DHN's

MO diagrams for 1.5-and 2.6-DHN's are sketched in Figs. 5 and 6. They belong to the C_{2h} point-group and have a point of symmetry so that the transitions to the symmetric states are dipole-forbidden. The remaining states are antisymmetric which mutually interact with each other irrespective of their polarization directions. This property of the states is also obvious from Tables V and VI. Once again, the first two transitions in these systems are pure I-type excitations $\Phi_6 \rightarrow \Phi_7$ and $\Phi_5 \rightarrow \Phi_7$, respectively; the former being symmetry-forbidden, while most of the intensity confined in the second one. The pattern of the next three transitions is almost identical to those for the previous cases. The symmetry-allowed B transitions result from interaction among different configurations with the dominant

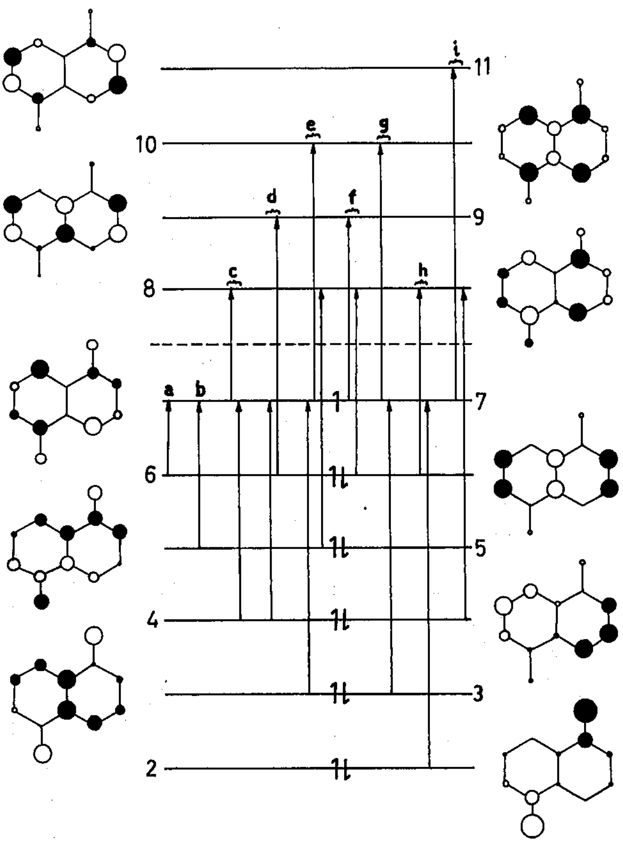

Fig. 5. MO diagram for 1.5-dihydroxynaphthalene cation and different modes of excitation. The letters (a, b, c, etc.) correspond to the transitions in Table V. Also see caption to Fig. 1.

contributions from $\Phi_7 \rightarrow \Phi_9$ and $\Phi_6 \rightarrow \Phi_8$. In the case of 1.5-DHN$^+$, the higher B transition has a large *f*-value, whereas both the allowed B transitions have comparable intensities in 2.6-DHN$^+$.

3.4 Correlation among electronic transitions

To investigate the behaviour of different electronic transitions of radical cations of DHN's in moving from one system to another, we have presented in Fig. 7 a correlation diagram with their calculated energies and intensities. For the sake of comparison, the calculated electronic transitions for 1-naphthol (1N) and 2-naphthol (2N) cations are also plotted in the same diagram. To facilitate discussions, different DHN's are enumerated as given at the bottom of the figure.

From the viewpoint of ionic systems, it is the lower-energy transitions that

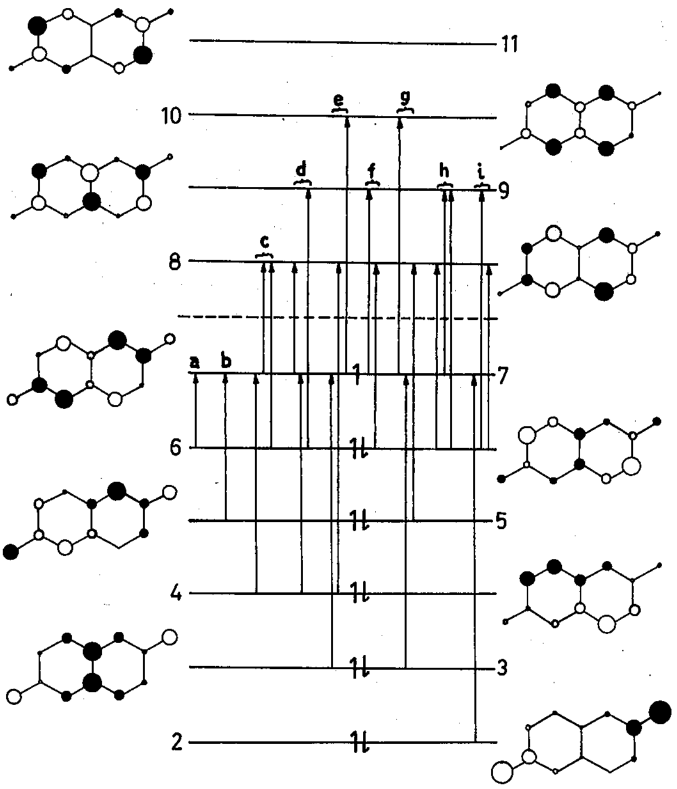

Fig. 6. MO diagram for 2.6-dihydroxynaphthalene cation and different modes of excitation. The letters (a, b, c, etc.) correspond to the transitions in Table VI. Also see caption to Fig. 1.

are particularly important and need special mention. The first I transition is greatly red-shifted in moving from system 1 to 2. This energy-shift consistently decreases for the pairs (3, 4) and (5, 6). This transition is either very poor in intensity or symmetry-forbidden. On the other hand, the behaviour of the second I transition is somewhat erratic. It shows only a marginal shift in energy for a particular pair and has a relatively large oscillator strength. The energy difference $\Delta E(\mathrm{I}_1, \mathrm{I}_2)$, between the two I transitions shows a consistent decrease in moving from (1, 2) to (5, 6).

The AI and IA transitions are very close to each other in 1, but their separation increases in 2 accompanied by the reversal in their ordering. For the AI transition, the intensity increases in moving from 1 to 2, but for the IA transition, the oscillator strength shows an appreciable decrease. A similar trend is noticed for other systems as well. Furthermore, the energy separation $\Delta E(\mathrm{AI}, \mathrm{IA})$ gradually increases for the systems 1,3 and 5, while it remains almost constant for 2,4 and 6.

The next transition is of BI- or IB-type and is either very weak in intensity or

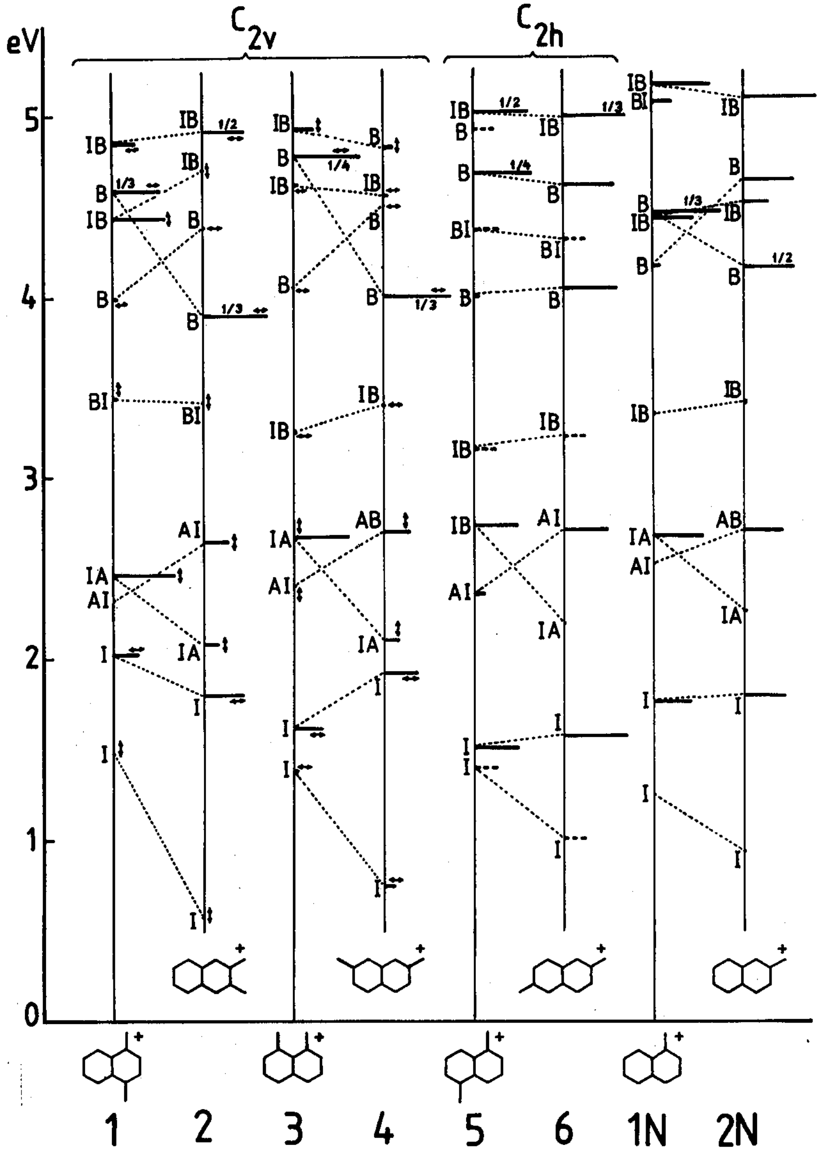

Fig. 7. Correlation diagram for the calculated electronic transitions of radical cations of some dihydroxynaphthalenes, 1-naphthol (1N) and 2-naphthol (2N). The one-letter and two-letter symbols represent their classes. Horizontal solid lines give the measure of the calculated relative oscillator strengths (f) of the transitions and the fractional numbers indicate the amount by which the f-values have been reduced in the figure. The polarizations of electronic transitions are indicated by arrows and the broken horizontal lines correspond to the forbidden transitions. The enumeration of DHN's is given at the bottom together with their structures where the open-ended lines represent OH substitutions.

symmetry-forbidden. Its energy changes only marginally in different ionic systems. A systematic trend is also noticed for the higher-energy transitions above 4 eV.

A comparison of the lower-energy transitions of radical cations of DHN's with those of naphthols reveals that the spectrum of 1.4-DHN$^+$(1) shows a greater resemblance with that of 1-naphthol$^+$(1N) as regards the energy pattern of the transitions, their separation from one another and the oscillator strengths. Similarly, the electronic states of systems 3 and 5 also resemble to some extent with that of 1N. On the other hand, the spectrum of 2N shows some similarity with those of 2, 4 and 6. This means that all those systems which have the hydroxyl substitution at the position 1 of naphthalene, have somewhat similar spectra. In a like manner, the spectra of the systems with hydroxyl group at the position 2 of naphthalene show resemblance with the spectrum of 2N.

3.5 Determination of the first IP's of DHN's

In a recent paper [18] we proposed an entirely new concept for calculating the first IP's of condensed-ring aromatics from the energy of the optical A band for their cations. For such cases where the relevant experimental data are not available, the energy of the electronic transition A, which is of non-Koopmans-type, can be obtained from the theory and a suitable formula based on this can be derived. Fitting the experimental data for the first IP's for some forty polycyclic aromatic hydrocarbons with the energy of the lowest non-Koopmans state A for their radical cations calculated from the open-shell SCF–CI method, yields the following regression:

$$\mathrm{IP}_1^{\mathrm{cal}} = 5.35 + 0.43E_A^{\mathrm{SCF-CI}} + 16.43/N, \tag{7}$$

$$SE(\mathrm{IP}_1) = 0.12 = \ \mathrm{eV},$$

where $E_A^{\mathrm{SCF-CI}}$ is the energy of the electronic state A and N is the number of carbon atoms in the molecule. The last factor in Eq. (7) represents the "size factor" which can be considered as to compensate the deficiency of the model that does not include structural relaxation. In its present form, the above equation can be applied to substituted systems as well if N is taken as the total number of π atomic centres in the molecule (e.g. carbon and oxygen atoms in hydroxy-substituted naphthalenes). The above equation yields the values of 7.75 and 7.88 eV for the first IP's of 1- and 2-naphthols which are very close to the observed IP_1 values of 7.78 and 7.90 eV, respectively [19]. From the calculated energy of the A state for the cations of DHN's with C_{2v} and C_{2h} symmetry, the first IP's of their respective neutral precursors are predicted and the results are collected in Table VII.

TABLE VII

Estimated values of the first IP's of dihydroxynaphthalenes and 1- and 2-naphthols calculated from open-shell SCF–CI energies of the A type transition for their cations and those obtained from Koopmans' theorem with energy correction and their comparison with available experimental data. All energies are in eV.

Substituted hydrocarbon	E_A^{SCF-CI}	IP_1[a]	IP_1[b]	IP_1[c]
1.4-Dihydroxynaphthalene	2.31	7.71	8.89	—
2.3-Dihydroxynaphthalene	2.64	7.85	7.87	—
1.8-Dihydroxynaphthalene	2.39	7.75	7.80	—
2.7-Dihydroxynaphthalene	2.68	7.87	7.89	—
1.5-Dihydroxynaphthalene	2.34	7.73	7.83	—
2.6-Dihydroxynaphthalene	2.70	7.88	7.91	—
1-naphthol	2.39	7.75	7.88	7.78
2-naphthol	2.70	7.88	7.91	7.90

[a] Calculated from Eq. (7): $IP_1^{cal} = 5.35 + 0.43\ E_A^{SCF-CI} + 16.43/N$.
[b] Calculated from Eq. (8): $IP_1^{cal} = 5.52 + 3.46\ \varepsilon^{HMO} + 7.58\ \Delta\varepsilon^{HMO}$.
[c] The experimental values of IP_1 taken from Ref. [19].

To evaluate the usefulness of the above approach, the first IP's of DHN's have also been computed from the following regression [20] which is based on the Koopmans' theorem [21] and incorporates bond perturbation in the Hückel model:

$$IP_1^{cal} = 5.52 + 3.46\ \varepsilon^{HMO} + 7.58\ \Delta\varepsilon^{HMO}, \qquad (8)$$

$$SE(IP_1) = 0.10\,\mathrm{eV}.$$

In this expression, ε^{HMO} is the Hückel eigenvalue of the highest-filled MO and $\Delta\varepsilon^{HMO}$ is the correction in energy due to change in the equilibrium bondlengths of a molecule when it gets ionized. The IP's for DHN's thus computed are also given in Table VII from which it is obvious that the present approach for estimating IP's from the IP_1 vs. E_A relation is at least as good as that estimated by the HMO model with energy correction. In general, the first IP's of different DHN's normally lie in the range 7.7 to 7.9 eV. Moreover, these values are slightly smaller than the vertical first ionization potential (8.15 eV) of naphthalene. This can be qualitatively explained on the basis of the fact that the highest-occupied MO of naphthalene does not have any node at positions 1 and 2 as a result of which the π orbital of naphthalene can interact with the n orbitals of hydroxyl groups (cf. Figs. 1–6), thus lowering the first IP's of dihydroxynaphthalenes.

Conclusions

The open-shell SCF–CI calculations have provided a great insight into the understanding of the nature of electronic transitions of radical cations of dihydroxynaphthalenes. In particular, the correlation diagram is very helpful in studying the behaviour of the transitions in moving from one molecular system to another and reveals the spectral changes due to the substitution of hydroxyl groups at different positions. The IP_1 versus E_A relation offers an interesting approach for estimating the first IP's of substituted systems from the energy of the lowest non-Koopmans state for their cations and its predictions are comparable to that of the Hückel model with energy correction.

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References

[1] Y. Taniazaki, S. Kubodera, *J. Mol. Spectrosc.* **24**, 1 (1967).

[2] H. Baba, S. Suzuki, *Bull. Chem. Soc. Japan* **34**, 1 (1961); *J. Chem. Phys.* **35**, 1118 (1961).

[3] L. Klasinc, U. Sommer, *Chem. Phys. Lett.* **3**, 107 (1969).

[4] S. Suzuki, T. Fujii, H. Baba, *J. Mol. Spectrosc.* **47**, 243 (1973).

[5] T. Fujii, S. Suzuki, *Bull. Chem. Soc. Japan* **49**, 2892 (1976).

[6] J.R. Maple, E.L. Wehry, *Anal. Chem.* **53**, 266 (1981).

[7] J. Bello, R. Hurtubise, *J. Appl. Spectrosc.* **40**, 790 (1986).

[8] G. Schürmann, M. Klessinger, *Chem. Phys.* **113**, 241 (1987).

[9] J.R. Johnson, K.D. Jordon, D.F. Plusquellic, D.W. Pratt, *J. Chem. Phys.* **93**, 2258 (1990).

[10] Z.H. Khan, Z.U. Khan, Z.H. Zaidi, *Can. J. Spectrosc.* **33**, 170 (1988).

[11] A.D. Broadbent, W.D. Hewson, H.A. McDonald, R.J. Melanson, *Can. J. Chem.* **55**, 2946 (1977).

[12] A.R. Baharvand, Z.H. Zaidi, M.K. Machwe, *Curr. Sci.* **60**, 171 (1991).

[13] J. Wasilewski, *Acta Phys. Pol.* **A38**, 349 (1970).

[14] H.C. Longuet-Higgins, J.A. Pople, *Proc Phys. Soc. A* **68**, 591 (1955).

[15] C.C.J. Roothaan, *Rev. Mod. Phys.* **32**, 179 (1960).

[16] Z.H. Khan, *Spectrochim. Acta A* **46**, I (1990).

[17] N. Mataga, K. Nishimoto, *Z. Phys. Chem. Neue Folge* **13**, 140 (1957).

[18] Z.H. Khan, *Spectrochim. Acta A* **44**, 1125 (1988).

[19] C. Utsunomiya, T. Kobayashi, S. Nagakura, *Bull. Chem. Soc. Japan* **48**, 1852 (1975).

[20] A.K. Sharma, Z.H. Khan, Z.H. Zaidi, *Z. Phys. Chem., Leipz.* **271**, 1205 (1990).

[21] T. Koopmans, *Physica* **1**, 104 (1934).