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INDO Calculations on Electronic Spectra of Organic Molecules†

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Using the INDO method of Salahub and Sandorfy and bonding parameters of RINDO method after slightly modifying the weighting factor, the electronic spectra of 9,10-anthraquinone (AQ) and a few diamino anthraquinones (AQ's), were calculated after including lowest thirty singly excited Hartree-Fock states in the configuration interaction process. The results are found to be good in agreement with experiment.

Keywords: INDO, Excited states, Configuration interaction, Electronic transition, Oscillator strength.

INTRODUCTION

9,10-Anthraquinone and its derivatives form a very important group of synthetic and natural colourants [1]. Since the work of Rodionova, Krutovskaya, Rodionov, Tuchin and Karpov [2] on diamino anthraquinones, there has been increased interest in the investigation of spectral characteristics of derivatives of 9,10-anthraquinones [3-17]. Theoretical *ab initio* [7] or density functional theory [15] and the semi-empirical ZINDO [12,18-22] methods have been used to calculate the electronic spectra of 9,10-anthraquinone and its derivatives. The *ab initio* or density functional method is costly and time consuming for relatively large molecules. The ZINDO method yields good transition energies and oscillator strengths for $\pi \rightarrow \pi^*$ transitions, but it poorly represents the $\sigma \rightarrow \sigma^*$ and even $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ transitions which might arise at relatively higher energy.

Salahub and Sandorfy (SS) INDO method promises good results for excited states of relatively large saturated and unsaturated organic molecules involving both σ and π systems [23-26]. Using this INDO method, the present authors calculated the electronic spectra of 9,10-anthraquinone and diamino-substituted 9,10-anthraquinone's, considering the lowest thirty singly excited Hartree-Fock states in the configuration interaction (CI) process and compared the results with experiment carried out by Khan and Khan [12]. But, they were not quite satisfactory. The prominently sharp absorption peak, in particular, observed experimentally at 249.4 nm in 9,10-anthraquinone was not reproduced by this INDO scheme. This led us to consider reparametrization of the bonding parameters used in Salahub and Sandorfy INDO scheme [24].

To calculate the electronic spectra of saturated and unsaturated organic molecules, Salahub and Sandorfy [24] had selected a single value of bonding parameter β°_{AB} for a pair of atoms A and B in the INDO method of Pople and Beveridge [27]. But they had used average of separate values of bonding parameters for the two atoms A and B to obtain the molecular Rydberg transitions apart from valence shell transitions by their RCNDO method [23]. Similar bonding parameters were also used in the RINDO theory with good results [28].

This recipe of bonding parameter was also used in the ZINDO [18-22] and the CNDO-CI [29-32] methods. But the ZINDO or CNDO-CI methods emphasize the π-system of organic molecules and somewhat underplay the σ-system. As a result, some of the higher energy states fail to show character of $\sigma \rightarrow \sigma^*$ transition in this region in the ZINDO or CNDO-CI scheme.

To remove the anomalies, the present authors chose the same methodology for bonding parameters here, except for a slight difference in the weighting factor. This renders the present INDO method consistent with the RINDO method at the valence shell level. Such an INDO method was required to be tested for a number of molecules. In fact, using this method the authors calculated the electronic spectra of molecules like

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water, methane, ethane, ethylene, propene, ammonia, nitroalkanes, nitro alkenes and fullerenes [33].

In the present paper, results of calculations of low-lying transitions are, for brevity, reproduced only on 9,10-anthraquinone and a few diamino substituted 9,10-anthraquinone's, by the new method and compared to those obtained by Salahub and Sandorfy INDO method and Khan and Khan results [12].

METHODOLOGY

The INDO Hartree-Fock equations may be written as suggested by Salahub and Sandorfy [24] except that the resonance integral, $H_{\mu\nu}$ is given by:

$$H_{\mu\nu} = \beta^0_{AB} S_{\mu\nu} \qquad (1)$$

where $S_{\mu\nu}$ is overlap integral for molecular orbitals ψ_μ and ψ_ν belonging to atoms A and B respectively and

$$\beta^\circ_{AB} = \eta\ (I_A + I_B) \qquad (2)$$

with I_A and I_B as the average of σ and π ionization potentials for atoms A and B respectively. Value of η was taken to be 0.362.

Geometries of the molecules were taken from the work of Khan and Khan [12]. The energy of the ground state was first minimized in the usual way. The method of configuration interaction (CI) which included the lowest thirty singly excited configurations was then applied for singlets.

The algorithm of INDO method used by Salahub and Sandorfy has been slightly modified by us to obtain the present result as given below.

To solve the INDO Hartree-Fock equations, Jacobi diagonalization process was continued until all the off-diagonal terms of the secular Hamiltonian were smaller than 10^{-4} a.u. and the SCF procedure was discontinued after the difference between successive eigen values became less than 10^{-3} a.u.

RESULTS AND DISCUSSION

The results of new INDO calculations on electronic spectra of 9,10-anthraquinone and diamino anthraquinones like 1,2-diamino-9,10-anthraquinone (1,2-DAAQ), 1,4-diamino-9,10-anthraquinone (1,4-DAAQ), 1,5-diamino-9,10-anthraquinone (1,5-DAAQ) and 2,6-diamino-9,10-anthraquinone (2,6-DAAQ) are given in Tables 1-5. The theoretical values of oscillator strengths obtained for different transitions plotted against their wavelengths are shown in Figs. 1-5 and compared with plots of values of absorbance against wavelength [12].

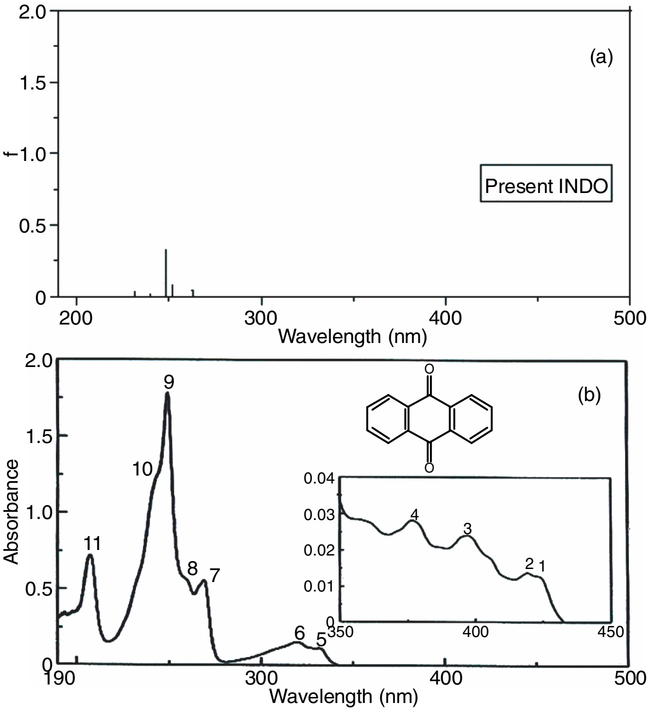

Fig. 1. (a) Plot of present INDO f (oscillator strength) against λ (wavelength) in units of nm for 9,10-anthraquinone, (b) Experimental absorbance against wavelength [Ref. 12]

Electronic transitions in 9,10-anthraquinone: The lowest energy bands are found at 498.6 nm (f = 0.00) and 394.8 nm (f = 0.00) in the parent molecule *i.e.*, 9,10-anthraquinone. Both are weak (f = 0.00) bands and can be assigned to an n→π* transition (Table-1). Such a band is also found in diamino substituted 9,10-anthraquinones except that they are somewhat blue shifted. Experimentally, they are observed at 424.0 nm and 397.6 nm, respectively. In INDO scheme of Salahub and Sandorfy they appear at 451.1 and 361.9 nm, respectively.

TABLE-1
INDO ELECTRONIC SPECTRA OF 9,10-ANTHRAQUINONE

S. No.	Observed [Ref. 12]		Calculated					
			INDO (Salahub & Sandorfy)			Present INDO		
	λ_{max} (nm)	Relative intensity	λ (nm)	f	Symmetry of transition	λ (nm)	f	Symmetry of transition
1	331.8	Moderate	451.1	0.00	(n→π*)	498.6	0.00	(n→π*)
2	319.4	Moderate	361.9	0.00	(n→π*)	394.8	0.00	(n→π*)
3	269.0	Strong	238.1	0.00	(n→π*)	288.7	0.00	(σ→π*)
4	249.4	Very strong	224.6	0.00	(n→π*)	262.7	0.04	(π→π*) + (σ→σ*)
5	207.8	Strong	223.5	0.07	(π→π*)	251.8	0.08	(π→π*)
6			212.7	0.01	(π→π*)	249.2	0.00	(n→σ*)
7			209.1	0.27	(π→π*)	248.6	0.34	(π→π*)
8						240.1	0.01	(π→π*)
9						231.6	0.03	(π→π*)
10						226.7	0.00	(σ→π*)
11						215.9	0.093	(π→π*) + (σ→σ*)
12						198.7	0.02	(π→π*) + (σ→σ*)

The strongest transition calculated at 248.6 nm (f = 0.338), corresponds well to the experimentally observed band at 249.4 nm, whereas the INDO method of Salahub and Sandorfy [24] does not reproduce this band. The ZINDO method of Zerner reproduces it at 244.2 nm (f = 1.29) [12]. This has π→π* symmetry character. Another band observed at 207.8 nm is found at 215.9 nm (f = 0.09). This has a mixed (σ→σ* + π→π*) character for transition. The INDO method of Salahub and Sandorfy gives it as π→π* transition at 209.1 nm (f = 0.27). The other prominent band observed at 269 nm can be seen to agree with a calculated band at 262.7 nm (f = 0.04). This is not found by the INDO calculation of Salahub and Sandorfy.

Electronic transitions in 1,2-DAAQ: The lowest energy transition found at 448.54 nm (f = 0.00) has a n→π* transition symmetry. Experimentally a band of moderate intensity is found at 461 nm (Table-2).

The strongest band observed at 247.6 nm is obtained at 247.57 nm (f = 0.43) by the present INDO calculation. This is of the π→π* type. While this is not obtained by the INDO method of Salahub and Sandorfy, but was reported at 258.9 nm (f = 0.87) by the ZINDO method [12].

Another strong band is found at 205.08 nm (f = 0.41) has π→π* transition. This corresponds well to a strong band observed at 208 nm (Fig. 2).

The corresponding three transitions calculated by Salahub and Sandorfy method are shown respectively at 392.6, 326.4 and 195.8 nm (Table-2). It may be seen that the results of calculation by the new method appear to be better than that by Salahub and Sandorfy method.

Electronic transitions in 1,4-DAAQ: The three observed bands with increasing energy occur at 578.4 (m), 247.2 (vs) and 204.8 (s) nm.

They appear to have been calculated at 494.56 (f = 0.00), 276.33 (f = 0.35) and 206.33 (f= 0.08) nm respectively (Table-3). Their symmetry are respectively n→π*, (π→π* + σ→σ*) and (π→π* + σ→σ*). The mixing of excited states is due to the configuration interaction (CI) process and the way the bonding parameter is being used. The corresponding transitions by Salahub and Sandorfy method are found at 408.4 (f = 0.00), 212.4 (f = 0.65) and 203.3 (f = 0.09) nm, respectively. The results by the new method are in good agreement with experiment. All the three transitions correspond fairly to observed bands at 578.4, 247.2 and 204.8 nm respectively (Fig. 3).

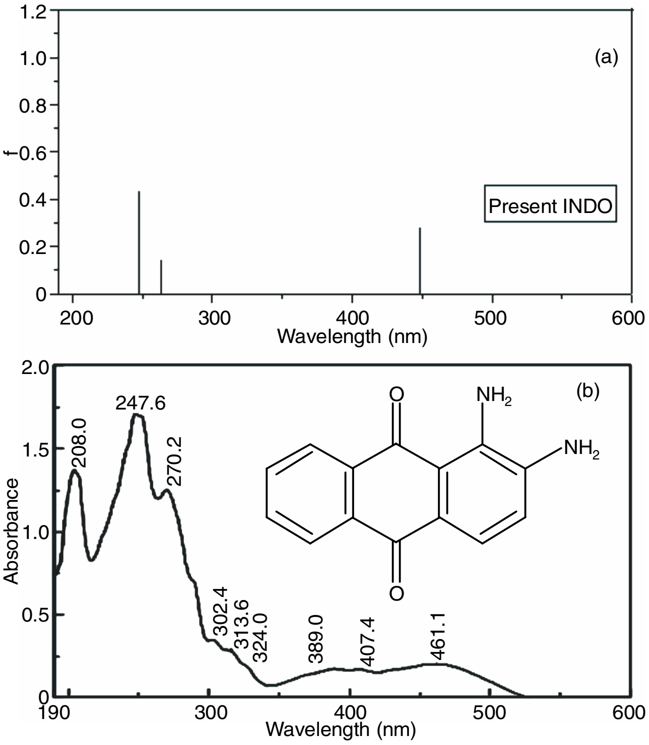

Fig. 2. (a) Plot of present INDO f (oscillator strength) against λ (wavelength) in units of nm for 1,2-DAAQ, (b) Experimental absorbance against wavelength [Ref. 12]

Electronic transitions in 1,5-DAAQ: The three bands of increasing energy were observed respectively at 469.6, 273.6 and 231.8 nm. The lowest wavelength band appears to be very strong. Our calculations show three bands respectively at 485.16 (f = 0.00), 346.62 (f = 0.44) and 246.28 (f = 0.46) nm (Fig. 4). They correspond well to the observed bands. These may be assigned symmetry character of n→π*, π→π* and again π→π* respectively. It can be seen from Table-4 that Salahub and Sandorfy INDO results do not appear to fair as well.

TABLE-2
INDO ELECTRONIC SPECTRA OF 1,2-DAAQ

S. No.	Observed [Ref. 12]		Calculated					
			INDO (Salahub & Sandorfy)			Present INDO		
	λ_{max} (nm)	Relative intensity	λ (nm)	f	Symmetry of transition	λ (nm)	f	Symmetry of transition
1	461.0	Moderate	392.6	0.00	(n→π*)	448.5	0.00	(n→π*)
2	270.0	Strong	326.4	0.58	(π→π*)	373.8	0.00	(n→σ*)
3	247.6	Very strong	320.1	0.00	(π→π*)	364.8	0.00	(n→π*)
4	208.0	Strong	314.0	0.00	(n→σ*)	352.8	0.48	(π→π*)
5			286.8	0.00	(n→σ*)	263.4	0.13	(π→σ*)
6			243.1	0.00	(n→σ*)	247.6	0.43	(π→π*)
7			239.9	0.00	(π→π*)	240.5	0.00	(π→π*)
8			216.0	0.01	(π→π*)	227.9	0.02	(π→π*)
9			208.5	0.01	(π→π*)	216.4	0.02	(σ→σ*)
10			195.8	0.14	(π→π*)	205.1	0.41	(π→π*)
11			188.3	0.03	(π→π*) + (σ→σ*)	200.5	0.05	(π→π*)

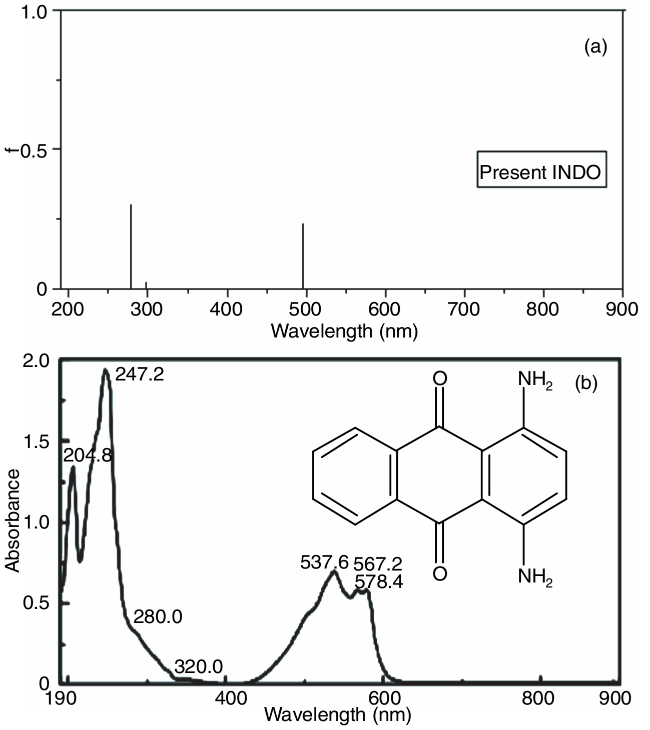

Fig. 3. (a) Plot of present INDO f (oscillator strength) against λ (wavelength) in units of nm for 1,4-DAAQ, (b) Experimental absorbance against wavelength [Ref. 12]

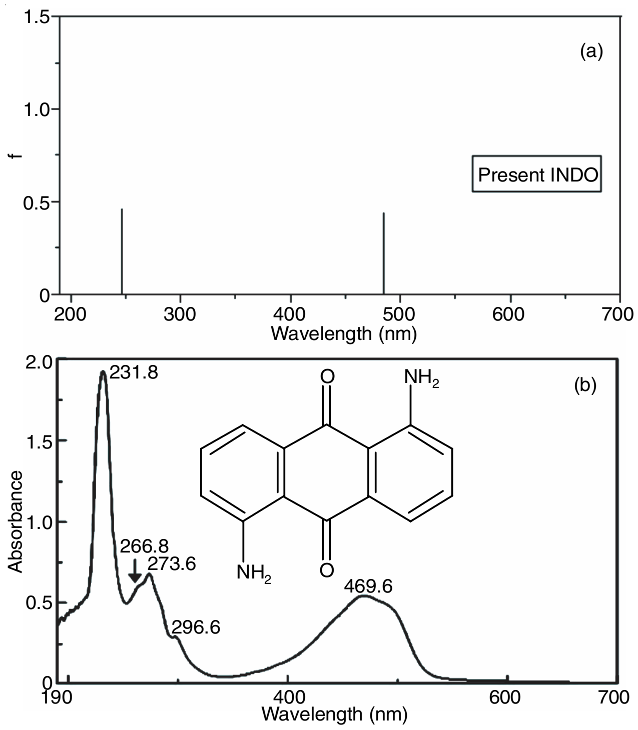

Fig. 4. (a) Plot of present INDO f (oscillator strength) against λ (wavelength) in units of nm for 1,5-DAAQ, (b) Experimental absorbance against wavelength [Ref. 12]

TABLE-3
INDO ELECTRONIC SPECTRA OF 1,4-DAAQ

S. No.	Observed [Ref. 12]		Calculated					
			INDO (Salahub & Sandorfy)			Present INDO		
	λ_{max} (nm)	Relative intensity	λ (nm)	f	Symmetry of transition	λ (nm)	f	Symmetry of transition
1	578.4	Moderate	408.4	0.00	(n→π*)	494.60	0.00	(n→σ*)
2	247.2	Very strong	392.1	0.66	(π→π*)	473.10	0.00	(n→π*)
3	204.8	Strong	248.7	0.00	(π→π*)	438.90	0.25	(π→π*)
4			222.3	0.04	(π→π*)	386.00	0.00	(σ→π*)
5			212.4	0.65	(π→π*)	298.30	0.02	(n→σ*)
6			206.4	0.01	(σ→σ*)	278.00	0.11	(π→π*) + (σ→σ*)
7			202.5	0.00	(n→σ*) + (π→π*)	276.30	0.35	(π→π*) + (σ→σ*)
8			203.3	0.09	(π→π*)	241.20	0.06	(π→σ*)
9						238.90	0.02	(π→σ*)
10						229.10	0.09	(π→π*) + (σ→σ*)
11						219.10	0.02	(π→π*)
12						212.24	0.02	(π→π*)
13						206.33	0.08	(π→π*) + (σ→σ*)

TABLE-4
INDO ELECTRONIC SPECTRA OF 1,5-DAAQ

S. No.	Observed [Ref. 12]		Calculated					
			INDO (Salahub & Sandorfy)			Present INDO		
	λ_{max} (nm)	Relative intensity	λ (nm)	f	Symmetry of transition	λ (nm)	f	Symmetry of transition
1	469.6	Strong	431.5	0.00	(n→π*)	485.2	0.00	(n→π*)
2	273.6	Strong	333.4	0.00	(n→π*)	377.0	0.00	(n→π*)
3	231.8	Very strong	315.4	0.58	(π→π*)	346.6	0.44	(π→π*)
4			291.7	0.00	(π→π*)	321.6	0.00	(π→π*)
5			252.5	0.00	(n→σ*)	319.7	0.00	(π→σ*)
6			246.7	0.00	(n→σ*)	304.8	0.00	(π→σ*)
7			212.3	0.00	(n→π*)	252.6	0.00	(n→σ*)
8			209.9	0.79	(π→π*)	250.6	0.00	(σ→π*)
9			208.3	0.00	(n→π*)	246.3	0.46	(π→π*)
10			207.9	0.00	(π→π*)	222.9	0.00	(n→π*)
11			201.3	0.00	(n→π*)	214.2	0.16	(π→π*)

TABLE-5
INDO ELECTRONIC SPECTRA OF 2,6-DAAQ

S. No.	Observed [Ref. 12]		Calculated					
			INDO (Salahub & Sandorfy)			Present INDO		
	λ_{max} (nm)	Relative intensity	λ (nm)	f	Symmetry of transition	λ (nm)	f	Symmetry of transition
1	426.5	Moderate	383.0	0.00	(n→π*)	435.49	0.00	(n→π*)
2	321.0	Strong	314.0	0.00	(n→π*)	357.33	0.00	(σ→π*)
3	291.0	Very strong	255.0	0.00	(π→π*)	298.97	0.00	(σ→π*)
4	227.0	Very strong	251.0	0.24	(π→π*)	283.33	0.00	(π→π*)
5			232.0	1.13	(π→π*)	262.68	0.65	(n→σ*)
6			210.0	0.00	(π→π*)	252.76	0.00	(n→σ*)
7			207.9	0.00	(π→π*)	239.74	0.60	(π→σ*)
8			205.1	0.28	(π→π*)	231.12	0.00	(n→π*)
9			193.1	0.22	(π→π*)	219.05	0.20	(π→π*)
10						211.29	0.41	(π→π*)
11						205.20	0.01	(π→π*) + (σ→σ*)

Electronic transitions in 2,6-DAAQ: The lowest energy transition in 2,6-DAAQ calculated at 435.49 (f = 0.00) has symmetry of (n→π*) and corresponds well to the band at 426.5 nm (Table-5).

In the case of 2,6-DAAQ the strong band is observed at 291 nm and next such band at 227.0 nm correspond well to respective INDO calculated bands at 262.68 nm (f = 0.68) and 239.7 nm (f = 0.60) (Fig. 5). These are of the (π→π*) type. Under Salahub and Sandorfy INDO method they respectively appear at 232 nm (f = 1.13) and 205.1 nm (f = 0.28).

Conclusions

The new INDO method is found more suitable for calculating the electronic spectra of organic molecules. Reasonably good energy values for low-lying transition bands are obtained. The energy values of transitions and their oscillator strengths are more consistent with observed bands in all 9,10-anthraquinones investigated here. The symmetry obtained for the excited states in question appears to be reasonable, as is generally expected of such transitions.

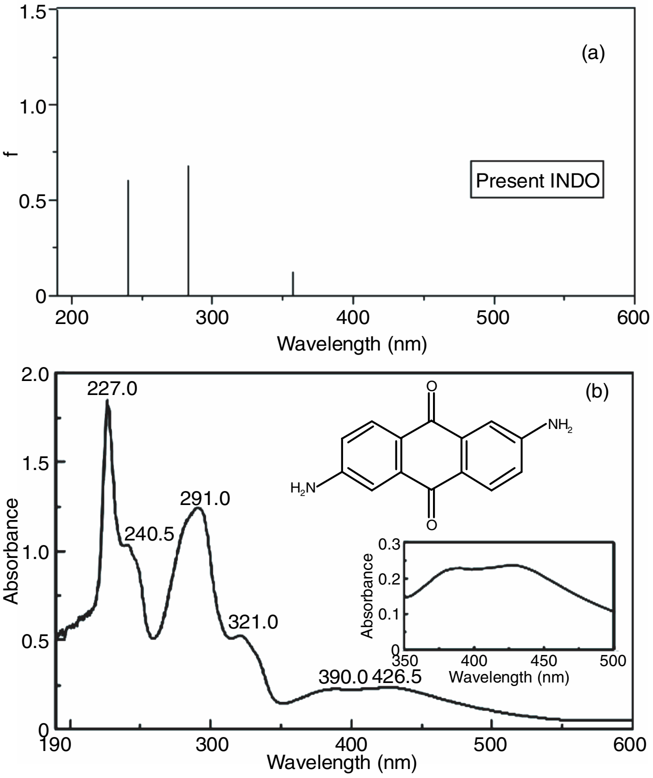

Fig. 5. (a) Plot of present INDO f (oscillator strength) against λ (wavelength) in units of nm for 2,6-DAAQ, (b) Experimental absorbance against wavelength [Ref. 12]

The new INDO method described here gives results better than Salahub and Sandorfy method and sometimes even better than the ZINDO method. It also describes the σ→σ* character of high energy transitions. The experimental results of Khan and Khan [12] do not show the lowest energy weak transitions (f = 0.00) generally expected in molecules containing oxygen non-bonding electrons.

The INDO method of Salahub and Sandorfy has been modified by changing the way the bonding parameter was calculated. Numerous calculations have been made on a good number of molecules by the present INDO method, as pointed out above. The transitions are reasonably described.

In the present paper, however, we have shown only the prominent results on 9,10-anthraquinone and some substituted diamino anthraquinones such as 1,2-diamino-9,10-anthraquinone (1,2-DAAQ), 1,4-diamino-9,10-anthraquinone (1,4-DAAQ), 1,5-diamino-9,10-anthraquinone (1,5-DAAQ) and 2,6-diamino-9,10-anthraquinone (2,6-DAAQ).

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REFERENCES

1. D. Jacquemin, X. Assfeld, J. Preat and E.A. Perpète, *Mol. Phys.*, **105**, 325 (2007).
2. G.N. Rodionova, I.V. Krutovskaya, A.N. Rodionov, Yu.G. Tuchin and V.V. Karpov, *J. Appl. Spectrosc.*, **32**, 344 (1980).
3. H. Nakahara and K. Fukuda, *J. Colloid Interface. Sci.*, **83**, 401 (1981).
4. M. Nepras, J. Fabian, M. Titz and B. Gas, *Collect. Czech. Chem. Commun.*, **47**, 2569 (1982).
5. M. Nepras, B. Gas, J. Fabian and M. Titz, *Collect. Czech. Chem. Commun.*, **47**, 2583 (1982).

6. M. Nepras, M. Titz, B. Gas and J. Fabian, *Collect. Czech. Chem. Commun.*, **47**, 2594 (1982).
7. J.D. Petke, P. Butler and G.M. Maggiora, *Int. J. Quantum Chem.*, **27**, 71 (1985).
8. Y. Iino, T. Tani, M. Sakuda, H. Nakahara and K. Fukuda, *Chem. Phys. Lett.*, **140**, 76 (1987).
9. A.N. Diaz, *J. Photochem. Photobiol. Chem.*, **53**, 141 (1990).
10. P.Y. Kuo, H. Du, L.A. Corkan, K. Yang and J.S. Lindsey, *Chemom. Intell. Lab. Syst.*, **48**, 219 (1999).
11. T. Itoh, M. Yamaji and H. Shizuka, *Spectrochim. Acta A*, **58**, 397 (2002).
12. M.S. Khan and Z.H. Khan, *Spectrochim. Acta A*, **59**, 1409 (2003).
13. J.M. Dixon, M. Taniguchi and J.S. Lindsey, *Photochem. Photobiol.*, **81**, 212 (2005).
14. S.V. Makarov, E.A. Vlasova, I.Yu. Vashurina and A.S. Pogorelova, *Russ. J. Gen. Chem.*, **77**, 1775 (2007).
15. D. Jacquemin, V. Wathelet, J. Preat and E.A. Perpète, *Spectrochim. Acta A*, **67**, 334 (2007).
16. D.W. Cho, K.D. Song, S.K. Park, K.S. Jeon and M. Yoon, *Bull. Korean Chem. Soc.*, **28**, 647 (2007).
17. Z. Markovic, N. Manojlovic and S. Zlatanovic, *J. Ser. Soc. Comp. Mech.*, **2**, 73 (2008).
18. Y. Caro, L. Anamale, M. Fouillaud, P. Laurent, T. Petit and L. Dufosse, *Nat. Prod. Bioprospect.*, **2**, 174 (2012).
19. A.D. Bacon and M.C. Zerner, *Theor. Chim. Acta*, **53**, 21 (1979).
20. J.D. Head and M.C. Zerner, *Chem. Phys. Lett.*, **122**, 264 (1985).
21. J.D. Head and M.C. Zerner, *Chem. Phys. Lett.*, **131**, 359 (1986).
22. W.P. Anderson, W.D. Edwards and M.C. Zerner, *Inorg. Chem.*, **25**, 2728 (1986).
23. M. Kotzian, N. Roesch and M.C. Zerner, *Theor. Chim. Acta*, **81**, 201 (1992).
24. D.R. Salahub and C. Sandorfy, *Theor. Chim. Acta*, **20**, 227 (1971).
25. D.R. Salahub and C. Sandorfy, *Chem. Phys. Lett.*, **8**, 71 (1971).
26. D.R. Salahub, *Theoret. Chim. Acta (Berl.)*, **22**, 325 (1971).
27. D.R. Salahub, *Theoret. Chim. Acta (Berl.)*, **22**, 330 (1971).
28. J.E. Del Bene and H.H. Jaffe, *J. Chem. Phys.*, **48**, 1807 (1968).
29. J.E. Del Bene and H.H. Jaffe, *J. Chem. Phys.*, **48**, 4050 (1968).
30. J.E. Del Bene and H.H. Jaffe, *J. Chem. Phys.*, **49**, 1221 (1968).
31. J.E. Del Bene and H.H. Jaffe, *J. Chem. Phys.*, **50**, 1126 (1969).
32. J.A. Pople and D.L. Beveridge, Approximate Molecular Orbital Theory, McGraw-Hill, New York (1970).
33. W.H. Ansari, *J. Chem. Phys.*, **67**, 3629 (1977).