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In this paper we present a study concerning the basicity of some new carbanion monosubstituted pyridazinium, 3-methyl-pyridazinium, 3-(*p*-halogenophenyl)-pyridazinium and phtalazinium ylids. The pK_a values of the conjugated acids (salts) of ylids have been experimentaly determinated. Consequently, we have evaluated their basicity (k_b) using the titration curves. The basicity depends mainly on the structure of the ylids carbanion itself, however the heterocycle's structures also has some influence on bacisity. Having in view the basicity, we have established certain correlations between basicity, structure and stability of the analised ylids.

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Intoduction.

In previous research work [1-10] we studied the synthesis, structure and reactivity of some new pyridazinium and phtalazinium ylids type **1** and **2**, Figure 1. Zugravescu and colaboratores [11] have shown that one of the most important factors concerning the stability of cycloimmonium ylids is the nature of the substituent linked to the ylidic carbanion. Delocalization of the anionic charge is enhanced by the donor-acceptor effect exerted by the *para*

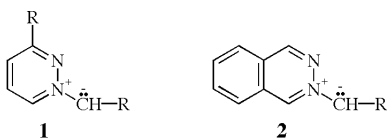


Figure 1

substituent of the phenacyl-group or by the esteric group bound to the carbanion. It has also been shown [11] that the nucleophilic character of cycloimmonium ylids is dependant on how much of the negative charge is localised on carbon (carbanionic character), because the carbanion is the basic centre of the ylid.

The most general method used for the synthesis of cycloimmonium- ylids **4**, developed by Kröhnke [12], consists in dehydrohalogenation of cycloimmonium salts **3** according to the general reaction (pathway a). Because of its nucleophilic character, the ylidic carbanion can bind a molecule of hydrobromic acid, thus reforming the salt **3** (pathway b), Figure 2.

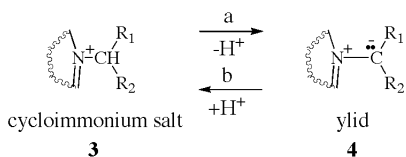


Figure 2

By studying the reaction of cycloimmonium ylids **4** with mineral acids one can determine their basicities, and establish a correlation between the stability and basicity of

ylids. According to Ratts and collaborators [13,14], the basicity and nucleophilicity of ylids can be evaluated using the pK_a values of their conjugate acids.

The emphasis of this work is to determine the basicity of some formerly synthesised pyridazinium and phtalazinium ylids and, consequently, to established correlations between structure and stability of the analised ylids. Thus, we synthesised the conjugate acids (the salts) presented in the following reaction scheme (Figure 3).

Results and Discussion.

The pK_a , k_a , pK_b and k_b values are listed in Table I. Analysing the pK_a data listed in table I, the following results were found.

a) The basicity constant of conjugate acids (salts) that contain a *para* R substituted phenacyl group show the following variation: for conjugate acids **5-8**, derived from pyridazinium ylids, the basicity constant varies between 2.63×10^{-12} for $R = NO_2$ and 1.41×10^{-8} for $R = OCH_3$. When a $COOC_2H_5$ esteric group is linked directly to the carbanion (compound **9**), the basicity constant is 7.76×10^{-13} . For the conjugate acids **10-12**, derived from 3-methyl-pyridazinium ylids, the basicity constants vary between 3.23×10^{-12} ($R = NO_2$) and 1.66×10^{-8} ($R = OCH_3$); for the acid **13**, the $k_b = 1.38 \times 10^{-12}$. For the conjugate acids **14-17**, derived from 3-(*p*-chlorophenyl)-pyridazinium ylids, the k_b values vary between 1.41×10^{-12} ($R = NO_2$) and 5.75×10^{-8} ($R = OCH_3$); for the acid **19**, $k_b = 3.63 \times 10^{-13}$. For the conjugated acids **19-22** derived from phtalazinium ylids, the k_b values vary between 1.12×10^{-12} ($R = NO_2$) to 1.44×10^{-11} ($R = OCH_3$).

This collection of data shows that, in the case of type A conjugate acids, when R is an electron withdrawing group, such as nitro (NO_2), the basicities have the lowest values, while when R is an electron donating group, such as methoxy (OCH_3), the basicities have the highest values. The basicities of type B conjugated acids are lower than type A. The latter result is expected because the esteric group is more electron withdrawing than the benzoic group ($-CO-C_6H_5-R$). These observations show that a strong correlation between the basicity of ylid and the structure of ylid carbanion exists.

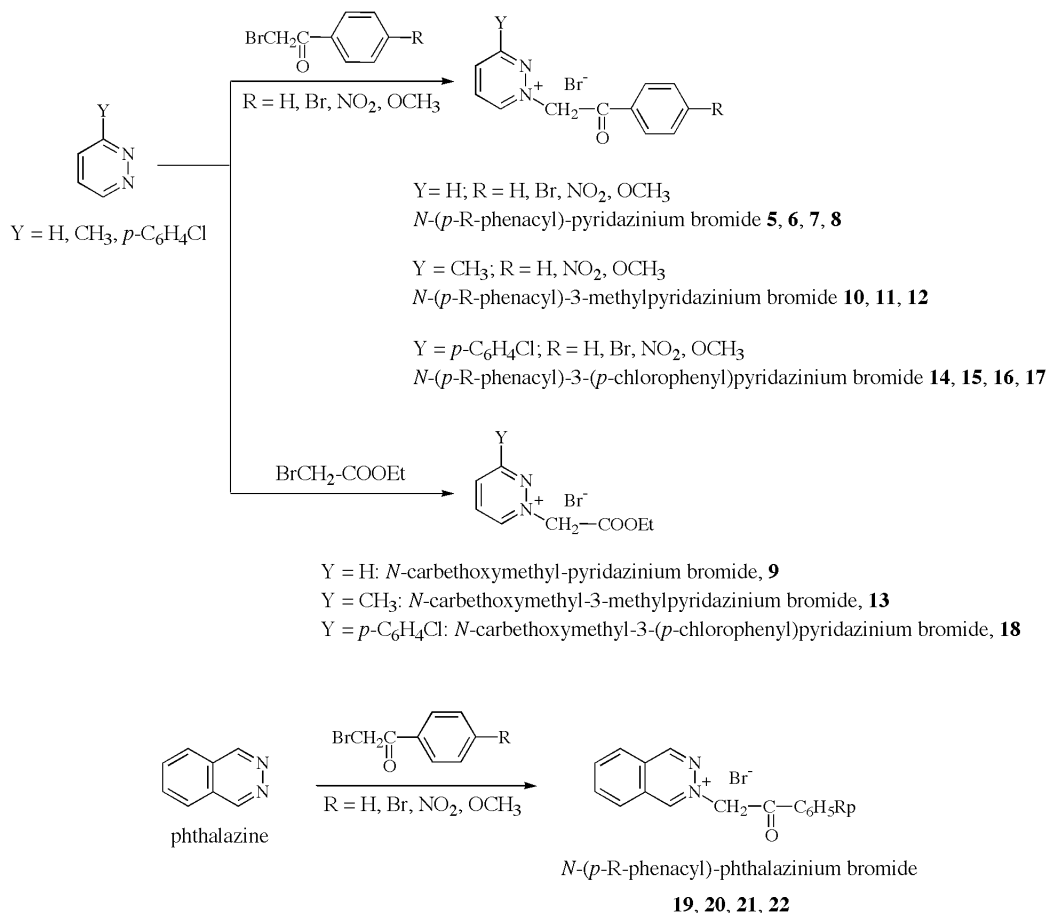


Figure 3. Reaction pathway to get the conjugated acids

Table I
 The p*K*_a, p*K*_b, *K*_a and *K*_b Values of Conjugate Acids

Product	p <i>K</i> _a	<i>K</i> _a	p <i>K</i> _b	<i>K</i> _b
5	7.65	2.23 x 10 ⁻⁸	9.04	9.12 x 10 ⁻¹⁰
6	7.21	6.16 x 10 ⁻⁸	9.48	3.31 x 10 ⁻¹⁰
7	5.11	7.76 x 10 ⁻⁶	11.58	2.63 x 10 ⁻¹²
8	8.84	1.44 x 10 ⁻⁹	7.85	1.41 x 10 ⁻⁸
9	4.58	2.63 x 10 ⁻⁵	12.11	7.76 x 10 ⁻¹³
10	7.81	1.54 x 10 ⁻⁵	8.88	1.32 x 10 ⁻⁹
11	5.20	6.30 x 10 ⁻⁶	11.49	3.23 x 10 ⁻¹²
12	8.91	1.23 x 10 ⁻⁹	7.78	1.66 x 10 ⁻⁸
13	4.83	1.47 x 10 ⁻⁵	11.86	1.38 x 10 ⁻¹²
14	6.26	5.49 x 10 ⁻⁷	10.43	3.41 x 10 ⁻¹¹
15	5.43	3.71 x 10 ⁻⁶	11.26	5.49 x 10 ⁻¹²
16	4.84	1.44 x 10 ⁻⁵	11.85	1.41 x 10 ⁻¹²
17	9.45	3.58 x 10 ⁻¹⁰	7.24	5.75 x 10 ⁻⁸
18	4.25	5.75 x 10 ⁻⁵	12.44	3.63 x 10 ⁻¹³
19	5.66	2.18 x 10 ⁻⁶	11.03	9.33 x 10 ⁻¹²
20	5.42	3.80 x 10 ⁻⁶	11.27	5.37 x 10 ⁻¹²
21	4.75	1.77 x 10 ⁻⁵	11.94	1.12 x 10 ⁻¹²
22	5.85	1.41 x 10 ⁻⁶	10.84	1.44 x 10 ⁻¹¹

b) A correlation between the basicity, the anionic charge delocalisation and the stability of ylid has also been found. The greater the delocalisation of anionic charge, the lower the basicity, and lower basicity corresponds to greater stability of the ylid. On the contrary, if the basicity is greater (low delocalisation of anionic charge), the ylid will be less stable. These conclusions are also confirmed by other experimental data related to pyridazinium and phthalazinium ylids [11].

c) The influence of the heterocycle on the basicity and stability of ylids can not be neglected. As can be seen from table 1, if we consider the conjugate acids with the same carbanion but different heterocycle (for example acids **7**, **11**, **16**, **21**), the *K*_b of these compounds are slightly different. In the case of acid **21**, where the heterocycle is phthalazine, the electron withdrawing effect of the fused benzene ring on pyridazine is the strongest and, the basicity constant has the lowest value. On the other hand, in the case of acid **11** where the heterocycle is 3-methylpyridazine, the basicity is the highest, probably because of the electron donating

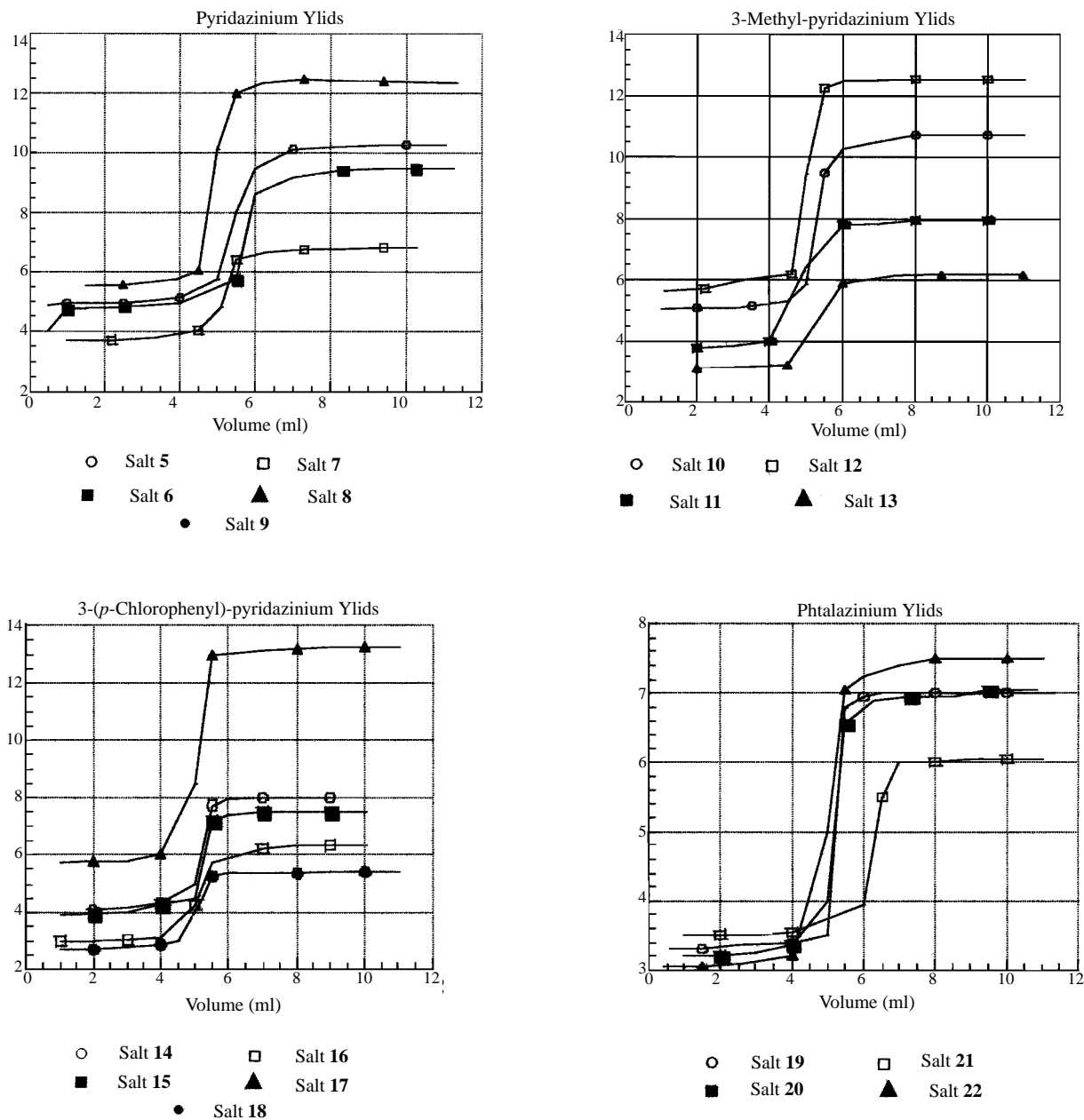


Figure 4

effect of the methyl group. To our knowledge, the influence of substituents linked to heterocycle, is being studied for the first time, and it will be studied in greater detail studied in the future.

Conclusion.

The basicity constants of conjugated acids of some carbanion monosubstituted 1,2-diazinium ylids (**5-22**) have been determined. The electron withdrawing substituents linked to carbanion induce delocalisation of negative charge, thus decreasing the basicity of conjugated acids. The electron donating substituents increase the

basicity by fixing the negative charge to the carbanion. The different substituents on the pyridazinic ring have also influence about the basicities of the analysed conjugated acids. In all these cases, a strong correlation between the basicity and stability of the ylids also exists.

EXPERIMENTAL

We determined the pK_a values of the conjugated acids using the semineutralization pH method [15]. According to this method, it was considered that at the moment of semineutralization a quantity of 50% of weak acid was neutralized, the pH value being

dependent on the autoprotolysis constant value of the solvent used. A 10^{-2} M methanol solution of the conjugated acids (the salts) were prepared and then titrated with a 10^{-2} M solution of sodium hydroxide (NaOH) in methanol. The titrations were carried out using a MP 220 potentiometer pH-meter apparatus (type Mettler Tolédo), at 20 °C, using a glass electrode. The pH values were determined using the titration curves (Figure 4) and the pK_a values were calculated from the following equations:

$$\begin{aligned} pH_{1/2} &= pK_a; \\ pK_a + pK_b &= pK_{\text{methanol}}; \\ pK_{\text{methanol}} &= 16.69; K_{\text{methanol}} = 2 \times 10^{-17}. \end{aligned}$$

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