

Studies of the Absorption Spectra of Azo Dyes and their Metal-complexes. I^{*1}. The Absorption Spectra of Phenylazoacetoacetanilide and its Related Compounds

By Yoshiharu YAGI

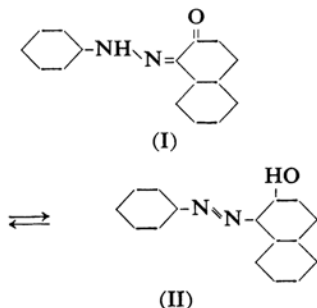
(Received June 12, 1962)

Although the recent development of neutral-dyeing metal-complex azo dyes has been remarkable¹⁾, the chemical properties of the metal complexes of azo dyes, particularly of *o*, *o'*-disubstituted monoazo dyes, have not been fully investigated. It has, therefore, been considered important for the further progress of these complex dyes to study the structures of ligand azo dyes and their metal-complexes.

In this connection, the author tried to make clear the structure of phenolazoacetoacetanilides, which form yellow-dyeing metal-complexes. As the first step, the electronic and infrared absorption spectra of α -phenylazoacetoacetanilide^{*2} and its related compounds were studied.

Results and Discussion

The Electronic Absorption Spectra of Phenylazoacetoacetanilide in Various Solvents.—It had long been studied whether *o*- and *p*-hydroxy azo compounds have the azo form or the hydrazone form²⁾. For example, 1-phenylazo-2-naphthol in solution was found³⁾ to be in a



tautomeric equilibrium between azo- and quinonehydrazone-forms, as is shown in I and II.

An electronic absorption spectrum of phenylazoacetoacetanilide in *n*-hexane shows three bands in the region of 200~400 m μ (Fig. 1).

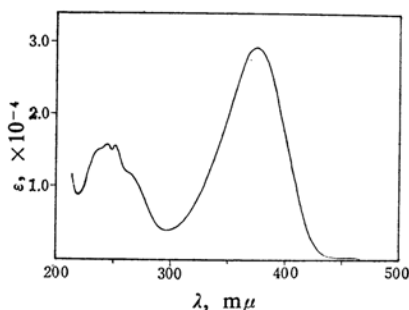


Fig. 1. Phenylazoacetoacetanilide in *n*-hexane.

These bands are referred to as A, B and C—D from the longer wavelength side. Band A is considered to arise from a transition involving electron migration along the whole conjugate system of the molecule. In Table I are shown the absorption spectra of this compound in various solvents. The absorption maxima of band A shift toward a shorter wavelength in the following order: pyridine > chloroform > acetic acid > *n*-hexane > standard solvent^{*3}. The relatively small differences in λ_{\max} suggest that the displacement of band A is due to the polarity change of the absorbing system caused by solute-solvent interaction; that is, it is due to the general solvent effect.

Burawoy³⁾ investigated the absorption spectra of 1-phenylazo-2-naphthol in the above-mentioned solvents and concluded that the tautomeric equilibrium of azo \rightleftharpoons quinonehydrazone depends upon the polarity of the solvent.

With respect to phenylazoacetoacetanilide, however, the locations of each absorption band in *n*-hexane and in the standard solvent almost coincide. This indicates that the compound is not in a tautomeric equilibrium but may

1) H. Pfizner, *Melliand Textilber.*, **35**, 649 (1954); *Angew. Chem.*, **62**, 242 (1950); C. Schetty, *J. Soc. Dyers Colourists*, **71**, 705 (1955).

*1 Presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

*2 For the sake of convenience, the compounds in this study are named as azo compounds; α -phenylazoacetoacetanilide, for example, is abbreviated as phenylazoacetoacetanilide.

2) K. Auwers et al., *Ann.*, **378**, 210 (1911); **487**, 79 (1931); A. Burawoy et al., *ibid.*, **503**, 180 (1933); **504**, 71 (1933); **509**, 60 (1934); H. Shingu, *J. Chem. Soc. Japan*, (*Nippon Kagaku Kaishi*), **60**, 542, 595 (1939); A. Burawoy et al., *J. Chem. Soc.*, **1953**, 1443; **1952**, 3734.

3) A. Burawoy, A. G. Salem and A. R. Thompson, *ibid.*, **1952**, 4793.

*3 The term "standard solvent" denotes 80% aqueous methanol containing 0.1 g. of acetic acid per liter.

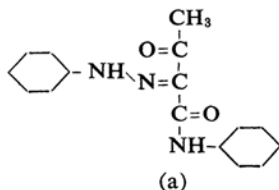
TABLE I. ABSORPTION SPECTRA OF PHENYLAZOACETOACETANILIDE

| Solvent | A | B | C-D |
|------------------|--------------|---------------|--|
| <i>n</i> -Hexane | 373.7 (2.93) | 270.0* (1.04) | 251.2(1.57), 243.3(1.58), 231.7*(1.44) |
| Standard solvent | 373.4 (3.03) | 271.5* (1.00) | 251.2(1.40), 243.5(1.45), 231.5*(1.34) |
| Chloroform | 379.8 (2.62) | 273.5* (0.92) | 254.1(1.38) — — |
| Acetic acid | 376.2 (2.86) | 274.6* (0.88) | — — — |
| Pyridine | 380.9 (2.73) | — | — — — |

Wavelengths (λ) in $m\mu$; Molar extinction coefficients (ϵ) $\times 10^{-4}$ in parenthesis

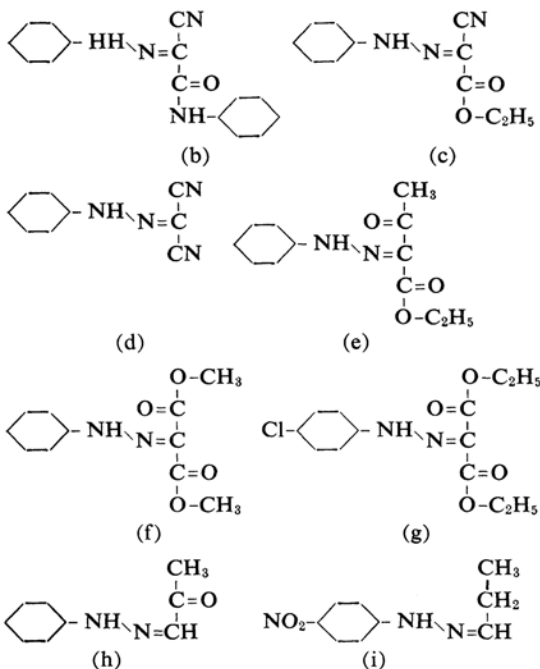
* Inflection

exist as a hydrazone form, as is shown in a, irrespective of the nature of the solvents.



The Infrared Absorption Spectra of Phenylazoacetoacetanilide and its Related Compounds.—

In order to confirm the presumption derived in the preceding paragraph, the following analogous compounds were synthesized: Phenylazocycanoacetanilide (b), phenylazocycanoacetic acid ethylester (c), phenylazomalonic dinitrile (d), phenylazoacetoacetic acid ethylester (e), phenylazomalonic acid dimethylester (f), *p*-chlorophenylazomalonic acid diethylester (g), α -ketopropionaldehydephenylhydrazone (h), and propionaldehyde-*p*-nitrophenylhydrazone (i). Table II shows the carbonyl stretching vibrations, and Table III, the NH stretching vibrations of hydrazone groups:

TABLE II. THE CARBONYL STRETCHING VIBRATIONS (cm^{-1})

| Compound | Ketone | Ester | Amide I |
|----------|-------------|----------------------------|------------|
| a | 1623(1633)* | — | 1667(1665) |
| b | — | — | 1652(1655) |
| c | — | 1750(1757) | — |
| e | 1620(1630) | 1718(1720) | — |
| f | — | { 1653(1676) 1728(1733) | — |
| g | — | { 1675(1678) 1723(1733) | — |
| h | 1649(1670) | — | — |

Values in paraffin-oil and in CCl_4 (in parenthesis) were tabulated.

TABLE III. THE NH STRETCHING VIBRATIONS (cm^{-1})

| Compound | Nujol mull | CCl_4 |
|----------|--------------|----------------|
| c | 3250 | 3320 |
| d | 3240 | 3333 |
| h | 3310 | 3390 |
| e | not detected | 3200 |
| f | 3115 | 3210 |
| g | 3160 | 3195 |
| i | 3280 | 3370 |

Compounds, a—i, exhibit strong bands in the region of $1590\sim 1600\text{ cm}^{-1}$ (in paraffin-oil) or $1585\sim 1600\text{ cm}^{-1}$ (in a carbon tetrachloride solution). These are considered to be due to C=C skeletal in-plane vibrations of phenyl rings. Although it is generally known that the NH deformation vibration of the secondary amine shows a weak band in the $1550\sim 1650\text{ cm}^{-1}$ region⁴, compounds d and i have no band in this region. This suggests that bands due to the NH vibration of the hydrazone group do not appear at frequencies higher than 1600 cm^{-1} . In the region of $1640\sim 1690\text{ cm}^{-1}$ also, the C=N stretching vibration may be expected to appear⁵, but, as will be seen in d and i, this band seems to be too weak to detect. Consequently, the bands in the $1620\sim 1760\text{ cm}^{-1}$ region in this study are ascribed to the carbonyl stretching vibration.

4) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", John Wiley & Sons, Inc., New York (1958), p. 251.

5) Ibid., p. 263.

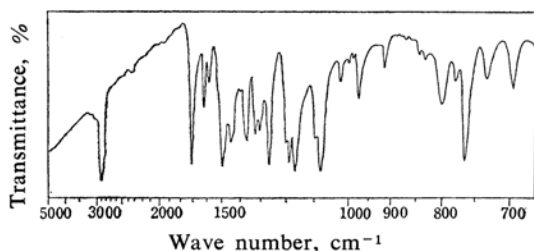


Fig. 2. Infrared spectrum of e (Nujol mull).

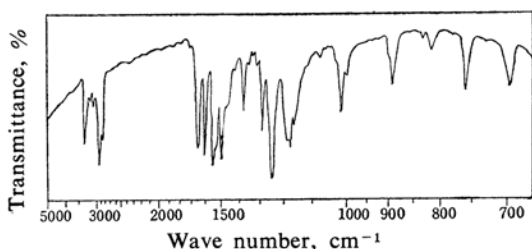
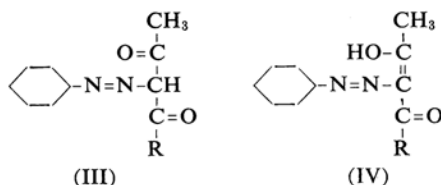


Fig. 3. Infrared spectrum of h (Nujol mull).

Solid 2-hydroxyazobenzene⁶⁾ and 3-methyl-1-phenyl-4-phenylazo-5-pyrazolone⁷⁾ were found to exhibit $\nu_{C=O}$ at 1610 and 1650 cm^{-1} respectively. The azo compounds in this study also exhibit the C=O absorption in the same region.

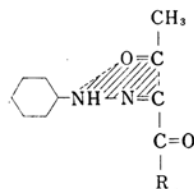
As to the acetyl derivatives in Table II, h shows $\nu_{C=O}$ at 1649 cm^{-1} , and a and e, at lower frequencies of about 1620 cm^{-1} . In these cases, a band at about 1665 cm^{-1} in the spectrum of a is assigned to the amide I band, while a strong absorption at 1720 cm^{-1} in the spectrum of e is attributed to the ester carbonyl. The derivatives of alkylmalonates, f and g, have two absorption bands in this region. It is evident that either of these two bands arises from the C=O stretchings of ester carbonyls.

The C=O stretching vibration of the acetyl derivative and that of one ester group in the alkylmalonate derivative are markedly lower in frequency than those of ordinary α, β -unsaturated carbonyl systems. This indicates that the compounds, a, e, f and g, form intramolecular hydrogen bonds in the solid state and in a non-polar solvent, as is shown in V.



6) K. Ueno, *J. Am. Chem. Soc.*, **79**, 3066 (1957).

7) S. Toda, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **80**, 402 (1959).



(V)

(R = $-\text{OC}_2\text{H}_5$, $-\text{NHPh}$, etc.)

In Table III are illustrated the NH stretching vibrations of the hydrazone group belonging to the group of compounds having no acid amide group. Compounds i and d have a sharp absorption at 3370 and 3333 cm^{-1} respectively. These agree with Ramirez and Kirby's value reported⁸⁾ for the NH stretching vibrations of hydrazone groups.

The compounds in Table III are classified into two groups, one showing relatively broad bands in the 3195~3210 cm^{-1} region, such as e, f and g (Fig. 4) and the other having sharp bands at higher frequencies in the 3320~3390 cm^{-1} region such as c, d and i. The former group consists of the compounds which have been deduced from the $\nu_{C=O}$ values to have an intramolecular hydrogen bond. It is considered that the ν_{NH} and $\nu_{C=O}$ markedly decrease, owing to the chelate ring formation between a carbonyl oxygen and a hydrazone hydrogen atom. Randall⁹⁾ investigated the infrared absorption bands of e and found the ketone and ester carbonyls (1706 cm^{-1}), the azo group (1626 cm^{-1}) and the C=C stretching (1511 cm^{-1}) in an enolized form, as is shown in IV. However, α, α -dimethyl ethylacetoacetate, which is not enolizable, was reported to have a ketonic carbonyl band (1718 cm^{-1}) and an ester carbonyl band (1742 cm^{-1})¹⁰⁾. The azo

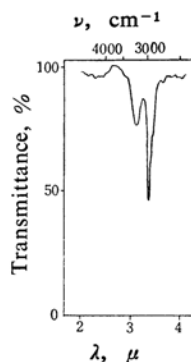


Fig. 4. Infrared spectrum of g in CCl_4 .

8) F. Ramirez and A. F. Kirby, *J. Am. Chem. Soc.*, **76**, 1037 (1954).

9) H. M. Randall et al., "Infrared Determination of Organic Structures", van Nostrand Co., New York (1949), p. 231.

10) R. S. Rasmussen and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1073 (1949).

TABLE IV. ELECTRONIC ABSORPTION SPECTRA

| Compound | Solvent | A | B | C-D |
|----------|---------|-------------|--|--|
| a | { S | 373.4(3.03) | 271.5*(1.00) | 251.2 (1.40), 243.5 (1.45), 231.5*(1.34) |
| | { H | 373.7(2.93) | 270.0*(1.04) | 251.2 (1.57), 243.3 (1.58), 231.7*(1.44) |
| b | { S | 370.2(2.13) | 285.5*(0.39) | 239.0 (1.98) |
| | { H | 361.5(1.74) | 294.5*(0.45), 284.5*(0.39), 276.0*(0.32) | 251.5*(0.74), 243.9*(1.52), 235.7 (2.00) |
| j | S | 356.0(1.95) | — | 251.3*(0.67), 237.7 (1.02) |
| c | { S | 357.4(2.19) | 281.5*(0.14) | 251.8*(0.63), 241.5 (0.82) |
| | { H | 347.8(2.02) | 294.5*(0.28), 285.1 (0.21), 275.2*(0.15) | 250.3*(0.60), 243.0*(0.83), 235.2 (0.89) |
| d | { S | 357.3(2.12) | — | 252.0*(0.65), 243.5 (0.78) |
| | { H | 353.2(1.90) | — | 252.5*(0.64), 244.0 (0.76), 238.5*(0.71) |
| e | { S | 355.7(2.12) | — | 249.2*(0.89), 239.8 (1.19) |
| | { H | 354.5(1.99) | 295.8*(0.24), 286.5 (0.21) | 251.6*(0.78), 238.0 (1.34) |
| f | { S | 350.6(2.16) | 285.5 (0.24) | 233.6 (1.09) |
| | { H | 348.4(2.12) | 294.5*(0.29), 284.8 (0.27), 275.0*(0.21) | 246.6*(0.58), 231.1 (1.04) |
| g | { S | 350.3(2.33) | 301.8 (0.57), 291.5 (0.50) | 241.7*(1.28) |
| | { H | 350.6(2.29) | 303.1 (0.61), 293.1 (0.50) | 235.1 (1.10) |
| h | { S | 348.8(2.32) | 296.0 (0.44), 285.5*(0.36) | 237.3 (1.12) |
| | { H | 326.5(1.89) | 292.5 (0.82), 282.2*(0.62) | 232.0 (1.13) |
| i | { S | 393.1(2.22) | — | 249.9 (0.90) |
| | { H | 341.4(0.68) | — | 274.2 (1.19) |

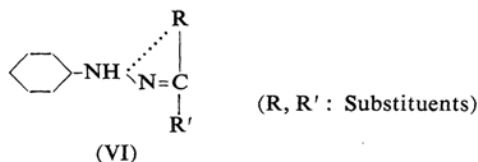
S, Standard solvent; H, *n*-Hexane

group usually does not exhibit distinct absorption¹¹⁾. Further, the author was unable to detect the OH stretching vibration in this study. Consequently, it can not be considered that e has such a structure as III or IV.

In the latter group, the ν_{NH} values do not differ from that of i. It is conceivable that the intramolecular hydrogen bond between the cyano nitrogen and the hydrazone hydrogen atom is almost negligible or does not exist at all. This is supported by the fact that the proton-accepting power of the cyano group is generally weak¹²⁾.

The Electronic Absorption Spectra of Phenylazoacetoacetanilide and its Related Compounds.

—The electronic absorption spectra of the series of compounds in *n*-hexane and the standard solvent are tabulated in Table IV. The three groups of characteristic bands in the 200–400 $\text{m}\mu$ region are abbreviated as A, B and C–D.



Generally a $>\text{C}=\text{N}$ linkage was reported¹³⁾ to have properties spectrally analogous to an ethylenic linkage. Hence, an electronic effect of R or R' in VI will be transmitted to the whole conjugate system through the π - p con-

jugation between a nitrogen atom and a phenyl nucleus in $\text{Ph}-\text{NH}-\text{N}=\text{C}$, exerting a considerable influence upon band A. As will be seen in Table IV, every substituent, such as $-\text{COCH}_3$, $-\text{CONH}_2$, etc., when introduced as R or R', has a bathochromic effect on the bands A.

The intensity and the maximum wavelength of band A in the spectra of a are the most notable in Table IV, and a comparison of b with phenylazocycanoacetamide (j) indicates that the introduction of a phenyl ring into the carboxylic acid amide group causes a marked red-shift of band A. This suggests that the π - p conjugation at a carboxylic acid anilide group contributes much to the transition along the whole conjugate system.

In the compounds a, e, f and g, the absorption maxima of the bands A are almost equal in *n*-hexane and in the standard solvent. On the other hand, in the compounds b, c, d and h, the bands A in *n*-hexane are at appreciably shorter wavelengths. The former are the compounds having the internal hydrogen bond in the solid state and in non-polar solvents.

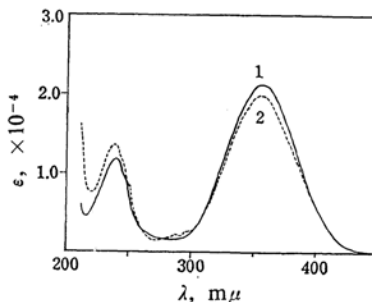


Fig. 5. Absorption spectra of e in the standard solvent (1) and in *n*-hexane (2).

11) Cf. Ref. 4, p. 272.

12) S. Seki et al., "Hydrogen-bond" (Suiso-Ketsugo), Iwanami-Shoten, Tokyo (1956), p. 24.

13) E. A. Braude and E. R. H. Jones *J. Chem. Soc.*, 1945, 498; 1946, 948; 1949, 1898; 1952, 1068.

It is considered that the six-membered chelate ring in *n*-hexane, as shown in V, stabilizes the excited state and decreases the electronic transition energy^{3,8,14}.

In the ultraviolet region, the bands B are usually situated in the region of 270–300 m μ , and their intensities are generally small. In some cases, these consist of three peaks in *n*-hexane, but they are apt to disappear in polar solvents. Undoubtedly, the bands B are thought to originate from the carbonyl group, since d and i exhibit no absorption in this region. The true molar extinction coefficients of the B bands seem rather small (10^2 – 10^3), taking into account the fact that these are superposed by the slopes of the bands A or C–D. These B bands are tentatively ascribed to the $n \rightarrow \pi$ transition (R-band)¹⁵ of carbonyl. However, the band B of a alone absorbs at a shorter wavelength and has a relatively high intensity. This may be a conjugation band (K-band)¹⁶ of another origin.

The bands C–D are located in the 230–250 m μ region. Some of them show fine structures. It is not possible, however, to make a full examination of these bands on the basis of the present knowledge alone.

Experimental

Preparation of Azo Compounds.—*Phenylazoacetoacetanilide (a)*.—This was prepared from diazotized aniline and acetoacetanilide. Recrystallization from ethanol gave green-yellow needles; m. p., 107–108°C. (reported 107–108°C)¹⁷.

Phenylazocycanoacetanilide (b).—Cyanoacetanilide was prepared according to the method described in the literature¹⁸. Compound b was obtained by the treatment of cyanoacetanilide with diazotized aniline. Recrystallization from ethanol gave rectangular yellow plates; m. p., 199–200°C.

Found: C, 68.35; H, 4.18; N, 21.01. Calcd. for $C_{15}H_{12}ON_4$: C, 68.18; H, 4.58; N, 21.19%.

Phenylazocycanoacetic Acid Ethylester (c).—An aqueous alcoholic solution containing ethyl cyanoacetate and an excess of sodium acetate was treated with diazotized aniline to yield yellow needles. This was recrystallized from ligroin, giving yellow needles with an m. p. of 126°C (reported 125°C)¹⁹.

Phenylazomalonic Dintrile (d).—This was obtained in the same manner as c and was recrystallized from ethanol, giving orange-yellow plates; m. p., 145°C (decomp.) (reported 146–147°C (decomp.))¹⁹.

Phenylazoacetoacetic Acid Ethylester (e).—This was obtained in the manner described in c. Recrystallization from ligroin gave pale-yellow rectangular plates; m. p., 82–83.5°C (reported 82–83°C)²⁰.

Phenylazomalonic Acid Dimethylester (f).—This was obtained in the same manner as c. Recrystallization from ligroin gave yellow prisms; m. p., 62–63°C (reported 63.5°C)¹⁹.

p-Chlorophenylazomalonic Acid Diethylester (g).—This was obtained in a manner similar to that above. Recrystallization from ligroin yielded pale-yellow rectangular plates; m. p., 59–61°C.

Found: C, 52.39; H, 4.85; N, 9.09. Calcd. for $C_{13}H_{15}O_4N_2Cl$: C, 52.36; H, 5.06; N, 9.37%.

α -Ketopropionaldehydephenylhydrazone (h).—Acetoacetic acid prepared by the method of Schechter et al.²¹ was treated with diazotized aniline. An orange precipitate was recrystallized from benzene, affording pale-yellow rectangular plates; m. p., 151–152°C (reported 149–150°C)²².

Propionaldehyde-p-nitrophenylhydrazone (i).—This was prepared by the treatment of *p*-nitrophenylhydrazine with propionaldehyde in ethanol. Recrystallization from 50% ethanol gave orange-yellow needles; m. p., 124°C (reported 124°C)²³.

Phenylazocycanoacetamide (j).—Cyanoacetamide was prepared by the method described in the literature²⁴. Compound j was obtained in the same manner as c and was recrystallized from ethylacetate, giving rectangular yellow plates; m. p., 249–251°C (decomp.).

Found: C, 57.88; H, 4.23; N, 29.46. Calcd. for $C_9H_8ON_4$: C, 57.44; H, 4.30; N, 29.76%.

Measurements of the Spectra.—The infrared spectra were measured by two infrared spectrophotometers, a Perkin-Elmer model 21 and a Shimadzu model IR-27, equipped with NaCl optics. In the case of the solution measurements, the spectra were determined at concentration of 10^{-3} – 10^{-4} M.

Visible and ultraviolet absorptions were carried out using two recording spectrophotometers, a Beckman model DK-2 and a Shimadzu model RS-27. The concentration of samples was 2.5×10^{-5} M.

Summary

Phenylazoacetoacetanilide and its related compounds have the hydrazone structure. The phenylazoacetoacetic acid ethylester, for example, forms an intramolecular hydrogen bond between a ketone group and a hydrazone group in the solid state and in non-polar solvents.

The electronic absorption spectra exhibit three groups of bands—A, B and C–D. The effects upon the spectra of the intramolecular hydrogen bond and of the π - p conjugation at

14) P. H. Gore and O. H. Wheeler, *J. Am. Chem. Soc.*, **78**, 2160 (1956).

15) A. Burawoy et al., *J. Chem. Soc.*, 1952, 2310; 1955, 3721.

16) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold and Co., London (1954), p. 111.

17) W. F. Whitmore and S. Zuckerman, *Am. Ink Maker*, **34**, 28 (1959).

18) K. G. Naik and Y. N. Bhat, *J. Indian Chem. Soc.*, **4**, 547 (1927); *Chem. Zentr.*, **1928** I, 1759.

19) A. Hantzsch and K. J. Thompson, *Ber.*, **38**, 2266 (1905).

20) C. Kjellin, *ibid.*, **30**, 1966 (1897).

21) N. S. Schechter et al., *J. Am. Chem. Soc.*, **71**, 3165 (1949).

22) F. R. Japp and F. Klingemann, *Ann.*, **247**, 217 (1888).

23) C. D. Harris and K. Oppenheim, *Chem. Zentr.*, **1916** II, 991.

24) H. Gilman (Editor-in-Chief), "Organic Syntheses", Coll. Vol. I, 179 (1932).

the carboxylic acid amide group have been discussed.

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