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# Unsymmetrical Azines of 4-Acetyl-3-Methyl-1-Phenyl-5-Pyrazolone. Spectral Characteristics and Structure

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*ABSTRACT*

*The spectral characteristics of some unsymmetrical azines derived from 4-acetyl-3-methyl-1-phenyl-5-pyrazolone have been studied. The compounds exhibit a weak fluorescence ($Q_F < 0{\cdot}01$) in the region 23000–18000 $cm^{-1}$ in solution, and fluorescence intensely in the solid phase in the range 21000–17000 $cm^{-1}$. The compounds can exist in four tautomeric forms, namely keto, enol and two imino configurations. On the basis of the experimental data, and the results of PPP-SCF-CI quantum chemical calculations it is concluded that the enol form predominates in solution.*

## 1 INTRODUCTION

The unsymmetrical azines of 4-acetyl-3-methyl-1-phenyl-5-pyrazolone (UAP) used in this investigation contained two structural fragments, i.e. a 1-phenyl-5-pyrazolone moiety and an azine moiety (see Table 1). Pyrazolone derivatives have been described for practical applications such as synthetic dyes, luminophores and pharmaceuticals. Their pharmaceutical activity, attributed to the presence of the 1-phenyl-5-pyrazolone fragment, depends on the substituent in the 4-position.[1,2] 4-Acetyl-3-methyl-1-phenyl-5-pyrazolone derivatives are also physiologically active.[3,5] Hydrazones, and particularly azines, also possess biological activity and have been

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**TABLE 1**
Compounds Investigated

| *Compound no.* | *Aryl substituent* |
|---|---|
| **1** | Phenyl |
| **2** | 4-$CH_3$-Phenyl |
| **3** | 4-$OCH_3$-Phenyl |
| **4** | 4-Cl-Phenyl |
| **5** | 4-F-Phenyl |
| **6** | 4-CHO-Phenyl |
| **7** | 4-$NO_2$-Phenyl |
| **8** | 4-$N(CH_3)_2$-Phenyl |
| **9** | 4-$N(C_2H_5)_2$-Phenyl |
| **10** | 4-(1-Piperidyl)-phenyl |
| **11** | 4-(4-Morpholinyl)-phenyl |
| **12** | 4-(1-Pyrolidinyl)-phenyl |
| **13** | 2-Naphthyl |
| **14** | 9-Anthracenyl |
| **15** | 9-Ethyl-3-carbazolyl |
| **16** | 4-$N(CH_3)$-Styryl |

evaluated for possible use in analytical and synthetic chemistry.[6] Some unsymmetrical azines have antibacterial properties,[7,8] some are used as organic luminophores,[9] and others have been used in the synthesis of unsymmetrical diarylethylenes.[10,11] The combination of the two structural fragments (pyrazolone and azine) suggests a specific potential biological activity of UAP, as well as possibilities for the application of these compounds in analytical and synthetic chemistry.

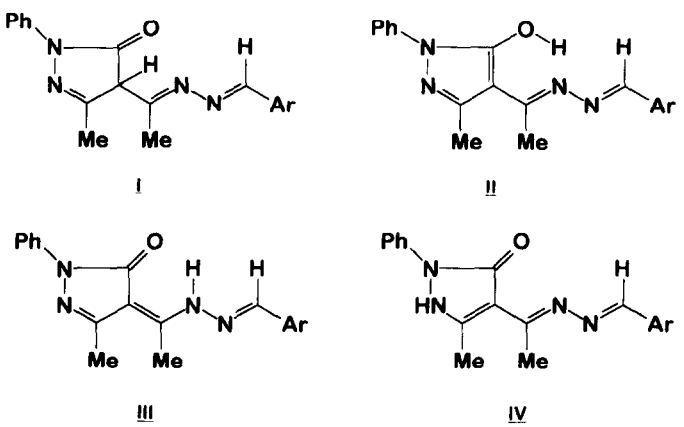


**Fig. 1.** Possible tautomeric forms of the compounds.

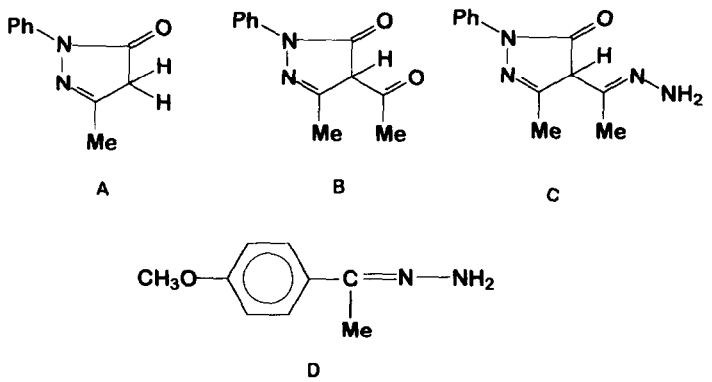


**Fig. 2.** Model compounds.

1-Phenyl-5-pyrazolone derivatives may exist in different tautomeric forms depending on the substituent in the 4-position and on the solvent.[12–15] For UAP, four tautomeric structures are possible, namely keto (**I**), enol (**II**) and two imino forms (**III** and **IV**) (see Fig. 1).

The present work reports on the spectral characteristics of some unsymmetrical azines derived from 4-acetyl-3-methyl-1-phenyl-5-pyrazolone and different aldehydes (see Table 1). Comparison of the electronic spectra of these compounds with those of model compounds (see Fig. 2), and the results of NMR and IR studies and also PPP-SCF-CI quantum chemical calculations, suggests that the predominant tautomeric form of these compounds in solution has been established in this investigation.

## 2 EXPERIMENTAL

The unsymmetrical azines were synthesized by condensation of the hydrazone of 4-acetyl-3-methyl-1-phenyl-5-pyrazolone[4] with the corresponding aromatic aldehydes.[16,17] Equimolar amounts of the hydrazone and the aldehyde were refluxed in ethanol for 12–13 h; the azines were isolated in crystalline form with yields of 95–99%.

All compounds were characterized by melting points, elemental analysis, NMR, IR, absorption and fluorescence spectra.

Fluorescence and excitation spectra were recorded on a Perkin Elmer MPF-44 spectrofluorimeter and absorption spectra on a Specord M40 (Carl Zeiss, Jena). The fluorescence quantum yields were determined relative to 3-aminophthalimide ($Q_F$ = 0·6 in ethanol).[18] IR spectra were measured on a Bruker IFS 113v and NMR spectra on a Bruker-WM-250 and a Tesla BS 487C-80.

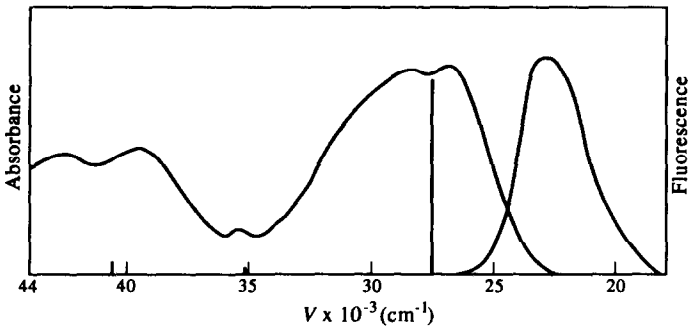


**Fig. 3.** Absorption and fluorescence spectrum of compound **1** in ethanol. The vertical lines indicate the calculated $\pi$-$\pi^*$ transitions of its enol tautomeric form.

## 3 RESULTS AND DISCUSSION

### 3.1 Absorption and fluorescence spectra

Figure 3 shows the absorption and fluorescence spectra of the parent compound **1** in ethanol. The vertical lines denote the position and intensity of the $\pi$-$\pi^*$ transitions of the enolic tautomeric form **II** (see Section 3.2), computed by the PPP-SCF-CI method with standard parameterization, taking into consideration all singly excited configurations.[19–22]

The azines of pyrazolone have two main absorption bands in solution, one in the region 42000–40000 $cm^{-1}$ (molar absorptivity around 30000) and another with a maximum around 25000 $cm^{-1}$ (molar absorptivity around 50000) (see Table 2).

The position of the longest wavelength absorption maximum depends on the length of the conjugated system (Table 2) and is at 27000 $cm^{-1}$ for the parent compound **1**. Elongation of the conjugated system by one double bond (compound **16**), or with a change of the phenyl substituent for 9-anthracenyl, leads to bathochromic displacements of 2000 $cm^{-1}$ and 4000 $cm^{-1}$, respectively. Electron releasing and electron withdrawing substituents in the *p*-position of the phenyl ring lead generally to an insignificant red shift of the longest wavelength absorption maximum, except for compounds containing a *p*-dialkylamino group (compounds **8–12**), which absorb at around 3200 $cm^{-1}$ to the red relative to **1** (see Table 2).

The absorption spectra were measured in hexane, dichloromethane, ethanol and DMSO and it is observed that the solvent polarity had practically no effect on the absorption spectra; the energy difference between the longest wavelength absorption maxima in hexane and ethanol was 200 $cm^{-1}$.

**TABLE 2**

Spectral Characteristics of the Compounds in Ethanol and in the Solid State. Numbering Corresponds to that given in Table 1; $\nu_{abs}$ and $\nu_{fl}$ are Energy of Absorption and Fluorescence Respectively for Franck–Condon Transitions ($cm^{-1}$); — Indicates no Fluorescence Observed

| *Compound no.* | *Ethanol* | | *Solid state* | |
|---|---|---|---|---|
| | $\nu_{abs}$ | $\nu_{fl}$ | $\nu_{exc}$ | $\nu_{fl}$ |
| **A** | 40650 | — | — | — |
| **B** | 37690 | — | — | — |
| **C** | 29940 | — | — | — |
| **D** | 30300 | — | — | — |
| **1** | 26650 | 22990 | 22730 | 19230 |
| **2** | 26320 | 21740 | 22730 | 19800 |
| **3** | 25970 | 20000 | 22730 | 20410 |
| **4** | 26320 | 23260 | 22730 | 19610 |
| **5** | 27320 | 20000 | 21740 | 19610 |
| **6** | 25640 | 20620 | 21280 | 20200 |
| **7** | 25970 | — | — | — |
| **8** | 24690 | 20000 | 21280 | 19800 |
| **9** | 23810 | 20000 | 21280 | 19800 |
| **10** | 24390 | 19800 | 21280 | 19800 |
| **11** | 25640 | 20200 | 21280 | 19610 |
| **12** | 23980 | 19800 | 21740 | 19230 |
| **13** | 26060 | — | 21740 | 19610 |
| **14** | 23100 | — | 18520 | 16950 |
| **15** | 24980 | 21740 | 21640 | 19610 |
| **16** | 22730 | 17860 | 20830 | 17860 |

The model compounds (see Fig. 2) represent structural analogs of fragments of the studied molecules, with gradual extension of the conjugated system.

Compounds **A**, **B** and **C** characterize the pyrazolone part of the UAP, and absorb in the region 45500–33000 $cm^{-1}$ (Table 2). The model compound **D**, characteristic of the azine fragment, has two absorption maxima around 43500 $cm^{-1}$ and 30000 $cm^{-1}$ (Table 2). The large bathochromic shift (3300 $cm^{-1}$ for compound **1**) of the longest wavelength maximum of UAP relative to the model compounds (Table 2) demonstrates the existence of conjugation between the azine and the pyrazolone parts of the molecule.

Most of the compounds studied exhibited a weak fluorescence in solution (ethanol) at room temperature ($Q_F < 0{\cdot}01$). The Franck–Condon fluorescence transitions were in the region 23000–18000 $cm^{-1}$ (Table 2). The weak fluorescence of these compounds may be attributed to the

possibility of rotation around the single C–C and N–N bonds. However, the fluorescence intensity of the UAP was slightly enhanced (2–3 times) with an increase in the viscosity of the solution or on freezing at 77 K. None of the compounds exhibited phosphorescence in 'frozen' solution and all the solutions studied were photostable. On the basis of these experimental results, it can be assumed that the intramolecular motions of the different fragments of UAP, connected by single bonds, are not the reason for the low fluorescence intensity and that another mechanism of radiationless deactivation is operative. Only in the case of the 9-anthracenyl derivative, which is non-fluorescent at room temperature, was the fluorescence intensity enhanced to a greater extent upon freezing (around 30 times), becoming comparable with that of the 'frozen' solutions of the other compounds. This shows that the rotation of the anthracenyl substituent around the single C–C bond is a significant mode for the radiationless deactivation at room temperature.

UAP containing a dialkylamino group in the *p*-position of the phenyl ring exhibit a relatively more intense fluorescence ($Q_F$ around 0·1), and compounds with a methoxy, methyl or halogen substituent in the *p*-position have a much weaker fluorescence ($Q_F < 0{\cdot}01$). The latter observation also holds when the substituent is an aldehyde group (compound **6**), as well as in the case of the 9-ethyl-3-carbazolyl derivative (compound **15**). The compound with a nitro group in the *p*-position (compound **7**), and those with a 2-naphthyl (compound **13**) or a 9-anthracenyl group (compound **14**) were practically non-fluorescent in any solvent.

As with absorption, the energy of the fluorescence transition of the unsymmetrical azines of the pyrazolones did not depend substantially on the solvent polarity. The fluorescence intensity was lowest in hexane and increased with increasing solvent polarity.

All compounds studied, except the nitro derivative (compound **7**), fluoresced intensely in the solid phase in the region 20500–17000 $cm^{-1}$, as did compounds **13** and **14**, which were non-fluorescent in solution. This intense fluorescence suggests that the UAP studied may be of practical interest as additives to daylight fluorescent pigments.

### 3.2 Structure of the unsymmetrical azines of 4-acetyl-3-methyl-1-phenyl-5-pyrazolone

It was noted above that the unsymmetrical azines of 4-acetyl-3-methyl-1-phenyl-5-pyrazolone may exist in four tautomeric forms in solution (Fig. 1).

The electronic spectra of the UAP demonstrate the existence of conjugation between the two parts of the molecule (see Section 3.1), also supported by the results of the quantum chemical calculations. Table 3

**TABLE 3**
Computed and Experimental Energies of the Franck–Condon Absorption Transitions of Compound **1**

| *Form* | $\nu_{calc}$ (*f*) | $\nu_{exp}$ (*ε*) |
|---|---|---|
| | 26420 (1·18) | |
| **I** | 36670 (0·0004) | |
| | 37090 (0·05) | |
| | 27690 (1·20) | 26900 (49000) |
| **II** | 36200 (0·0008) | 35400 (9100) |
| | 40650 (0·06) | 39400 (29600) |
| | 26420 (1·18) | |
| **IV** | 35700 (0·0003) | |
| | 37100 (0·05) | |

shows the computed energies of the $\pi$-$\pi^*$ transitions of the different tautomeric forms of the parent compound **1**. It is apparent that the calculated $\pi$-$\pi^*$ transition energies of the tautomeric forms **II** and **IV** are in good agreement with the experimental data.

On the basis of the electronic spectra and the PPP quantum chemical calculations, it can be concluded that the keto tautomeric form **I**, in which there is no conjugation, is not present in solution.

The band at 1720 $cm^{-1}$ in the IR spectrum of the unsubstituted pyrazolone,[12] characteristic of the carbonyl group, is not observed in the IR spectrum of the parent UAP **1**. Consequently, it can also be concluded that there is no carbonyl-containing tautomeric form in solution (i.e. forms **I**, **III** and **IV**). Additionally, no band was observed in the IR spectra in tetrachloromethane, which is typical of an NH or OH group, although absence of a band for the OH group may also be attributed to the fact that it is chelated.[23] The IR results suggest that the enol form **II** may be present in solution.

$^{13}C$ NMR results also show that forms **I**, **III** and **IV** are not present, as they all contain a carbonyl group, while the $^{13}C$ NMR spectrum of **1** shows no signals in the region of the carbonyl carbon atoms, but shows signals at 162·5 ppm (enol carbon atom) and 99·1 ppm ($sp^2$ carbon atom of the type C=C—OH).[24] In the $^1H$ NMR spectra, there is a signal in the region 13–15 ppm characteristic of enols. The position of the signal does not change upon dilution, which, together with the shape of the signal, indicates the existence of a strong intramolecular hydrogen bond (O—H . . . N). The NMR results clearly indicate that the enol form **II** of the unsymmetrical azines of 4-acetyl-3-methyl-1-phenyl-5-pyrazolone predominates in solution.

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