

## Acid Dissociation Constants and The Conformations of 2-Furfural and 2-Thiophene Aldehyde Benzenesulphonylhydrazones

ABDELGAWAD A. FAHMI\* and GAMAL R. SAAD  
*Department of Chemistry, Faculty of Science,  
Cairo University, Giza, Egypt*

**ABSTRACT.** Acid dissociation constants,  $pK_a$ , of 2-furfural benzene-sulphonylhydrazone, (1) and 2-thiophene aldehyde benzenesulphonylhydrazone, (2) have been determined spectrophotometrically in ethanol-water media of various composition over the temperature range 15-40°C. The results were used to calculate the enthalpy  $\Delta H$  and the entropy  $\Delta S$  for the ionization process. The slight difference observed between the  $pK_a$  values of the studied compounds (1) and (2) revealed that the ring heteroatom is not involved in the formation of hydrogen-bonded chelate ring. This was confirmed by dipole moment, IR, and NMR spectral measurements.

### Introduction

Aldehyde benzenesulphonylhydrazones of type  $Ar-CH = N-NH-SO_2C_6H_5$  were first prepared by Grammaticakis<sup>[1]</sup> in 1952, and since then, these compounds have only been used as intermediates in the preparation of 5-arenesulphonylformazenes<sup>[2]</sup> and 2,5-disubstituted tetrazoles<sup>[3,4]</sup>. In continuation of our previous work on the chemistry of such compounds<sup>[4]</sup>, we wish to report the results of the study of the acidity of the two compounds (1) and (2) in different solvents and at different temperatures.

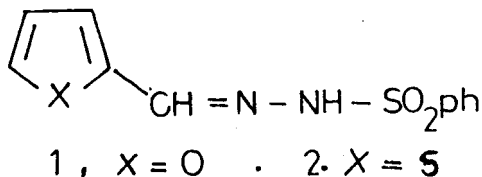


FIG. 1. Compounds studied in the present work

\* To whom correspondence should be addressed.

This study was carried out to determine the effect of the heteroatom on the acidity and chelating properties of (1) & (2) and to correlate their acid dissociation constants with solvent composition and temperature.

### Experimental

2-Furfural benzenesulphonylhydrazone (1) and 2-thiophenealdehyde benzenesulphonylhydrazone (1) and 2-thiophenealdehyde benzenesulphonylhydrazone (2) were prepared as describe elsewhere<sup>[4]</sup>. Measurements of pH were made with a Hanna pH-meter, model H1 8417 equipped with combined glass electrode. The pH-meter readings were converted to hydrogen ion concentration ( $H^+$ ) by means of the Van Uitert relation<sup>[5]</sup>. Electronic absorption spectra were measured on Perkin-Elmer Lambda 3 Spectrophotometer.

For the spectrophotometric determination of the acid dissociation constant,  $pK_a$ , an aliquot of the stock hydrazone solution is diluted with perchloric acid solution, absolute ethanol, and water to give an overall ionic strength of 0.1 M and hydrazone concentration of  $10^{-3}$  M and contain the required ethanol content (20, 40, 60 and 80% v/v). The ionic strength was kept constant at 0.1 M using  $HClO_4$  while the concentration of the hydrazones used were  $10^{-3}$  M. The change of pH was performed by using very small amounts of NaOH, this keeps the ionic strength constant. The absorption spectra of each of these solutions were examined at different pH values and at temperatures of 15-40°C. For pH measurements, the temperature was controlled by using double jacket cell connected to an ultrathermostate adjusted to the required temperature ( $\pm 0.1^\circ C$ ). This thermostate is connected at the same time to the spectrophotometric cell in order to verify the same temperature for both measurements. Static dielectric constants of solutions were measured on a Dipolemeter DM01 manufactured by WTW, West Germany. Dielectric constants ( $\epsilon$ ), densities ( $d$ ), and refractive indexes ( $n_D$ ) for solutions of the hydrazones were measured at 30°C as described earlier<sup>[6]</sup>. The dipole moments  $\mu_2$  in benzene were determined by the refractivity method employing the Debye equation.

$$\mu_2 = 0.01273 \sqrt{(P_{2\infty} - {}_D P_2) T}$$

where  ${}_D P_2$  is the molar deformation polarization of the solute obtained by extrapolating the measured molecular refraction for the sodium-D line to infinite wavelength<sup>[7]</sup>; and  $P_{2\infty}$  is the molecular polarization of the solute at infinite dilution, taken as the average of that determined graphically and those calculated from Hedestrand's<sup>[8]</sup> and Palit-Banerjee's<sup>[9]</sup> equations.

I.R. spectra were obtained for samples in KBr discs with a Pye Unicam SP3-300.  $^1H$  NMR spectra were measured in  $CDCl_3$  with a Varian GIMNI 200 MHz NMR-spectrometer.

### Results and Discussion

The acid dissociation constants,  $pK_a$ 's of (1) and (2) were determined spectrophotometrically in 20, 40, 60 and 80% (v/v) ethanol-water media over the temper-

ature range 15 to 40°C. The acid dissociation constant was calculated from the absorbance (A)-pH data by the equation :

$$pK_a = pH + \log \frac{(A_{\max} - A)}{(A - A_{\min})} \quad (1)$$

where,  $A_{\max}$  and  $A_{\min}$  are the absorbance values in the basic and acidic media (pH 10 and pH 1), respectively. The results obtained are given in Table 1. The values of the dielectric constant of the solvents used in the temperature range 15-40°C are given in Table 2.

TABLE 1.  $pK_a$  values of compounds (1) and (2) ( $\pm 0.01$  unit) in ethanol-water media of various ethanol content and at different temperatures.

Temp. (°C)	Vol. % of ethanol			
	20	40	60	80
Compound (1)				
15	7.18	7.86	8.57	9.26
20	7.11	7.78	8.45	9.12
25	7.04	7.67	8.33	8.97
30	6.97	7.59	8.121	8.85
35	6.90	7.50	8.09	8.69
40	6.84	7.41	7.98	8.55
Compound (2)				
15	7.30	8.06	8.76	9.47
20	7.20	7.92	8.60	9.31
25	7.10	7.78	8.46	9.15
30	7.01	7.68	8.34	9.00
35	6.91	7.57	8.22	8.66
40	6.83	7.46	8.08	8.72

TABLE 2. Dielectric constant ( $\pm 0.05$ ) of ethanol-water mixtures of various ethanol content and at different temperatures.

Temp. (°C)	Vol. % of ethanol			
	20	40	60	80
15	73.08	62.67	50.67	42.05
20	71.13	60.23	49.31	38.04
25	68.93	57.74	46.50	35.42
30	65.93	54.40	43.05	32.98
35	63.76	52.42	41.60	30.78
40	60.55	49.60	40.09	29.96

The results show that at any given temperature, an increase of ethanol content results in an increase of the  $pK_a$  value, as a consequence of the decrease of the dielectric

constant of the solvent mixture<sup>[10]</sup>. Also, in a given solvent an increase of temperature results in a decrease in the  $pK_a$  value.

From these data, both the enthalpy  $\Delta H^\circ$  and entropy  $\Delta S^\circ$  of the dissociation were calculated using the equation

$$\ln K_a = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (2)$$

The results are summarized in Table 3. It is clear that  $\Delta H^\circ$  values are positive whereas the values of entropy change  $\Delta S^\circ$  are negative in all solvent mixtures used.

TABLE 3. Thermodynamic parameters of compounds (1) and (2) dissolved in ethanol-water media of varying ethanol content.

	Vol. % of ethanol			
	20	40	60	80
Compound (1)				
$\Delta H^\circ$ (kJ mol <sup>-1</sup> ) (± 1)	23.70	32.49	40.93	49.10
$\Delta S^\circ$ (JK <sup>-1</sup> mol <sup>-1</sup> ) (± 3)	- 55.22	- 38.50	- 21.97	- 6.61
Compound (2)				
$\Delta H^\circ$ (kJ mol <sup>-1</sup> ) (± 2)	32.56	40.65	45.65	57.80
$\Delta S^\circ$ (JK <sup>-1</sup> mol <sup>-1</sup> ) (± 5)	- 26.08	- 11.64	7.69	- 19.00

Harned *et al.*<sup>[11]</sup> investigated the temperature variation of the acidity of acetic acid in water and in aqueous dioxane, as well as the acidity of other acids in water<sup>[12,13]</sup>. A parabolic relationship between  $pK_a$  and temperature was found; the relation being

$$pK_a - pK_m = C (t - \theta)^2 \quad (3)$$

Here, the temperature is expressed in degrees centigrade,  $pK_m$  is the minimum value of  $pK_a$  at temperature  $\theta$ .  $C$  is a constant of the order of  $5 \times 10^{-5} \text{ K}^{-2}$ .

When the latter equation was applied to our experimental data, values of  $pK_m$  and  $\theta$  were found as shown in Table 4. The data indicate that as the ethanol content in the solvent mixture increases, the value of  $\theta$  increases whereas  $pK_m$  decreases. The increase in  $\theta$  values with the increase of ethanol content is in agreement with the above finding that ionization is opposed with the increase of ethanol content.

A comparison of the  $pK_a$  data of compound (1) with those of compound (2) (Table 1) reveals that replacement of the 2-furyl group in (1) by 2-thienyl as in (2) resulted in a slight increase in the  $pK_a$  value. This effect is observed at any temperature in any solvent mixture.

TABLE 4.  $pK_m$  and  $\theta$  determined for compounds (1) and (2) in ethanol-water media of varying ethanol content.

	Vol. % of ethanol			
	20	40	60	80
Compound (1)				
$\theta$	165.18	214.92	264.64	312.07
$pK_m$	6.06	5.88	5.46	4.85
Compound (2)				
$\theta$	216.81	264.29	293.79	326.47
$pK_m$	5.26	4.94	4.86	4.61

In general, compounds (1) and (2) can be represented by either of the following two structures

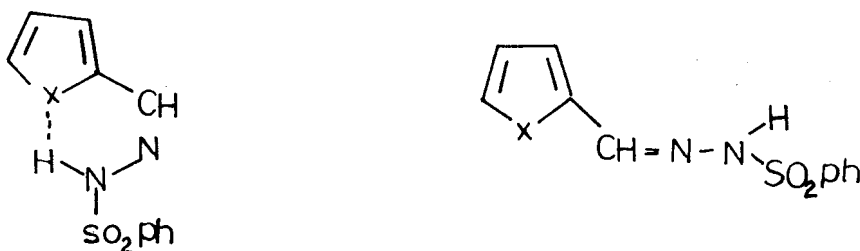


FIG. 2. Possible geometric structures of compounds (1) and (2).

According to structure (i) it might be expected that the acidity is most likely dependent upon the strength of the intramolecular hydrogen bond.  $X \cdots H-N$ , such that, the stronger the bond the less is the acidity. The electronegativity of the X atom will affect the strength of the H-bond and hence the acidity of the H-N group through an inductive effect; that is, the higher the electronegativity of the X atom the higher is the acidity. Referring to structure (i) the acidity is governed by the predominance of one of the above two opposing effects. On the other hand, structure (ii) suggests that the acidity is mainly governed by the electronegativity. This means that the greater the electronegativity of the X atom the greater will be the inductive effect, and hence, the higher the acidity.

Based on the above arguments, structure (ii) seems to be more appropriate for both compounds than structure (i), since the observed  $pK_a$  values for (1) are less than those of (2). This conclusion was confirmed by dipole moment measurements of both compounds in benzene at 30°C and comparing the results obtained with those calculated, using the method of bond moments<sup>[14]</sup>, for the various possible conformations (figure 3). The experimental results are given in Table 5 and those calculated for conformations (I-VIII) in Table 6. A comparison of the data in Tables 5 and 6, necessitates that conformations II-V and VII and VIII should be excluded, since their calculated dipole moments values are significantly different from the experimental values,

which are 4.92 and 4.77 D for compounds (1) and (2), respectively. The calculated dipole moments 5.01 and 4.94 D for compounds (1) and (2) respectively are close to the calculated ones based on conformation VI.

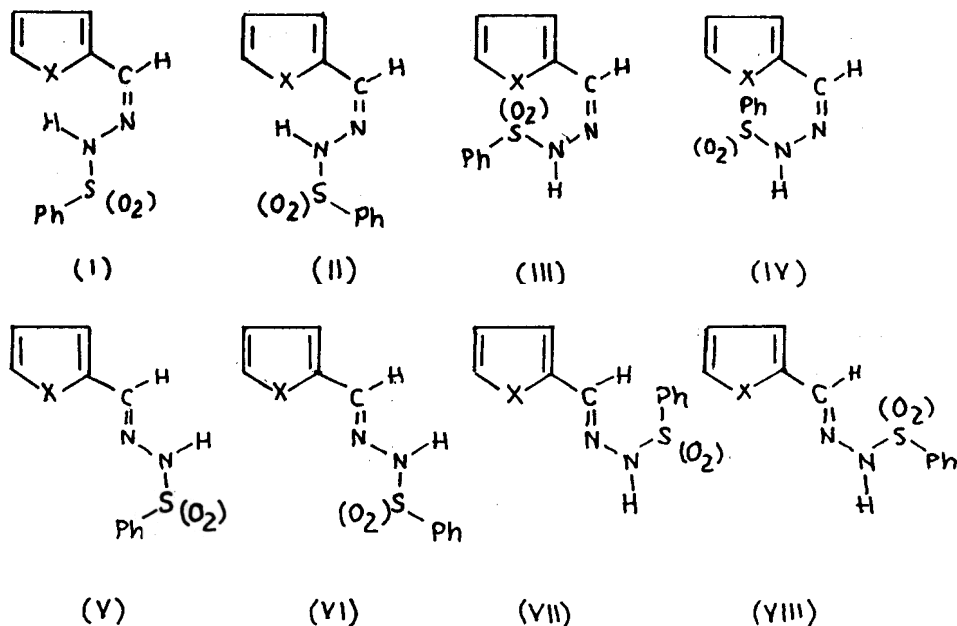


FIG. 3. Various hypothetical conformations for compounds (1) or (2).

The nonchelated structure (ii) was further confirmed by the observation that no metal complex could be detected spectrophotometrically with both compounds (1) and (2), since all trials to prepare the FeIII, CoII, NiII, and CuII complexes with (1) and (2) were unsuccessful.

TABLE 5. Dipole moment and polarization data of compounds (1) and (2) in benzene at 30°C.

Compound	${}_D P_2$		$P_{2\infty}$ (cm <sup>3</sup> )		$P_{2\infty}$ (cm <sup>3</sup> )	$\mu$ (D)
	(cm <sup>3</sup> )	graph.	Hedestrand	Palit-Banerjee		
(1)	68.90	563.76	563.81 $\alpha = 10.717$ $\beta = 0.304$	555.47 A = 0.342 $\gamma = 1.862$	561.01	4.92
(2)	70.15	536.43	536.49 $\alpha = 9.504$ $\beta = 0.191$	527.18 A = 0.342 $\gamma = 1.640$	533.37	4.77

TABLE 6. Calculated dipole moments for various conformations (I-VIII) of compounds (1) and (2).

Compound	Conformations							
	I	II	III	IV	V	VI	VII	VIII
(1)	5.01	3.50	2.87	2.96	3.50	4.93	3.03	2.66
(2)	4.94	3.49	3.00	2.88	3.39	4.85	2.38	1.98

The IR and  $^1\text{H}$  NMR spectra of the two compounds were compared with that of benzaldehyde benzenesulphonylhydrazide, (3). The stretching frequencies,  $\nu_{\text{NH}}$ , and the proton chemical shifts of the NH proton of compounds 1-3 are given in Table 7. The close similarity of the stretching frequencies of NH bond and the chemical shifts values of the NH proton resonance for the three compounds 1-3 substantiate further our previous conclusion that compounds 1 and 2 exist in a non-chelated form.

TABLE 7. Chemical shifts of NH proton ( $\sigma_{\text{NH}}$ ) and NH stretching frequencies ( $\nu_{\text{NH}}$ ) for compounds (1-3).

Compound no.	(1)	(2)	(3)
$\delta_{\text{NH}}$ (ppm)	8.30	8.35	8.44
$\nu_{\text{NH}}$ $\text{cm}^{-1}$	3200	3160	3180

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## ثابت التفكك الحامضي والشكل الفراغي لمركبات ٢-فيرفورال ، و ٢-ثيوفين ألدهايد بنزين سلفونيل هيدرازون

عبد الجواد علي فهمي و جمال سعد

قسم الكيمياء ، كلية العلوم ، جامعة القاهرة

الجيزة - مصر

المستخلص . تم قياس ثابت التفكك الحامضي للمركبات ٢-فيرفورال ، ٢-ثيوفين ألدهايد بنزين سلفونيل هيدرازون طيفياً في تراكيز مختلفة لخليط كحول-ماء في درجة حرارة من ١٥-٤٠ م° . وقد أظهرت النتائج أن زيادة الكحول في الخليط عند أي درجة حرارة تؤدي إلى زيادة في ثابت التفكك الحامضي كنتيجة لانخفاض ثابت العزل الكهربائي لخليط الإذابة كما أن زيادة درجة الحرارة لأي مذيب ينتج عنها انخفاض في ثابت التفكك . كما تم حساب كل من المستوى الحراري والإنتروبي للتفكك من هذه النتائج .