

THE ABSORPTION SPECTRA OF SOME 4(3H) QUINAZOLINONES

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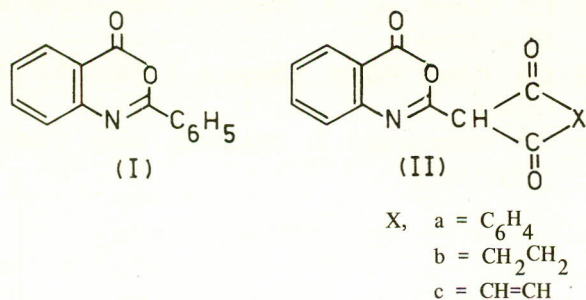
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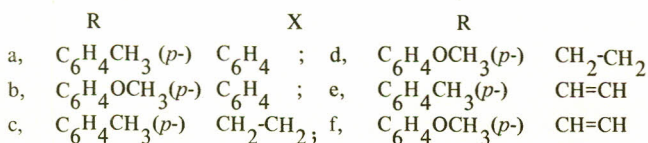
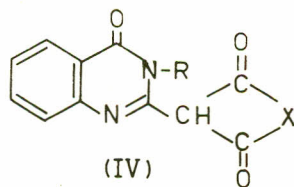
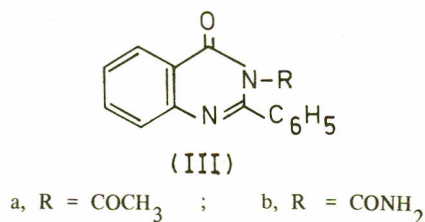
Electronic absorption spectra of 2-phthalonyl-4H-3,1-benzoxazin-4-one and various 4(3H)-quinazolinones have been taken at room temperature in different organic solvents. Spectral changes due to substitution and change of solvent are interpreted in relation to molecular structure. The important bands in the IR spectra are assigned and discussed in relation to molecular structures.

INTRODUCTION

The preparation of some 2-substituted-4H-3,1-benzoxazin-4-ones (I and II) were previously reported [1,2].

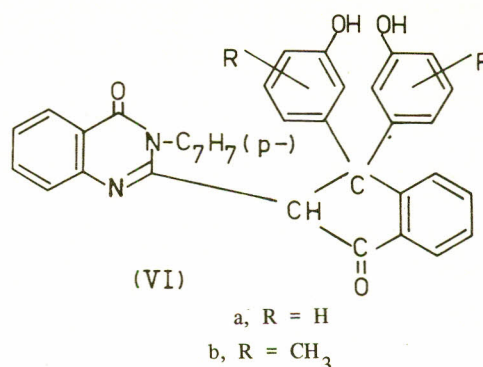
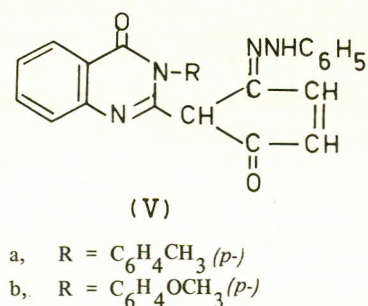


Condensation of I and II with some amines gives the corresponding 2,3-disubstituted 4(3H) quinazolinones (IIIa, b) and (IVa-f) [3,4].



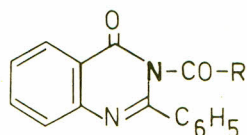
The condensation of IVe, f with phenylhydrazine gives the corresponding monophenylhydrazones (Va, b) [5].

Moreover, the condensation of IV with phenol and/or *p*-cresol gives the corresponding condensation products (VIa, b).



The condensation of (IIIa, b) with aromatic aldehydes gives the corresponding 2,3-disubstituted 4(3H) quinazolinones (VIIa-k). The structure of compounds VII were confirmed by the following assignments:

(i) IR spectral studies. (ii) The ¹H-NMR spectrum of compound VIIa, using DMSO as solvent, shows the following assignments: A singlet at δ = 6.0 ppm corresponding to 2H (CH=CH-). Multiplet at δ = 7.1-8.0 ppm corresponding to 14 H (aromatic and quinazolone protons).



(VII)

- | | | |
|--|---|--|
| R | | R |
| a. CH=CH-C ₆ H ₅ | ; | g. CH=CH-C ₄ H ₃ O (furyl) |
| b. CH=CH-C ₆ H ₄ OCH ₃ (<i>p</i> -) | ; | h. N=CH-C ₆ H ₅ |
| c. CH=CH-C ₆ H ₄ OH (<i>p</i> -) | ; | i. N=CH-C ₆ H ₄ OCH ₃ (<i>p</i> -) |
| d. CH=CH-C ₆ H ₄ OH (<i>o</i> -) | ; | j. N=CH-C ₆ H ₄ OH (<i>o</i> -) |
| e. CH=CH-C ₆ H ₃ -O ₂ CH ₂ 3;4 | ; | k. N=CH-C ₄ H ₃ O |
| f. CH=CH-C ₆ H ₄ -N(CH ₃) ₂ | | |

RESULTS AND DISCUSSION

The products were prepared and crystallized several times from the appropriate solvents. The solvents used for spectral measurements were purified by recommended procedures [6]. The absorption spectra in the UV and visible regions were recorded on a Unicam SP 8000 spectrophotometer using 1.0 cm matched silica cells. The IR spectra were scanned by means of a Unicam SP 1200 IR spectrophotometer using the KBr disc technique.

(A) *Band Assignment and Substituent Effect.* The UV spectra of 4(3H) quinazolinones in ethanol, Table 1, exhibit three absorption bands in 205–305 nm region. The bands due to possible transitions within the present compounds would be a combination of electronic substituents at position 2.

The UV spectra of 2-phenyl-4(3H) quinazolinones in ethanol showed five absorption bands. The two bands lying at 219 and 237 nm region correspond to $1L_a$ of the phenyl ring and to $\pi-\pi^*$ transition of quinazolinones nucleus respectively. The third band at 287 nm is composite one consisting of two overlapping transitions and is assigned to $1L_b$ and $\pi-\pi^*$ transition of the carbonyl group. The two bands at 305 and 322 nm can be assigned to two types of intermolecular charge transfer (C.T.) with the molecule. On the other hand the UV spectra of 2-phenyl-5 nitro-indan-1:3-dione in ethanol exhibits four absorption bands. The first two bands at 230 and 245 nm correspond to transitions $1L$ and $1L_b$ states respectively [7]. The third band was observed at 290 nm attributable to $\pi-\pi^*$ transition of the carbonyl group, while the charge transfer band appears at 370 nm. Thus, the first band lying in 206–220 nm region, in the spectra of 4(3H) quinazolinones can be assigned to $1L$ transition. The band in most cases, was not affected by changing the substituent of position 2 and 3. The band located within 235–241 nm region is a composite one consisting of two bands and is characterised by high excitation values. The band is due to the local transitions, and may be assigned to transition of $1L_b$ state overlapping with the $\pi-\pi^*$ transition of the quinazolinones nucleus.

The broad band at the longer wavelength side appears near 300 nm. The band splits into two bands lying near 272 and 300 nm in the spectra of IIa and Va, b. Thus, the band corresponds to two types of transitions. The band near 272 nm can be assigned to $\pi-\pi^*$ transition of

Table 1. UV Absorption spectra of IIa and IV-VI(in ethanol).

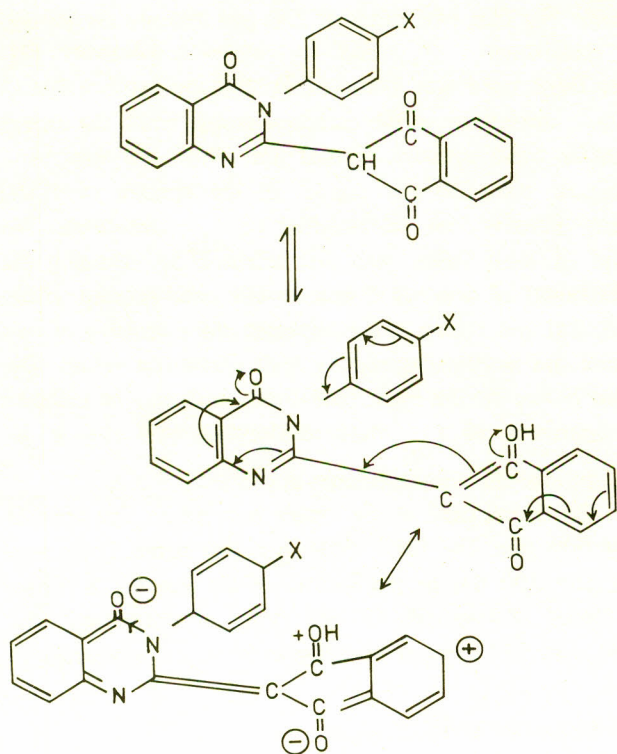
Compound	$1L_a$		$1L_b + \pi-\pi^*$ trans. of Quinaz.		$\pi-\pi^*$ trans. of C=O + C.T.	
	λ max.	ϵ max. 10^{-4}	λ max.	ϵ max. 10^{-4}	λ max.	ϵ max. 10^{-4}
IIa	225	4.31	231,264	4.01	273-314 ^b	2.31-2.70
IVa	220	5.60	235 ^b	5.14	298 ^b	0.53
IVb	206	2.01	236 ^b	3.41	300 ^b	2.01
IVc	206	1.88	236 ^b	2.29	292 ^b	0.44
IVd	206	1.28	236 ^b	2.15	291 ^b	0.58
IVe	206	1.45	236 ^b	1.89	291 ^b	0.44
Va	207	2.47	238 ^b	1.63	272 ^b -300 ^{sh}	2.47-0.93
Vb	210	2.02	241 ^b	2.34	275 ^b -305 ^{sh}	2.24-0.79
VIa	215	2.61	235 ^b	2.72	290 ^b	0.87
VIb	206	2.12	236 ^b	2.51	290 ^b	0.56

b= broad; sh= shoulder; λ max. in nm; ϵ max. in $\text{cm}^2 \text{mole}^{-1}$

the carbonyl group. The $\pi-\pi^*$ transition of the carbonyl group at position 4 is influenced by C.T. from donor systems at position 2 and 3.

All compounds display keto-enol tautomerism. The enol form favours the C.T. to the carbonyl group at position 4. The band position is affected by changing the nature of the substituent at position 2 and 3.

The last band lying near 300 nm can be attributed to C.T. within the whole molecule. The C.T. band originates mainly from the substituents at position 2 and 3 to the carbonyl group at position 4 acting as acceptor. The C.T.



from the substituent at position 2 to the carbonyl group at position 4 is antagonised by the C.T. from the substituent at position 3. The band is the net resultant of the two types of C.T.

(B) *Solvent Effect* [8]. Intramolecular C.T. bands are solvent sensitive, while locally excited bands are relatively insensitive to change of solvent. The spectra in different organic solvents are shown in Table 2. Practically, no shift occurs due to change of solvent from cyclohexane, ether to ethanol for the 1L_a band. The 1L_b band is slightly shifted in ether than ethanol and cyclohexane. The band at longer wavelength, located near 300 nm shows some solvent dependence. The magnitude of red shift goes in the order: ether > chloroform > ethanol > carbon tetrachloride = cyclohexane.

The shift is not only due to the dipole-dielectric interaction, but also due to hydrogen bonding, which is usually much stronger than the dielectric stabilization. Thus, the observed shift would be the resultant of the shift due to the increased polarity of the medium and blue shift due to the intermolecular hydrogen bond formation between the solute molecule and the solvent molecules.

(C) *IR Spectra*. The spectra of compounds under investigation were reported to the extent that appears possible. IR spectra are recorded within the 4000–650 cm^{-1} region, Tables 3,4. The spectra show a broad band in the 3400–3270 cm^{-1} region (for compounds II, IV–VI) corresponding to the stretching vibrations of the OH group which appears due to keto-enol tautomerism. Also, a strong band is observed in the spectra of Va, b due to the stretching vibration of the NH group. The spectra exhibit four bands near 1700, 1680, 1630 and 1610 cm^{-1} . These bands correspond to the ν C=O, the ν C=N and the ν C=C

Table 2. UV Absorption spectra of IV–VI (in different solvents).

Compound*	Ether			CHCl_3 C.T.	CCl_4 C.T.	Cyclohexane		
	1L_a	1L_b	C.T.			1L_a	1L_b	C.T.
IVa	215	236	298	293	290	217	238	290
IVb	208	240	310	305	304	207	233	300
IVc	208	241	298	295	294	208	232	290
IVd	208	240	309	306	298	208	236	298
IVe	209	242	298	294	290	207	237	289
Va	208	242	290 ^b	276-300	275	207	235	275
VIa	215	235 ^b	295	285	297	217	240 ^b	281
VIb	207	241	298	295 ^b	296	206	236	291

* Saturated solution; λ max. in nm.

Table 3. Solid state IR data for IIa and IV-VI (KBr cm^{-1}).

IIa	IVa	IVb	IVc	IVd	IVe	Va	Vb	VIa	VIb	Band Assign
3400 ^b		3270 ^s	3270 ^s	3280 ^s	3370 ^s	3320 ^s	3320 ^s	3400 ^b	3400 ^b	ν OH
1700 ^{vs}	1700 ^{vs}			1685 ^s	1690 ^m	3260 ^s	3270 ^s	1705 ^s	1695 ^s	ν NH
1680 ^{sh}	1663 ^{sh}	1660 ^m	1655 ^{sh}	1655 ^{sh}		1680 ^s	1682 ^b	1665 ^b		ν C=O
1640 ^m		1635 ^{sh}	1630 ^{sh}		1638 ^{sh}	1670 ^{sh}		1665 ^b	1632 ^{sh}	ν C=O
1610 ^s	1610 ^{sh}	1615 ^w	1610 ^s	1610 ^s	1610 ^{sh}	1635 ^{sh}	1635 ^{sh}		1610 ^w	ν C=N
*1600 ^s	1600 ^w	1595 ^w		1595 ^m	1600 ^{sh}	1605 ^{vs}	1600 ^s	1605 ^s		ν C=C ethyl
*1595 ^s		1575 ^s	1575 ^s	1580 ^s	1580 ^{vs}	1585 ^s	1580 ^s		1580 ^{vs}	Quinazol.I
*1510 ^s	1510 ^s	1510 ^s	1510 ^s	1510 ^s	1510 ^s	1495 ^{vs}	1490 ^{vs}	1500 ^s	1510 ^{vs}	Quinazol.II
	1330 ^m	1300 ^s	1310 ^m	1300 ^s	1315 ^s	1305 ^s	1315 ^m	1310 ^m	1308 ^{sh}	Quinazol.III
1115 ^s	1095 ^m	1105 ^{vs}	1095 ^s	1100 ^{vs}	1095 ^{vs}	1100 ^w	1100 ^w	1120 ^w	1095 ^{vs}	ν C=N
								882 ^m	910 ^m	ν C-C
	820 ^s	825 ^{vs}	820 ^s	823 ^{vs}	825 ^s	855 ^s	855 ^s		825 ^s	γ C-H ¹
								820 ^s		γ C-H ²
										γ C-H ³
755 ^s	770 ^{vs}	730 ^s	735 ^m	730 ^{vs}	735 ^m	775 ^{vs}	770 ^{vs}	765 ^s	740 ^m	γ C-H ⁴
						740 ^{vs}	755 ^{vs}			γ C-H ⁵
						700 ^{vs}	695 ^s			γ C-H ⁵

Intensity of bands is given in : vs = very strong ; s = strong ; m = medium b = broad ; sh = shoulder ; w = weak.

*Benzoxazone I, II and III

1-5 are the number of adjacent ring hydrogen atoms.

Table 4. IR Spectral data of compounds VII (KBr cm^{-1})

Compound	ν C=O		ν C=N	Quinazolone			ν C-N
	hetero	side chain		I	II	III	
VIIIa	1660 ^{vs}	1700 ^{sh}	1615 ^m	1605 ^s	1530 ^m	1490 ^{sh}	1330 ^m
VIIIb	1680 ^s	1705 ^{sh}	1610 ^s	1595 ^m	1530 ^s	1490 ^{sh}	1320 ^m
VIIIc	1660 ^s	1690 ^s	1615 ^m	1600 ^{sh}	1525 ^{sh}	1495 ^m	1320 ^m
VIIId	1665 ^{vs}	1690 ^{sh}	1610 ^m	1605 ^{sh}	1530 ^s	1500 ^m	1330 ^m
VIIe	1660 ^s	1680 ^{sh}	1615 ^s	1605 ^{sh}	1525 ^m	1495 ^m	1325 ^m
VIIIf	1665 ^s	1680 ^{sh}	1620 ^m	1600 ^s	1525 ^s	1500 ^m	1320 ^m
VIIg	1670 ^{vs}	1690 ^{sh}	1615 ^m	1600 ^s	1525 ^m	1490 ^m	1315 ^m
VIIIh	1660 ^{vs}	1700 ^s	1620 ^m	1595 ^{vs}	1530 ^m	1490 ^m	1330 ^m
VIIIi	1665 ^s	1680 ^{sh}	1620 ^{sh}	1600 ^{vs}	1525 ^m	1500 ^w	1325 ^m
VIIIj	1670 ^s	1690 ^s	1615 ^s	1600 ^{sh}	1525 ^s	1490 ^s	1320 ^m
VIIIk	1670 ^{vs}	1685 ^{sh}	1620 ^m	1595 ^s	1530 ^m	1500 ^{sh}	1325 ^m

ethylenic respectively. In the spectra of some compounds, these bands appears as a broad band or as a shoulder.

There are three distinct strong bands in the 1600-1500 cm^{-1} region. These are due to skeletal vibrations of the quinazolone or benzoxazone nucleus [9]. A medium to strong band appears near 1300 cm^{-1} attributable to ν C-N, while ν C-C absorbs near 1100 cm^{-1} . The out of plane deformation frequencies for aromatic and aliphatic C-H

bands are expected in the 1000-850 cm^{-1} region.

Table 4, represents the characteristic features of the IR spectra for compounds VII.

EXPERIMENTAL

Action of Phenylhydrazine on IVe, f. A solution of IVe and/or IVf (0.01 mole) and phenylhydrazine (1.1 g;

Table 5. Compounds Va, b; VIa, b and VIIa-k.

Compound	M.P.	Formula (Mol. wt.)	Analysis % (Calcd./Found)		
			C	H	N
Va	209	$C_{26}H_{20}N_4O_2$	74.06	4.79	13.33
		(420)	73.98	5.00	13.09
Vb	214-15	$C_{26}H_{20}N_4O_3$	71.56	4.59	12.84
		(436)	71.20	4.73	12.47
VIa	218-20	$C_{36}H_{26}N_2O_4$	78.53	4.76	5.09
		(550)	78.12	5.03	5.17
VIb	246	$C_{38}H_{30}N_2O_4$	78.89	5.19	4.84
		(578)	78.67	5.36	4.92
VIIa	230	$C_{23}H_{16}N_2O_2$	78.41	4.55	7.95
		(352)	78.20	4.63	8.14
VIIb	236	$C_{24}H_{18}N_2O_3$	75.39	4.71	7.33
		(382)	75.01	4.99	7.30
VIIc	265	$C_{23}H_{16}N_2O_3$	75.00	4.35	7.61
		(368)	74.86	4.61	7.94
VIId	234	$C_{23}H_{16}N_2O_3$	75.00	4.55	7.62
		(368)	75.04	4.59	7.62
VIIe	243	$C_{24}H_{16}N_2O_4$	72.73	4.04	7.07
		(396)	72.39	4.36	7.41
VIIf	226-27	$C_{25}H_{21}N_3O_2$	75.95	5.32	10.63
		(395)	75.66	5.51	10.99
VIIg	248	$C_{21}H_{14}N_2O_3$	73.68	4.09	8.19
		(342)	73.36	4.42	8.20
VIIh	236	$C_{22}H_{15}N_3O_2$	74.97	4.25	11.99
		(353)	74.51	4.55	12.29
VIIi	224	$C_{23}H_{17}N_3O_3$	72.06	4.44	10.97
		(383)	72.00	4.67	11.21
VIIj	230	$C_{22}H_{15}N_3O_3$	71.29	4.32	11.60
		(369)	71.09	4.06	11.22
VIIk	240	$C_{20}H_{13}N_3O_3$	69.97	3.79	13.99
		(343)	70.10	4.11	13.82

All melting points are not corrected.

0.01 mole) in 30 ml ethyl alcohol was heated under reflux for 5 hr. The yellow products separated on cooling, were crystallized from ethyl alcohol to give the corresponding monohydrazones (Va, b). Yield 60–65 %. The results are listed in Table 5.

Condensation of IVa with Phenols. A mixture of IVa (3.8 g; 0.01 mole), and phenol and/or *p*-cresol (0.02 mole) and zinc chloride 0.5 g, was heated in an oil bath at 170–180 for 5 hr. The product obtained was crystallized from ethyl alcohol to give the yellow crystalline products

(VIa, b). Yield is almost quantitative. The data are given in Table 5.

Reaction of (III) with Aromatic Aldehydes. A mixture of (IIIa or b) [3] (0.01 mole), the appropriate aromatic aldehyde (0.015 mole), and 0.5 g zinc chloride, was heated in an oil-bath for 5 hr at 180°. The solid obtained was washed with hot water. The crystalline products obtained were recrystallized from ethanol. Yield is almost quantitative. The results are listed in Table 5.

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