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INFRARED SPECTROSCOPIC INVESTIGATION OF SOME ACETANILIDE DERIVATIVES

By

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INFRARED SPECTROSCOPIC INVESTIGATION OF SOME ACETANILIDE DERIVATIVES

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SUMMARY

The infrared spectra as KBr disc of ring substituted acetanilides were recorded. The important bonds were assigned to their modes of vibration. The effects of substituents on the ν_{NH}, Amide I, Amide II and δasy. CH_3 are investigated. The free energy relations are given. The results indicate the coplanarity of the molecules.

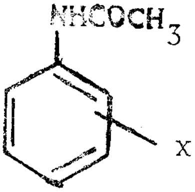
INTRODUCTION

Acetanilides are used as antipyretic and analgesics to lower the temperature of a fever and for relief of headaches and neuralgic pains. Acetanilide (antifebrin) is liable to exert a toxic action by the gradual liberation of aniline in the system, and for this reason, it has been largely replaced by p-ethoxyacetanilide (phenacetin) [1,2]. The NMR absorption spectra of several substituted acetanilides were reported [3,4]. The δ_{CH3} and δ_{NH} were correlated to the hammett constant. Several IR investigations were devoted to study the tautomeric structures of some amides and related compounds [5].

The present investigation is a systematic study of the of substituent on the IR-absorption spectra of some substituted acetanilides.

EXPERIMENTAL

The substituted acetanilides were prepared by acetylation of the corresponding amines using the previously described method [6]. The resulting compounds were crystalized to constant m.p. C. The following acetanilides were prepared.



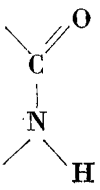
where x = H(a). o—Cl(b), m—Cl(c), p—Cl(d), p—Br(e), o—CH_3(f), m—CH_3(g), p—CH_3(h), o—OCH_3(i), m—OCH_3(j), p—OCH_3(k), o—NO_2(l), m—NO_2(m), p—NO_2(n), o—COOH(o), m—COOH(p), p—COOH(q), p—$N(CH_3)_2$(r), 2,4—diCl(s) and p—$COCH_3$(t).

The infrared spectra were obtained using the KBr disc technique with the aid of a PYE UNICAM SP 1000 infrared spectrophotometer.

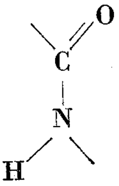
RESULTS AND DISCUSSION

Amides may be characterized by means of the absorption bands due to the N—H nd C=O stretching vibrations, N—H deformations and due to certain mixed vibrations (amide bands). The amide I band is essentially due to C=O stretching. The amide II and is essentially due to N-H bending and C—N stretching in the case of secondary amides. The important group frequencies of different acetanilides listed in Table (1).

The presence of a nitrogen atom in molecule often results in conjugation because of the lone pair electrons of the nitrogen atom. The important group frequencies of amines are those associated with the NH stretching, N—H deformation ana C—N stretching vibrations while primary amines show two absorption bands in the region 3500—3300 cm^{-1} due to asymmetric and symmetric stretching vibrations of the NH_2 group [7]. Secondary amines show only a single NH stretching band in the range 3500—3300 cm^{-1}. Russell and Thompson [8] have investigated the intensity and frequency of N—H stretching vibrations in a number of secondary amines and have found that both are very sensitive to structural changes. The band is found in the range 3350—3310 cm^{-1} in aliphatic secondary amines and $\sim$ 3450 cm^{-1} in alkyl aryl amines. Just like primary amines simple primary amides exhibit two broad bands around 3350—3180 cm^{-1}. The twin bands have been assigned to the cis and trans-rotational isomers [9] thus,



Cis



trans

The acetanilides under investigation display mostly two bands in the region 3360—3230 cm^{-1} and 3270—3230 cm^{-1} which may be assigned to υ_{NH} stretching frequency (Table 1).

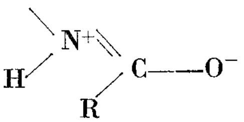
The band in the region 1550—1515 cm^{-1} is due to the (δ_{NH}) deformation vibration of the NH group (Amide II band).

Bands due to the C—H stretching modes of alkanes are found in the region 3000—2850 cm^{-1} [10]. Fox and Martin [11] have found that two strong bands appear at 2962 ± 10 and 2872 ± 10 cm^{-1} in hydrocarbons containing methyl groups due to the asymmetrical and symmetrical stretching modes of methyl group. The acetanilides display two bands in the regions 2990—2950 and 2870—2820 cm^{-1} (Table 1) which may be assigned to ν_{CH_3} asym and ν_{CH_3} sym. For compounds f, g, h, j, k, r and t another band was observed in the region 2950—2910 which may be attributed to the second CH_3 group on the ring as substituent or part of. The asymmetrical CH_3 deformation band is found in the region 1480—1448 cm^{-1} while the band in the region 1277—1238 cm^{-1} was assigned to the symmetrical CH_3 deformation band.

The bands due to the asymmetric and symmetric stretching vibration of the aromatic CH were observed in the region 3130—3080 and 3080—3030 cm^{-1} respectively.

Weak absorption bands are observed in the region 1200—970 cm^{-1} which are assigned to C—H in-plane-deformation in the benzene ring (δ CH∅). These bands are not very useful for structural studies. Intense absorption bands are observed in the 900—700 cm^{1-} region due to the C—H out of -plane deformation vibration (γ CH∅). These vibrations are highly characteristic of the substitution type in the benzene rings.

The carbonyl group is the most useful and effective available for characterization and structural analysis. The carbonyl stretching vibration is highly localized and can be identified by the strong absorption in the region 1900—1580 cm^{-1}. Primary amides show the carbonyl absorption near 1650 cm^{-1}. The relatively low C=O frequency in amide is due to the importance of the resonance forms of the type.



1650 cm^{-1}, however another band at lower wave number was observed in the region 1697—1665 cm^{-1}.

Effect of substituents.

The effect of substitution on the benzene ring on the band position in the ir-spectra of the mono-substituted acetanilide was investigaed applying the free energy relation:

$$\bar{\upsilon}_X = \bar{\upsilon}_H + \rho\sigma_X$$

The relations between the Hammett constant (σ) and the absorption bands due to the υ_{NH}, amide I band, Amide II band and δasym. CH_3 were investigated and the regressions representing the straight lines are:

$$\bar{\upsilon}_{x(NH)} = 3250 + 65\,\sigma_X \qquad (1)$$

$$\bar{\upsilon}_{(Amide\ I)} = 1659 + 22.1\sigma_X \qquad (2)$$

$$\bar{\upsilon}_{(Amide\ II)} = 1552 + 31.6\,\sigma_X \qquad (3)$$

$$\bar{\upsilon}_{\delta asy.CH_3} = 1460 + 40.3\sigma_X \qquad (4)$$

The correlation coefficients (r) amounts to 0.96, 0.93, 0.93 and 0.96 for the four bands respectively. The standard deviation as calculated from the least squares method [12] amount to 7.5, 3.7, 4.7 and 3.5 cm^{-1} respectively.

From the results obtained it can be concluded that the substituents exert their normal action to the ring, NH, C=O and CH_3 groups. This may be taken as the coplanarity of the acteanilide molecules and the action of the nitrogen atom as conductor through the lone pair of electrons.

Table 1 Important Infrared Absorption Bands of Acetanilides.

	X	νNH	νCH ∅ asym.	νCH ∅ sym.	νCH_3 asym	νCH_3 sym	C=O Amide	σNH Amide II	σCH_3 asym.	σCH_3 asym.
a	H	3280 ,3240	3080	3040	2950	2840	1658	1525	1465	1262
b	o–Cl	3270 ,3250	3090	3040	a	a	1660	1530	1470	a
c	m—Cl	3290 ,3260	3110	3050	2970	2860	1672	1535	1478	1265
d	p—Cl	3300 ,3270	3110	3060	a	a	1672 ,1665	1535	1468	1260
e	p—Br	3280 ,3230	3110	3030	a	a	1670	1535	1465	1265
f	o—CH_3	3270 ,3230	3090	3030	2970 ,2930	2850	1655	1525	1458	1270
g	m—CH_3	3290 ,3250	3130	3070	2970 ,2920	2860	1660	1520	1460*	1260
h	p—CH_3	3300 ,3250	3130	3070	2980 ,2930	2860	1662	1515	1450	1265
i	o—OCH_3	3260 ,3240	3110	3050	2960	2860	1652	1525	1410	1258
j	m—OCH_3	3295 ,3250	3120	3080	2970 ,2930	2850	1657	1515	1450*	1252
k	p—OCH_3	3260 ,3230*	3110	3070	2990 ,2950	2830	1650 ,1638	1515	1448*	1246
l	o—NO_2	3260 ,—	3110	3060	2960	2840	1705* ,1697	1535	—	1277
m	m—NO_2	3300 ,3270	3090	3050	2960	2870	1685 ,*1672	1545	1478	1273
n	p—NO_2	3300 ,3270	3100	3040	2960	2870	1690 ,*1677	1547	a	1268
o	o—COOH	3200^X	—	—	a	a	1688	a	a	a
p	m—COOH	3230	—	—	a	a	1703	a	a	1270
q	p—COOH	3300	—	—	a	a	1685 ,1675	a	a	1265
r	p—$N(CH_3)_2$	3270 ,3230	3100	3040	2960 ,2910	2820	1685 ,1645	1515	1448	1238
s	2,4—diCl	3290 ,3260	3090	3030	2960	2850	1690	1535	1473	1263
t	p—$COOH_3$	3310 ,3260	3100	3060	2970 ,2930	2865	1670 ,1675 ,1668*	1535	1480	1275

a: not detectable, *Shoulder-mashed by νOH broad band with 3100—2400 cm–1 indicates strong intermolecular hydrogen bonding
X O-COOH chelated with NH group in the intermolecular hydrogen bonding.

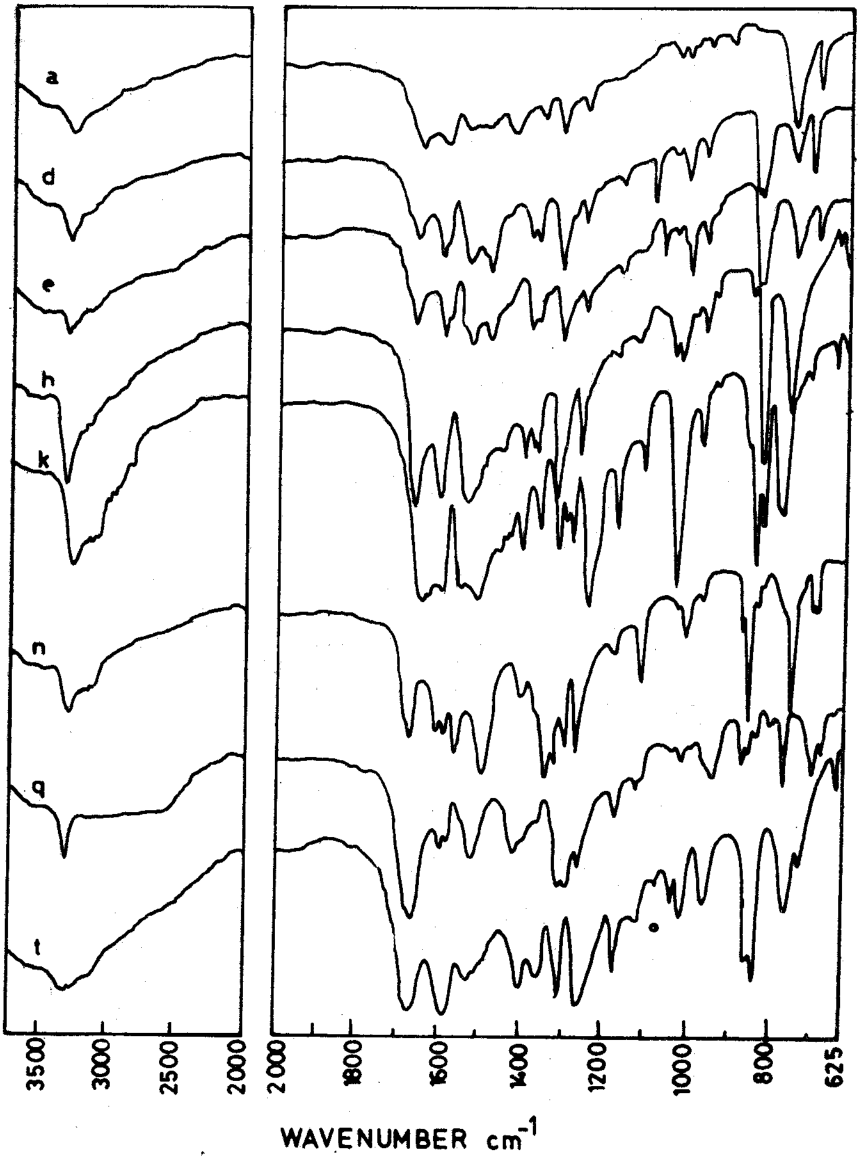

a
d
e
h
k
n
q
t
3500
3000
2500
2000
2000
1800
1600
1400
1200
1000
800
625
WAVENUMBER cm^{-1}

Fig (1)

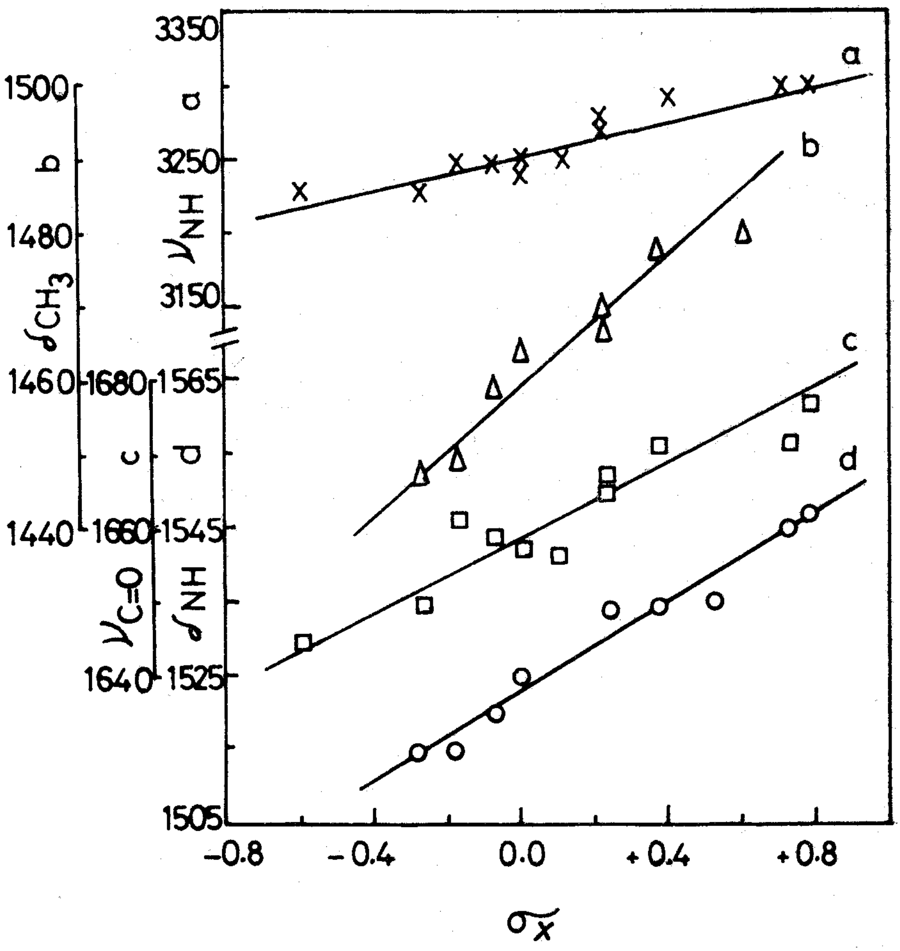

3350
3250
3150
1500
1480
1460
1440
1680
1660
1640
1565
1545
1525
1505
a
b
c
d
δCH_3
$\nu_{C=O}$
ν_{NH}
δ_{NH}
−0.8
− 0.4
0.0
+ 0.4
+ 0.8
σ_x

Fig (2)

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