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Note

Ultraviolet and Infrared Spectra of Some *p*-Nitrobenzyl Phenyl Ethers

A. M. G. Nassar, A. M. Hindawey, S. H. Etaiw, R. M. Issa*, and F. M. Issa*

Chemistry Department, Faculty of Science, Alexandria University, Alexandria, and *Tanta University Egypt

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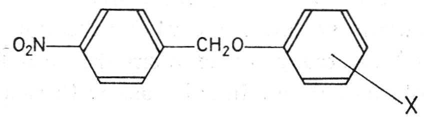
The UV-spectra of substituted *p*-nitrobenzyl phenyl ethers in ethanol and carbon tetrachloride were recorded. The effect of substitution on band position and intensity is correlated with the electronic nature of the group. The IR-spectra are analysed and the position of certain bands is discussed in terms of molecular structure.

INTRODUCTION

The UV-spectra of nitrobenzenes have been the subject of many investigations[1-4]. We have recently reported the electronic absorption spectra of some *p*-nitrobenzyl derivatives[5]. The present investigation is devoted to the study of UV- and IR-spectra of some *p*-nitrobenzyl phenyl ethers. Assignment of bands due to C. T. or to local excitation are studied. The important bands in the IR-spectra especially the nitro group were found to be sensitive to electronic nature of the substituent in the phenyl group.

EXPERIMENTAL

The *p*-nitrobenzyl phenyl ethers were prepared according to the method of Reid[6], and have the general formula:



X = H(I), p-CH_3(II), p-Cl(III), p-Br(IV), p-CHO(V), p-NO_2(VI), and o-NO_2(VII).

The UV-spectra were recorded on a UNICAM SP-800 spectrophotometer using 1 cm matched silica cells. The IR-spectra were measured on a UNICAM SP-200 spectrophotometer using KBr disc technique.

RESULTS AND DISCUSSION

The UV-spectra of the *p*-nitrobenzyl phenyl ethers in ethanol comprise three main absorption bands in the 210—325 nm region, while the spectrum of the unsubstituted compound (I) shows only two bands at 216 and 273 nm.

The broad band near 270 nm resembles that observed in the spectra of nitrobenzenes[3,4]. It could be considered as a complex band corresponding to

$^1L_a \leftarrow {}^1A$ transition of the phenyl ring and an intramolecular charge transfer (C. T.)$_1$ from the highest occupied orbital of the phenyl ring to the lowest unoccupied orbital of the nitro-group.

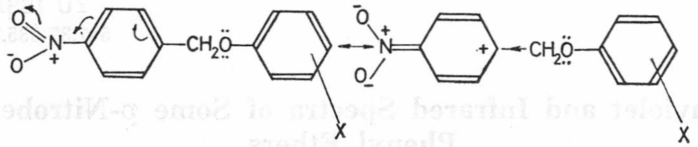


TABLE I

UV-Spectra Obtained in Ethanol and Carbon Tetrachloride Solutions[a]

Compound	Ethanol						CCl$_4$			
	^1L_a		^1L_b+(C. T.)$_1$		(C. T.)$_2$		^1L_b+(C. T.)$_1$		(C. T.)$_2$	
	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$
I	216	0.64	273	1.05	—	—	270	1.37	—	—
II	222	0.85	269	0.91	280	0.74	270	1.49	—	—
III	227	1.43	269	1.20	288	0.81	266	1.35	289	0.75
IV	227	1.50	268	1.31	289	0.77	265	1.32	291	0.55
V	219	1.78	276	3.03	284[b] 290	2.80 2.27	270	S	282[b] 290	S S
VI	220	0.84	264	0.92	300	1.37	—	—	288	S
VII	218	1.35	263	1.27	324	0.25	—	—	319	S

[a] λ_{max} in nm; ε_{max} in mol^{-1} cm^{-1} $\times 10^{-4}$, S saturated solution used; — not apparent.

[b] $\pi - \pi^*$ transition of the C = O group.

A support for the C. T. origin of the band could be obtained from the calculation of the energy of C. T. in CCl$_4$ solutions[5], where the observed values agreed well with the calculated ones, except for compounds (II), (VI) and (VII). This could be attributed to strong antagonism through the molecule since the phenyl group acts mainly as a donor in this case with respect to the nitro group.

Compound	$E_{C.T.}$/eV Calcd.	Obsd.
I	5.05	4.65
II	4.62	4.59
III	4.87	4.67
IV	4.78	4.68
V	5.33	4.59
VI	5.72	4.70*
VII	5.72	4.72*

* Using data from ethanol.

The complexity of the substituted phenyl, XC_6H_4—O—CH_2—, portion renders the $\pi - \pi^*$ and $(^1B_{2u} \leftarrow {}^1A_{1g})$ transition appear submerged under the more intense band, while the longer wavelength band, 280—323 nm appears as a shoulder. It is presumably of the $n - \pi^*$ type involving the transition of a n-electron from the highest nonbonding molecular orbital of the oxygen atom to the lowest antibonding π^* molecular orbital of the phenyl ring.

The spectrum of the compound (V) containing a *p*-aldehyde group comprises four absorption bands, the new band located at 284 nm probably due to the $\pi - \pi^*$ transition of the C=O group.

Interesting changes in the IR-spectra are those with the NO_2 and C—O—C stretching bands. Two strong bands were observed near 1520 and 1350 cm^{-1} regions, corresponding to the asymmetric and symmetric stretching vibrations of the nitro group, respectively. The asymmetric band was found to shift to a lower frequency as the electron acceptor character of the substituent increases. On the other hand, the asymmetric and symmetric stretching vibrations of the C—O—C link observed near 1250 and 1050 cm^{-1}, respectively, shifted to a higher frequency on increasing the acceptor character of the substituent X. In the case of the compound (VII), the presence of an *ortho*-nitro group to the C—O—C link results in splitting of the ether band into two medium bands laying at 1256 and 1275 cm^{-1}. This doublet structure is in accordance with previous observations[7].

TABLE II

Some Important IR-Frequencies (in cm^{-1}) of Substituted p-*Nitrobenzyl Phenyl Ethers*

I	II	III	IV	V	VI	VII	Assignment
1538	1525	1532	1531	1522	1520	1523	NO_2 asym. str.
1356	1354	1358	1354	1357	1358	1349	NO_2 sym. str.
1224	1245	1258	1255	1260	1270	1275 1256	C—O asym. str.
1012	1070	1060	1030	1042	1050	1030	C—O sym. str.
1118	1178	1175	1176	1166	1180	1166	C—N str.

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SAŽETAK

Ultraljubičasti i infracrveni spektri nekih *p*-nitrobenzil fenil etera

A. M. G. Nassar, A. H. Hindawey, S. H. Etaiw, R. M. Issa, and F. M. Issa

Snimljeni su ultraljubičasti spektri otopina *p*-nitrobenzil fenil etera u etanolu i tetraklorugljiku. Utvrđena je korelacija između utjecaja supstituenata na položaj i intenzitet apsorpcijskih vrpci i elektronske naravi skupina. Na temelju položaja karakterističnih vrpci u infracrvenim spektrima analizirana je molekulska struktura.

CHEMISTRY DEPARTMENT
FACULTY OF SCIENCE
ALEXANDRIA UNIVERSITY
ALEXANDRIA, EGYPT

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