Electronic Absorption Spectra of Some 1,4-Benzoquinone Diazides. A Molecular-Orbital Treatment

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The electronic absorption spectra of some 1,4-benzoquinone diazides were investigated in different solvents. The results indicate that the studied molecules pertain to the quinonoid structure. A common feature of the observed spectra is the overlap of the spectral bands. A Gaussian analysis was used to resolve the overlapping bands, and the minimum residue method was used to obtain the best fit between the analyzed and observed spectra. The observed spectra were assigned to π–π^* transitions, and none of the n–π^* transitions were observed. Molecular-orbital calculations with geometry optimization were performed using the ab initio method and different basis sets through the GAMESS package, whereas excited-state calculations were performed using the SCF-AM1-CI procedure through the MOPAC 5 package. For a comparison, MO-calculations were performed on 1,4-benzoquinone.

Quinone diazides have a peculiar electronic structure which is responsible for their physical and chemical behavior. Both carbonyl and diazo groups are electron-withdrawing and retard the effect of each other. Also, the quinonoid ring possesses low-lying π^* molecular orbitals and acts as an electron acceptor in intramolecular electronic interactions.

1,4-Benzoquinone diazides (4-diazo-2,5-cyclohexadien-1-one) are mutagenic, and are formed in the stomach by the action of phenol (widely distributed in smoked foods and some medical drugs) with nitrite under gastric conditions of temperature and pH.[1,2] This mutagenicity was found to be inhibited by the action of most amino acids.[3]

Anderson and Roedel[4,5] were the first to study the UV spectra of quinone diazides, and correlate them with the electronic structure of the molecules. Many studies followed, all of which proved that the spectra are characteristic of the quinonoid structure and that the spectra are dependent on the solvent polarity.[6,7]

X-Ray studies[8,9] have shown that the molecule is almost planar. The C–O bond length was found to be close to that in benzoquinone, whereas the C–N and N–N bond lengths were close to those of benzenediazonium chloride.

The ^{13}C NMR spectra of *p*-quinone diazide and some of its derivatives[9,10] had shown that the chemical shift C(4) did vary with the solvent used. The results indicated the transformation of *p*-quinone diazide from a quinonoid structure to an aromatic structure upon changing the solvent.

The only reported MO-calculations on quinone diazide were those using the HMO method.[11] The results showed that the type of substituent had no essential effect on the nature of bonding.

In this work the electronic spectra of some 1,4-benzoquinone diazides were investigated in different solvents, and the spectra were interpreted in terms of the quinonoid–benzenoid structure transformation. A common feature of the spectra was the persistence of broad bands, each of which represent a number of overlapping transitions. A Gaussian analysis was used to analyze the overlapping transitions; the method of minimum-residue was adopted. Molecular-orbital calculations with geometry optimization were performed on the ab initio level using the GAMESS program for the different structures and conformers of the studied molecules. The obtained results correlate nicely with the spectral observations. The excited states of the studied molecules were investigated by SCF-CI molecular-orbital calculations using the AM1 procedures.

Experimental

Solvents. Ethanol, Methanol, and Dioxane (Prolabo); Acetonitrile (99%, Aldrich), Dimethyl Sulfoxide (Merck) and *N*,*N*-Dimethylformamide (BDH) are all AR-grade reagents. The solvents were used without further purifications.

Compounds. The studied compounds were prepared as reported in the literature.[12,13] In some cases the compounds decompose with extreme violence rather than melting. The measured melting points were 1,4-benzoquinone diazide, 100 °C (100 °C);[12] 3-methyl-1,4-benzoquinone diazide, 75 °C; 3-carboxy-1,4-benzoquinone diazide, 180 °C; and 3-nitro-1,4-benzoquinone diazide, 118 °C (119 °C).[13]

Apparatus. The spectra were scanned on a Perkin–Elmer Lambda 4B UV/vis spectrophotometer in the 900—190 nm range using 1.0 cm fused silica cells.

Results and Discussion

Electronic Absorption Spectra. The interconjugation between the reaction centers, carbonyl and diazo groups, with a system of multiple bonds is the responsible for their unique electronic structure. In fact, many structural formulae were assigned to quinone diazides.[6] Some formulae contain penta-valent nitrogen, whereas the others contain bicyclic structures with an oxadiazole ring.

The shown structure describes the physicochemical and chemical properties of quinone diazides only partially; (Chart 1) a more accurate description is through a hybrid of two interionic boundary structures, quinonoid (a) and benzenoid (b) ones (Scheme 1.).

In this work an attempt was made to throw more light, and to draw confirming evidence about the structure of benzoquinone diazides.

i. 1,4-Benzoquinone Diazide. The electronic absorption spectra of 1,4-benzoquinone diazide were scanned using water (double distilled), ethanol, methanol, DMF, DMSO, dioxane, 1,2-dichloroethane, and acetonitrile as solvents. The main feature of the spectra is the observation of a broad band. A Gaussian analysis of the scanned spectra was performed with a model built using the MATHCAD package. The best fitting was decided on the basis of a comparison of the intensities of the analyzed and the experimental bands, and minimizing the residual difference between the experimental intensity and that obtained after a Gaussian analysis through the entire range of the wavelengths scanned by the spectra. The best fitting was obtained through a compromise between the above two variables.

The spectrum of 1,4-benzoquinone diazide is given in Fig. 1, where water was used as a solvent. Two regions of absorption appear in the spectrum, a long-wavelength one (ca. 350 nm) and a short-wavelength one (ca. 250 nm). Each region, clearly corresponds to a number of overlapping bands. The absorption in the long-wavelength region is resolved by a Gaussian analysis to bands with maxima at 348, 335, and 328 nm. The intensity varies from 5000 to 26800 $mol^{-1}\,L^{-1}\,cm^{-1}$ for the values of the molar-extinction coefficient, which excludes that any of them corresponds to an n–π^* transition.

The short-wavelength absorption extends from 300—200 nm. A Gaussian analysis gives three overlapping transitions with band maxima at 276, 251, and 226 nm. As given in Table 1, the intensities of the analyzed bands range from 370 to 26800 $mol^{-1}\,L^{-1}\,cm^{-1}$ for the value of the molar extinction

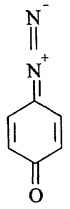
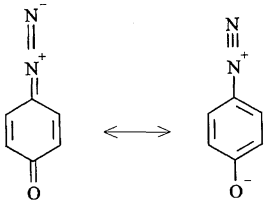


Chart 1.



(a) (b)

Scheme 1.

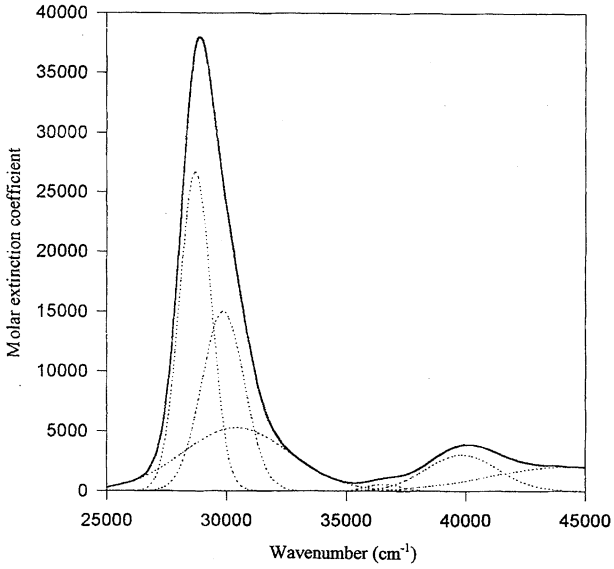


Fig. 1. Absorption spectrum of 1,4-benzoquinone diazide in water and its Gaussian analysis.

coefficients. Again, these values exclude the assignment of any of the bands to an n–π^* transition. Hence, one assigns the bands observed and analyzed in the spectrum of 1,4-benzoquinone diazide to localized π–π^*.

Benzoquinone diazides are very sparingly soluble in nonpolar solvents, except in dioxane and diethyl ether. Figure 2 shows the absorption spectrum of 1,4-benzoquinone diazide in dioxane and Fig. 3 that in ethanol. The general features of the spectra are the same in both solvents. A slight variation in band maxima is observed. A Gaussian analysis of the spectra in both solvents indicates a slight variation in the band maxima with the variation of the solvent, a result which means that the quinonoid structure is predominate and that the contribution of the benzenoid structure is undetectable. On the other hand, the variation in the band intensity with the type of solvent is significant.

Intramolecular charge-transfer transitions are not expected in 1,4-benzoquinone diazide. Both the N=N and C=O groups are electron-withdrawing and retard the effects of each other. The absence of n–π^* as well as charge-transfer transitions in the spectra of 1,4-benzoquinone diazide has been confirmed by an undetectable solvent effect on the values of the band maxima. It is an experimental fact that benzoquinone diazides absorb light at a significantly longer wavelength than the corresponding benzenoid compounds. The spectral results at hand prove that, in all solvents, the molecule 1,4-benzoquinone diazide did not isomerize to the corresponding benzenoid compound.

ii. 3-Methyl-1,4-benzoquinone Diazide. Figures 4a, b show the spectra of 3-methyl-1,4-benzoquinone diazide in ethanol. A Gaussian analysis shows the existence of absorption bands with maxima at 354, 341, 325, 259, and 231 nm. The resolved spectra confirms the phenomena of overlapping electronic transitions and the apparent degeneracy of the electronic states of the molecule. A Gaussian analysis of the spectra in different solvents indicates a slight variation

Table 1. Band Maxima and Intensities of the Studied Compounds in Different Solvents

Compound	Solvent	λ_{max} (nm)	ν (cm^{-1})	ε (mol^{-1} L cm^{-1})	f
1,4-Benzoquinone diazide	Water	348	28730	26800	0.19
		335	29850	15000	0.15
		328	30490	5000	0.12
		276	36230	370	0.00
		251	39840	2720	0.04
		226	44250	2010	0.09
	Dioxane	361	27700	9120	0.04
		348	28730	5130	0.02
		343	29150	22840	0.31
		317	31540	3770	0.05
		268	37310	2080	0.04
		236	42370	1730	0.04
	1,2-Ethane	356	28090	15260	0.143
		337	29670	12070	0.123
		320	31250	2910	0.045
		318	31440	980	0.008
		272	36760	1100	0.019
		249	40160	1410	0.040
	Ethanol	356	28090	20220	0.11
		344	29070	20650	0.17
		335	29850	15270	0.25
		293	34130	550	0.00
		257	38910	2630	0.05
		228	43860	1960	0.09
3-Methyl-1,4-benzoquinone diazide	Ethanol	354	28250	25230	0.15
		341	29320	24170	0.19
		325	30770	2580	0.09
		325	30770	8110	0.07
		259	38610	3320	0.05
		231	43290	2690	0.10
3-Carboxy-1,4-benzoquinone diazide	Ethanol	370	27030	4430	0.03
		358	27930	6780	0.07
		338	29580	3030	0.07
		267	37450	2330	0.08
		231	43290	3150	0.07
3-Nitro-1,4-benzoquinone diazide	Ethanol	388	25770	6350	0.13
		317	31540	6240	0.08
		273	36630	4800	0.12

of the band maxima with the solvent polarity, while the band intensity shows a significant change with the solvent type. The values of the molar-extinction coefficients exclude the assignment of any of the bands to an n–π^* transition.

iii. 3-Carboxy-1,4-benzoquinone Diazide. The perturbation effect of the –COOH group is stronger than that of the $-CH_3$ group. This has been reflected in the spectra (Fig. 5) in two ways: The red shift of the band maxima of the carboxy derivative compared to that of the methyl derivative and the decrease in the extent of band-overlap specially in the short-wavelength region. A striking observation is the relatively low intensity of the band maxima of the carboxy derivative compared to the methyl derivative or the parent compound, 1,4-benzoquinone diazide (Table 1). In spite of that, all of the bands in the spectrum of 3-carboxy-1,4-benzoquinone diazide correspond to localized π–π^* transitions.

iv. 3-Nitro-1,4-benzoquinone Diazide. Figure 6 shows the absorption spectrum of 3-nitro-1,4-benzoquinone diazide using ethanol as a solvent. Three important observations are obvious: The phenomenon of transitions-overlap, that was clearly encountered in 1,4-benzoquinone diazide as well as its methyl derivative, is absent in the spectra of 3-nitro-1,4-benzoquinone diazide; a red shift in the band maxima as compared to those of 1,4-benzoquinone diazide or its methyl derivative. Both effects are the result of a strong perturbation effect of the nitro group. Another general feature of the spectra of the nitro derivative is the lower intensity than in the 1,4-benzoquinone diazide or its methyl derivative. In spite of that, all of the observed bands in the spectrum of the nitro derivative are due to localized π–π^* transitions. None of the observed bands is assigned to an n–π^* or a charge-transfer transition as a result of the high intensity and

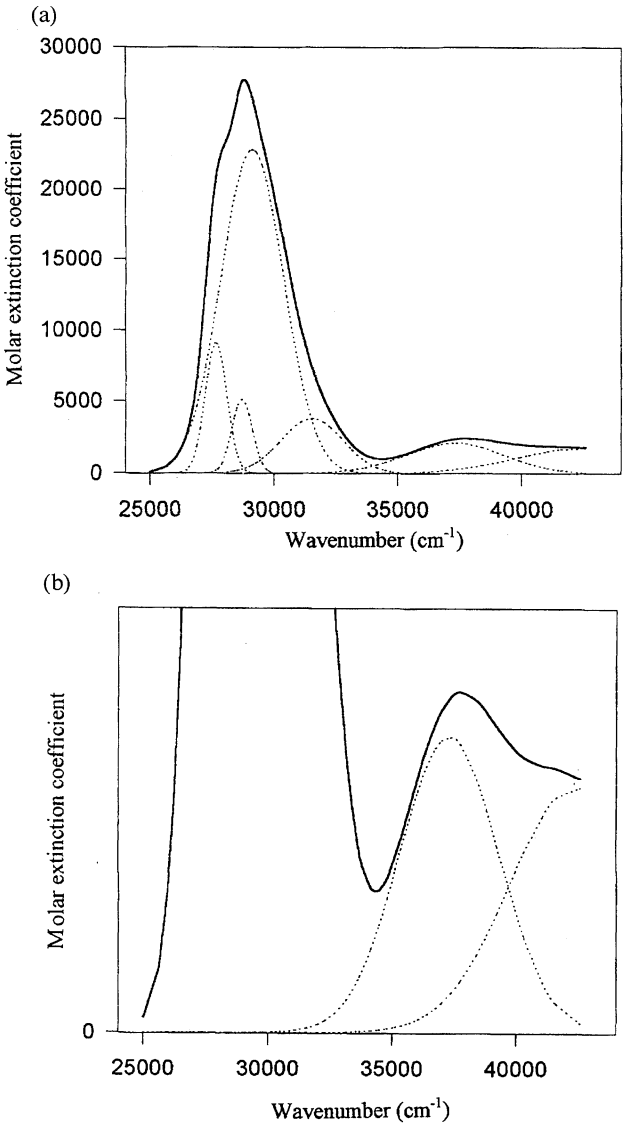


Fig. 2. Absorption spectrum of 1,4-benzoquinone diazide in dioxane and its Gaussian analysis.

a nondetectable solvent effect on the band maxima.

Molecular Orbital Calculations. The interpretation of the results of quantum-mechanical calculations is significant to determine: The equilibrium geometry, the charge distribution, and compare the stability of the quinonoid and the benzenoid isomers of the molecule.

In this work, MO calculations were carried out on the ground state using ab initio procedures through the GAMESS package.[14] Different basis sets (N-21G, N-31G, and N-311G) were tried. On the other hand, calculations on the excited states were performed using the SCF-AM1-CI procedure with a MOPAC 5-package.[15]

i. 1,4-Benzoquinone Diazide. The results of ab initio calculations are given in Table 2. Seven basis sets were tried; expanded basis sets gave a lower (better) energy for the molecule. Geometry optimization has shown that the N=N group falls on the same axis passing with the C_4, C_1, and O-atom (Chart 2); that is, one deals with a planar structure

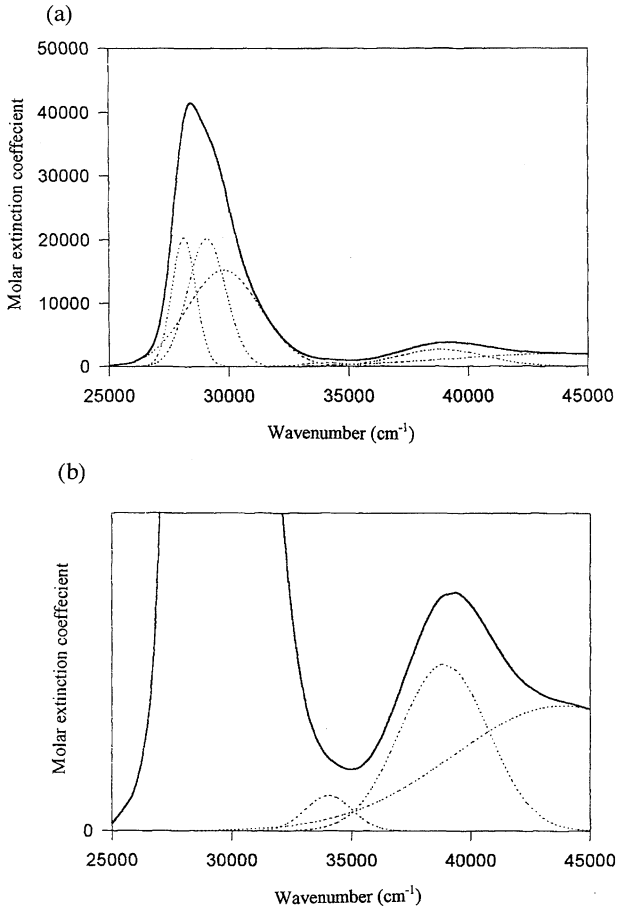


Fig. 3. Absorption spectrum of 1,4-benzoquinone diazide in ethanol and its Gaussian analysis.

following the C_{2v} symmetry point group. The basis sets (6-311G and DZV) lead to the best results nearest to those of the experiment.

A number of resonating structures are possible for 1,4-benzoquinone diazide (Scheme 2).

The bond lengths (C_4–N_8 and N_8–N_9) are diagnostic of the charge distribution in these molecules. For 9-diazofluorene, a C–N distance of 132(4) pm and an N–N distance of 112.4(4) pm were reported (Chart 3).[16] The corresponding values for benzenediazonium chloride are 138.5(9) and 109.7(6) pm.[17] In both compounds, the N–N distance is much closer to that of a triple bond (109.75 pm in N_2) than for a double bond (ca. 124 pm in azo compounds). The N–N distance calculated for 1,4-benzoquinone diazide (Table 2) varies between 111.6 and 113.1; these values are very close to the bond length in 9-diazofluorene, but very far from bond length in azo compounds. They correspond nicely with the experimental value (111.5(2)) obtained from X-ray measurements.[9] The C–N bond length (130.7 pm) is slightly shorter than the experimental one (134.5(2)). The C–O distance is 123.0 pm compared to 125.0(2) pm, as obtained from the X-ray data.

The infrared spectrum of 1,4-benzoquinone diazide[9] showed that ν_{N-N} is between the corresponding vibrations in 9-diazofluorene and benzenediazonium chloride. Also, the C=O vibration is at a lower frequency than the corresponding

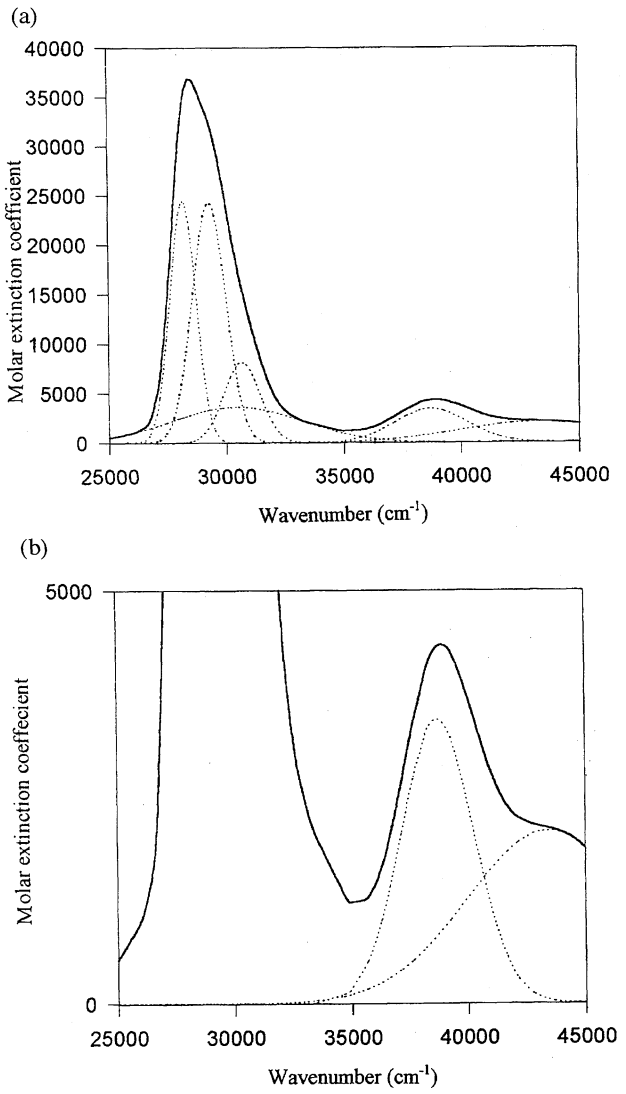


Fig. 4. Absorption spectrum of 3-methyl-1,4-benzoquinone diazide in ethanol and its Gaussian analysis.

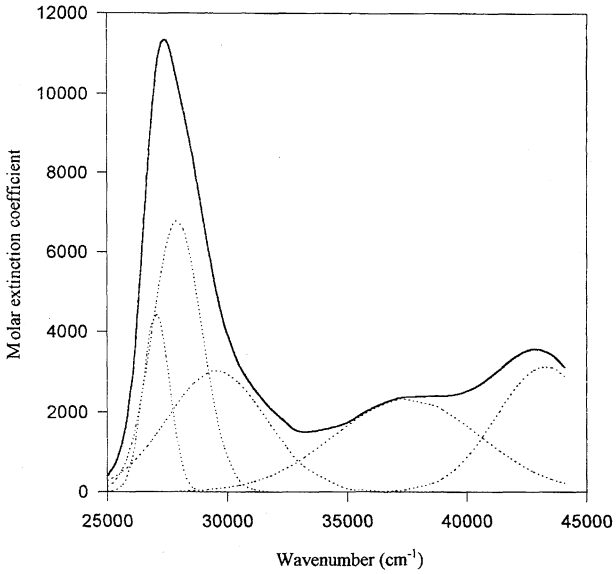


Fig. 5. Absorption spectrum of 3-carboxy-1,4-benzoquinone diazide in ethanol and its Gaussian analysis.

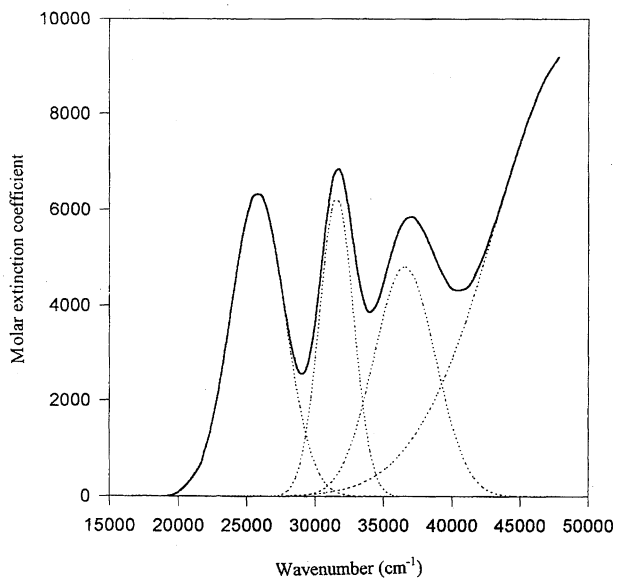


Fig. 6. Absorption spectrum of 3-nitro-1,4-benzoquinone diazide in ethanol and its Gaussian analysis.

vibration in quinones, a result which means an elongation of the C–O bond in 1,4-benzoquinone diazide.

The measured dipole moment of 1,4-benzoquinone diazide is 5.0 D, using benzene as a solvent.[5] The calculated value in this work varies between 5.28 and 5.69 D, depending on the basis set used. The calculated value corresponds nicely with the experimental one, and both indicate the contribution of the benzenoid and quinonoid forms to the structure of the molecule.

The excited states of the studied molecules were investigated using the AM1-SCF procedures. The three highest occupied MO's of 1,4-benzoquinone diazide; (ψ_{20}, ψ_{21}, and ψ_{22}) are π, σ, and π molecular orbitals, whereas the three lowest unoccupied MO's (ψ_{23}, ψ_{24}, and ψ_{25}) are π^*, σ^*, and π^* molecular orbitals. Also, one notices that ψ_{20} is 100% localized over the ring, whereas ψ_{24} is almost localized over the diazo group. The form of the wave functions of the MO's has indicated only a weak conjugation between the diazo group and the cyclohexadiene ring, and the absence of conjugation between the oxygen atom and the same ring. These results mean that the quinonoid structure is predominating, whereas the benzenoid structure is only of a minor contribution. These results are reflected in the spectrum of the molecule.

The calculated bond orders using the AM1 procedure are given in Table 3. The triple-bond character is significant between N_9 and N_8; the double-bond character is weak between C_4–N_8, but is significant between the C_5–C_6 and C_1–O_7 atoms. The bond orders between the C_4–C_5 and C_6–C_1 atoms are significantly less than those between the C_5–C_6 and C_2–C_3 atoms, which indicate a cyclohexadiene character rather than a benzenoid character. It is important to notice that the bond orders between C_6–C_1 and C_1–C_2 are

Table 2. Results of Geometry Optimization of 1,4-Benzoquinone Diazide Using Different Basis Sets

Basis set	Symm. point group	Geometrical parameters	pm or °	Dipole moment[b]	Total energy a. u.	Overlap population	Net charge			
							N_9	N_8	O_7	ϕ[a]
3-21G	C_1	N_9–N_8	111.6	5.28	−410.877799	0.810	0.013	−0.420	−0.625	1.032
		C_4–N_8	130.3			0.009				
		C_1–O_7	122.2			1.126				
		C_4–N_8–N_9	179.9							
4-31G	C_1	N_9–N_8	111.7	5.48	−412.590060	0.614	−0.018	−0.348	−0.645	1.011
		C_4–N_8	130.3			−0.025				
		C_1–O_7	122.7			0.974				
		C_4–N_8–N_9	179.9							
5-31G	C_1	N_9–N_8	112.1	5.52	−412.935762	0.607	−0.019	−0.323	−0.614	0.956
		C_4–N_8	130.7			−0.034				
		C_1–O_7	123.1			1.027				
		C_4–N_8–N_9	179.9							
6-31G	C_1	N_9–N_8	112.1	5.53	−413.024739	0.600	−0.019	−0.316	−0.606	0.944
		C_4–N_8	130.8			−0.030				
		C_1–O_7	123.2			1.040				
		C_4–N_8–N_9	179.9							
6-31G	C_{2v}	N_9–N_8	112.1	5.53	−413.024739	0.600	−0.019	−0.316	−0.606	0.944
		C_4–N_8	130.8			−0.030				
		C_1–O_7	123.2			1.040				
		C_4–N_8–N_9	180.0							
6-311G	C_{2v}	N_9–N_8	112.0	5.66	−413.112801	0.453	0.072	−0.348	−0.530	0.806
		C_4–N_8	130.7			0.044				
		C_1–O_7	123.0			0.01				
		C_4–N_8–N_9	180.0							
DZV	C_{2v}	N_9–N_8	113.1	5.69	−413.073280	1.095	0.023	−0.089	−0.414	0.480
		C_4–N_8	131.5			0.292				
		C_1–O_7	123.7			1.209				
		C_4–N_8–N_9	180.0							
X-Ray results[40]		N_9–N_8	111.5							
		C_4–N_8	134.5							
		C_1–O_7	125.0							

a) Cyclohexadiene ring. b) Experimental value = 5.0.[7]

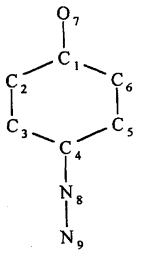
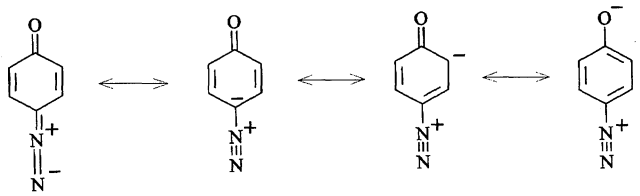


Chart 2.



Scheme 2.

very much near to its value for a C–H bond.

A 6×6- CI matrix was solved considering the interaction between the three highest occupied and the three lowest unoccupied MO's. The wave functions of the lowest seven excited states are given in Table 4. Five absorption bands have been observed in the accessible UV region, whereas seven electronic transitions were calculated in the same region, a result which indicates the overlap of some electronic transitions. The third (λ_{max} = 311 nm) and the fourth (λ_{max} = 308 nm) electronic transitions are expected to be highly overlapping. The same behavior was encountered with the fifth (λ_{max} = 283 nm) and the sixth (λ_{max} = 281 nm) transitions. The mathematical form of the wave functions of the excited states

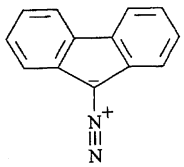


Chart 3.

Table 3. Bond Order Between the Different Atoms in 1,4-Benzoquinone Diazide

Bond	6-311G basis set	AM1 method		
	Total bond order	Total bond order	π bond order	σ bond order
N_9–N_8	2.10	2.39	1.47	0.92
N_8–C_4	0.84	1.22	0.38	0.84
C_4–C_5	1.04	1.05	0.13	0.92
C_5–C_6	1.73	1.77	0.80	0.97
C_6–C_1	1.00	0.98	0.08	0.90
C_1–O_7	1.75	1.83	0.86	0.97
C_5–H_{13}	0.95	0.95	0.00	0.95

(Table 4) and those of the MO's indicate the absence of a pure n–π* transition. This result was confirmed experimentally. However, σ(n)–π* and π–π* transitions are overlapping in a number of the calculated transitions. The lowest energy transition (λ_{max} = 256 nm) and the next transition (λ_{max} = 337 nm), both in 1,2-dichloroethane as a solvent, are very intense ($16000 > \varepsilon > 14000$), a result which confirms that both are allowed transitions. A theoretical analysis, (Table 4) has shown that the lowest energy transition is an allowed π–π* transition, whereas the next transition (λ = 337 nm) has contributions of both the π–π* and σ(n)–π* transitions. The correspondence between the calculated and experimental transition energies is adequate (Table 4).

Some conclusions are evident from the results of the MO-calculations. The conjugation between either the diazo group or the oxygen atom and the cyclohexadieneyl ring is weak. In addition, the N–N triple bond and the C–O double bond characters are evident. These results indicate a trivial contribution of the benzenoid resonance structures of 1,4-benzoquinone diazide (Chart 4).

MO-calculations using the 6-311G basis set were performed on 1,4-benzoquinone (Chart 4) assuming a C_{2v} sym-

Table 4. State Wave Functions and Energies of 1,4-Benzoquinone Diazide

State functions	λ / nm	ΔE / eV
$\Psi_{EXI} = \pm 0.628\psi_{22}^{-1}\psi_{23} + 0.321\psi_{22}^{-1}\psi_{23}\psi_{22}^{-1}\overline{\psi}_{23} + 0.118\psi_{22}^{-1}\psi_{25}\psi_{20}^{-1}\overline{\psi}_{23} + 0.118\psi_{22}^{-1}\overline{\psi}_{25}\psi_{20}^{-1}\psi_{23}$	364 (356)[a)]	3.41 (3.48)[a)]
$\Psi_{EXII} = \pm 0.640\psi_{21}^{-1}\psi_{23} + 0.275\psi_{22}^{-1}\psi_{23}\psi_{21}^{-1}\overline{\psi}_{23} - 0.275\psi_{22}^{-1}\overline{\psi}_{23}\psi_{21}^{-1}\psi_{23}$	345 (337)	3.59 (3.67)
$\Psi_{EXIII} = \pm 0.670\psi_{22}^{-1}\psi_{25} + 0.202\psi_{22}^{-1}\psi_{23}\psi_{22}^{-1}\overline{\psi}_{25} - 0.202\psi_{22}^{-1}\overline{\psi}_{23}\psi_{22}^{-1}\psi_{25}$	311 (320)	3.98 (3.87)
$\Psi_{EXIV} = \pm 0.521\psi_{20}^{-1}\psi_{24} + 0.185\psi_{22}^{-1}\psi_{23}\psi_{20}^{-1}\overline{\psi}_{25} - 0.185\psi_{22}^{-1}\overline{\psi}_{23}\psi_{20}^{-1}\psi_{25} - 0.209\psi_{22}^{-1}\psi_{23}\psi_{20}^{-1}\overline{\psi}_{24} - 0.209\psi_{22}^{-1}\overline{\psi}_{23}\psi_{20}^{-1}\psi_{24} + 0.383\psi_{22}^{-1}\psi_{24}\psi_{22}^{-1}\overline{\psi}_{25} - 0.383\psi_{22}^{-1}\overline{\psi}_{24}\psi_{22}^{-1}\psi_{25}$	308	4.02
$\Psi_{EXV} = \pm 0.609\psi_{21}^{-1}\psi_{24} + 0.236\psi_{22}^{-1}\overline{\psi}_{23}\psi_{21}^{-1}\overline{\psi}_{24} + 0.236\psi_{22}^{-1}\psi_{23}\psi_{21}^{-1}\psi_{24} - 0.249\psi_{22}^{-1}\psi_{23}\psi_{21}^{-1}\overline{\psi}_{24} - 0.249\psi_{22}^{-1}\overline{\psi}_{23}\psi_{21}^{-1}\psi_{24}$	283	4.37
$\Psi_{EXVI} = \pm 0.643\psi_{20}^{-1}\psi_{23} + 0.166\psi_{22}^{-1}\psi_{23}\psi_{22}^{-1}\overline{\psi}_{25} - 0.166\psi_{22}^{-1}\overline{\psi}_{23}\psi_{22}^{-1}\psi_{25} + 0.229\psi_{22}^{-1}\psi_{23}\psi_{20}^{-1}\overline{\psi}_{23} - 0.229\psi_{22}^{-1}\overline{\psi}_{23}\psi_{20}^{-1}\psi_{23}$	281 (272)	4.41 (4.56)
$\Psi_{EXVII} = \pm 0.681\psi_{21}^{-1}\psi_{25} + 0.125\psi_{22}^{-1}\psi_{23}\psi_{21}^{-1}\overline{\psi}_{25} - 0.125\psi_{22}^{-1}\overline{\psi}_{23}\psi_{21}^{-1}\psi_{25}$	243 (249)	5.08 (4.98)

a) Experimental value.

Table 5. State Wave Functions and Energies of 1,4-Benzoquinone

State functions	λ / nm	ΔE / eV
$\Psi_{EXI} = \pm 0.692\psi_{20}^{1}\psi_{21}$	389	3.18
$\Psi_{EXII} = \pm 0.689\psi_{18}^{-1}\psi_{21}$	297	4.17
$\Psi_{EXIII} = \pm 0.690\psi_{20}^{-1}\psi_{22}$	236	5.24
$\Psi_{EXIV} = \pm 0.681\psi_{19}^{-1}\psi_{21} \pm 0.149_{18}^{-1}\psi_{22}$	231	5.35
$\Psi_{EXV} = \pm 0.654\psi_{20}^{-1}\psi_{23} + 0.248\psi_{20}^{-1}\psi_{21}\psi_{19}^{-1}\overline{\psi}_{21} - 0.248\psi_{20}^{-1}\overline{\psi}_{21}\psi_{19}^{-1}\psi_{21}$	226	5.47

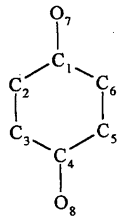


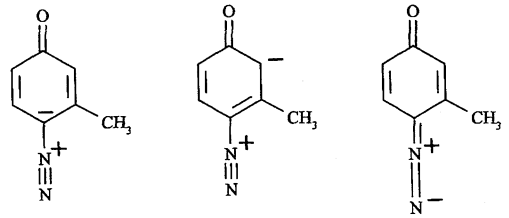
Chart 4.

metry point group. The C–O bond length was found to be 121.8 pm compared 123.0 pm in benzoquinone diazide. The slight bond elongation indicates a slight benzenoid contribution. Also, the C_1–C_2 bond length is 147.8 pm, whereas that of C_2–C_3 is 132.5 pm. The corresponding bond lengths in 1,4-benzoquinone diazide are 146.4 and 133.8 pm, a result which indicates the heavy weight of the quinonoid structure of 1,4-benzoquinone diazide.

Bond-order calculations were illuminating. The total C–O bond order in 1,4-benzoquinone is 1.9091, analyzed to the 0.9368 π-bond order and the 0.9723 σ-bond order. The corresponding π-bond order of the C–O bond in 1,4-benzoquinone diazide is only 0.8591; similarly, the bond order between the carbon atoms in 1,4-benzoquinone differs from the corresponding values in 1,4-benzoquinone diazide. All of these results indicate that the contribution of the benzenoid resonance structure in 1,4-benzoquinone diazide has a certain weight. Another important result is that MO-calculations on the excited states of 1,4-benzoquinone indicated the existence of a discrete n–π* transition (λ_{max} = 389 nm) that does not overlap the π–π* transitions (Table 5), as was the case in 1,4-benzoquinone diazide. Also, the conurbation of both σ(n)–π* and π–π* to an electronic transition (Ψ_{EXIV}, λ_{max} = 231 nm) is exists.

ii. 3-Methyl-1,4-benzoquinone Diazide. It has been reported that alkyl substitution at a position ortho to the C=O group causes small red shifts of both the $\nu_{C=O}$ and $\nu_{N=N}$ vibrations, whereas methyl groups at the C-atom *ortho* to the N–N group cause a small blue shift of $\nu_{N=N}$.[9] The influence of the alkyl group is small. The red shift of $\nu_{N=N}$ is explained by the destabilization of resonance structures (a), (b), thus increasing the weight of (c) (Chart 5).

MO-calculations were carried out; the results obtained using the 6-31G basis set are shown in Table 6. The results show that methyl substitution has a minor effect on the structure of the molecule; the N_9–N_8 and C_1–O_7 bonds have been slightly elongated compared with their length in 1,4-benzo-



(a) (b) (c)

Chart 5.

Table 6. Results of ab initio MO-Calculations on Some 1,4-Benzoquinone Diazide Derivatives Using 6-31G Basis Sets

Compound	Symm. point group	Geometrical parameters	pm, °	Dipole moment	Total energy a.u.	Overlap population	Net charge				
							N_9	N_8	O_7	Me	ϕ[a]
3-Methyl-1,4-benzoquinone diazide	C_1	N_9–N_8	112.2	5.73	−452.0487840	0.592	−0.023	−0.334	−0.610	0.092	0.876
		C_4–N_8	130.7			−0.059					
		C_1–O_7	123.2			1.041					
		C_3–C_{13}	150.6			0.468					
		C_4–N_8–N_9	179.9								
							N_9	N_8	O_7	COOH	ϕ[a]
3-Carboxy-1,4-benzoquinone diazide	C_1	N_9–N_8	111.2	4.11	−600.5467100	0.716	0.023	−0.295	−0.600	−0.016	0.888
		C_4–N_8	131.9			−0.134					
		C_1–O_7	123.2			1.042					
		C_{13}–O_{14}	121.5			1.135					
		C_{13}–O_{15}	134.1			0.421					
		O_{15}–H_{16}	95.4			0.529					
		C_4–N_8–N_9	179.1								
							N_9	N_8	O_7	NO_2	ϕ[a]
3-Nitro-1,4-benzoquinone diazide	C_1	N_9–N_8	111.0	5.56	−616.3620904	0.713	0.040	−0.285	−0.581	−0.575	1.401
		C_4–N_8	132.0			−0.114					
		C_1–O_7	122.9			1.043					
		C_3–C_{13}	145.4			−0.177					
		N_{13}–O_{14}	122.9			0.081					
		N_{13}–O_{15}	121.8			0.168					
		C_4–N_8–N_9	178.0								

a) Cyclohexadiene ring.

quinone diazide. The electronic transitions were considered between the three highest occupied molecular orbitals and the three lowest unoccupied molecular orbitals. The forms of the CI wave functions of the excited states are given in Table 7. Again, no transition is assigned to a pure n–π* one. The overlapping nature of the electronic transitions in 3-methyl-1,4-benzoquinone diazide is apparent.

iii. 3-Carboxy-1,4-benzoquinone Diazide. The above compound can exists in a number of conformers (Chart 6).

MO-calculations were performed on different conformers using the ab initio method and 6-31G basis. The conformer (b) was found to have the lowest energy, and the height of the barrier of internal rotation of the O–H bond around the C–O bond is 13.71 kcal mol^{-1}. The results of MO-calculations are given in Table 6. The value of the atomic charge density, bond length, overlap population as well as the dipole moment are different for the carboxy derivative than for the parent compound. In the carboxy derivative the C_4–N_8 and the C_1–O_7 bonds have been elongated, which means a greater contribution of the aromatic resonating structure. The wave functions of the excited states were obtained through SCF-CI-MO calculations by solving a 6×6-CI matrix; the results are given in Table 8. The behavior of transition overlap persists, and no pure n–π* transition has been observed. Also, many of the calculated transitions are degenerate, a behavior that is observed with 1,4-benzoquinone diazide and its derivatives. The correspondence between the calculated transition energies and the experimental ones is adequate.

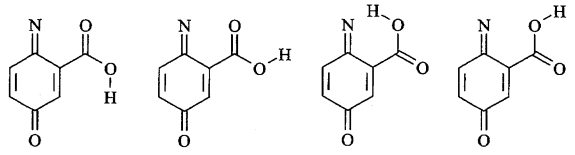


Chart 6.

iv. 3-Nitro-1,4-benzoquinone Diazide. The results of MO calculations using the 6-31G basis sets are given in Table 6. Substitution by a nitro group has significantly affected the N–N, C–O as well C–C bond lengths. It is important to find that, in spite of the strong perturbation effect of the $-NO_2$ group, a rather weak conjugation exists between the cyclohexadiene ring and both of the diazo and the nitro groups.

The CI-wave functions of the excited states are given in Table 9. Reduced symmetry has led to a significant mixing between a large number of molecular orbitals.

Conclusions. 1,4-Benzoquinone diazide is a planar molecule that follows the C_{2v} point group. Both spectral studies and MO-calculations proved to give only a minor contribution of the bezenoid resonating structure; also, the quinonoid structure persists in different solvents, since only a minor shift of the band maxima was observed with solvent variation. The calculated bond order and bond length (C–C, C–N, N–N, and C–O) in 1,4-benzoquinone diazide and 1,4-benzoquinone support the quinonoid structure over the benzenoid one in the former molecule. A theoretical investigation indicated a minor-if any-conjugation between either the diazo group, N_2 or the oxygen atom, O, and the cyclohexadiene ring as well as the degeneracy of many electronic states. These results were reflected in the spectral observations. The observed bands were rather broad, and a Gaussian analysis revealed that each band covers a number of overlapping transitions. Both the experimental and theoretical results proved the absence of any n–π* transition in the UV-vis spectra of the studied benzoquinone diazides, whereas it exists in the spectrum of 1,4-benzoquinone.

Substitution in the benzoquinone diazide ring with a $-CH_3$, $-COOH$ or $-NO_2$ group has a varying effect on the structural

Table 7. State Wave Functions and Energies of 3-Methyl-1,4 benzoquinone Diazide

State functions	λ / nm	ΔE / eV
$\Psi_{EXI} = \pm 0.628\psi_{25}^{-1}\psi_{26} - 0.102\psi_{25}^{-1}\psi_{26}\psi_{23}^{-1}\psi_{28} + 0.315\psi_{25}^{-1}\psi_{26}\psi_{25}^{-1}\overline{\psi}_{26} - 0.106\psi_{25}^{-1}\overline{\psi}_{28}\psi_{25}^{-1}\psi_{28} + 0.120\psi_{25}^{-1}\psi_{28}\psi_{23}^{-1}\overline{\psi}_{28} + 0.120\psi_{25}^{-1}\overline{\psi}_{28}\psi_{23}^{-1}\psi_{28}$	361 (358)[a]	3.42 (3.46)[a]
$\Psi_{EXII} = \pm 0.639\psi_{24}^{-1}\psi_{26} + 0.277\psi_{25}^{-1}\psi_{26}\psi_{24}^{-1}\overline{\psi}_{26} - 0.277\psi_{25}^{-1}\overline{\psi}_{26}\psi_{24}^{-1}\psi_{26}$	343 (343)	3.61 (3.61)
$\Psi_{EXIII} = \pm 0.546\psi_{23}^{-1}\psi_{27} + 0.195\psi_{25}^{-1}\psi_{26}\psi_{23}^{-1}\psi_{27} - 0.195\psi_{25}^{-1}\overline{\psi}_{26}\psi_{23}^{-1}\overline{\psi}_{27} + 0.216\psi_{25}^{-1}\psi_{26}\psi_{23}^{-1}\overline{\psi}_{27} + 0.216\psi_{25}^{-1}\overline{\psi}_{26}\psi_{23}^{-1}\psi_{27} - 0.336\psi_{25}^{-1}\psi_{27}\psi_{25}^{-1}\overline{\psi}_{28} + 0.336\psi_{25}^{-1}\overline{\psi}_{27}\psi_{25}^{-1}\psi_{28}$	318 (328)	3.90 (3.78)
$\Psi_{EXIV} = \pm 0.667\psi_{25}^{-1}\psi_{28} \pm 0.135\psi_{23}^{-1}\psi_{26} + 0.179\psi_{25}^{-1}\psi_{26}\psi_{25}^{-1}\overline{\psi}_{28} - 0.179\psi_{25}^{-1}\overline{\psi}_{26}\psi_{25}^{-1}\psi_{28}$	311 (313)	3.98 (3.96)
$\Psi_{EXV} = \pm 0.110\psi_{24}^{-1}\psi_{27} \pm 0.625\psi_{23}^{-1}\psi_{26} + 0.167\psi_{25}^{-1}\psi_{26}\psi_{25}^{-1}\overline{\psi}_{28} - 0.167\psi_{25}^{-1}\overline{\psi}_{26}\psi_{25}^{-1}\psi_{28} + 0.215\psi_{25}^{-1}\psi_{26}\psi_{23}^{-1}\overline{\psi}_{27} - 0.215\psi_{25}^{-1}\overline{\psi}_{26}\psi_{23}^{-1}\psi_{27}$	289	4.28
$\Psi_{EXVI} = \pm 0.598\psi_{24}^{-1}\psi_{27} \pm 0.109\psi_{23}^{-1}\psi_{26} - 0.234\psi_{25}^{-1}\psi_{26}\psi_{24}^{-1}\psi_{27} - 0.234\psi_{25}^{-1}\overline{\psi}_{26}\psi_{24}^{-1}\overline{\psi}_{27} - 0.248\psi_{25}^{-1}\overline{\psi}_{26}\psi_{24}^{-1}\psi_{27} - 0.248\psi_{25}^{-1}\psi_{26}\psi_{24}^{-1}\overline{\psi}_{27}$	281 (264)	4.40 (4.69)
$\Psi_{EXVII} = \pm 0.674\psi_{24}^{-1}\psi_{28} - 0.156\psi_{25}^{-1}\psi_{26}\psi_{24}^{-1}\psi_{28} - 0.156\psi_{25}^{-1}\overline{\psi}_{26}\psi_{24}^{-1}\overline{\psi}_{28} - 0.106\psi_{25}^{-1}\psi_{26}\psi_{24}^{-1}\overline{\psi}_{28} - 0.106\psi_{25}^{-1}\overline{\psi}_{26}\psi_{24}^{-1}\psi_{28}$	239 (238)	5.18 (5.21)

a) Experimental value.

Table 8. State Wave Functions and Energies of 3-Carboxy-1,4-benzoquinone Diazide

State functions	λ / nm	ΔE / eV
$\Psi_{EXI} = \pm 0.653\psi_{30}^{-1}\psi_{31} + 0.133\psi_{30}^{-1}\psi_{31}\psi_{30}^{-1}\overline{\psi}_{33} - 0.133\psi_{30}^{-1}\overline{\psi}_{31}\psi_{30}^{-1}\psi_{33} + 0.206\psi_{30}^{-1}\psi_{31}\psi_{30}^{-1}\overline{\psi}_{31}$	371 (363)[a)]	3.34 (3.41)[a)]
$\Psi_{EXII} = \pm 0.644\psi_{29}^{-1}\psi_{31} + 0.264\psi_{30}^{-1}\psi_{31}\psi_{29}^{-1}\overline{\psi}_{31} - 0.264\psi_{30}^{-1}\overline{\psi}_{31}\psi_{29}^{-1}\psi_{31}$	342 (349)	3.62 (3.55)
$\Psi_{EXIII} = \pm 0.652\psi_{30}^{-1}\psi_{33} + 0.265\psi_{30}^{-1}\psi_{31}\psi_{30}^{-1}\overline{\psi}_{31} \pm 0.143\psi_{28}^{-1}\psi_{31}$	328 (333)	3.78 (3.72)
$\Psi_{EXIV} = \pm 0.542\psi_{28}^{-1}\psi_{32} - 0.210\psi_{30}^{-1}\psi_{33}\psi_{28}^{-1}\psi_{32} - 0.210\psi_{30}^{-1}\overline{\psi}_{33}\psi_{28}^{-1}\overline{\psi}_{32} + 0.146\psi_{30}^{-1}\psi_{31}\psi_{29}^{-1}\overline{\psi}_{32} - 0.146\psi_{30}^{-1}\overline{\psi}_{31}\psi_{29}^{-1}\psi_{32} + 0.217\psi_{30}^{-1}\psi_{31}\psi_{28}^{-1}\overline{\psi}_{32} + 0.217\psi_{30}^{-1}\overline{\psi}_{31}\psi_{28}^{-1}\psi_{32} + 0.292\psi_{30}^{-1}\psi_{32}\psi_{30}^{-1}\overline{\psi}_{33} - 0.292\psi_{30}^{-1}\overline{\psi}_{32}\psi_{30}^{-1}\psi_{33}$	278	4.45
$\Psi_{EXV} = \pm 0.579\psi_{29}^{-1}\psi_{32} + 0.233\psi_{30}^{-1}\overline{\psi}_{31}\psi_{29}^{-1}\overline{\psi}_{32} + 0.233\psi_{30}^{-1}\psi_{31}\psi_{29}^{-1}\psi_{32} \pm 0.197\psi_{28}^{-1}\psi_{31} - 0.247\psi_{30}^{-1}\overline{\psi}_{31}\psi_{29}^{-1}\psi_{32} - 0.247\psi_{30}^{-1}\psi_{31}\psi_{29}^{-1}\overline{\psi}_{32}$	272	4.55
$\Psi_{EXVI} = \pm 0.181\psi_{29}^{-1}\psi_{32} \pm 0.589\psi_{28}^{-1}\psi_{31} \pm 0.117\psi_{28}^{-1}\psi_{33} + 0.188\psi_{30}^{-1}\psi_{31}\psi_{30}^{-1}\overline{\psi}_{31} - 0.147\psi_{30}^{-1}\psi_{33}\psi_{30}^{-1}\overline{\psi}_{33} + 0.183\psi_{30}^{-1}\psi_{31}\psi_{28}^{-1}\overline{\psi}_{31} - 0.183\psi_{30}^{-1}\overline{\psi}_{31}\psi_{28}^{-1}\psi_{31}$	267 (262)	4.64 (4.73)
$\Psi_{EXVII} = \pm 0.654\psi_{29}^{-1}\psi_{33} + 0.176\psi_{30}^{-1}\psi_{31}\psi_{28}^{-1}\overline{\psi}_{33} - 0.176\psi_{30}^{-1}\overline{\psi}_{31}\psi_{29}^{-1}\psi_{33} - 0.143\psi_{30}^{-1}\psi_{32}\psi_{29}^{-1}\overline{\psi}_{33} - 0.143\psi_{30}^{-1}\overline{\psi}_{32}\psi_{29}^{-1}\psi_{33}$	248	5.00
$\Psi_{EXVIII} = \pm 0.111\psi_{30}^{-1}\psi_{32} \pm 0.319\psi_{28}^{-1}\psi_{32} + 0.339\psi_{30}^{-1}\psi_{31}\psi_{30}^{-1}\overline{\psi}_{32} - 0.339\psi_{30}^{-1}\overline{\psi}_{31}\psi_{30}^{-1}\psi_{32} + 0.475\psi_{30}^{-1}\psi_{33}\psi_{30}^{-1}\overline{\psi}_{32} + 0.475\psi_{30}^{-1}\psi_{33}\psi_{30}^{-1}\overline{\psi}_{32} - 0.141\psi_{30}^{-1}\psi_{33}\psi_{28}^{-1}\overline{\psi}_{33} - 0.141\psi_{28}^{-1}\psi_{33}$	223 (226)	5.56 (5.48)
$\Psi_{EXIX} = \pm 0.142\psi_{30}^{-1}\psi_{31} \pm 0.193\psi_{30}^{-1}\psi_{33} \pm 0.217\psi_{28}^{-1}\psi_{31} \pm 0.449\psi_{28}^{-1}\psi_{33} - 0.393\psi_{30}^{-1}\psi_{31}\psi_{30}^{-1}\overline{\psi}_{31} + 0.336\psi_{30}^{-1}\psi_{33}\psi_{30}^{-1}\overline{\psi}_{33} - 0.123\psi_{30}^{-1}\psi_{31}\psi_{28}^{-1}\psi_{33} - 0.123\psi_{30}^{-1}\overline{\psi}_{31}\psi_{28}^{-1}\overline{\psi}_{33} + 0.103\psi_{30}^{-1}\psi_{31}\psi_{30}^{-1}\overline{\psi}_{33} - 0.103\psi_{30}^{-1}\overline{\psi}_{31}\psi_{30}^{-1}\psi_{33} + 0.120\psi_{30}^{-1}\psi_{31}\psi_{28}^{-1}\overline{\psi}_{31} - 0.120\psi_{30}^{-1}\overline{\psi}_{31}\psi_{28}^{-1}\psi_{31}$	218	5.67

a) Experimental value.

Table 9. State Wave Functions and Energies of 3-Nitro-1,4-benzoquinone Diazide

State functions	λ / nm	ΔE / eV
$\Psi_{EXI} = \pm 0.685\Psi_{30}^{-1}\Psi_{31} + 0.102\Psi_{30}^{-1}\Psi_{31}\Psi_{30}^{-1}\overline{\Psi}_{33} - 0.102\Psi_{30}^{-1}\overline{\Psi}_{31}\Psi_{30}^{-1}\Psi_{33}$	369 (386)[a)]	3.35 (3.21)[a)]
$\Psi_{EXII} = \pm 0.635\Psi_{30}^{-1}\Psi_{33} \pm 0.199\Psi_{28}^{-1}\Psi_{31} - 0.235\Psi_{30}^{-1}\Psi_{31}\Psi_{30}^{-1}\overline{\Psi}_{32} + 0.130\Psi_{30}^{-1}\Psi_{31}\Psi_{30}^{-1}\overline{\Psi}_{33} - 0.130\Psi_{30}^{-1}\overline{\Psi}_{31}\Psi_{30}^{-1}\Psi_{33}$	334	3.70
$\Psi_{EXIII} = \pm 0.638\Psi_{29}^{-1}\Psi_{31} \pm 0.124\Psi_{29}^{-1}\Psi_{33} + 0.235\Psi_{30}^{-1}\Psi_{31}\Psi_{29}^{-1}\overline{\Psi}_{31} - 0.235\Psi_{30}^{-1}\overline{\Psi}_{31}\Psi_{29}^{-1}\Psi_{31}$	331 (315)	3.74 (3.93)
$\Psi_{EXIV} = \pm 0.603\Psi_{29}^{-1}\Psi_{32} + 0.232\Psi_{30}^{-1}\Psi_{31}\Psi_{29}^{-1}\Psi_{32} + 0.232\Psi_{30}^{-1}\overline{\Psi}_{31}\Psi_{29}^{-1}\overline{\Psi}_{32} - 0.247\Psi_{30}^{-1}\Psi_{31}\Psi_{29}^{-1}\overline{\Psi}_{32} - 0.247\Psi_{30}^{-1}\overline{\Psi}_{31}\Psi_{29}^{-1}\Psi_{32}$	278 (276)	4.63 (4.49)

a) Experimental value.

parameters of the molecule. The smallest effect was for the $-CH_3$ group and the largest effect was for the $-NO_2$ group. However, methyl substitution strengthens the quinonoid structure, whereas the carboxyl substitution strengthens the benzenoid structure. The best conformer of 3-carboxy-1,4-benzoquinone diazide was predicted theoretically.

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