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A Molecular Orbital Treatment of the Electronic Structure and Spectra of Aryl Nitrones

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ABSTRACT. The electronic structures of some aryl nitrones have been investigated using the MNDO-MO method. Equilibrium geometries, and charge density distributions have been computed. Various electronic differences between nitrones and the corresponding imines have been analyzed and discussed. The electronic absorption spectra of the studied nitrones have been analyzed and interpreted using the results of MO computation. Charge density distribution, dipole moments and the extent of delocalization of the MO's were used to interpret the observed solvent effects. Comparison between the spectra of aryl nitrones and that of the corresponding imines led to conclusions regarding the structural differences between the two classes of compounds.

Introduction

Compounds containing the C = N - O, nitrone, group attracted increasing attention in the last two decade. The high chemical reactivity of nitrones is underlined by the 1,3-dipolar cycloadditions to electrophiles. This thermally⁽¹⁾ allowed cycloaddition lead to the formation of several chemically and biologically important heterocycles.

The electronic spectra of a number of aryl nitrones have been reported^(2,3) and some qualitative relations concerning substituent effect have been observed⁽⁴⁾. However, the literature does not seem to contain any quantitative and systematic investigation of the electronic spectral properties of this class of compounds. The aim of the present work is to carry out a quantitative investigation of the electronic spectra of aryl nitrones in comparison with the corresponding imines. Quantitative assignments

of the observed electronic transitions, solvent and substituent effects are facilitated via MO computation.

Experimental

Arylnitrones studied in this work were synthesized by condensing the ethanolic solutions of equimolar quantities of an arylaldehyde and phenylhydroxylamine¹⁶. The products were purified by repeated crystallization. Compounds studied in the present work are systematically sketched in figure (1).

All UV spectra were recorded at room temperature on a Cary-17 D spectrophotometer using 1.0 cm pathlength cells.

Molecular orbital computations were carried out using the MO package MOPAC 5 which is based on the MNDO formalism¹⁷. Details of the method are given elsewhere¹⁷. All molecular geometries are fully optimized, first using a molecular mechanics steepest descent procedure followed by MNDO optimization. The configuration adopted throughout the present work is shown in Fig. 1. Configuration interaction carried out involves all possible single and double excitations involving the highest three occupied and lowest three vacant MO's (all of 100 states).

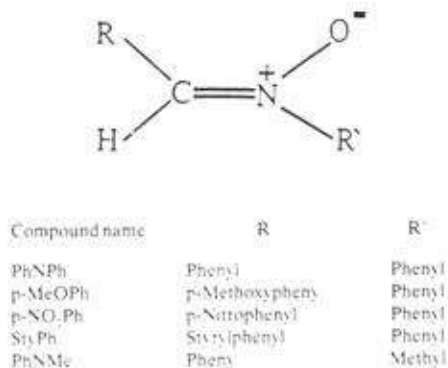


FIG. 1. Compounds studied in the present work.

Results and Discussion

1 - Aryl - NPhenylnitrones

The electronic absorption spectrum of 1-phenyl N-phenylnitronium, in ethanol, is presented in Fig. 2. The spectrum shows a broad intense absorption profile centered at ≈ 313 nm and a moderate intensity band at ≈ 236 nm. The width of the main long wavelength envelope and its asymmetry at the peak maximum suggest that this absorption profile might, very well, enclose more than one transition. Gaussian deconvolution of the spectrum predicted four well defined overlapping bands with

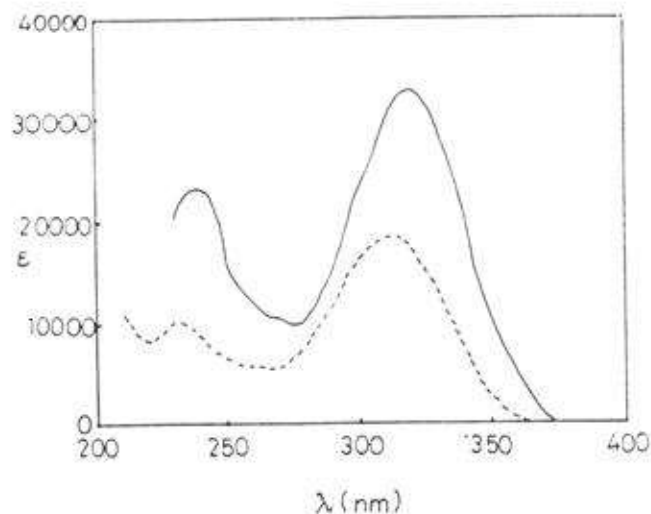


FIG. 2. Electronic absorption spectra of PhNPh nitron in (---) ethanol and (—) 1, 2-dichloroethane.

peak maxima at 320, 285, 250 and 236 nm. In a non-polar solvent, 1, 2-dichloroethane, all observed bands undergo a red shift and lowering in intensity. Decreasing solvent polarity obviously resolved the overlapping of the first and second transitions.

Table I presents a comparison between the theoretically computed and experimentally observed transition energies. All transitions observed in the spectra of 1-phenyl N-phenylnitron can be safely assigned as $\pi - \pi^*$ transitions (cf. E values). Although, computation predicted several $n - \pi$ transitions to occur, yet none is observed experimentally, probably because they are hidden by the stronger and broader $\pi - \pi^*$ ones.

Two allowed $\pi - \pi^*$ transitions are predicted to occur in the wavelength range covered by the first absorption profile at 319 and 288 nm. These two transitions can be assigned as a mixture of the two configurations $\psi_{11} - \psi_{12}$ and $\psi_{13} - \psi_{14}$. The MO ψ_{11} is a π -MO delocalized over the entire molecule with $\approx 50\%$ of its density localized on the nitron group. A transition either to ψ_{12} or ψ_{14} will transfer electron density onto the N-phenyl subsystem, i.e. against the dipole moment vector. Hence, the excited states I and II are of lower polarizability than the ground state. This would explain the observed blue shift of the first absorption profile, upon increasing solvent polarity.

The short wavelength absorption profile seems to enclose three distinct transitions

TABLE I. Comparison between the theoretically computed and experimentally observed transition energies.

Band system	E, eV		Assignment	Origin
	Obs.	Calc.		
I	-	2.20	$\pi - \pi^*$	$\psi_{20} - \psi_{21}^*$
	-	2.01	$\pi - \pi^*$	$\psi_{10} - \psi_{11}^*$
II	3.89	3.88	$\pi - \pi^*$	$\psi_{12} - \psi_{13}^*$
III	4.15	4.32	$\pi - \pi^*$	$\psi_{14} - \psi_{15}^*$
	-	4.47	$\pi - \pi^*$	$\psi_{16} - \psi_{17}^*$
IV	5.06	5.02	$\pi - \pi^*$	$\psi_{22} - \psi_{23}^*$
V	5.25	5.27	$\pi - \pi^*$	$\psi_{18} - \psi_{19}^*$
	-	5.20	$\pi - \pi^*$	$\psi_{24} - \psi_{25}^*$

ψ = HOMO and ψ^* = LUMO.

with peak maxima at 245, 235 & 220 nm. The overlap between these three transitions seems to be somewhat resolved upon increasing solvent polarity. This is simply because the corresponding configurations $\psi_{12} - \psi_{13}^*$ and $\psi_{14} - \psi_{15}^*$, which form the corresponding (π, π^*) states, would lead to transfer of electron density in opposite directions. That is, why the polarizability of the former is greater than that of the ground state, while that of the latter is much lower. Therefore, increasing solvent polarity would increase the separation between the two transitions. Figure 3 presents the nodal properties of the highest three occupied and lowest three vacant MO's.

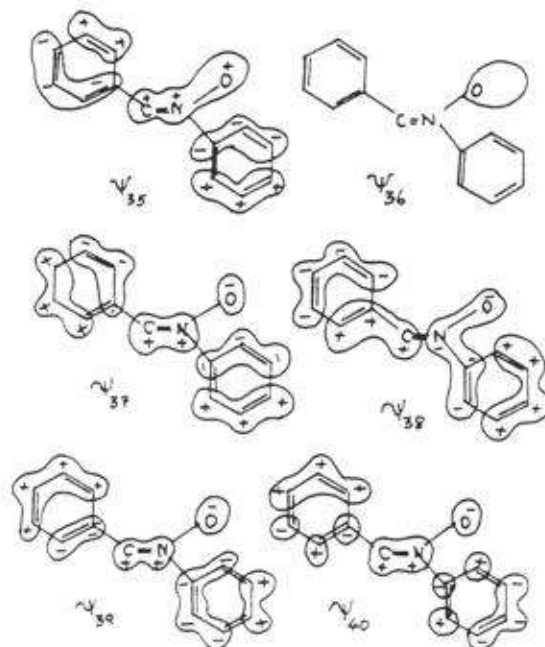


FIG. 3. Nodal properties of HOMO and LUMO in PhNph nitron.

In order to establish the type of conjugation predominant in aryl nitrones, let us compare the spectrum of aryl nitrones with that of the corresponding imine. Figure 4 presents such a comparison, using ethanol as a solvent. The spectrum of 1,2-diphenyl imine shows a low intensity band at ≈ 280 nm and a much stronger broad one at 240 nm. It is quite clear that this spectrum is different both in band position and in the intensity ratio of the first to the second absorption profiles, as compared to that of 1-phenyl-N-phenylnitron. The long wavelength band at 280 nm is a conjugate band reflects the linear conjugated nature of the imine. Interpretation of the spectrum of nitrones cannot, therefore, be made by simple relations with that of the corresponding imines.

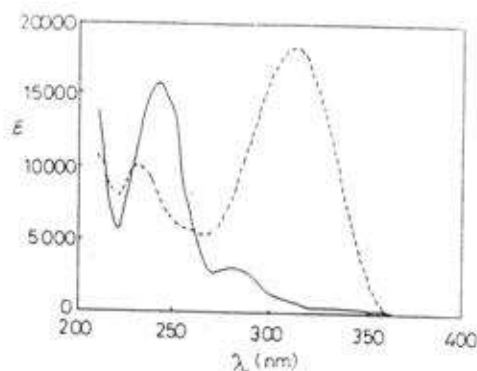


FIG. 4. Comparison of the spectra of (---) PhNPh nitron and (—) PhNPh imine in ethanol.

Figure 5 presents the spectrum of 1-phenyl-N-methylnitron, in ethanol as a solvent. Two main absorption profiles centered at 290 and 230 nm appear in the spec-

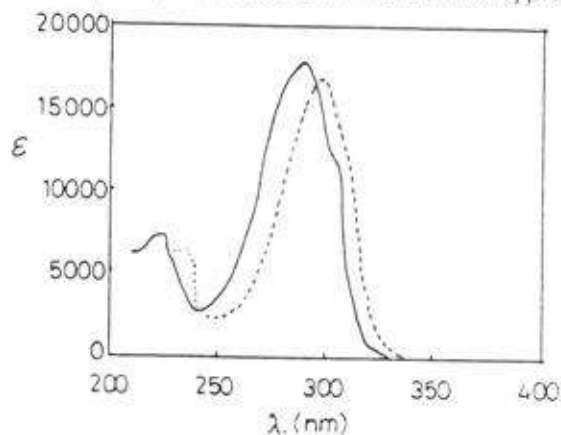


FIG. 5. Electronic absorption spectra of PhNMe nitron in (—) ethanol and (---) 1,2-dichloroethane.

trum of the N-methyl derivative. Careful gaussian fitting of these two envelopes indicates that the long wavelength broad one, encloses a shoulder at 315 nm and a peak at 295 nm. These two transitions show a blue shift upon increasing solvent polarity. The short wavelength envelope encloses two peak maxima at 235 and 228 nm, and again show blue shift by solvent polarity.

MO calculations are in good agreement with the observed spectra and elaborates upon the assignment that all observed bands are of the $\pi - \pi^*$ type. Furthermore, the inductive effect of the methyl group, shows a perturbation which is very similar to that of the phenyl moiety. This has been reflected in the similarity of the spectra of the N-methyl and that of the N-phenyl nitrones. On this basis one might safely assume cross-conjugation to predominate in aryl nitrones. Conjugation extends linearly over the 1-phenyl nitrone subsystem while the N-phenyl sub system has only a perturbing effect on the observed spectrum.

Further investigation of the type and the extent of binding between the 1-phenyl ring and the nitrone group may be established by studying substituent effects. Figure 6 presents a comparison between the spectra of 1-phenyl N-phenyl nitrone and its p-methoxy and p-nitro derivatives. Electron donating (methoxy) and electron withdrawing (nitro) groups have a pronounced effect on the spectrum, both cause a red shift of the two observed absorption profiles, as compared to the unsubstituted parent compound. In the case of the p-methoxy derivative, the general shape of the spectrum greatly resembles that of the parent compound with a typical effect of the methoxy group. The main long wavelength absorption profile encloses two bands at 335 and 315 nm while two bands at 260 and 240 nm are enclosed in the short wavelength envelope.

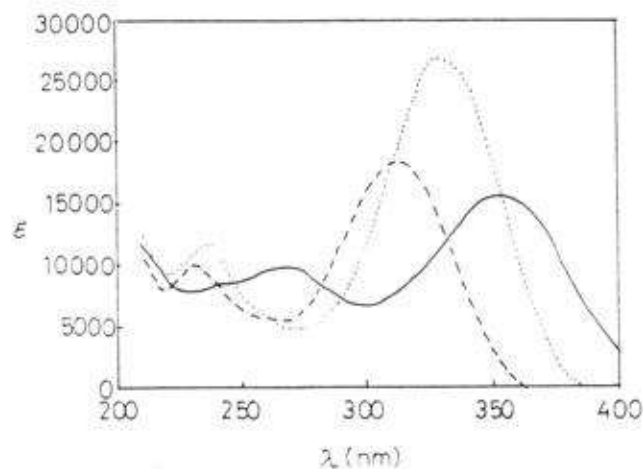


FIG. 6. Comparison of the electronic absorption spectra of (---) p-MeOPh and (—) p-NO₂ with that of (- - -) PhNPh nitrone in ethanol solvent.

The fact that the first absorption profile in the spectrum of diarylnitrone is the one that is affected by N-phenyl substitution elaborates upon our previous conclusion regarding the extent of conjugation in this class of compounds. The 1-phenyl nitrono moiety enjoys linear conjugation and is responsible for the absorption profile in the 350-290 nm region. MO computation of p-methoxy N-phenyl nitrono indicates that the first two ($\pi - \pi^*$) states are localized to considerable extent on the 1-aryl nitrono subsystem and show little charge transfer from the N-phenyl moiety. On the other hand, the short wave length profile does not show any major change both in band position and intensity upon p-methoxy substitution, suggesting that it originates from transitions localized to great extent on the n-phenyl subsystem.

p-Nitro substitution has perturbed the spectrum considerably, yet without changing the general assignment of the observed transitions. Perturbation due to a nitro group is known to be pronounced⁷ and may be interpreted by the stabilization due to resonance of this group.

Figure 7 presents the spectra of 1-styryl n-phenyl nitrono in ethanol as well as 1,2 dichloroethane, as solvents. Extending the conjugation between the nitrono group and the phenyl ring via the ethylene double bond leads to a dramatic change in the spectrum as compared to the spectrum of nitronos studied previously. The spectrum shows three main absorption profiles. The long wavelength band at 350 nm shows a considerable decrease in intensity and red shift ($\Delta\nu = 1013$) upon going from polar to non-polar solvent. The second absorption profile shows exactly the opposite trend, i.e. doubling of band intensity and a blue shift of 870 cm^{-1} . The 350 nm band can thus be interpreted as a conjugation transition which involves an excited state that is less polar than the ground state. MO computation indicated that the first ($\pi - \pi^*$)' state involves a considerable transfer of charge onto the N-phenyl ring. This migration of charge is opposite to the dipole moment vector and hence lowering the polarizability of the excited state. The second absorption profile encloses two transitions at 305 and 280 nm, which involve excited states localized to great extent on the styryl nitrono moiety with little perturbation by the N-phenyl ring. The third band system in the 250-210 nm region shows two peak maxima at 245 and 222 nm. One may thus summarize the effect of the ethylene linkage between the nitrono group and the phenyl ring by :

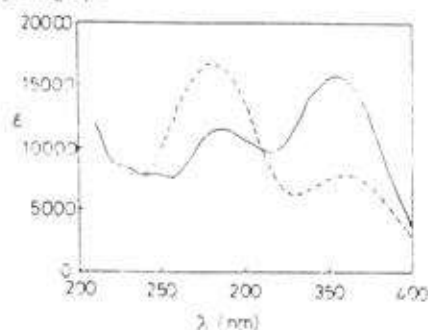


Fig. 7. Electronic absorption spectra of StyPh nitrono in (—) ethanol and (---) 1,2 dichloroethane.

1. A new band at 350 nm is generated which is absent in the spectra of aryl nitrones and is most probably due to intramolecular charge transfer transition.
2. In general, the intensity is reduced considerably compared to that in the spectra of aryl nitrones.

Table 2 presents band maxima, extinction coefficients, and transition probabilities for the observed transitions in the spectra of the studied nitrones.

TABLE 2. Band maxima, extinction coefficients and transition probabilities for the observed transitions in the spectra of the studied compounds in ethanol.

	ϵ_{\max}	λ_{\max}	$D_{if} \times 10^3$	$A_{if} \times 10^{-15}$	$B_{if} \times 10^{-17}$	$\tau \times 10^7$
PhNPh	319	19 000	4.6	11.1	8.0	0.9
	300	16 500	5.3	6.4	5.7	1.5
	237	8 500	68.2	0.6	1.2	15.2
	228	10 190	94.2	0.8	1.6	12.4
PhNMe	305	11 842	1.7	3.5	3.0	2.8
	290	17 894	3.7	6.5	6.5	1.5
	230	5 789	30.7	0.2	0.5	37.0
	224	7 368	48.4	0.4	0.8	25.4
p-MeOPh	337	27 586	0.1	28.0	18.0	0.3
	315	23 448	6.8	16.0	12.0	0.6
	238	11 628	1.3	1.3	2.2	8.0
	228	10 344	97.1	0.8	1.7	12.0
p-NO ₂ Ph	360	15 400	91.7	3.1	3.6	3.2
	335	12 000	49.6	1.4	0.9	7.4
	266	9 800	32.6	0.4	0.6	22.5
	245	8 600	19.0	0.2	0.5	49.3
StyPh	353	15 800	87.7	2.8	1.5	3.6
	305	10 200	31.6	6.5	0.6	15.4
	250	8 000	26.9	3.0	0.5	32.9
	245	7 600	15.6	1.7	0.5	60.2
	222	9 000	18.7	1.5	0.3	67.5

Spectral characteristics namely, transition probability of emission (A_{if}) and of absorption (B_{if}) and life time of excited states (τ) are determined using the expression

$$A_{if} = 7.24 \times 10^{10} (\nu^2) D_{if}$$

$$B_{if} = 14.5 \times 10^{24} D_{if}$$

$$\tau = 1 / A_{if}$$

Where the dipole strength D_{if} is given by

$$D_{if} = 3.98 \times 10^{-20} \int \nu \epsilon(\nu) d\nu$$

معالجة التركيب الإلكتروني والظيف الجزئي لمركبات الأريل نيسترون باستخدام نظرية الأفلاك الجزيئية

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للتلخيص - تمت دراسة التركيب الإلكتروني لبعض مركبات الأريل نيسترون باستخدام طريقة MNDO-MO ، وذلك لحساب شكل اهتزازي عند الأتزان وتوزيع الكثافة الإلكترونية في هذه الجزيئات . وقد تم التمسك ومناقشة الفروق في الخواص الإلكترونية المختلفة بين النيوترونات والأمينات المقارنة . وقد تم شرح وتحليل طيف الامتصاص الإلكتروني للمركبات المقروسة باستخدام نتائج حسابات الأفلاك الجزيئية . كما تم شرح تأثير المذيب على أساس التغير في توزيع كثافة الشحنة والتغير في عزم ثنائي القطب والتشاور الأفلاك الجزيئية . وقد أدت المقارنة بين طيف الامتصاص الإلكتروني للنيوترونات والأمينات المقابلة لها إلى استنتاجات خاصة بالفروق في التركيب الإلكتروني بين هاتين المجموعتين من مركبات .