The new values are not due to impurities as evidenced by determinations at slightly higher concentrations of the same copper salt solution. In each case the height of both the Cu(II) and Cu(I) waves were equal.

The results here show that in any polarographic determination involving maxima, the influence of even exceedingly small concentrations of maxima suppressors should be known or tested. In general a concentration of maximum suppressor equal to the M.S.P. value is sufficient and any concentration above this value is likely to alter the half-wave potential and/or diffusion current. Conclusions reached in two recent investigations[21] do not seem warranted on the basis of the polarographic evidence presented here.

Cetyltrimethylammonium bromide and Triton X-100 are available commercially. Since their stock solutions do not decompose as do gelatin and agar, these materials are suggested as desirable suppressors in polarographic investigations.

Acknowledgment.—The author wishes to express his appreciation to Dr. L. Meites for the use of his polarographic equipment.

Summary

The critical concentration for micelle formation is shown to be identical with the concentration necessary to suppress maxima (M.S.P.). The great adsorptivity of the colloidal agents at concentrations corresponding to their M.S.P. values seems to account for the ability to suppress maxima by displacing the less actively adsorbed non-surface-active ions from the mercury drop surface.

Concentrations of maxima suppressors greater than the M.S.P. values can influence polarographic properties. Specific influences have been noted and discussed.

During the main investigation half-wave potential values for the two step reduction of Cu(II) in potassium thiocyanate, in severe disagreement with those previously reported, were noted.

NEW HAVEN, CONN. RECEIVED JUNE 15, 1949

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[21] (a) Buckley and Taylor, *J. Res. Natl. Bureau Standards*, **34**, 97(1945); (b) Coe and Rogers, THIS JOURNAL, **70**, 3276 (1948); (c) see published correspondence in this regard: Meites and Colichman, *Anal. Chem.*, **21**, 758 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

The Spectra of Some 2,4-Dinitrophenylhydrazones[1]

BY H. HARRY SZMANT AND HENRY J. PLANINSEK

The color of the 2,4-dinitrophenylhydrazones (DNPH) is thought[2,3] to be an indication of the degree of unsaturation present in the parent carbonyl compound. Since the characteristic behavior associated with unsaturation in organic compounds is caused by the presence of readily excited η electrons, it was of interest to us to observe a curious gradation of color in the DNPH of the *p*-acetyl derivatives of phenyl sulfide, sulfoxide and sulfone which were prepared in the course of another investigation.[4] In this paper we wish to report the results of the study of the absorption spectra in the ultraviolet and visible range of the above mentioned and several reference compounds.

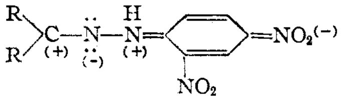
Experimental and Results

The DNPH were prepared by the customary method.[5] The compounds required repeated crystallizations until a constant melting point was obtained; toluene was the most favorable solvent from the viewpoint of solubility. In order to remove traces of toluene occluded in the crystals, the final products were recrystallized once from ethanol. It is probable that the low melting points of the DNPH as they are first obtained are due to the existence of geometrical isomers rather than to the presence of impurities (or starting materials). It can thus be assumed that repeated crystallizations simply serve to isolate the higher melting isomer.

The physical and spectral data are summarized in Table I. The absorption spectra reproduced in Figs. 1 and 2 were determined by means of a Beckman DU spectrophotometer using solutions containing approximately 10 mg. of the compound per liter of 95% ethanol.

Discussion

Braude and Jones[3] pointed out that the absorption spectrum of the DNPH of a carbonyl compound is more useful for the interpretation of the electronic nature of a given structure than that of the parent carbonyl compound. This is presumably the result of the polarizing effect of the 2,4-dinitrophenyl portion of the molecule on the residue of the carbonyl compound. This polarizing force dampens the various resonance possibilities in the carbonyl compound and causes an adjustment of the electron distribution around the polarized carbon-nitrogen double bond (I). In the DNPH of a simple ketone such



(I)

as acetone the maximum of 2,4-dinitrophenylhydrazine (352 mμ)[3] is displaced toward the visible (360 mμ).[2]

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[1] Presented in part before the Organic Division of the American Chemical Society, San Francisco, Calif., April, 1949.

[2] Roberts and Green, THIS JOURNAL, **68**, 214 (1946).

[3] Braude and Jones, *J. Chem. Soc.*, 498 (1945).

[4] Szmant and Palopoli, THIS JOURNAL, **72**, 1757 (1950).

[5] Shriner and Fuson, "Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

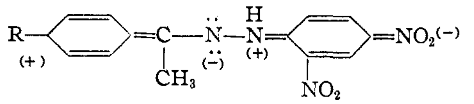
TABLE I

PHYSICAL AND SPECTRAL DATA OF SOME 2,4-DINITROPHENYLHYDRAZONES

No.	DNPH of $RCOCH_3$ R	M. p., °C.[a]	Color	$\lambda_{max.}$ mμ	$\Delta\lambda_{max.}$[b] mμ	$\epsilon_{max.} \times 10^{-2}$	$\Delta\epsilon_{max.} \times 10^{-2}$[c]
1	C_6H_5	252[d]	Light red	376[e]	...	238	...
2	*p*-$C_6H_5C_6H_4$[f]	241	Deep red	382	6	127	−109
3	*p*-$C_6H_5CH_2C_6H_4$[g]	201	Light red	381	5	367	129
4	*p*-$C_6H_5OC_6H_4$[h]	216	Deep red	383	7	266	28
5	*p*-$C_6H_5SC_6H_4$	167	Light red	384	8	301	63
6	*p*-$C_6H_5SOC_6H_4$	215	Deep red	372	−4	294	56
7	*p*-$C_6H_5SO_2C_6H_4$	245	Orange	373	−3	281	43
8	2-Thienyl	245[i]	Light red	392	16	255	17

[a] All melting points are uncorrected. [b] $\Delta\lambda_{max.}$ = ($\lambda_{max.}$ of compound − $\lambda_{max.}$ of acetophenone DNPH). [c] $\Delta\epsilon_{max.}$ = ($\epsilon_{max.}$ of compound − $\epsilon_{max.}$ of acetophenone DNPH). [d] Campbell (*Analyst*, **61**, 345 (1936)) reports m. p. 249–250°. [f] *Anal.* Calcd. for $C_{20}H_{16}N_4O_4$: C, 63.83; H, 4.28. Found: C, 63.60; H, 4.15. [g] *Anal.* Calcd. for $C_{21}H_{18}N_4O_4$: C, 64.60; H, 4.65. Found: C, 64.45; H, 4.50. [h] Calcd. for $C_{20}H_{16}N_4O_5$: C, 61.22; H, 4.11. Found: C, 61.11; H, 4.02. [i] Hartough and Kosak (THIS JOURNAL, **68**, 3629 (1946)) reported m. p. 245°.

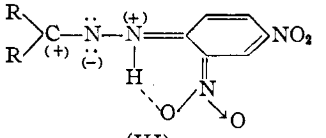
In para-substituted acetophenone DNPH, such as the series of compounds used in this study, the ability of the substituent to interact with the positive charge in the benzene ring of the polarized structure (II) will determine the nature of the spectrum.



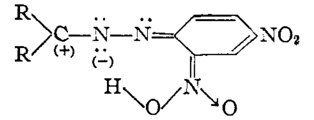
(II)

Before discussing the specific results obtained in this study we would like to comment on the existence of other DNPH structures in addition to those represented by II.

It is noted from the comparison of the available spectral data of 4-nitrophenylhydrazones and DNPH that the latter exhibit a maximum at a *shorter* wave length. Thus, the 4-nitrophenylhydrazone and DNPH of benzaldehyde have the maxima at 407[6] and 478[2] mμ, respectively. Also the absorption intensity of the DNPH is lower than that of the 4-nitrophenylhydrazone (ε 34,200 and 29,200, respectively). A possible explanation of this unexpected difference may lie in the existence of the DNPH as the hydrogen-bonded structure III which in turn can tautomerize to give IV. It is noteworthy that in the probable structures III and IV the major axis of electron oscillation[7] is shortened. The above comments concerning the DNPH of benzaldehyde apply also to the DNPH of methyl aryl ketones since unlike in the azines[8] the presence of the



(III)



(IV)

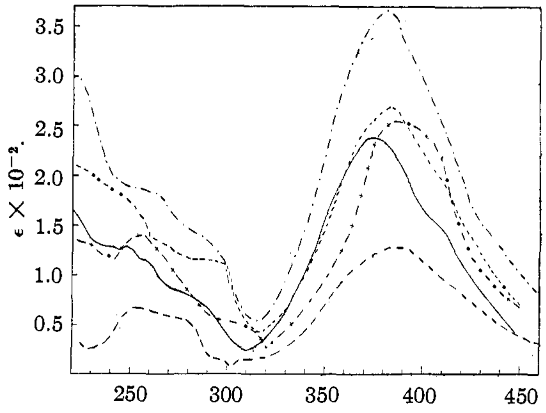


Fig. 1.—Absorption spectra of DNPH of: —, acetophenone; — —, *p*-phenylacetophenone; —·—·, *p*-benzylacetophenone; ----, *p*-phenoxyacetophenone; — + — +, 2-thienyl methyl ketone.

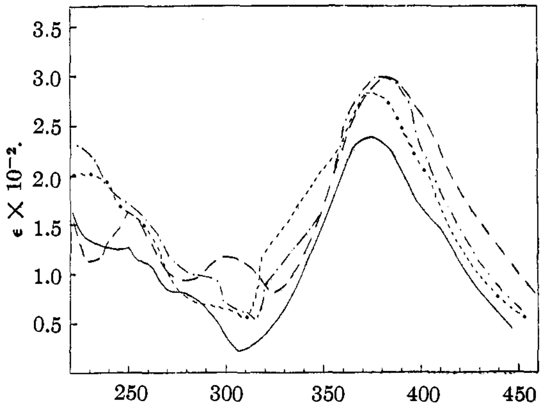


Fig. 2.—Absorption spectra of DNPH of: —, acetophenone; — —, *p*-phenylmercaptoacetophenone; —·—, *p*-phenylthionylacetophenone; - - - - -, *p*-phenylsulfonylacetophenone.

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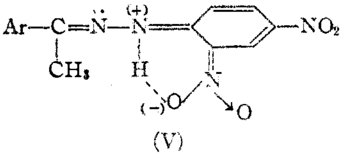
(6) Ferguson and Robinson, THIS JOURNAL, **71**, 342 (1949).

(7) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

(8) Szmant and Planinsek, THIS JOURNAL, in press.

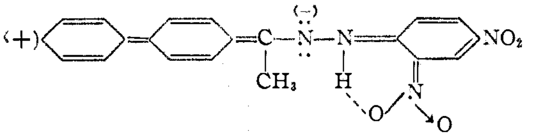
alpha methyl group has little if any effect on the position of the absorption maximum.[9]

The examination of the near ultraviolet portion of the DNPH spectra reveals in several compounds the presence of absorption bands characteristic of the aryl group of the parent ketone. Thus, it may be concluded that the DNPH also has structures of type V in which the aryl group is permitted an independent resonance.



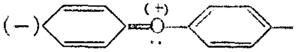
(V)

The substituents in compounds 2 to 6 cause a bathochromic shift of the maximum of 6 to 8 mμ. All these substituents are electron-donating groups and thus would be expected to favor resonance structures corresponding to II. Considerable differences are, however, observed in the absorption intensities of these compounds. Compound 2 has a remarkably low absorption intensity in the 280 mμ band, and in the near ultraviolet region it shows a shoulder extending from 250 to 280 mμ with secondary maximum at 250 mμ. This suggests that in addition to the resonance represented by VI there is in this case a strong contribution from the resonance of the diphenyl unit[10] (in a structure of type V).

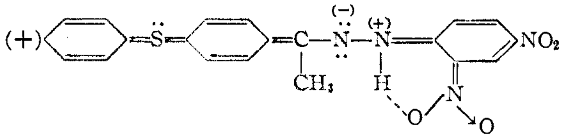


(VI)

Compound 3, unlike compound 2, shows a remarkably high absorption intensity. The bathochromic shift caused by the benzyl group is of the same magnitude as that reported for the methyl group[11] but the slight increase in absorption intensity noticed with the methyl group is here very much magnified. This and the steep absorption in the 220–240 mμ range suggests that hyperconjugation of the benzyl group plays an important part in the excited state. Braude[12] recently examined the contribution of hyperconjugation to the spectrum of diphenylmethane and other structures and concluded that such contributions are significant. In the case of compound 3 the strong polarization of the molecule in the direction of the dinitrophenyl group should facilitate the hyperconjugation process.

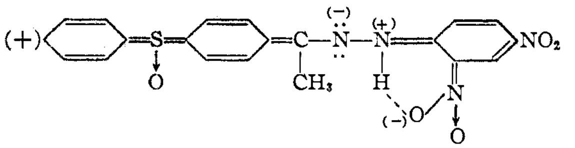
The results obtained with compound 4 are of interest because of the rather small bathochromic effect of the phenoxy group (7 mμ).[13] Competitive resonance within the diphenyl ether unit with contributions by structures containing the unit  explain satisfactorily the behavior of compound 4.

The *p*-phenylmercapto group (compound 5) caused a greater bathochromic shift and higher absorption intensity than the *p*-phenoxy group. This is in accord with the smaller electronegativity of the sulfur atom as compared with oxygen, and may result also from the contribution of structures such as VII. Compound 5 also shows sharp maxima at 250 and 300 mμ. Both bands are characteristic of the absorption spectrum of phenyl sulfide,[14,15] with the 300 mμ band corresponding to the shifted 280 mμ band of the unsubstituted phenyl sulfide molecule.

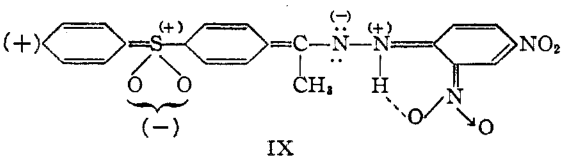


(VII)

The electronegative character of the sulfoxide and sulfone groups (in compounds 6 and 7, respectively) opposes the typical polarization of the DNPH structure, and thus there is observed a shift of the maximum toward shorter wave lengths. The ability of sulfur to expand its octet, however, makes possible an increase of absorption intensity (particularly in the high energy (*i. e.*, short wave length) range). Thus structures of type VIII and IX probably contribute to the excited states of these compounds. Similar structures for aryl sulfones were recently proposed by Fehnel and Carmack[16] and by Koch.[17]



VIII



IX

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(9) This statement is limited to the comparison of aromatic aldehydes and alkaryl ketones. Thus, the DNPH of benzaldehyde and acetophenone have maxima at 378[2] and 376-377[3] mμ respectively. Bathochromic shifts caused by alpha methyl groups were observed in aliphatic structures.[3]

(10) O'Shaughnessy and Rodebush, THIS JOURNAL, 62 2906 (1940) reported the major absorption maximum of biphenyl at 251 mμ with a minor absorption at 280 mμ.

(11) Roberts and Green (ref. 2) give λ 383 mμ, ε 27,600 for *p*-methylacetophenone DNPH.

(12) Braude, *J. Chem. Soc.*, 1902 (1949).

(13) The introduction of a *p*-hydroxyl group in benzaldehyde DNPH caused a bathochromic shift of 17 mμ (Ref. 2), and a *p*-methoxy group in benzalacetone displaced the maximum by 32 mμ (Wilds, *et al.*, THIS JOURNAL, 69, 1985 (1947)).

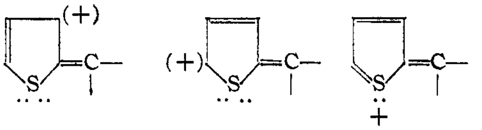
(14) Koch, *J. Chem. Soc.*, 387 (1949).

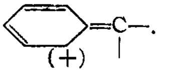
(15) Fehnel and Carmack, THIS JOURNAL, 71, 84 (1949).

(16) Fehnel and Carmack, *ibid.*, 71 231 (1949).

(17) Koch, *J. Chem. Soc.*, 408 (1949); Barnard, Vabian and Koch, *ibid.*, 2442 (1949).

The thiophene compound of this series (compound 8) shows the greatest displacement of the maximum and thus it appears that the thiophene ring is a ready source of electrons. The electron deficiency on the thiophene ring distributes itself over three atoms as indicated in the following structures:



It may be of significance that the last of the resonance structures shown contains a continuous conjugated system absent in the corresponding resonance structure with a benzene ring: . This difference may be in part responsible for the great "basicity"[18] of the 2-thienyl group as compared to the phenyl group. In the ultraviolet range compound 8 exhibits a secondary maximum at 255 mμ which probably corresponds to the independent absorption of the thiophene nucleus[19] in the DNPH structure of type V.

Summary

The absorption spectra of *p*-phenyl-, benzyl-, phenoxy-, phenylmercapto-, phenylthionyl- and phenylsulfonylacetophenone 2,4-dinitrophenylhydrazones and of 2-thienyl methyl ketone 2,4-dinitrophenylhydrazone were examined in the ultraviolet and visible range and compared with the spectrum of the unsubstituted acetophenone derivative. Evidence with regard to the expansion of the valence shell of the sulfur atom is presented.

[18] Brooker, *et al.*, THIS JOURNAL, **67**, 1875 (1945).

[19] Sease and Zechmeister, *ibid.*, **69**, 270 (1947), report the 231 mμ band for thiophene in hexane.

PITTSBURGH, PENNSYLVANIA

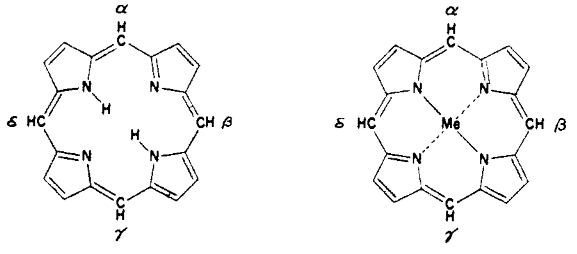
RECEIVED JANUARY 11, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

Exchange and Replacement Reactions of $\alpha,\beta,\gamma,\delta$-Tetraphenyl-metalloporphins[1]

BY J. W. BARNES[2] AND G. D. DOROUGH

It has been known for many years that the two imino hydrogens of free base porphin compounds are replaceable by a great variety of metal ions to produce metallo-derivatives designated as metalloporphins (Fig. 1). It is apparent from even the most cursory examination of the properties of these metal compounds that they may be divided into two large categories with a minimum of overlapping. In one category are the metalloporphins derived from small divalent metal ions such as copper(II), nickel(II), zinc(II), and many others. These metalloporphins not only possess spectra which are similar in shape and extinction coefficient (see Fig. 2), but also exhibit on the whole a considerable reluctance to part with the bonded metal. Copper, for example, is so tightly bonded in the porphin ring that it is removed only by methods so drastic as to cause decomposition of the porphin structure. Although there is no definite relationship between bond type and rate of isotopic exchange,[3] it is not surprising that even after long contact times such metalloporphins have been found not to exchange with the corresponding metal ion in solution. Copper,[4] iron,[4] magnesium[5] and tin,[6] have been among the metalloporphins upon which exchange experiments have been conducted.



(a) Porphin free base. (b) Metalloporphin.

Fig. 1.

The second group of metalloporphins is derived from the large divalent metals such as lead and mercury, and the alkali metals. These metalloporphins show no great affinity for the bonded metal; the action of water or dilute acetic acid is quite sufficient to convert the metalloporphin rapidly and completely to the free base. For one porphin, at least, $\alpha,\beta,\gamma,\delta$-tetraphenylporphin, the spectra of the lead, mercury, and alkali metal derivatives are somewhat similar, being characterized by broad absorption in the red region, and as a group differ markedly from the characteristic spectra shown by the metalloporphins derived

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[1] Second in a series of papers on "Fundamental Properties of Porphyrin Systems."

[2] Monsanto Research Fellow, 1948. Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

[3] A. C. Wahl, editor, "Radioactivity Applied to Chemistry," Chapter 3, John Wiley and Sons, Inc., New York, N. Y. in preparation.

[4] Ruben, Kamen, Allen and Nahinsky, THIS JOURNAL, **64**, 2297 (1942). The iron in this case was trivalent.

[5] Ruben, Kamen and Frankel, *J. Phys. Chem.*, **46**, 710 (1942).

[6] Prof. R. B. Duffield, private communication.