[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA]

THE ULTRAVIOLET ABSORPTION SPECTRA OF SUBSTITUTED PYRAZOLES

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The ultraviolet absorption spectra of heterocyclic compounds have been compared variously to analogous carbon compounds (1). Pyrrole has been compared to cyclopentadiene, though differences arise due to the presence of the closed π orbital system present in the former. Comparison of indole with both indene and naphthalene reveals a qualitative similarity to both, but no more striking agreement with one than with the other (2). Other comparisons have been made with compounds in which changes have been made in the heteroatom (1).

In connection with investigations of the behavior of β-dicarbonyl compounds we have had opportunity to prepare several simple alkyl substituted pyrazoles, and to examine their spectra. Mangini and Dal Monte (3) have recently reported the spectra of pyrazole (I) and 3-methyl (II), 4-methyl- (III), and 3,5-dimethylpyrazole (IV). Our results are in agreement with those of Mangini and Dal Monte, and extend their observations.

The pyrazoles were prepared in general by standard procedures. Many of the compounds are new, and data characterizing them are given in full in the experimental section. In the case of some of the previously known compounds the previous reports are divergent. Whereas von Auwers and Cauer (4) report a picrate of m.p. 150–152° for 3-*n*-propylpyrazole, Nesmeyanov, Krochetkov, and Rybinskaya (5) report a melting point of 113–114°. We find that the picrate melts at 141–142°. 3,5-Diethylpyrazole has been reported briefly without further description (6).

The pyrazoles are in general low-melting solids, and therefore are not satisfactory for the characterization of mixtures which might result from condensation of unsymmetrical ketones with esters.

Pyrazole itself shows an absorption maximum in 95% ethanol at about 210 mμ which is near the limit of the Beckman DU spectrophotometer, and therefore subject to considerable error, both in the exact position and intensity of this maximum (7). This maximum may be compared with that reported (1) at 210 mμ for pyrrole, at 200 mμ for furan, and 200 mμ for cyclopentadiene.

Substitution of alkyl groups leads to a bathochromic shift of the position of the maximum. The position and intensity of the absorption maximum for each compound studied in the present investigation are summarized in Table I.

It is clear that substitution in the 4 position leads to a much larger bathochromic shift than does substitution in the 3 or the 5 position. In fact, it appears that a 3-substituted pyrazole has its position of maximum absorption at effectively the same position as does a 3,5-disubstituted pyrazole. The spectral shifts observed are suitable for the supplemental characterization of the position of substitution in the pyrazole ring.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF ALKYL SUBSTITUTED PYRAZOLES IN 95% ETHANOL

Compound	λ_{max}, mμ	log ϵ_{max}
Pyrazole (I)	210–211	3.53
3-Methylpyrazole (II)	214	3.58
4-Methylpyrazole (III)	220	3.47
3-*n*-Propylpyrazole	215, 218	3.60
3-*n*-Butylpyrazole	218	3.60
3,4-Dimethylpyrazole	221–223	3.63
3-Ethyl-4-methylpyrazole	222–223	3.63
3,5-Dimethylpyrazole (IV)	216–217	3.61
3,5-Diethylpyrazole	214	3.67
3,5-Di-*n*-propylpyrazole	216	3.69
3-Ethyl-5-*n*-propylpyrazole	215	3.69
3-Methyl-5-*n*-propylpyrazole	216	3.66
3,4-Dimethyl-5-ethylpyrazole	223	3.70
3,5-Diethyl-4-methylpyrazole	224	3.71
3,5-Di-*n*-propyl-4-ethylpyrazole	223	3.72

In the case of 3-*n*-propylpyrazole and 3-*n*-butylpyrazole it appears that there may be present some of the isomeric 3,4-disubstituted pyrazole, since these materials were prepared by the condensation of formate esters with 2-pentanone and 2-hexanone. In the case of the condensation of ethyl formate with 2-pentanone Mariella and Stansfield (8) have discussed the possibility that some of the isomeric hydroxymethylene ketone is formed.

The spectral shifts observed may be compared with those reported by Andon, Cox, and Herington (9) for alkyl substituted pyridines, in which a 4-alkyl group exerts much less influence on the position of the maximum than does a 2 or a 3 substituent. Longuet-Higgins and Sowden (10) have also shown that an hypsochromic shift is to be expected in non-alternant hydrocarbons (such as azulene) on methyl substitution in certain positions.

In acidic solution somewhat similar results are observed, which are summarized in Table II.

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA OF ALKYL SUBSTITUTED PYRAZOLES IN 6 *N* HYDROCHLORIC ACID

Compound	λ_{max}, mμ	log ϵ_{max}
Pyrazole	217	3.67
4-Methylpyrazole	226	3.65
3,4-Dimethylpyrazole	229	3.78
3,5-Di-*n*-propylpyrazole	221–222	3.97
3,5-Di-*n*-propyl-4-ethylpyrazole	231–232	3.93
3-Methylpyrazole (3)	218 (1 *N*)	3.77
3,5-Dimethylpyrazole (3)	220 (1 *N*)	3.87

Alkyl substitution in the 4 position appears to lead to a bathochromic shift of about 9 mμ, while substitution in the 3 or the 5 position appears to lead to a bathochromic shift of 2 or 3 mμ. The last two examples in the table are taken from the work of Mangini and Dal Monte Casoni (3), and were carried out in 1 *N* alcoholic hydrogen chloride (note that *Chemical Abstracts*, by error, refers to ether as the solvent). A recent report by Dal Monte Casoni, Mangini, and Passerini (11) gives additional data on 3,4-dimethylpyrazole and 3,4,5-trimethylpyrazole. Unfortunately the original is not available to us.

EXPERIMENTAL[1]

Pyrazole (I). Pyrazole was prepared by the condensation of 1,1,3,3-tetraethoxypropane[2] with hydrazine as described by Jones (12). The yield was 70%, m.p. 67.5–69.2° [lit. (11) m.p. 70°], b.p. 96° (16 mm.).

3-Methylpyrazole (II). II was prepared by the method of Knorr (13), b.p. 108° (25 mm.).

4-Methylpyrazole (III). III was prepared by the reaction of diazomethane with methyl crotonate, following the procedure of von Pechmann and Burckard (14). Decarboxylation of 4-methylpyrazole-3-carboxylic acid proceeded at 300° to give III, b.p. 98.5–99.5° (18 mm.) [lit. (14) b.p. 204–206°], m.p. 15.8–18.5°, n_D^{22} 1.4913.

Anal. Calc'd for $C_4H_6N_2$: N, 34.12. Found: N, 33.78.

3,4-Dimethylpyrazole. (*General Procedure A.*) To alcohol-free sodium isopropoxide, prepared from 11.5 g. of sodium and 200 ml. of dry isopropyl alcohol, isopropyl formate (132 g.) was added with cooling in an ice-bath. Butanone, 36 g., was added dropwise with stirring over a period of 30 minutes, during which time the solid sodium isopropoxide dissolved. The mixture was stirred in an ice-bath for an additional two hours, and then was allowed to stand at room temperature for 16 hours. The very viscous product was poured into 300 ml. of water, and the aqueous solution was extracted with two 100-ml. portions of ether, which were combined and washed with two 50-ml. portions of *cold* 1 *N* sodium hydroxide, and these were added to the original aqueous phase. Hydrazine hydrate (85%), 60 g., was added to the aqueous phase with swirling, the mixture was heated to reflux and acetic acid, 31 ml., was added cautiously and the mixture was again heated to reflux briefly. The pyrazole layer was separated, and the aqueous layer was extracted with three 50-ml. portions of ether. The combined pyrazole layer and ether extracts were washed with dilute sodium hydroxide, dried, and fractionated. 3,4-Dimethylpyrazole, 34.8 g. (72%), was obtained, b.p. 106–107° (11 mm.). A sample crystallized from petroleum ether melted at 57–58° [lit. (15) m.p. 58°]. The *picrate* melted at 151–153° [lit. (15) m.p. 153°].

A small sample of the sodium salt of the keto-aldehyde was allowed to react with 2,4-dinitrophenylhydrazine to give *1-(2,4-dinitrophenyl)-3,4 (4,5)-dimethylpyrazole*, m.p. 136.5–137.5° as crystallized from aqueous ethanol.

Anal. Calc'd for $C_{11}H_{10}N_4O_4$: N, 21.37. Found: N, 21.50.

The use of sodium methoxide in methanol in procedure *A* for the condensation of butanone with methyl formate afforded a 55% yield of 3,4-dimethylpyrazole.

3-n-Propylpyrazole. From the condensation of 2-pentanone (86 g.) with ethyl formate (222 g.) in the presence of sodium methoxide by procedure *A* outlined above, followed by the addition of hydrazine, there was isolated 64 g. (58%) of 3-*n*-propylpyrazole, b.p. 117–118° (11 mm.); reported (4) b.p. 117° (13 mm.), n_D^{24} 1.4897.

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[1] Analyses are by the Microanalytical Laboratory of the University of California. Melting points are corrected; boiling points are uncorrected. All distillations were carried out with a two foot modified Podbielniak column.

[2] We are grateful to Carbide and Carbon Chemicals Corp. for a generous supply of 1,1,3,3-tetraethoxypropane.

Anal. Calc'd for $C_6H_{10}N_2$: C, 65.41; H, 9.15; N, 25.44; C-CH_3, 13.8.
Found: C, 65.61; H, 9.12; N, 25.48; C-CH_3, 9.6.

The *picrate*, crystallized from aqueous ethanol, melted at 142.5–143.0° [reported m.p. 150–152° (4), m.p. 113–114° (5)].

Anal. Calc'd for $C_{12}H_{13}N_5O_7$: C, 42.48; H, 3.86; N, 20.65.
Found: C, 42.66; H, 3.74; N, 20.92.

Using sodium sand as catalyst, there was obtained from 45 g. of 2-pentanone 46.7 g. (82%) of 3-*n*-propylpyrazole.

3-n-Butylpyrazole. In the usual manner 11.5 g. of sodium, 100 ml. of dry ethanol, 50 g. of 2-hexanone, and 111 g. of ethyl formate were allowed to react. Following treatment with hydrazine, 47.3 g. (75.3%) of 3-*n*-butylpyrazole was obtained, b.p. 127–128° (10.5 mm.), $n_D^{18.5}$ 1.4870.

Anal. Calc'd for $C_7H_{12}N_2$: C, 67.70; H, 9.74; N, 22.56.
Found: C, 67.62; H, 9.52; N, 22.55.

The *picrate*, crystallized from benzene-hexane, melted at 105.0–106.5°.

Anal. Calc'd for $C_{13}H_{15}N_5O_7$: C, 44.19; H, 4.28; N, 19.82.
Found: C, 44.70; H, 4.27; N, 19.86.

3-Ethyl-4-methylpyrazole. 3-Ethyl-4-methylpyrazole was prepared by the condensation of diethyl ketone with ethyl formate in the presence of sodium methoxide, followed by treatment with hydrazine; yield 70%, b.p. 124–125° (17 mm.), n_D^{25} 1.4917.

Anal. Calc'd for $C_6H_{10}N_2$: C, 65.41; H, 9.15; N, 25.44.
Found: C, 65.38; H, 8.64; N, 25.08.

The *picrate*, crystallized from benzene-petroleum ether, melted at 132.0–132.5°.

Anal. Calc'd for $C_{12}H_{13}N_5O_7$: C, 42.48; H, 3.86; N, 20.65.
Found: C, 42.73; H, 3.88; N, 20.67.

3,5-Dimethylpyrazole was obtained from acetylacetone and hydrazine m.p. 106.5–107.5° [lit. (16) 107–108°].

3,5-Diethylpyrazole. Dipropionylmethane, n_D^{25} 1.4533, prepared by the method of Sprague, Beckham, and Adkins (17), was allowed to react with hydrazine in slightly alkaline solution. 3,5-Diethylpyrazole, m.p. 22–24°, n_D^{25} 1.4853, b.p. 116–117° (8 mm.) [reported b.p. 119–120° (9 mm.) (6)], was obtained in 20% yield.

Anal. Calc'd for $C_7H_{12}N_2$: C, 67.69; H, 9.74; N, 22.56.
Found: C, 67.80; H, 9.55; N, 22.51.

The *picrate*, crystallized from benzene-hexane, melted at 149–150°.

Anal. Calc'd for $C_{13}H_{15}N_5O_7$: C, 44.19; H, 4.28; N, 19.82.
Found: C, 45.14; H, 4.64; N, 19.61.

3,5-Di-n-propylpyrazole. Dibutyrylmethane, prepared by the procedure of Adams and Hauser (18), was not isolated, but was treated directly with hydrazine hydrate and acetic acid to give 3,5-di-*n*-propylpyrazole (31%), $n_D^{23.5}$ 1.4792, m.p. 35–36°, b.p. 147–148° (13 mm.).

Anal. Calc'd for $C_9H_{16}N_2$: C, 71.00; H, 10.61; N, 18.40.
Found: C, 70.44; H, 10.58; N, 18.67.

An attempt to prepare the picrate was unsuccessful.

3-Methyl-5-n-propylpyrazole. Acetylbutyrylmethane, prepared by the general method of Adams and Hauser (18), was allowed to react with hydrazine in slightly basic solution. The pyrazole was obtained in 35% yield, b.p. 130–132° (15 mm.), n_D^{25} 1.4847, d_4^{25} 0.9489.

Anal. Calc'd for $C_7H_{12}N_2$: C, 67.69; H, 9.74; N, 22.56.
Found: C, 67.83; H, 9.81; N, 22.29.

The *picrate*, m.p. 109.8–110.2°, was recrystallized from benzene.

Anal. Calc'd for $C_{13}H_{15}N_5O_7$: C, 44.19; H, 4.28; N, 19.82.
Found: C, 44.59; H, 4.22; N, 20.00.

3-Ethyl-5-n-propylpyrazole was prepared in 35% yield by a similar procedure, b.p. 135–135.5° (12 mm.), n_D^{25} 1.4828, d_4^{25} 0.9358, m.p. 19–21°.

Anal. Calc'd for $C_8H_{14}N_2$: C, 69.52; H, 10.21; N, 20.27.
Found: C, 69.53; H, 10.06; N, 20.31.

The *picrate*, m.p. 105.5–106.5°, was slightly orange instead of the usual yellow.

Anal. Calc'd for $C_{14}H_{17}N_3O_7$: C, 45.78; H, 4.67; N, 19.07.
Found: C, 46.13; H, 4.60; N, 18.96.

3,4-Dimethyl-5-ethylpyrazole. Condensation of ethyl acetate with 3-pentanone by sodium methoxide, followed by treatment with hydrazine hydrate, gave 3,4-dimethyl-5-ethylpyrazole, b.p. 130–131° (15 mm.), n_D^{25} 1.4928, in 20% yield.

Anal. Calc'd for $C_7H_{12}N_2$: C, 67.69; H, 9.74; N, 22.56.
Found: C, 67.81; H, 10.03; N, 22.71.

The *picrate* melted over a wide range after several crystallizations from benzene, m.p. 191–201°.

Anal. Calc'd for $C_{13}H_{15}N_5O_7$: C, 44.19; H, 4.28; N, 19.83.
Found: C, 44.02; H, 4.25; N, 20.18.

3,5-Diethyl-4-methylpyrazole was prepared in 38% yield by the sodamide condensation of ethyl propionate and 3-pentanone, followed by treatment with hydrazine, b.p. 136–137° (13 mm.), m.p. 56.0–57.0°.

Anal. Calc'd for $C_8H_{14}N_2$: C, 69.52; H, 10.21; N, 20.27.
Found: C, 69.67; H, 10.05; N, 20.50.

The *picrate* crystallized from benzene-hexane, m.p. 147–149°.

Anal. Calc'd for $C_{14}H_{17}N_5O_7$: C, 45.78; H, 4.67; N, 19.07.
Found: C, 46.01; H, 4.66; N, 19.14.

3,5-Di-n-propyl-4-ethylpyrazole was prepared in 25% yield by the sodamide method, b.p. 160–161° (14 mm.), m.p., on crystallization from pentane, 60–62°.

Anal. Calc'd for $C_{11}H_{20}N_2$: C, 73.28; H, 11.18; N, 15.54.
Found: C, 73.29; H, 11.01; N, 15.52.

The *picrate* was crystallized from benzene-hexane, m.p. 85.6–87.7°.

Anal. Calc'd for $C_{17}H_{23}N_5O_7$: C, 49.88; H, 5.66; N, 17.11.
Found: C, 50.05; H, 5.61; N, 16.83.

Determination of spectra. All spectra were determined with a Beckman DU spectrophotomer, with concentrations of the pyrazoles such that the observed optical density was about 0.5, at the position of maximum absorption.

SUMMARY

The ultraviolet spectra of several simple alkyl substituted pyrazoles have been examined. It is found that there is a pronounced bathochromic shift induced by the introduction of an alkyl group at the 4 position of the pyrazole ring, and a lesser shift by substitution at the 3 or the 5 position. In acid solution, similar shifts are observed.

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