

FTIR spectroscopic studies and AM1 semi-empirical calculations of some hydrogen-bonded complexes of 2,5-dihydroxy-3,6-dichlorobenzoquinone and anilines

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Abstract. Fourier transform infrared (FTIR) spectra of a series of 1 : 1 hydrogen-bonded complexes between 2,5-dihydroxy-3,6-dichlorobenzoquinone (chloranilic acid, CA) and anilines in the crystalline form were investigated. The correlation between the center of gravity of the protonic vibration bands (ν_{cg} , cm^{-1}) and the calculated proton affinities of the investigated anilines (PA, kcal/mol) as well as the Hammett substituent constants, (σ_{H}) were presented. A deep minimum was located at PA = 210–211 kcal/mol and $\sigma_{\text{H}} = 0.1$ suggesting the existence of a critical behavior. The semi-empirical quantum mechanical method, AM1 was utilized to correlate the experimental FTIR data. The obtained data showed a reasonable consistency with the experimental results. An intersection point was recorded at PA = 210–211 kcal/mol in the correlations between the oxygen and nitrogen atomic charges, (q_{O} and q_{N} , esu), the OH and NH bond distances (R_{OH} and R_{NH} , Å) and PA values of the substituted anilines. The strict correlation between the experimental and the calculated results confirmed the validity of the AM1 semi-empirical method for studying chloranilic acid – anilines hydrogen-bonded complexes.

1. Introduction

Intra- and intermolecular proton transfer reactions are among the most common and fundamental chemical processes [1–6]. They play a significant role in both inorganic and organic/biochemical reaction mechanisms. Because of the great experimental difficulty related to the study of this topic, especially in the gas phase, ab initio quantum mechanical calculations [7–9] and semi-empirical methods are employed as a valuable source of information's to address the problems of hydrogen bond formation [10–12]. The MNDO – PM3 and AM1 procedures are the modified of MNDO methods which able to describe the structure of the hydrogen-bonded complexes. The AM1 method is applied satisfactorily in many hydrogen-bonded systems specially in pentachlorophenol and dihydroxybenzoquinone–amine systems [13–15]. It is known however, that the quality of semi-empirical results depends on the nature of the investigated system and its chemical properties which are the targets of the study. For such reasons, these methods need to be extensively tested before employed with confidence.

Consequently, the aim of the present contribution was to test the AM1 method through its correlation with the FTIR spectral data of an interesting hydrogen-bonded complexes between chloranilic acid and

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anilines. The wide applications of quinones [16–19] encouraged us to study such correlation. An important aim of this work was studying the influences of the chemical substitution on the proton transfer process and the strength of the hydrogen bond from the experimental and theoretical points of view. The PA is a direct measure of the Bronsted base strength of the molecule and it was used as a basicity scale in many hydrogen-bonded systems [20,21]. Thus, the present investigation was devoted to calculate the proton affinities of the studied anilines by using AM1 approach and using it as a basicity scale in the system under investigation.

2. Experimental

Chloranilic acid, acetonitrile and the solid anilines were of spectroscopic grade. Liquid anilines were dried over KOH and double distilled through a 25-cm fractionating column shortly before use and stored in brown bottles. The crystalline complexes of CA with different anilines were prepared by precipitation from equimolar solution of the components in acetonitrile. The stoichiometry of the complexes were confirmed by carbon, hydrogen and nitrogen elemental analyses. These analyses provided that 1 : 1 solid complexes were formed. FTIR spectra of the solid complexes were recorded on a Perkin Elmer Paragon 1000 Spectrophotometer with a resolution power of 4 cm^{-1} in KBr pellets. The used KBr was Perkin–Elmer IR spectroscopic grade which was oven dried at 140°C .

3. Methods of calculations

The gravity center of the protonic vibration bands, ν_{cg} (cm^{-1}) were estimated as described previously [20–22]. The proton affinity, PA of an aniline (B) is defined as minus the heat of formation of its combination with a proton, Eq. (1)

$$\text{PA(B)} = \Delta H_f(\text{H}^+) + \Delta H_f(\text{B}) - \Delta H_f(\text{B}^+\text{H}), \quad (1)$$

where $\Delta H_f(\text{H}^+)$ is the experimental proton heat of formation and equal to 367 kcal/mol [23]. The heat of formations of neutral anilines $\Delta H_f(\text{B})$, their conjugate acids $\Delta H_f(\text{B}^+\text{H})$, the hydrogen bonded complexes $\Delta H_f(\text{HB})$, and the proton transfer complexes $\Delta H_f(\text{PT})$ were calculated using AM1 (gas phase) method [24]. The AM1 calculations were performed using either SPARTAN or MOPAC programs [25,26] running on Hewlett-Packard 720 workstation running HP-UX Ian and utilizing the Restricted Hartree–Fock (RHF) with AM1 semi-empirical Hamiltonian. Standard bond lengths and bond angles were used as starting geometries. Planarity of the aromatic rings was assumed, but conformations of the substituent group were optimized. Heats of formation were calculated with complete geometry optimization. The hydrogen bonding energies for the molecular and proton transfer species, $(\Delta E)_{\text{HB}}$ and $(\Delta E)_{\text{PT}}$, respectively, were calculated using Eqs (2) and (3)

$$(\Delta E)_{\text{HB}} = \Delta H_f(\text{HB}) - [-121.49 + \Delta H_f(\text{B})], \quad (2)$$

$$(\Delta E)_{\text{PT}} = \Delta H_f(\text{PT}) - [-177.41 + \Delta H_f(\text{B}^+\text{H})], \quad (3)$$

where -121.49 and -177.41 are the heat of formations of chloranilic acid, CA and the chloranilate anion (HA^-), respectively.

4. Results and discussion

4.1. FTIR spectra of the solid complexes

Chloranilic acid, Fig. 1, is a strong enough ($pK_1 = 1.07$ and $pK_2 = 2.24$) [27] to form a variety of complexes ranging from non polar, relatively weak adducts to strongly polar proton transfer species. Figure 2 represents the FTIR spectra of chloranilic acid and some of its hydrogen bonded complexes in the stretching frequency region ($4000\text{--}2000\text{ cm}^{-1}$). Figure 2a represents the spectrum of CA, where a sharp band appeared at 3232 cm^{-1} representing the ν_{OH} . Figure 2b represents the spectrum of CA-p-chloroaniline as a representative example of the molecular complexes. The spectrum showed two bands at 3184 and 3060 cm^{-1} attributed to $\nu_{NH_2}^{as}$ and $\nu_{NH_2}^s$ vibrations, respectively. The absorption band at 2822 cm^{-1} represents the ν_{OH} , which is shifted to a lower frequency compared to that of CA due to the hydrogen-bond formation. The band appeared at 2569 cm^{-1} could be ascribed to the in-plane bending overtone of the OH group. Passing near the critical region complexes represented by aniline complex, Fig. 2c, one observes the weakness of the absorption above 2500 cm^{-1} where a continuum is formed [28] extending to a frequency lower than 2500 cm^{-1} . Two weak bands can be detected at 3030 and 2962 cm^{-1} , representing $\nu_{NH_3^+}^{as}$ and $\nu_{NH_3^+}^s$ vibrations respectively. Figure 2d represents CA-m-methoxyaniline proton transfer complex where a broad band appeared at 2909 cm^{-1} that might be attributed to the asymmetric and symmetric $\nu_{NH_3^+}$ stretching vibration bands overlapping with the ν_{C-H} vibration.

Simultaneously with the change of the protonic vibration band, the evolution of $\nu_{C=O}$, ν_{C-O} , δ_{OH} and ν_{C-NH_2} vibrations take place. Hence, the FTIR spectra were studied in the range of $2000\text{--}1000\text{ cm}^{-1}$, Fig. 3. Figure 3a represents the spectrum of CA with a doublet located at 1664 and 1630 cm^{-1} , represents the asymmetric and symmetric stretching carbonyl group frequencies, respectively. The absorption band at 1367 cm^{-1} could be assigned to be an in-plane bending vibration of OH group, δ_{OH} and that at 1271 cm^{-1} to be ν_{C-O} . The spectrum of the molecular complex, CA-p-chloroaniline, Fig. 3b showed the carbonyl group asymmetric and symmetric stretching vibration frequencies at 1644 and 1630 cm^{-1} , respectively. The absorption band at 1594 cm^{-1} is due to δ_{NH_2} and that at 1572 cm^{-1} could be assigned to the aromatic ring vibration mode. The broad absorption band at 1500 cm^{-1} is attributed to $\delta_{(O_9-H_{10})}$ and that at 1358 cm^{-1} to the in-plane bending band of $O_{12}-H_{13}$ group involved in the intramolecular hydrogen bonding with the neighboring carbonyl group, $\delta_{(O_{12}-H_{13})}$. One observes in Fig. 3b, two absorption peaks at 1260 and 1207 cm^{-1} , respectively, representing the $\nu_{C_2-O_9}$ and $\nu_{C_5-O_{12}}$ modes. The lower frequency band at 1092 could be ascribed to ν_{C-NH_2} . For complexes near the critical point represented by CA-aniline complex, Fig. 3c, the asymmetric and symmetric carbonyl absorption bands were appeared at

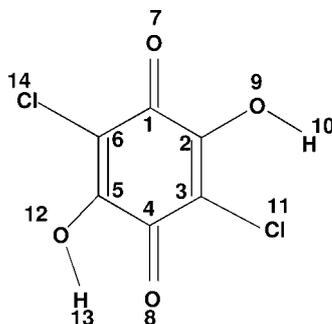


Fig. 1. Chloranilic acid.

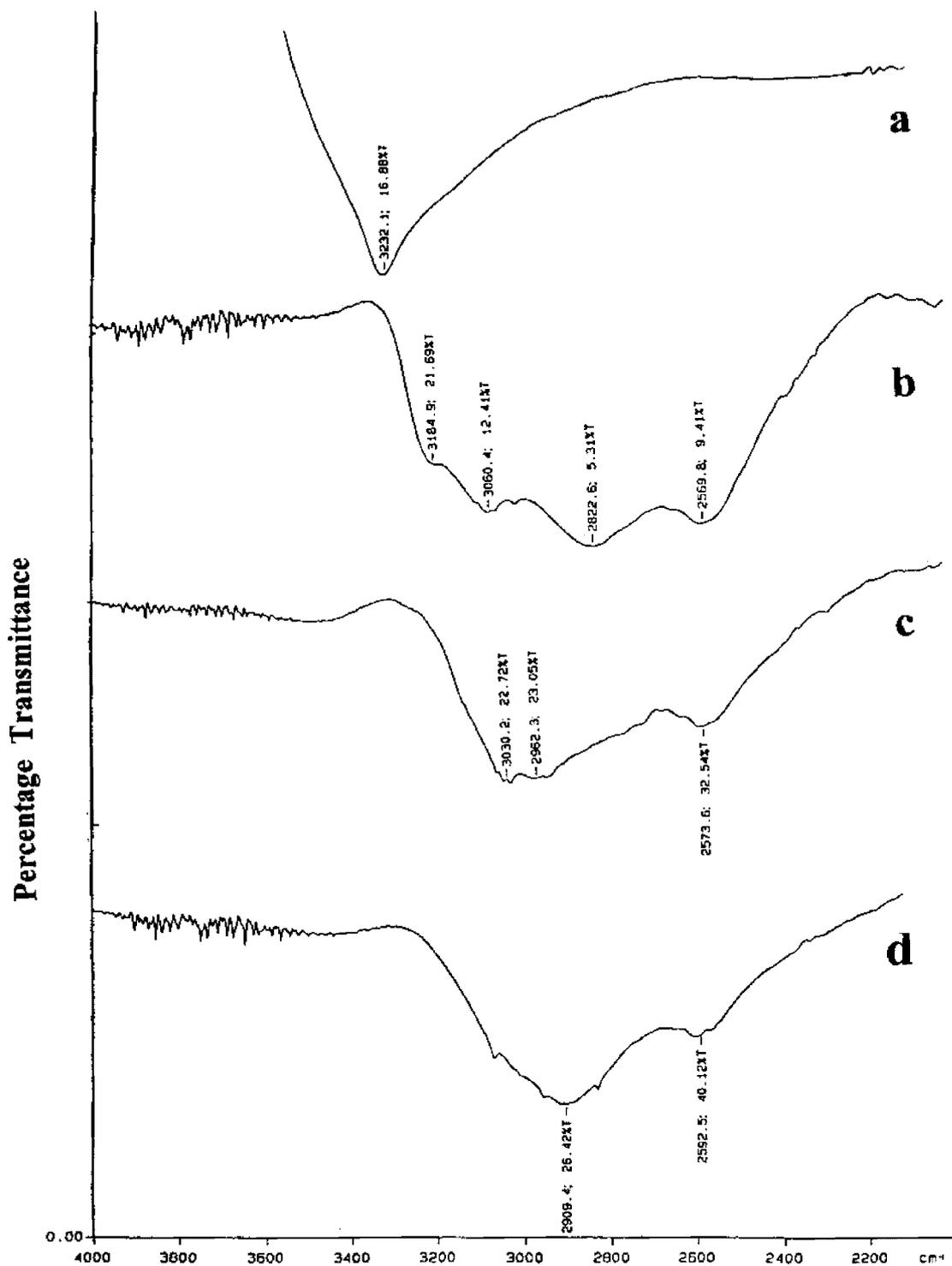


Fig. 2. FTIR spectra of (a) CA and its hydrogen-bonded complexes with (b) p-chloroaniline, (c) aniline and (d) m-methoxyaniline in the range 4000–2000 cm⁻¹.

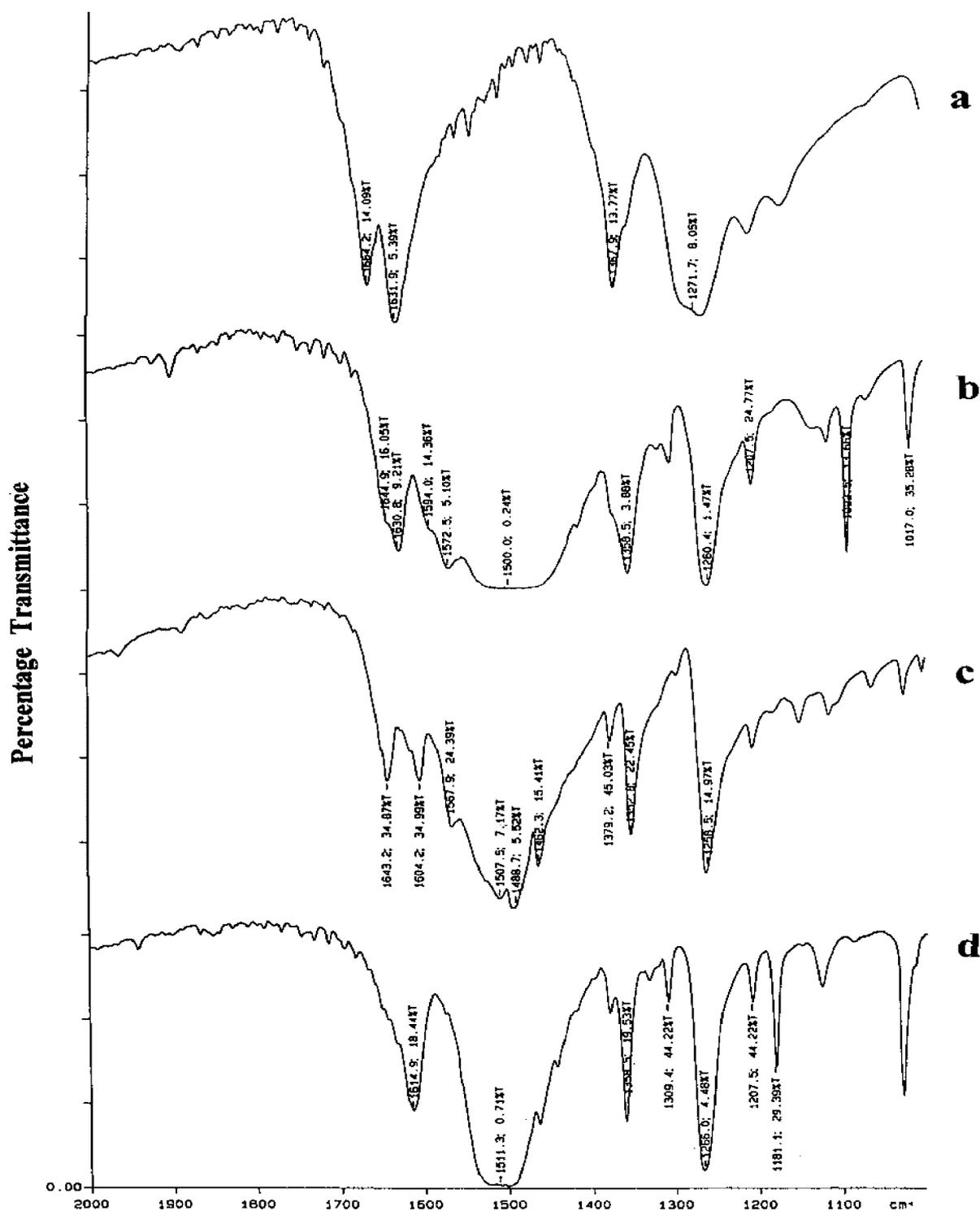
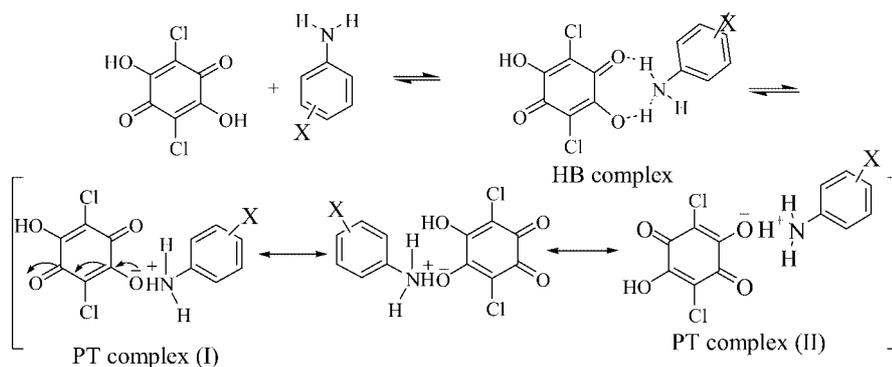


Fig. 3. FTIR spectra of (a) CA and its hydrogen-bonded complexes with (b) p-chloroaniline, (c) aniline and (d) p-methoxyaniline in the range 2000–1000 cm⁻¹.

1643 and 1604 cm^{-1} with equal intensities, a weak band representing δ_{NH_2} was appeared at 1567 cm^{-1} . The doublet at 1507 and 1488 cm^{-1} represents $\delta_{\text{O}_9\text{-H}_{10}}$ and $\delta_{\text{N-H}_{10}}$, respectively, where the proton is nearly lying between the O_9 and the N-atom of aniline, the absorption band at 1462 cm^{-1} could be assigned to be $\delta_{\text{O}_{12}\text{-H}_{13}}$. The two bands at 1379 and 1352 cm^{-1} are attributed to $\nu_{\text{C}_2\text{-O}_9}$ and $\nu_{\text{O}_5\text{-O}_{12}}$, respectively. The $\nu_{\text{C-NH}_2}$ absorption band locates at 1258 cm^{-1} , a frequency that is higher compared to that was detected for CA-p-chloroaniline complex.

The spectrum of the proton transfer complex of CA and p-anisidine is shown in Fig. 3d, where only one absorption band appeared at 1614 cm^{-1} for the carbonyl group stretching vibration. Also a broad band was observed at 1511 cm^{-1} which could be assigned to the combined $\delta_{\text{NH}_3^+}$ band with the symmetric carbonyl stretching vibration band. The band locates at 1358 cm^{-1} is presumably attributed to the in-plane bending band of $\text{O}_{12}\text{-H}_{13}$ group involving in the intramolecular hydrogen bonding with the neighboring carbonyl group, $\delta_{\text{O}_{12}\text{-H}_{13}}$. Also, two absorption bands representing the $\nu_{\text{C}_2\text{-O}_9}$ and $\nu_{\text{C}_5\text{-O}_{12}}$ were located at 1266 and 1207 cm^{-1} , respectively. The frequency band at 1181 cm^{-1} could be assigned to the C-NH₂ bond stretching vibration band, $\nu_{\text{C-NH}_2}$ that is relatively lower than that of CA-aniline complex. This could be explained by the fact of a complete proton transfer complex formation. It is worth noting that the proton transfer equilibrium constant between CA and p-anisidine in 1,4-dioxane has a higher value, which is in agreement with the obtained vibration spectral results [5]. In addition, the shift of the carbonyl frequency to a relatively lower one (1614 cm^{-1}) could be rationalized in terms of appreciable conjugation including the hydroxyl, and carbonyl groups of CA. This conjugation is favored by the co-planarity of the molecule and the lack of a hydrogen atom due to the protonation of the aniline NH₂ group [29]. Therefore, the proton transfer complex formation could be explained as indicated in Scheme 1.

It is very difficult to estimate the position of bands of $\nu_{\text{(OH)}}$ or $\nu_{\text{(NH}^+)}$ for both the molecular and proton transfer complexes because of the appearance of the asymmetric vibrations and overtones at the higher frequency region beside the contribution of the second OH group in the IR absorption profile. Consequently, the center of gravity of the protonic vibration bands ν_{cg} (cm^{-1}) was computed and correlated with both calculated proton affinity and σ_{H} of the substituents, Figs 4 and 5. The proton affinities of the studied anilines, the Hammett substituent constants, (σ_{H}), the ν_{cg} (cm^{-1}) values together with the carbonyl group frequencies $\nu_{\text{(C=O)}}$, are compiled in Table 1. Figure 4 represents the relationship between ν_{cg} and PA. This diagram showed a deep minimum at between PA = 210–211 kcal/mol, which might be assigned to the critical behavior, where ca. 50% PT exists [28]. The shape of the plots on both sides of the critical region is considerably asymmetric. The left-hand side represents the molecular complexes and



Scheme 1.

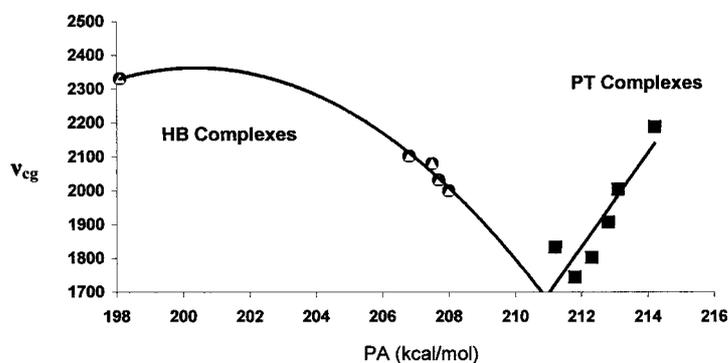


Fig. 4. Correlation between the center of gravity of the broad protonic absorption bands and PA values of anilines.

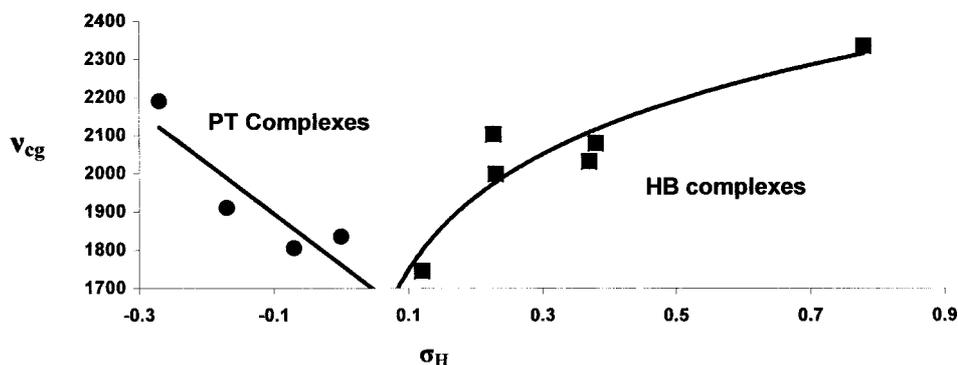


Fig. 5. Correlation between the center of gravity of the broad protonic absorption bands and Hammett substituent constants of anilines.

the right-hand side represents the proton transfer ones. The correlation diagram for the ν_{cg} values, against Hammett σ -constants Fig. 5, is quite similar in shape to that of the ν_{cg} against PA values, but they have exactly opposite manner on the experimental center of gravity of the protonic absorption bands, ν_{cg} . Also a deep minimum was found at $\sigma_H = 0.15$ that is parallel to the PA value between 210–211 kcal/mol corresponding to the critical region. On the other hand, it is obviously observed from these diagrams that the molecular complexes have higher ν_{cg} values than those recorded for the proton transfer complexes. This could be presumably attributed to the formation of bifurcated proton transfer complexes where the proton is attached to both the nitrogen atom of aniline and the carbonyl group of CA, hindering the proton transfer process [30–32]. The scattering of the experimental points could be explained on the ground that different packing of molecules in the crystal lattice would affect the regularity of the proton polarization.

Therefore, in conclusion the aniline proton affinities, PA is a good evidence for the capability of different substituted anilines for binding CA through either a hydrogen bond or proton transfer complex formation. In addition to this factor, another important one can be considered for preferential binding of such primary aromatic amines to CA as summarized by aniline structure and substituent effect. The general rule observed from the obtained correlations, Figs 4 and 5 is that, the higher possibility for PT increases as the electron donation power of the aniline substituent increases which could be transmitted to the N-center via inductive and resonance effects. Consequently, p-anisidine complex was found to exhibit the highest value of $\nu_{cg}(\text{NH}^+)$, 2187 cm^{-1} due to the strong electron donation power of the substituent

Table 1

Proton affinity, PA, Hammett substituent constants, σ_H , of different substituted anilines, the gravity center, ν_{cg} (cm^{-1}) and $\nu_{(C=O)}$ (cm^{-1}) of CA–anilines solid complexes

Aniline	PA (kcal/mol)	σ_H	ν_{cg} (cm^{-1})	$\nu_{(C=O)}$ (cm^{-1})
p-Nitroaniline	198.1	0.780	2331	1663, 1622
p-Bromoaniline	206.8	0.227	2101	1638, 1598
m-Bromoaniline	207.5	0.380	2078	1626, 1608
m-Chloroaniline	207.7	0.370	2030	1623, 1607
p-Chloroaniline	208	0.230	1998	1645, 1631
Aniline	211.2	0.000	1832	1664, 1632
m-Anisidine	211.8	0.120	1744	1633, 1605
m-Toluidine	212.3	−0.07	1802	1631, 1608
p-Toluidine	212.8	−0.17	1907	1617
N-methylaniline	213.1	—	2003	1643, 1604
p-Anisidine	214.2	−0.27	2187	1615

(p-OCH₃, $\sigma = -0.27$) leading to a sufficient electron density on the N-center and forming proton transfer complex (O[−] ···HN⁺). On the other hand, p-nitroaniline complex showed the highest value of ν_{cg} (OH), 2331 cm^{-1} , due to the stronger electron withdrawing power of the substituent (p-NO₂, $\sigma = 0.78$) leading to insufficient electron density at the N-center and suppressing the capability of N-atom to bind CA proton, i.e., molecular complex formation (OH ···N).

4.2. AM1 semi-empirical calculations

AM1 semi-empirical MO calculations were used to correlate with the experimental data [33–35]. The AM1 method gives a reasonably good description of the stereo, geometry, electron distribution and ground state properties compared with MINDO/3 and MNDO methods [36]. There are no evidences for the existence of the proton transfer equilibrium in the solid-state molecular complexes. Hence it is assumed that in the region of low PA values of anilines there is an asymmetric single minimum potential representing the species OH ···NH₂. Also, in the region of high PA there is an asymmetric single minimum potential corresponding to the proton transfer species, O[−] ···H⁺NH₂. Therefore, AM1 semi-empirical computations were performed by considering the hydrogen bond molecular complexes as to be of CA with p-nitroaniline, p-chloroaniline, p-bromoaniline, m-chloroaniline and m-bromoaniline and those of proton transfer to be of CA with aniline, N-methylaniline, p-methylaniline, p-methoxyaniline, m-methylaniline and m-methoxyaniline.

The calculated heat of formation of the neutral anilines $\Delta H_f(B)$, their conjugate acids $\Delta H_f(B^+H)$, the molecular complexes $\Delta H_f(HB)$, and of the proton transfer complexes $\Delta H_f(PT)$, based on the optimized molecular geometry of CA–anilines complexes, also, the binding energies (BE) of the hydrogen bonded complexes (HB) and those of the proton transfer complexes (PT) as well as the bond distances (BD) and the Mulliken charge populations (q) are collected in Table 2. It has been found that the hydrogen bond energies for the molecular complexes $-\Delta E_{HB}$, showed lower values, (≈ 3.0 kcal/mol), however, those of the proton transfer complexes, $-\Delta E_{PT}$, recorded higher values (84.4–146 kcal/mol). These results pinpoint to the weak hydrogen bonding of the molecular complexes where the heat of formation of the complex is nearly equal the sum of those of CA and free aniline (B). The higher $-\Delta E_{PT}$ values of the proton transfer complexes could be explained in terms of the electrostatic interaction that would give rise to the complex stability. On the other hand the hydrogen-bonded complexes locating near the

Table 2

Heat of formations ($-\Delta H_f$), of anilines (B), their conjugate acids, (BH^+), and of molecular and proton transfer complexes, (HB and PT) (kcal/mol), the hydrogen bond energies, $-\Delta E_{HB,PT}$ (kcal/mol), the R_{O-H} and R_{N-H} bond distances (\AA) and Mulliken charge populations (q), (e)

Anilines	ΔH_f (B)	ΔH_f (BH^+)	$-\Delta H_f$ (HB or PT)	$-\Delta E$ (HB or PT)	R_{O-H} (\AA)	R_{N-H} (\AA)	q_O (e)	q_N (e)
p-Nitroaniline	23.8	192.9	100.352	2.662	0.9769	2.711	-0.2094	-0.3498
p-Bromoaniline	24.5	184.9	99.756	2.866	0.9782	2.606	-0.2596	-0.3375
m-Bromoaniline	25.3	185.0	99.074	2.884	0.9787	2.585	-0.2096	-0.3367
m-Chloroaniline	13.2	178.7	111.154	2.874	0.9780	2.591	-0.2096	-0.3375
p-Chloroaniline	13.0	172.2	111.362	2.872	0.9785	2.587	-0.2098	-0.3377
Aniline	20.49	176.4	89.813	88.8	1.829	1.045	-0.4883	-0.2259
m-Anisidine	-17.7	137.7	164.84	125.1	1.813	1.046	-0.4952	-0.2409
m-Toluidine	12.90	167.8	93.96	84.4	1.905	1.045	-0.4892	-0.2219
p-Toluidine	12.80	167.2	143.31	133.1	2.109	1.030	-0.5189	-0.2377
N-methylaniline	24.1	178.2	124.43	125.2	1.939	1.030	-0.5337	-0.1894
p-Anisidine	-16.7	136.3	177.14	146.0	2.139	1.029	-0.5426	-0.1890

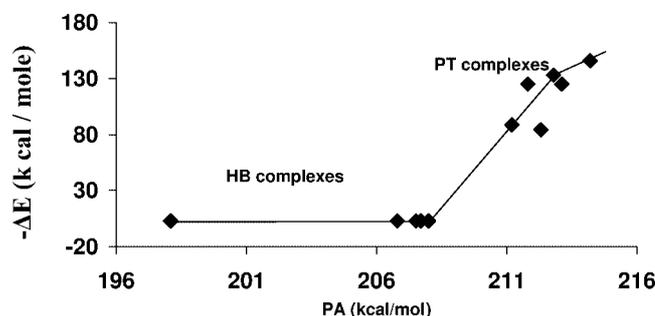


Fig. 6. The relationship between the hydrogen bond energies of CA-complexes and PA values of anilines.

critical point exhibit an intermediate values of the hydrogen bonding energy, such as CA-aniline and m-methoxyaniline having -88.4 and -84.4 kcal/mol energies, respectively.

The correlation between the hydrogen bonding energies of different complexes and the proton affinities of anilines is depicted graphically in Fig. 6. The obtained diagram is similar to that of a titration curve where the degree of proton transfer has a value near 0 or 100% in the two plateau regions. An inflection point was found at $PA \approx 211$ kcal/mol that represents the critical point. The same value was recorded in the correlation between ν_{cg} and PA, confirming the consistency between the experimental and AM1 results.

The dependence of the calculated R_{N-H} and R_{O-H} of the molecular and the proton transfer complexes on PA, showed two sigmoidal curves, Fig. 7. The two curves intersect at $PA = 211$ kcal/mol that corresponds to the critical point, a value was obtained from both previous experimental and theoretical correlations. The curve representing the variation of R_{N-H} with PA values starts with a large N-H bond distance 2.711 \AA for the molecular complex CA-p-nitroaniline where the proton is located at the oxygen atom of CA. As the proton affinity increases the hydrogen bond bridge polarization increases and the R_{N-H} value would decrease until it reaches to the lowest value at the proton transfer complex, CA-p-anisidine, $R_{N-H} = 1.029 \text{ \AA}$. Also, the R_{O-H} of the investigated hydrogen bond bridges are ap-

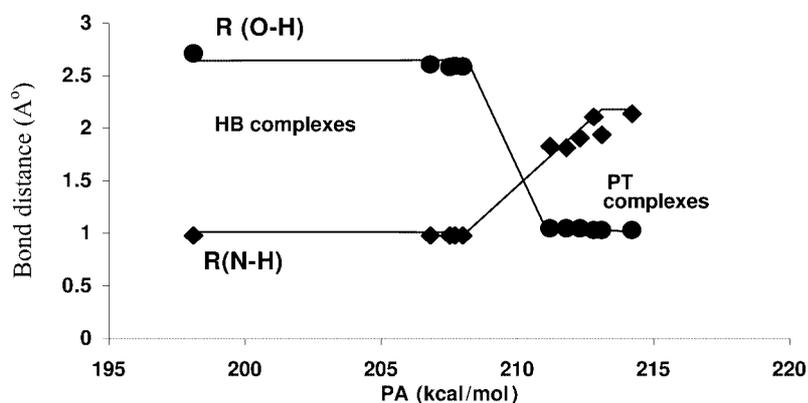


Fig. 7. Correlation between the O–H and N–H bond distances of the hydrogen bond bridges and PA values of anilines.

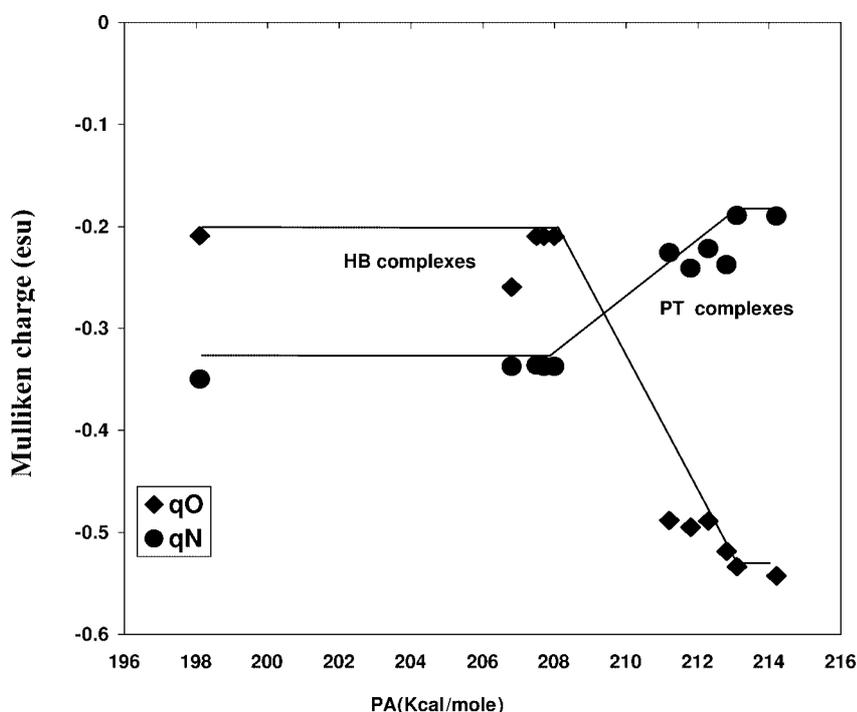


Fig. 8. The relationship between Mulliken charges q_O , q_N and PA values of anilines.

parently changed with the change of PA values of the anilines. The OH bond distance for the covalent complexes is 0.97 \AA , for the ionic complex, p-anisidine the OH bond distance recorded the longest one, 2.139 \AA where the proton is located at the nitrogen atom of the aniline moiety.

Concerning the charge populations on the nitrogen or oxygen atoms of different complexes, Table 2. It has been found that the charge populations of the hydrogen bond bridges oxygen atoms of the molecular complexes are quite similar to that of the free CA (-0.2123 e), however major perturbation of charges is caused by proton transfer complex formation. For example, the covalent complex, p-nitroaniline has a value of q_O (-0.2094 e), on the other hand, the ionic complex, p-anisidine has a

maximum q_O (-0.5426 e), where the proton is transferred to the N-atom. The dependence of q_O and q_N values on the PA values of the anilines revealed two sigmoidal shaped curves with an intersection at PA = 210 kcal/mol representing the critical point, Fig. 8.

Therefore, we conclude that there is a strict consistency between the experimental ν_{cg} (cm^{-1}) and the AM1 results. For the hydrogen bonded complex p-nitroaniline, ν_{cg} (OH) reached to the highest value 2331 cm^{-1} concurring with the lowest charge on the oxygen atom (-0.2094 e), the highest charge on the nitrogen atom (-0.3498 e), the largest R_{N-H} (2.711 \AA), the smallest R_{O-H} (0.9769 \AA) and the smallest hydrogen bonding energy (-2.662 kcal/mol). For the proton transfer complex, CA-p-anisidine, ν_{cg} (NH^+) reached to the highest value 2187 cm^{-1} consistent with the largest atomic charge on the oxygen atom (-0.5426 e), the lowest charge on the nitrogen atom (-0.1890 e), the largest R_{O-H} (2.139 \AA), the smallest R_{N-H} (1.029 \AA) and the highest proton transfer energy (146 kcal/mol).

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