[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FRANKLIN AND MARSHALL COLLEGE]

Infrared Study of Arylazopyrazolone Compounds and Their Copper Derivatives

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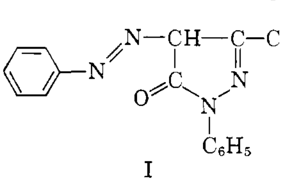
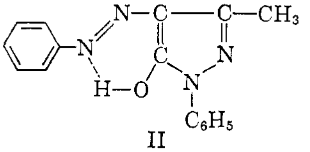
Through the infrared study of a number of substituted 4-benzeneazo-5-pyrazolones and their copper derivatives, it is proposed that the azo-keto form (I) is the principal structure. The azo stretching frequency N=N is assigned in the range 1565 to 1555 cm.$^{-1}$, the ring C=N band from 1610 to 1600 cm.$^{-1}$, and the carbonyl band from 1685 to 1665 cm.$^{-1}$ Nickel(II) coordinates with 1-phenyl-3-methyl-4-benzeneazo-5-thiopyrazolone to form a chelate ring with benzenoid type resonance through π-bonding from the metal to the ligand.

Recently it was reported[2] that the simple arylazopyrazolone compounds probably exist primarily in the azo-keto form (I) and that there was no evidence for the hydroxy-azo form (II), the quinonehydrazone form (III), the antipyrine form (IV), or the zwitterion structure that was proposed for the arylazo compounds.[3]


I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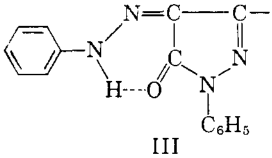
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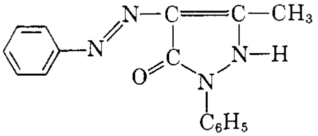
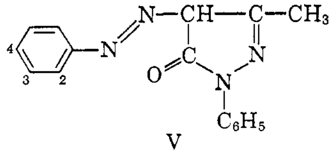
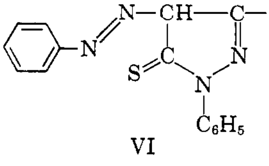

IV

As a continuation of the study of the structure of arylazopyrazolone compounds, the infrared spectra of several 2-, 3-, or 4-substituted arylazopyrazolones and related compounds were studied.

In the spectrum of each of the compounds of type (V), a sharp, well defined band was found in the range 1685 to 1665 cm.$^{-1}$ Although it is reasonable to assign this peak to the C=O on the basis of previous infrared studies of amides,[4] the assignment of this peak is confirmed by the following data. First, this peak is absent in the spectrum of 1-phenyl-3-methyl-4-benzeneazo-5-thiopyrazolone (VI). Secondly, the peak is absent in the spectrum of the *O*-methyl derivative of the unsubstituted compound VII but present in that of the *N*-methyl derivative VIII. Thirdly, this peak is absent in the spectra of all metal derivatives IX of the azo compounds studied.


V

Va = 2-CH_3
Vb = 3-CH_3
Vc = 4-CH_3
Vd = 2-Cl
Ve = 3-Cl
Vf = 4-Cl
Vg = 2-NO_2
Vh = 3-NO_2
Vi = 4-NO_2
Vj = 3-Br
Vk = 4-Br
Vl = 4-I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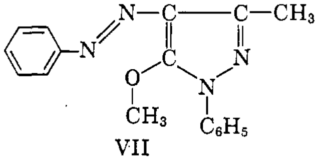
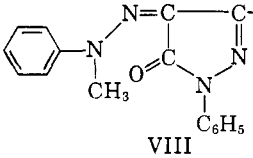
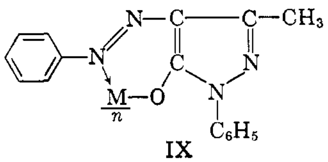
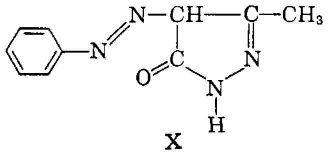

VII


VIII


IX

There are also no significant bands above 1700 cm.$^{-1}$ which can be assigned to either the —NH or the —OH group. However, in the spectrum of 3-methyl-4-benzeneazo-5-pyrazolone (X), which does contain an —NH group, a sharp band assigned to the —NH group occurred at 3600 cm.$^{-1}$ Although the possibility exists that if structure III represents the aryl azo pyrazolone compounds, the —NH absorption would be very broad and weak, due to hydrogen bonding, and thus unde-


X

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[1] Summer research fellow, 1960.

[2] F. A. Snavely and F. H. Suydam, *J. Org. Chem.*, **24**, 2039 (1959).

[3] M. Dolinsky and J. H. Jones, *J. Assoc. Offic. Agr. Chemists*, **37**, 197 (1954).

[4] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., J. Wiley & Sons, Inc., New York, 1958, p. 205.

TABLE I

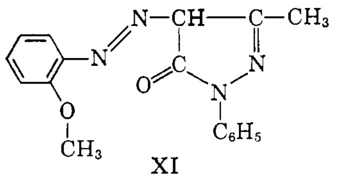
ELECTRONIC ABSORPTION PEAKS OF COMPOUNDS

Solvent	XI (in mμ)				XII (in mμ)			
	λ_{max}	log a_M	λ_{max}	log a_M	λ_{max}	log a_M	λ_{max}	log a_M
Dioxane[a]	253	4.41	412	4.35	255	4.45	415	4.38
95% C_2H_5OH	250	4.37	415	4.32	251	4.33	420	4.33
Benzene			415	4.34			418	4.36

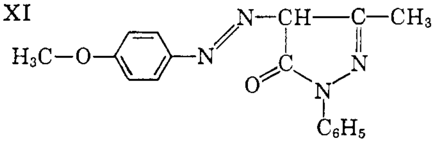
[a] These values are in agreement with those of D. D. M. Casoni, *Boll. Sci. facclta chim. ind. Bologna*, **9**, 4 (1951); *Chem. Abstr.*, **45**, 7353 (1951).

tectable,[5] structure I is more reasonable since the spectrum of VIII is significantly different from that of 1-phenyl-3-methyl-4-benzeneazo-5-pyrazolone (V). In addition the carbonyl absorption for VIII, 1670 cm.$^{-1}$, is about the same as that of V, 1665. If structure III were present one would expect a shift of the C=O band to lower frequencies due to hydrogen bonding.

Structure I is further confirmed by the electronic spectra of 1-phenyl-3-methyl-4-(2-methoxybenzeneazo)-5-pyrazolone (XI) and 1-phenyl-3-methyl-4-(4-methoxybenzeneazo-5-pyrazolone (XII), which are almost identical[6] (see Table I). Structure I explains this better than either structure II or III, since in structure I there is no hydrogen to interact with the methoxy group whether it is *ortho* or *para*. It is also to be noted that there is no significant difference in the visible spectra of XI and XII in benzene, dioxane or 95% ethanol as the solvents. Thus the tautomerism that Burawoy[7] finds with certain *o*-hydroxyarylazo compounds is also missing.



XI



XII

During the course of these studies, Pelz[8] *et al.*, reported infrared data on 1-phenyl-3-methyl-5-pyrazolone and its 4-benzeneazo derivative. An assignment of 1704 cm.$^{-1}$ was made for the carbonyl band in the pyrazolone. The absence of this band in the azo derivative (a new absorption at 1655 cm.$^{-1}$ is noted) leads them to the conclusion that the hydroxy-azo form II is present.

TABLE II

INFRARED ABSORPTION PEAKS OF THE ARYL AZO PYRAZOLONES AND RELATED COMPOUNDS, CM.$^{-1}$

Compound	C—H	C=O	C=N	N=N
V	3070	1665	1605	1560
VI	3050	—	1610	1555
VII	3080	—	1605	1560
VIII	3080	1670	1610	—
X[a]	3050	1675	1610	1560
Va	3050	1665	1600	1560
Vb	3080	1665	1600	1555
Vc	3080	1665	1610	1560
Cu of Vc	3050	—	1600	1565
Vd	3080	1665	1600	1560
Cu of Vd	[b]	—	1600	1565
Ve	3080	1665	1610	1560
Vf	3080	1665	1600	1560
Cu of Vf	[b]	—	1600	1565
Vg	[b]	1680	1610	1560
Vh	3080	1670	1610	1560
Vi	3080	1670	1610	1560
Vi (KBr pellet)[2]		1670		
Vj	3050	1665	1600	1560
Cu of Vj	[b]	—	1600	1565
Vk	3080	1665	1600	1560
Cu of Vk	[b]	—	1600	1565
Vl	3080	1670	1600	1560
Cu of Vl	[b]	—	1600	1565
Ni of VI	3050	—	1600	—

[a] Also N—H stretch at 3600 cm.$^{-1}$ [b] Solution too dilute to assign frequency.

Although a fair amount of infrared work has been done on azo compounds, no definite assignment of the N=N stretching frequency has been made.[9] Difficulty in assignment of the azo frequency has resulted from two main complications. First, it is doubtful if a true nitrogen-nitrogen double bond exists in many azo compounds, and secondly, most previously examined azo compounds were symmetrical in as much as the azo group was joined to two aromatic nuclei. Since the azo group itself is symmetrical, its stretching frequency would probably be weak or completely absent in symmetrical compounds such as azobenzene. However, conditional assignment of the azo group has been made in the region around 1579 cm.$^{-1}$ and 1406 cm.$^{-1}$ [10,11]

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(5) D. Hadzi, *J. Chem. Soc.*, 2143 (1956).

(6) A. Baidens, *Absorption Spectra of Azo Compounds*, Honors thesis, Franklin and Marshall College, 1954.

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(10) R. S. W. Le Fevre, M. F. O'Dwyer, and R. L. Werner, *Australian J. Chem.*, **6**, 341 (1953).

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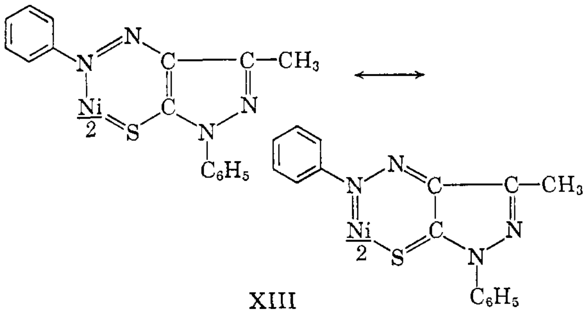
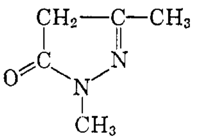
The arylazopyrazolone compounds studied do contain a true nitrogen-nitrogen double bond and are definitely not symmetrical. In the spectrum of each of the compounds examined, an intense peak was noted in the region from 1565 to 1555 cm.$^{-1}$ which has been assigned to the azo group. This peak contained a shoulder on the high frequency side which disappeared in the spectra of all of the metal derivatives. In the case of the nickel(II) derivative of VI the entire band disappeared. This peak is present in the spectrum of the *O*-methyl derivative VII. In the spectrum of the *N*-methyl derivative VIII, which does not contain an azo group, there is no peak from 1565 to 1555 cm.$^{-1}$, but a large peak is present at 1535 cm.$^{-1}$ However, the *O*-methyl derivative also shows a large peak at 1535 cm.$^{-1}$ Peaks in this region are also found in the simple azo derivatives.

The great intensity of the azo peak might result from the azo peak being superimposed on a peak due to ring vibrations. The intensity might also result from the definite asymmetry of the aryl azo pyrazolone compounds which would cause a large change of dipole moment during the stretching vibration mode and thus greater intensity. The complete disappearance of this peak in the spectrum of the nickel (II) derivative of the azo thiopyrazolone compound (VI) is probably explained by the benzenoid type resonance in the metal chelate ring (XIII). Measurements of the stability constants (to be reported later) confirm the dative π-bonding from the metal to the sulfur. This kind of ring structure cannot occur with the azo pyrazolone metal derivatives and thus the azo peak is either displaced slightly or reduced in intensity.

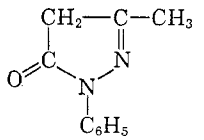


XIII

Gagnon *et al.*[12] assign a peak at 1600 cm.$^{-1}$ to the cyclic carbon-nitrogen double bond in 4-substituted 3-phenyl-5-pyrazolones and 4-substituted 1,3-diphenyl-5-pyrazolones. In the spectra of all of the arylazo compounds examined, a peak appeared in the region from 1610 to 1590 cm.$^{-1}$ which has been assigned to the pyrazolone C=N. W. Pelz[8] *et al.* call the peak in this region a ring vibration. A close inspection of our spectra show that the peak at 1610 cm.$^{-1}$ generally has a weak shoulder so that the C=N and the ring vibration may easily coincide. The spectrum of 1,3-dimethyl-5-pyrazolone (XIV) which does not contain a benzene ring has a sharp peak at 1610 cm.$^{-1}$ The spectrum of 1-phenyl-3-methyl-5-pyrazolone (XV) has two clearly defined peaks in this region, one at 1630 cm.$^{-1}$ and one at 1600 cm.$^{-1}$



XIV



XV

In the spectra of all of the metal derivatives of the arylazopyrazolone compounds, a broad, multipeaked absorption occurred from 1470 to 1385 cm.$^{-1}$, which was not present in the spectra of the free compounds. This broad absorption might be connected with the metal chelate ring vibration. However, a fairly similar absorption was also found with the *O*-methyl derivative VII and may possibly be the pyrazole ring vibration.

The region from 900 to 680 cm.$^{-1}$ shows the typical substituted benzene ring vibrations. A constant band at 690 cm.$^{-1}$, the monophenyl, is found with all of the azo derivatives. A band in the region from 835 to 825 cm.$^{-1}$ is found for the *para* substituted phenyl, and one in the region from 900 to 870 cm.$^{-1}$ for the *meta* substituted phenyl.

EXPERIMENTAL

All melting points are uncorrected.

The spectra were taken on a Perkin-Elmer infrared spectrophotometer Model 137 in chloroform as the solvent.

1-Phenyl-3-methyl-5-thiopyrazolone was prepared by the method of Michaelis.[13] The compound was recrystallized from 95% ethanol to give fine, white, needle-like crystals, m.p. 110°, reported[13] 109°.

1-Phenyl-3-methyl-4-benzeneazo-5-thiopyrazolone was prepared by coupling benzenediazonium chloride to the thiopyrazolone using a sodium acetate buffer. It was recrystallized from 95% ethanol to give dark red needles with a greenish luster, m.p. 97–98°, reported[14] 97°.

1,3-Dimethyl-5-pyrazolone was prepared by condensing acetoacetic ester with methylhydrazine in aqueous solution.[15] It was recrystallized from benzene to give a white crystalline product m.p. 122°, reported[15] 117°.

N-Methyl derivative of 1-phenyl-3-methyl-4-benzeneazo-5-pyrazolone. A mixture of 6.0 g. of 1-phenyl-3-methyl-4-benzeneazo-5-pyrazolone, 9.6 ml. of 5% sodium methylate solution, and 1.5 ml. of methyl iodide was refluxed for 3 hr. The red crystals, formed on cooling, were filtered and washed with 1:1 methyl alcohol-water. The residue was dissolved in dilute alcoholic potassium hydroxide and precipitated by the addition of water. The orange precipitate was recrystallized from 95% ethanol; m.p. 145°, reported[16] 144°.

O-Methyl derivative of 1-phenyl-3-methyl-4-benzeneazo-5-pyrazolone. A solution of 1-phenyl-3-methyl-4-benzeneazo-5-

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(12) P. E. Gagnon, J. I. Boivin, and R. J. Paquin, *Can. J. Chem.*, **31**, 1025 (1953).

(13) A. Michaelis and R. Pander, *Ann.*, **361**, 263 (1908).

(14) A. Michaelis, R. Leonhardt, and K. Wahle, *Ann.*, **338**, 193 (1905).

(15) K. Auwers and F. Niemeyer, *J. prakt. Chem.*, **110**, 153 (1925).

(16) K. Auwers, *Ann.*, **378**, 241 (1911).

pyrazolone in 0.6 g. of sodium hydroxide and 20 ml. of methyl alcohol was heated to reflux. Freshly distilled dimethyl sulfate, 1 ml., was added to the solution dropwise. One hour later 1 ml. of dimethyl sulfate was added to the dark red solution dropwise and 0.5 hr. later another 0.6 ml. was added. In a few moments an orange precipitate formed. The reaction mixture was cooled, suction filtered, and the residue extracted with 30 ml. of boiling methanol. The filtrate was treated with concd. sodium hydroxide and boiled 10 min. About 100 ml. of water was added and the orange-brown precipitate which formed was recrystallized repeatedly from methanol to yield dense yellow crystals; m.p. 80.5–81.5°; reported[16] 78°.

The 3-methyl-4-benzeneazo-5-pyrazolone was prepared by two different routes to establish the coupling of the diazonium salt in the 4-position.

Method 1. Benzenediazonium chloride was coupled to 3-methyl-5-pyrazolone in a dilute sodium hydroxide solution buffered with sodium acetate. The crude product was recrystallized from 95% ethanol in glittering yellow platelets, m.p. 203°, reported[17] 200-201°.

Method 2. Benzeneazoacetoacetic ester (30 g.) was dissolved in 100 ml. of glacial acetic acid. The solution was heated to reflux and 5.9 g. of 85% hydrazine hydrate was added over a period of 15 min. and refluxed for 2 hr. The reaction mixture was cooled, filtered, and the yellow crystals digested with dilute hydrochloric acid. The crude product was recrystallized from 95% ethanol, m.p. 202–203°. The infrared spectrum in chloroform was identical with that of the product from Method 1.

The derivatives of 1-phenyl-3-methyl-4-benzeneazo-5-pyrazolone were prepared by coupling the appropriate diazotized amines to the pyrazolone in dilute sodium hydroxide solution buffered with sodium acetate. The crude compounds were recrystallized from dioxane and tested for purity as previously reported.[18]

The unsubstituted azo compound V, orange needles, m.p. 155°, reported[18] 155°.

The 2-methyl derivative Va, orange needles, m.p. 184–185°, reported[19] 185°.

The 3-methyl derivative Vb, orange-red needles, m.p. 120°, reported[20] 119–120°.

The 4-methyl derivative Vc, orange needles, m.p. 139–140°, reported[18] 138–140°.

The 2-chloro derivative Vd, orange-red crystals, m.p. 193°, reported[21] 195°.

The 3-chloro derivative Ve, orange-red fibers, m.p. 134–135°, reported[20] 134–135°.

The 4-chloro derivative Vf, bright orange fibers, m.p. 141–142°, reported[18] 141–142°.

The 2-nitro derivative Vg, red-orange platelets, m.p. 217–218°, reported[21] 209°.

The 3-nitro derivative Vh, orange needles, m.p. 184°, reported[20] 183–184°.

The 4-nitro derivative Vi, red-orange platelets, m.p. 199–200°, reported[2] 199–200°.

The 3-bromo derivative Vj, tiny orange crystals, m.p. 158°, reported[20] 157–158°.

The 4-bromo derivative, Vk, orange fibers, m.p. 152–153°, reported[20] 152–153.5°.

The 4-iodo derivative Vl, orange needles, m.p. 156–157°, reported[20] 155–156°.

Copper(II) derivatives were generally prepared by dissolving 1 mmole of azo compound in a 100 ml. of 75:25 volume % dioxane–water which contained 1 mmole of nitric acid and 0.5 mmole of copper(II) nitrate. A dilute solution of sodium hydroxide was slowly added with stirring until the *p*H meter reading corresponded to the midpoint of the buffer zone of formation of the metal complex about 3.50. Upon standing at room temperature the complexes precipitated out. They were recrystallized from chlorobenzene.

Copper(II) derivative of Vc, dark brown needles, m.p. 223–224°, reported[6] 222–223°.

Copper(II) derivative of Vd, brown microcrystalline powder, m.p. 263–264°, reported[22] 263°.

Copper(II) derivative of Vf, red-purple needles, m.p. 269–270°, reported[18] 268–270°.

Copper(II) derivative of Vj, brown crystalline powder, m.p. 238–239°, reported[20] 238–239°.

Copper(II) derivative of Vk, brown crystalline powder, m.p. 258–259°, reported[20] 258–259°.

Copper(II) derivative of 1-phenyl-3-methyl-4-(4-iodobenzeneazo)-5-pyrazolone. To 50 ml. of dioxane were added 0.8084 g. (2 mmoles) of the azo compound, 1 mmole of copper(II) nitrate, 1 mmole of nitric acid 2 mmoles of urea, and 15 ml. of water. Dark brown crystals slowly formed from the solution during 6 hr. of reflux. The hot solution was suction filtered, washed with dioxane–water and hot water; yield 0.417 g. or 48% m.p. 266–267°.

Anal. Calcd. for $Cu(C_{16}H_{12}ON_4I)_2$: Cu, 7.30; N, 12.88. Found: Cu, 7.2; N, 12.8.

Nickel(II) derivative of VI. In 100 ml. of 75:25 dioxane–water is dissolved 1 mmole of VI and 0.5 mmole of the metal nitrate. Dilute sodium hydroxide is slowly added with stirring to a *p*H meter reading of 2.20, which corresponds to the midpoint of the buffer zone of formation of the metal complex. Upon standing the nickel derivative precipitated out as tiny black crystals, m.p. 233°.

Anal. Calcd. for $Ni(C_{16}H_{13}SN_4)_2$: C, 59.52; H, 4.03; N, 17.36. Found: C, 58.98; H, 4.12; N, 16.95.

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LANCASTER, PA.

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