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Spectroscopic Studies on 2-Pyrazolin-5-one Dyes*[1]

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The spectra of forty-five 2-pyrazolin-5-one dyes in the ultraviolet and visible regions are discussed on the basis of their hydrazone-keto structures. In particular, the effects of sterically-sensitive ortho-substitutions in the 1- and 4-positions on the pyrazolinone ring are investigated. The bathochromic effects on the visible absorption band of pyrazolinone dyes are caused by electron-attracting substituents in the 3-position, not by 1- and 4-substituents.

The visible spectroscopic examination of the 2-pyrazolin-5-one dyes on the basis of an azo-keto or an azo-enol form has been the subject of numerous publications.[1] In one investigation described previously,[2] the structure of 1, 3-disubstituted 2-pyrazolin-5-ones, in which 4-positions were coupled with diazotized anilines, has been disclosed to exist as only one tautomer, a strongly-chelated hydrazone-keto form, in the solid state and in solutions. It is desirable, therefore, to re-investigate the spectroscopic behavior of the pyrazolinone dyes on the basis of the hydrazone-keto structure.

The present investigation will describe the shift of the ultraviolet and visible absorption maxima affected by electron-attracting or electron-donating substituents directly attached to the phenylhydrazono moiety. In addition, the steric inhibition of resonance effects caused by *o, o'*-disubstituted aromatics in the 1- and/or 4-positions on the pyrazolinone ring will also be discussed. The compounds selected as most likely to exhibit these effects are 4-(2, 6-dinitrophenylhydrazono)-, 4-(2, 6-dimethylphenylhydrazono)-, and 4-(2, 6-dimethoxyphenylhydrazono)-1-phenyl-2-pyrazolin-5-ones, in which the 3-positions are replaced by methyl or phenyl groups, and 1-(2, 6-dimethylphenyl)-4-(2,6-dimethylphenylhydrazono)-3-ethoxycarbonyl-2-pyrazolin-5-one.

The forty-five dyes used in this study and the data for their absorptions are listed in Tables 1 and 2. The compounds studied were prepared in

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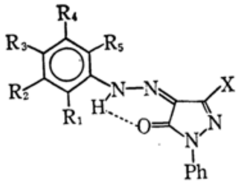
[*1] This work was performed at the Institute of Physical and Chemical Research, Bunkyo-ku, Tokyo

[1] R. H. Wiley and P. Wiley, "The Chemistry of Heterocyclic Compounds," Vol. 20, Chap. III, Interscience Publishers, N. Y. (1964).

[2] H. Yasuda and H. Midorikawa, *J. Org. Chem.*, **31**, 1722 (1966).

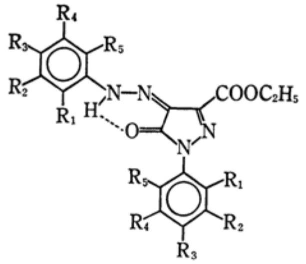
TABLE 1. 3-SUBSTITUTED 1-PHENYL-4-ARYLHYDRAZONO-2-PYRAZOLIN-5-ONES INVESTIGATED



Compound	R_1	R_2	R_3	R_4	R_5	X	Short-wave band (in EtOH)		Long-wave band (in EtOH)	
							λ_{max}	log ε	λ_{max}	log ε
III[a]	H	H	H	H	H	H	250	4.37	398	4.34
IV	H	H	H	H	H	Me	251	4.37	393	4.38
V	H	H	H	H	H	Ph	261	4.39	405	4.38
VI	H	H	H	H	H	$COOC_2H_5$	254 264	4.31 4.31	418	4.26
VII[b]	NO_2	H	H	H	H	Me	247	4.39	406	4.30
VIII[c]	H	NO_2	H	H	H	Me	248	4.34	381	4.32
IX	H	H	NO_2	H	H	Me	245	3.96	397	4.19
X	NO_2	H	NO_2	H	H	Me	244	4.08	400	4.20
XI[d]	NO_2	H	H	H	NO_2	Me	246	4.00	377	3.09
XII	Me	H	H	H	H	Me	252	4.30	402	4.32
XIII	H	Me	H	H	H	Me	254	4.32	396	4.37
XIV	H	H	Me	H	H	Me	254	4.32	400	4.35
XV	Me	Me	H	H	H	Me	254	4.30	403	4.32
XVI	Me	H	Me	H	H	Me	250	4.33	412	4.38
XVII	Me	H	Me	H	H	Me	251	4.23	407	4.26
XVIII	Me	H	H	H	Me	Me	253	4.28	386	4.25
XIX	OMe	H	H	H	H	Me	249	4.30	413	4.33
XX	H	OMe	H	H	H	Me	249	4.26	398	4.33
XXI	H	H	OMe	H	H	Me	250	4.33	419	4.38
XXII	OMe	H	H	OMe	H	Me	244	4.26	435	4.23
XXIII	OMe	H	H	H	OMe	Me	250	4.25	405	4.27
XXIV	NO_2	H	H	H	H	Ph	270	4.33	415	4.28
XXV[e]	H	NO_2	H	H	H	Ph	270	4.37	397	4.26
XXVI	H	H	NO_2	H	H	Ph	273	3.91	408	4.09
XXVII[f]	NO_2	H	NO_2	H	H	Ph	268	4.09	414	4.16
XXVIII[g]	NO_2	H	H	H	NO_2	Ph	266	4.41	393	4.26
XXIX	Me	H	H	H	H	Ph	263	4.54	414	4.49
XXX	H	Me	H	H	H	Ph	264	4.45	405	4.39
XXXI	H	H	Me	H	H	Ph	266	4.63	414	4.59
XXXII	Me	Me	H	H	H	Ph	266	4.23	416	4.13
XXXIII	Me	H	Me	H	H	Ph	267	4.38	422	4.27
XXXIV	Me	H	H	Me	H	Ph	265	4.41	419	4.33
XXXV	Me	H	H	H	Me	Ph	266	4.43	402	4.30
XXXVI	OMe	H	H	H	H	Ph	267	4.43	427	4.37
XXXVII	H	OMe	H	H	H	Ph	271	4.35	410	4.31
XXXVIII	H	H	OMe	H	H	Ph	272	4.53	430	4.43
XXXIX	OMe	H	H	OMe	H	Ph	274	4.31	447	4.18
XL	OMe	H	H	H	OMe	Ph	269	4.43	422	4.34

a) Taken from E. Chargaff and B. Magasanik, *J. Am. Chem. Soc.*, **69**, 1459 (1947). b) Mp 208—209°C, lit. mp 209°C, D. D. M. Casoni, *Boll. sci. facoltá chim. ind. Bologna*, **9**, 4 (1951); *Chem. Abstr.*, **45**, 7353 (1951). c) Mp 183—184°C, lit. mp 183°C, reference as footnote b). d) Recrystallization from dioxane-methanol in brown needles melting at 216—217°C. Found: C, 52.48; H, 3.08; N, 22.64%. Calcd. for $C_{16}H_{12}O_5N_6$: C, 52.17; H, 3.26; N, 22.83%. e) Mp 203—204°C, lit. mp 203°C, reference as footnote b). f) Three recrystallizations from pyridine-methanol in brown needles melting at 239—240°C. Found: C, 58.42; H, 3.12; N, 19.76%. Calcd for $C_{21}H_{14}O_5N_6$: C, 58.60; H, 3.28; N, 19.53%. g) Four recrystallizations from pyridine-methanol in deep violet needles melting at 258—259°C. Found: C, 58.80; H, 3.64; N, 19.62%. Calcd. for $C_{21}H_{14}O_5N_6$: C, 58.60; H, 3.26; N, 19.53%.

TABLE 2. 1-ARYL-4-ARYLHYDRAZONO-3-ETHOXYCARBONYL-2-PYRAZOLIN-5-ONES INVESTIGATED



Compound	R_1	R_2	R_3	R_4	R_5	Short-wave band (in EtOH) λ_{max}	Short-wave band (in EtOH) $\log \varepsilon$	Short-wave band (in EtOH) ε_{max}	θ[a)]	Long-wave band (in EtOH) λ_{max}	Long-wave band (in EtOH) $\log \varepsilon$
VI	H	H	H	H	H	254 260	4.31 4.31	20400 20500	(0°)	418	4.26
XLI	Me	H	H	H	H	253 260	4.09 4.03	12300 10800	41°	444	4.29
XLII	H	Me	H	H	H	258 262	4.33 4.33	21300 21300	0°	423	4.30
XLIII	H	H	Me	H	H	259 265	4.33 4.33	21400 21400	0°	430	4.31
XLIV	Me	Me	H	H	H	256 264	4.01 3.99	10200 9700	45°	446	4.28
XLV	Me	H	Me	H	H	258 266	4.14 4.08	13800 12000	37°	457	4.38
XLVI	Me	H	H	Me	H	245	4.12	13300	36°	447	4.34
XLVII	Me	H	H	H	Me	256 263	3.89 3.89	7700 7800	50°	435	4.31

a) The interplanar angles of the C_{arom}-N bond in the 1-position were calculated by applying the expression $\cos^2\theta=\varepsilon/\varepsilon_0$ assuming that ε_0 will be the same as avarage of two molecular extinction coefficients of the short-wave band for VI.

the course of other investigations,[3,4] except for some nitro compounds. In studying the effects produced upon the absorption by substituents, attention was directed to the long-wave band in the cases of the 3-methyl and 3-phenyl series, but to the short-wave band in the 3-ethoxycarbonyl derivatives.

Electronic Effects. In an attempt to understand the electronic mechanism guiding the absorption of the nitro-substituted dyes investigated, a probable structure contributing to the resonance form of a 4-(2, 4-dinitrophenylhydrazono) derivative will be discussed below.

The lactam group of the pyrazolinone ring plays an important part in the resonance hybrid of the dye concerned. In regard to the electron mobility in this group, it is well known[5] that the internal polarization of the $O{=}\underset{|}{C}{-}\underset{|}{N}{-}$ lactam system produces a net negative effect on the oxygen atom and a positive charge on a nitrogen atom such as $\overset{-}{O}{-}\underset{|}{C}{=}\underset{|}{\overset{+}{N}}{-}$, which has a high dipole moment and a high electron polarizability. The contribution of the resonance structures of the 2, 4-dinitrophenylhydrazones has been discussed exhaustively.[6] These interpretations are now applied to the contribution of the resonance structures of the 2, 4-dinitrophenylhydrazono moiety of the nitro-substituted dyes examined. Thus, the dinitro compound concerned is represented by Ia, b, c, d, e, and f, as illustrated in Chart 1.

In structures Ia, b, and c, the phenylhydrazono moiety is benzenoid, whereas in the other structures it is quinoid. In view of these resonance structures, the ground state should theoretically receive a limited contribution from ionic structures such as Ie and f; in turn, these structures should make large contributions to the electronically-excited state of the dye molecule. In consequence, a long-wave band with a high intensity may be expected throughout the whole combined system, in-

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[3] H. Yasuda and H. Midorikawa, This Bulletin, **39**, 1596 (1966).

[4] H. Yasuda, to be published.

[5] R. D. Brown, A. A. Hukins, R. J. W. LeFèvre, J. Northcott and I. R. Wilson, *J. Chem. Soc.*, **1949**, 2812.

[6] a) J. D. Roberts and C. Green, *J. Am. Chem. Soc.*, **68**, 214 (1946); b) C. Djerassi and E. Ryan, *ibid.*, **71**, 1000 (1949); c) H. H. Szmant and H. J. Planinsek, *ibid.*, **72**, 4042 (1950); d) F. Ramirez and A. F. Kirby, *ibid.*, **76**, 1037 (1954).

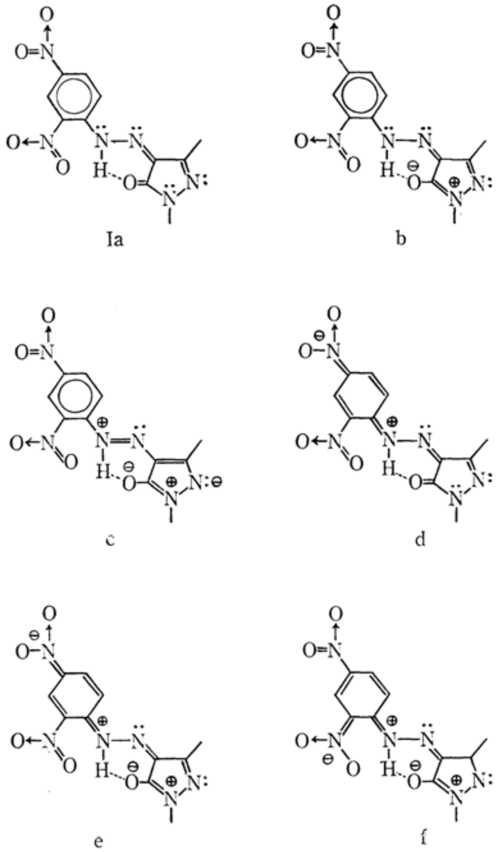


Chart 1.

volving both quinoid and the polarizable pyrazolinone ring.

The absorption maxima of the dyes examined in the ethanolic solution occur at longer wavelengths than those values in an *n*-hexane solution.[*2] It may be expected that low dielectric constant solvents will stabilize the nonpolar contributors in the high-energy state, while the excitation energy will be lowered by such ionic structures as Ie and and f, leaving those of the nonpolar structures unchanged in their high dielectric constant solvents. Thus, the decrease in excitation energy attributable to the former solution results in a bathochromic shift.

It is of interest to note that the substituents in the 3-position have a remarkable influence on the visible absorption region of the four typical compounds, III, IV, V, and VI; *i. e.*, the bathochromic effects increase in the order of substituents, $-CH_3 < H < -C_6H_5 < -COOC_2H_5$, as Table 1 shows. The same phenomena are also observed in all the other compounds. These observations make it reasonable to assume that the stability and contribution of hypothetically-isolated resonance structures, Ie and f, are affected directly by substituents increasing the electron-attracting effects. Conversely, the bathochromic-hypsochromic shifts ascribable to 3-substituents originate from the charge separation, through the conjugated system, between the substituents and the pyrazolinone ring.

Thus, when an electron-withdrawing substituent, for example, is introduced, the positive charge on the 1-nitrogen atom resulting from the mesomeric effect of the substituent is increased; this, by an inductive effect, then expedites the accumulation of the negative charge on the carbonyl-oxygen, stabilizing structures, Ie and f, leading to a bathochromic effect.

Despite the large positive Hammett σ-value and the large effect of the electrostatic interaction[7] of the *p*-nitro group, which would be expected to increase the weight of Ie, and to cause a bathochromic shift, the compounds, IX and XXVI, so substituted show very small Δ-values, $+3$ and $+4$ mμ, in comparison with the non-substituted dyes, IV and V respectively. Similarly, the bathochromic effects on the mono- or di-nitro substituted dyes, as compared with those observed for the corresponding methyl- and methoxy-substituted compounds, show only small differences, in contrast to the considerable bathochromic shift of the substituents at the 3-position on the pyrazolinone ring discussed above. These results suggest that no considerable transmission of the electronic effects across the $-NH-N=$ linkage occurs. Similar conclusion have appeared in the literature.[6a,b,8]

It may be noted from a comparison of the available spectral data on 2-nitro and 4-nitro substituted derivatives that the latter exhibits significant hypsochromic shifts. Thus, the 2-nitro and 4-nitro compounds, VII and IX, have their maxima at 406 and 397 mμ, and the maxima in the 2-nitro (XXIV) and 4-nitro (XXVI) compounds absorb at 415 and 408 mμ respectively. In the cases of the 2, 4-dinitro derivatives, X and XXVII, their absorption maxima resemble those of the corresponding *o*-nitro derivatives quite closely. The absorption maxima of *N*-methyl-2, 4-dinitrophenylhydrazones,[9] on the other hand, do not exhibit the bathochromic shift observed with 2, 4-dinitrophenylhydrazones.[10] The relatively large Δ-value for the *o*-nitro group can be ascribed to intramolecular hydrogen bonding, thus increasing the stability of the excited state by a resonance structure, Ig. The infrared studies[*3]

[*2] Unpublished investigation.

[7] G. W. Wheland, "Resonance in Organic Chemistry," John Wiely and Sons, N. Y. (1955), p. 353.

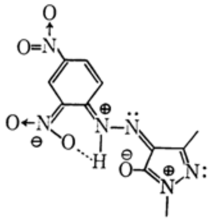
[8] L. A. Jones and N. L. Mueller, *J. Org. Chem.*, **27**, 2356 (1962).

[9] F. Bohlman, *Chem. Ber.*, **84**, 490 (1951).

[10] L. A. Jones, J. C. Holmes and R. B. Seligman, *Anal. Chem.*, **28**, 191 (1956).

[*3] The cyclic C=O stretching frequency of the ortho-nitro compound is increased by 10 cm^{-1} as compared with that of the para-nitro compound in the solid state and in a chloroform solution. This may be explained in terms of an N–O···H–N hydrogen bonding, which would weaken an C=O···H–N hydrogen bonding.

have confirmed the presence of hydrogen bonding between the NO_2 group and the N–H. Resonance stabilization of this kind in other *o*-nitro compounds has also been observed.[8,11a,b)]



Ig

The excitation energy of the *m*-nitro-substituted compounds, VIII and XXV, are considerably higher than those of the *o*- and *p*-substituted compounds with the same substituents. The *m*-substituted derivatives absorb in almost the same region as the corresponding unsubstituted derivatives, indicating that the inductive effect does not favor the stabilization of the excited state. The same phenomena may be expected to be observed in the methyl- and methoxy-substituted compounds.

The effects of the methyl and methoxy substituents on absorption are correlated with the Hammett σ-value, thus giving larger bathochromic shifts in the methoxy compounds than in the methyl compounds.

Steric Effects. In the 2, 6-dinitro compounds, XI and XXVIII, remarkable hypsochromic shifts of the absorption maxima result (see Table 1). These hypsochromic shifts are the result of a steric inhibition of resonance affecting the excited state through the resonance structures, Ie, f and g. The scale model of the 2, 6-dinitro derivative given in Fig. 1 indicates that, although this model cannot be accepted as more than an estimate, there must be some steric interference between the *o, o'*-disubstituted groups and the nitrogen atom directly attached to the pyrazolinone ring, if the dye molecule is to retain its planar strcuture.[*4]

Consequently, it may be assumed that the 2-nitrogen substituent is near-coplanar in the 2, 4-dinitro derivatives and completely non-planar in the 2, 6-dinitro derivatives, and that, therefore, a steric strain would require a greater deviation from planarity of the 2-nitro group in the latter compounds. The long-wavelength bands observed in both sterically hindered compounds show decreased intensities (XI, ε_{max} 8000; XXVIII, ε_{max} 18000), along with the above noted hypsochromic shifts, relative to the corresponding unsubstituted compounds (IV, ε_{max} 24000; V, ε_{max} 24200).

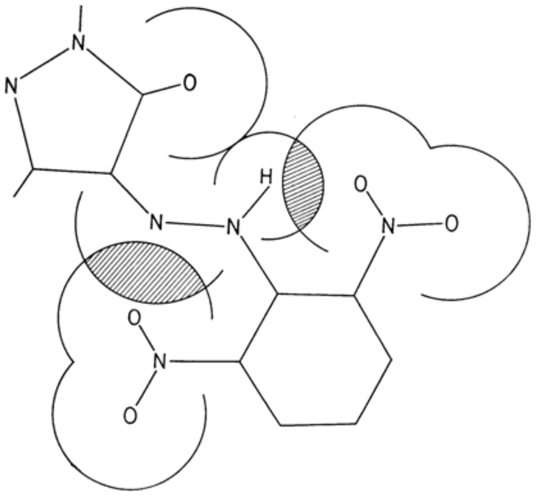


Fig. 1. Scale model for 1-phenyl-4-(2, 6-dinitrophenylhydrazono)-2-pyrazoline-5-one derivatives, XI and XXVIII. Bond lengths and van der Waals radii are those given by J. T. Edward and S. Nielsen, *J. Chem. Soc.*, **1957**, 5075; W. F. Forbes and W. A. Muetter, *Can. J. Chem.*, **34**, 1542 (1956); L. Pauling, "Nature of the Chemical Bond," 2nd ed., Cornell University Press, N. Y. (1945).

It may also be proposed that the hypsochromic shifts exhibited by the 2, 6-dinitro compounds are to be attributed to electronic transitions involving excited states to which resonance structures such as Ib may be supposed to make an appreciable contribution; *i. e.*, the non-planar nitro groups do not play an important part in attracting electrons of the nitrogen atom which are directly attached to the benzene ring; therefore, the charge separation through the conjugated system between the electron-donating –NH–N= group and the electron-attracting centers in the pyrazolinone will facilitate, by a mesomeric effect, the accumulation of the negative charge on the nitrogen atom at the 2-position, thus increasing the contribution of the resonance structure, Ib.

The intensities of the 2, 6-substituted compounds, abnormally lower than those observed in the corresponding unsubstituted derivatives, suggest that the Ib structure becomes more stable relative to the other resonance structures, Ie, f and g; this follows from the assumption noted above.

The introduction of methyl or methoxy substituents into the sterically-sensitive ortho-positions of the phenylhydrazono moiety leads to marked changes in its electronic absorption spectrum; *i. e.*, the 2, 6-dimethyl derivatives, XVIII and XXXV, are seen to produce more remarkable

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11) a) M. J. Kamlet, *Israel J. Chem.*, **1**, 428 (1963); b) M. J. Kamlet, H. G. Adolph and J. C. Hoffrommer, *J. Am. Chem. Soc.*, **86**, 4018 (1964).

[*4] In the transition states, applying to planar nitrogen atoms (in sp^3 hybridization) resulting from a decrease in the negative charge on the nitrogen atoms, the axis of symmetry of the 2p-lone pair electrons is the plane of the benzene rings.

hypsochromic shifts than those found for the 2, 3- 2, 4- and 2, 5-disubstituted derivatives. Furthermore, the same phenomena are also observed in the 2, 6-dimethoxy derivatives, XXIII and XL. Apparently, the size of the group in the *o*, *o*'-positions determines the steric interference of the dye molecule, as is shown in Fig. 2. The Stuart model indicates that the shielding effect of the methyl group is more effective than the ether-oxygen atom of the methoxy group.

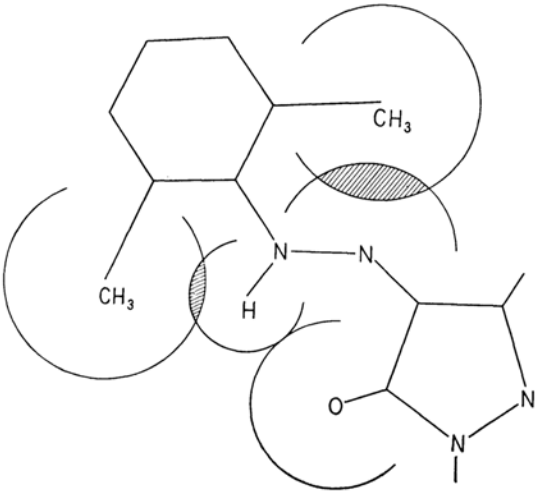

Fig. 2. Scale model for 1-phenyl-4-(2, 6-dimethylphenylhydrazono)-2-pyrazolin-5-one derivatives, XVIII and XXXV.

These changes are related to a transition probability[*5] between a non-planar hydrazono moiety and a polarizable pyrazolinone, as in the case of the 2, 6-dinitro derivatives, but definitive proof is lacking.

The spectra in the ultraviolet regions of 3-ethoxycarbonyl dyes are of particular interest. The introduction of a methyl substituent into the ortho-positions of the 1-phenyl group gives rise to a distinct decreases in intensity, without causing any unusual changes in wavelength, whereas the meta- and para-methyl compounds, XLII and XLIII, are similar to 1-phenyl itself (VI). The *o*, *o*'-disubstitution, XLVII, causes a very remarkable hypsochromic shift (see Table 2).

This means that the increasing deviations from coplanarity of the 1-aromatic group, which are due to the introduction of methyl groups into the sterically-sensitive ortho-positions, result in a reduction of conjugation across the C_{arom}-N bond, thus giving a decreased intensity resulting from a non-planar ground state to near-coplanar excited state. An examination of the molecular diagram (see Fig. 3) of the *o*, *o*'-dimethyl compound, for example, clearly indicates that the 1-aromatic ring is non-planar; there is a considerable overlap of the two methyl groups with 2-nitrogen and carbonyl-oxygen atoms.

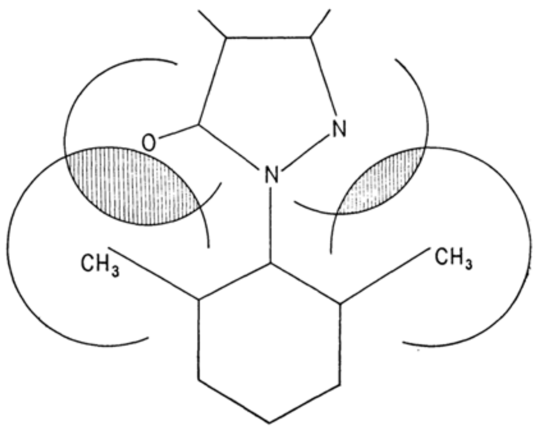

Fig. 3. Scale model for 1-(2, 6-dimethylphenyl)-3-ethoxycarbonyl-4-(2, 6-methylphenylhydrazono)-2-pyrazolin-5-one (XLVII).

It may be concluded from the spectroscopic behavior of the 3-ethoxycarbonyl derivatives investigated that the effects of the 1-aryl substituents are not imporatant factors in the visible region of pyrazolinone dyes.

Experimental

Materials. The nitro-substituted compounds prepared in this study are listed in Table 1. All of these were synthesized by the coupling reaction of diazotized anilines and 2-pyrazolin-5-ones. The general procedure for this coupling reaction will be described in detail.

The aniline (0.006 mol) was dissolved in glacial acetic acid (10 m*l*) containing concentrated hydrochloric acid (4 m*l*). To this acidic solution a small proportion of sodium nitrite (0.5 g) was added below 5°C with stirring. The resulting diazotized aniline was poured into a mixture of 3-methyl- or 3-phenyl-1-phenyl-2-pyrazolin-5-one (0.006 mol) and crystalline sodium acetate (10 g) in water (100 m*l*) under mechanical stirring at room temperature. The separated colored product was collected, washed with diluted methanol, and recrystallized from suitable solvents. The results are shown in Table 1 (footnotes b—g). All melting points are uncorrected.

Spectral Measurements. The electronic spectra were measured in spectroscopically-purified ethanol with a Cary Model-14 spectrophtometer.

The author is greatly indebted to Dr. Hiroshi Midorikawa of the Institute of Physical and Chemical Research and Professor Dr. Yoshihisa Kaneko of the University for their helpful discussions and encouragements. Thanks are also due to Professor Dr. Taro Hayashi of Ochanomizu University and Professor Dr. Tatsuo Takeshima of Chiba University for their valuable advice.

[*5] Unfortunately, we still lack a well-defined resonance structure of the methyl- or methoxy-substituted compounds.