[Contribution from the Department of Chemistry, State University of Iowa]

The Ultraviolet Absorption Spectra of Hydrazones of Aromatic Aldehydes

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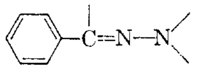
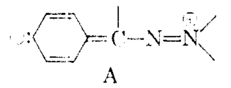
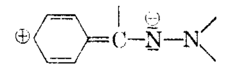
Ultraviolet absorption spectra are reported for a variety of hydrazones of benzaldehyde, substituted both on the terminal nitrogen and in the ring. The spectral features accord with the suggestion that the hydrazone group ($>C{=}N{-}N<$) is a strong electron-donor. *N*-alkyl- and *N*-acylhydrazone groups are also electron-donors. A close parallel exists between the spectral relationships of the aniline-acetanilide series, on the one hand, and the benzaldehyde hydrazone–benzaldehyde acylhydrazone series on the other. Explanations of properties of hydrazones based on assumptions of electron-withdrawal by the hydrazone group are shown to be unnecessary.

Benzaldehyde hydrazone and its derivatives which bear alkyl or acyl groups on the terminal nitrogen and no more than one nuclear substituent, have simple ultraviolet absorption spectra, characterized by two maxima, one in the region of 220–250 mμ, the other at longer wave lengths, 270–400 mμ. Benzophenone hydrazone and its nuclear-substituted derivatives have similar spectral features. When alkyl groups are introduced on the terminal nitrogen of benzaldehyde hydrazone, bathochromic and hyperchromic displacements are observed. This effect has been explained by invoking resonance forms of type A.[2] To explain the effect of ring substituents on the ultraviolet absorption spectra[3] and basicities[4] of a series of benzophenone hydrazones, resonance forms of type B have been used as well as those of type A. The latter would be aided by electron-withdrawing groups in the *ortho* and *para* positions, while the former would be favored by electron-donating substituents in the *ortho* and *para* positions.





A



B

The earlier work dealt only with the effect of substituents on the terminal nitrogen of benzaldehyde hydrazone, while the later work was concerned only with the effects of nuclear substituents in a series of benzophenone hydrazones. While the two series would be expected to parallel each other fairly closely, it would be of interest to compare the effects of substituents on the terminal nitrogen and in the nucleus of one series of compounds. In the course of studies on the chemistry of hydrazines we have prepared a number of hydrazones of benzaldehyde and its nuclear-substituted derivatives. For the present study we have determined the ultraviolet absorption spectra of these materials, as well as additional hydrazones which together form a series in which the substituents on the ring and the terminal nitrogen have been systematically varied.

The results, summarized in Table I (with additional data from the literature), show that the hydrazone group ($>C{=}N{-}N<$) is a strong electron-donating group, in the sense of formula A. The *N*-alkyl hydrazones are in the same class, the alkyl groups facilitating electron-release. The spectral changes, which accompany changes in the substituents *para* to the hydrazone or alkylhydrazone groups, are closely related to the changes observed when substituents *para* to the more familiar electron-donating groups are varied.[5] In the case of the hydrazones considered here, the in-

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[1] Present address: Union Carbide Research Institute, 32 Depot Plaza, White Plains, N. Y.

[2] D. Todd, *J. Am. Chem. Soc.*, **71**, 1353 (1949).

[3] H. H. Szmant and C. McGinnis, *J. Am. Chem. Soc.*, **74**, 240 (1952).

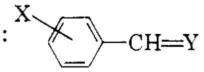
[4] H. F. Harnsberger, E. L. Cochran, and H. H. Szmant, *J. Am. Chem. Soc.*, **77**, 5048 (1955).

[5] L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947). The two bands which are observed in most of the spectra of hydrazones appear to be the displaced first and second primary bands of benzene, as described by Doub and Vandenbelt. Following their terminology, the band of longer wave length is referred to as the first primary band and that of shorter wave length as the second primary band. Throughout the discussion, references to displacements of peaks mean the first primary band, for which more data are available. The second primary bands show similar but smaller displacements. In their work the two primary bands were present (and the secondary band was absent) when the *para* substituents were of opposite and fairly strong electronic types (e.g. methoxyl and carbonyl).

Whether the bands of long and short wave length in the spectra of a series of *p*-disubstituted benzenes are in fact related to each other as first and second primary bands can be determined by the general method of G. N. Lewis and M. Calvin [*Chem. Rev.*, **25**, 273 (1939)], as applied to the benzene case by W. D. Kumler [*J. Am. Chem. Soc.*, **68**, 1184 (1946)]. This method states that the relationship is established if (1) the ratio of wave lengths of the first primary band (λ) to the second primary band (λ') is always less than 2 and increases as λ increases, and (2) the ratio of molar absorbancy indices ϵ'/ϵ decreases as λ increases. These criteria were adhered to sufficiently in the spectra of the hydrazones to serve as tentative establishment of the relationship. The hydrazones bearing nitro groups were anomalous although consistent within themselves. (Both Doub and Vandenbelt and Kumler have remarked the spectral anomalies introduced by nitro groups.) Furthermore, the semicarbazones do not fit the pattern established by the hydrazones, but are consistent within their own group.

TABLE I

ABSORPTION MAXIMA[a] OF AROMATIC ALDEHYDES AND HYDRAZONES:



X	Y				
	O	NNH$_2$	NNHCH$_3$	NN(CH$_3$)$_2$	NNHCONH$_2$
p-(CH$_3$)$_2$N	342(4.47)[b]	—	312[c]	313(4.40)	334(4.34)
		—	225[c]	223(3.99)	233(4.02)
p-CH$_3$O	277(4.17)[d]	281[c]	284(4.32)	291(4.31)	292(4.35)[e]
		—	sh 215(4.08)	sh 218(3.95)	[f]
H	246(4.12)[g]	273(4.07)[h]	285(4.12)[h]	297(4.21)[h]	283(4.30)[i]
		[f]	[f]	[f]	[f]
m-NO$_2$	257(3.87)[i]	268(4.30)[i]	294(4.27)	—	284(4.30)[i]
		[f]	210(4.20)	—	[f]
p-NO$_2$	268(4.02)[j]	343(4.10)	374(4.26)	392(4.28)[k]	328(4.20)[i]
		237(3.89)	246(4.01)	250(3.93)	[f]
p-CN	257(3.98)	306(4.31)	326(4.29)	—	303(4.47)
		226(3.96)	235(3.98)	—	218(4.14)
p-CH$_3$SO$_2$	243(3.96)	299(4.27)	320(4.39)	—	298(4.45)
		225(4.12)	227(3.96)	—	222(4.18)

[a] The solvent for the hydrazones was 95% ethanol; absolute ethanol was required to dissolve the semicarbazones. Figures in parentheses are values of log ε. [b] W. D. Kumler, *J. Am. Chem. Soc.*, **68,** 1184 (1946). [c] Log ε not determined. [d] R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, **1940,** 1347. [e] M. Ramart-Lucas and J. Klein, *Bull. soc. chim.*, [5], **16,** 454 (1949). [f] Portion of spectrum reported included only higher λ_{max}. [g] R. P. Mariella and R. R. Raube, *J. Am. Chem. Soc.*, **74,** 521 (1952). [h] D. Todd, *J. Am. Chem. Soc.*, **71,** 1353 (1949). [i] P. Grammaticakis, *Bull. Soc. chim.*, [5], **17,** 690 (1950). [j] P. Grammaticakis, *Bull. soc. chim.*, [5], **20,** 821 (1953). [k] For p-NO$_2$C$_6$H$_4$CH=NN(CH$_3$)CH$_2$C$_6$H$_5$ λ_{max} = 253,388 mμ; log ε = 4.04, 4.34 [R. L. Hinman, *J. Am. Chem. Soc.*, **78,** 2463 (1956)].

creased length of the resonating system causes both primary bands to be present when only the hydrazone group is on the ring (benzaldehyde hydrazone). No other nuclear substituent is necessary. Thus, the introduction of other electron-donating groups *para* to the hydrazone group causes only small displacements of the first primary band (λ) compared to that of the corresponding unsubstituted hydrazone. (Or, looking at it from the other end of the molecule, when an electron-donating group, such as methoxyl or dimethylamino is on the ring, increasing the electron-donating ability of the hydrazone group in the *para* position (by putting alkyl groups on the terminal nitrogen) causes but slight bathochromic shifts compared to the unmethylated hydrazone with the same nuclear substituent.) When electron-withdrawing groups are *para* to the hydrazone group, large bathochromic shifts are observed relative to benzaldehyde hydrazone, and the introduction of methyl groups on the terminal nitrogen causes large shifts toward the red.

These results are foreshadowed in the spectral changes which occur when the electron-withdrawing formyl group of the aldehyde is converted to the electron-donating hydrazone group. With electron-withdrawing groups on the ring, the conversion of aldehyde to hydrazone is accompanied by large bathochromic shifts of the first primary band. When electron-donating substituents are on the ring, however, the spectral changes are only slightly bathochromic (methoxyl), or actually hypsochromic (dimethylamino).[6]

The semicarbazones form an interesting class because the carbamyl group should withdraw electrons from the terminal nitrogen. It might be expected then that polarization of type B would be favored. If this were the case, however, it would be difficult to explain why the semicarbazones of aldehydes absorb at longer wave lengths than the aldehydes themselves, even when an electron-donating substituent (methoxyl) is in the *para* position. (The formyl group should withdraw electrons more effectively than the semicarbazone group.) These problems are not encountered if it is assumed that the semicarbazone group, like the hydrazone group, donates electrons, but less effectively than the latter.

An interesting parallel can be drawn between the hydrazone-semicarbazone pair and the aniline-acetanilide pair. The bathochromic shift and increased absorption of the high intensity band observed in passing from aniline to acetanilide has been ascribed to the extension of the conjugated system.[7] Similar spectral effects are observed when the terminal nitrogen of benzaldehyde hydrazone is substituted by a carbamyl group.[8] Conversion of p-methoxy-[7] or p-dimethylaminoaniline[9] to the corresponding acetanilide is also accompanied by bathochromic and hyperchromic displacements.

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(6) Similar effects are observed in the benzophenone series (ref. 3.)

(7) H. E. Ungnade, *J. Am. Chem. Soc.*, **76,** 5133 (1954).

(8) Substitution of the terminal nitrogen by an acyl group effects a similar spectral change. Thus, for C$_6$H$_5$CH = NNHY, when Y = CONH$_2$, λ_{max} = 283 (log ε 4.30); when Y = COCH$_3$, λ_{max} = 280 (log ε 4.30); Y = COC$_6$H$_5$, λ_{max} = 295 (log ε 4.35) [P. Grammaticakis, *Bull. soc. chim.*, (5), **17,** 690 (1950)].

(9) P. Grammaticakis, *Bull. soc. chim.*, (5), **18,** 534 (1951).

Similar shifts occur in passing from the hydrazone to the semicarbazone of a correspondingly nuclear-substituted benzaldehyde. When aniline bears an electron-withdrawing group in the *para* position, it absorbs at longer wave lengths than the corresponding acetanilide, although the intensity of absorption of the anilide is frequently the larger of the two (e.g. *p*-aminobenzoic acid,[5] λ_{max} 284, ϵ 14000; *p*-*N*-acetylaminobenzoic acid,[7] λ_{max} 270, ϵ 21,200). These changes are paralleled closely by those in a hydrazone-semicarbazone pair, substituted by electron-withdrawing groups. It is concluded, therefore, that the semicarbazone group (or any *N*-acylhydrazone group) donates electrons, like the acetylamino group and, like the latter, has less tendency to do so than the corresponding unacylated amino form.

When both an acyl group and a methyl group are on the terminal nitrogen, the value of λ_{max} is that observed when the acyl group alone is present plus a small increment for the effect of the methyl group. Thus, with *p*-nitrobenzaldehyde the methylhydrazone has λ_{max} 374 mμ, the acetylhydrazone,[3] λ_{max} 320 mμ, and the *N*-methyl-*N*-acetylhydrazone,[10] λ_{max} 327 mμ. Ramart-Lucas has reported a similar effect of introducing an acyl group in compounds such as anisaldehyde phenylhydrazone and anisaldehyde 1-acetyl-1-phenylhydrazone.[11]

It is interesting that the parallel between the aniline-acetanilide and hydrazone-acylhydrazone pairs breaks down at this point, for introduction of a methyl group in acetanilide causes a drop in both λ_{max} and ϵ from 242 mμ (14,400) for acetanilide[7] to 228 mμ (6000) for *N*-methylacetanilide.[12] A similar effect is observed when *p*-chloroacetanilide is converted to the *N*-methyl derivative.[9] This decrease, which does not seem to have been commented upon, is probably due to steric inhibition of resonance. The acetyl group would be about equivalent to an isopropyl group, which together with the methyl, might cause some interference with planarity due to hindrance at the *o*-hydrogens. The presence of two large alkyl groups on the anilino nitrogen has been shown to have this sort of effect on the ultraviolet spectrum,[13] and additional evidence can be found in the base strengths of *N*,*N*-dialkylanilines. Hindrance to planarity is evident even in *N*,*N*-diethylanilines.[14] The suggestion that steric interference exists in the *N*-methylacetanilides is supported by the spectra of the closely related phenylcyanamides. Phenylcyanamide itself shows λ_{max} 232 mμ, while *N*-methylphenylcyanamide has λ_{max} 235 mμ[15]; *p*-nitrophenylcyanamide: λ_{max} 313 mμ; *N*-methyl-*p*-nitrophenylcyanamide: λ_{max} 313 mμ.[16] The cyanamide group undoubtedly donates electrons like the acetylamino group. However, as the cyano group is much smaller than the acetyl group the steric effects do not appear on introduction of an *N*-methyl group. In the hydrazone series the groups on the terminal nitrogen would be too far removed from the ring hydrogens to interfere with planarity.[17]

In the foregoing discussion it has been shown that the spectral features of the benzaldehyde and related hydrazones can be explained in terms of resonance structure A and *without* invoking formula B. It is also unnecessary to use formula B to explain the increase in basicity observed when benzophenone hydrazone is substituted by an electron-donating group such as methoxyl.[4] Rather, the methoxyl groups merely decrease the ability of the hydrazone group to donate electrons to the ring. *p*-Methoxyaniline is likewise considerably more basic than aniline.[18]

Implicit in the discussion is the idea that hydrazones are like vinylogs of aniline, in both of which the amino group is operating in the same way. The hydrazone group is therefore closely related to the vinylamine group, in which the amino function donates electrons in the same manner.[19]

Styrylamine would of course be a true vinylog of aniline. In this context the oximino group is also closely related, and the limited data available suggest that it probably donates electrons by a similar mechanism. As the ability of *p*-orbitals to overlap for bond formation decreases from nitrogen to oxygen, the oximes should absorb at shorter wave lengths than the hydrazones (just as phenol absorbs at a shorter wave length than aniline), which is in fact observed: benzophenone oxime, λ_{max} 253 mμ,[20] *p*-methoxybenzophenone oxime, λ_{max} 270 mμ,[20] and *p*-nitrobenzophenone oxime, λ_{max} 310 mμ.[21]

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[10] R. L. Hinman and D. Fulton, *J. Am. Chem. Soc.*, **80**, 1895 (1958).

[11] M. Ramart-Lucas and J. Klein, *Bull. soc. chim.* [5], **16**, 454 (1949).

[12] P. L. Southwick, D. I. Sapper, and L. A. Pursglove, *J. Am. Chem. Soc.*, **72**, 4940 (1950).

[13] P. Rumpf and G. Girault, *Compt. rend.*, **238**, 1892 (1954).

[14] See the chapter by H. C. Brown, D. H. McDaniel, and O. Häfliger in E. A. Braude's *Determination of Organic Structures by Physical Methods*, Academic Press, New York, 1955.

[15] M. G. Seeley, R. E. Yates, and C. R. Noller, *J. Am. Chem. Soc.*, **73**, 772 (1951).

[16] R. Huisgen and H. Koch, *Ann.*, **591**, 200 (1955).

[17] Throughout the discussion the question of stereoisomerism of the hydrazone groups is ignored. It is assumed that all the compounds studied have the same configuration (presumably with the aldehyde hydrogen and the terminal nitrogen *cis*), not an unreasonable assumption in view of the common method of preparation.

[18] N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.*, **54**, 3469 (1932).

[19] N. J. Leonard and V. Gash, *J. Am. Chem. Soc.*, **76**, 2781 (1954), and subsequent papers.

[20] P. Grammaticakis, *Bull. soc. chim.*, [5], **8**, 427 (1941).

[21] A. Meisenheimer, *Ann.*, **502**, 162 (1933).

TABLE II

HYDRAZONES OF NUCLEAR SUBSTITUTED BENZALDEHYDES: X $C_6H_4CH{=}N{-}Y$

X	Y	M.P.	Formula	Calcd.			Found		
				C	H	N	C	H	N
p-$(CH_3)_2N$	$NHCH_3$	50–52°	$C_{10}H_{15}N_3$	67.74	8.53	—	67.41	8.69	—
p-$(CH_3)_2N$	$NHCONH_2$	224°(d)[a]	$C_{10}H_{11}N_4O$	59.10	5.46	—	59.22	5.41	—
p-CH_3O	$NHCH_3$	49–51°	$C_9H_{12}N_2O$	—	—	17.06	—	—	17.41
m-NO_2	$NHCH_3$	65–66°	$C_8H_9N_3O_2$	53.62	5.06	23.45	53.45	4.57	22.50
p-NO_2	$NHCH_3$	99–101°[b]	$C_8H_9N_3O_2$	53.61	5.06	23.43	53.74	5.10	23.65
p-CN	NH_2	66–67°	$C_8H_7N_3$	66.17	4.86	—	66.25	4.52	—
p-CN	$NHCH_3$	96–97°	$C_9H_9N_3$	67.90	4.53	—	67.74	5.03	—
p-CN	$NHCONH_2$	>250°	$C_9H_8N_4O$	57.44	4.28	—	57.36	4.19	—
p-CH_3SO_2	NH_2	149–150°	$C_8H_{10}N_2O_2S$	—	—	14.04	—	—	14.08
p-CH_3SO_2	$NHCH_3$	118–120°	$C_9H_{12}N_2O_2S$	50.94	5.70	—	51.35	5.66	—
p-CH_3SO_2	$NHCONH_2$	226–227°	$C_9H_{11}N_3O_3S$	44.80	4.60	—	45.13	4.38	—

[a] Reported m.p. 224° dec. (cor.) (F. Sachs and L. Sachs, *Ber.*, **38,** 525 (1905)). [b] Reported m.p. 93° (O. L. Brady and G. P. McHugh, *J. Chem. Soc.*, **121,** 1648 (1922).)

EXPERIMENTAL[22]

Hydrazones. With the exception of *p*-anisaldehyde hydrazone, these materials were prepared by the reaction of the aldehyde with a 10–20 fold molar excess of 85% hydrazine hydrate, according to the method of Curtius and Lublin.[23] *p*-Nitrobenzaldehyde hydrazone melted at 135–136° (lit.[23] m.p. 134°).

p-Anisaldehyde hydrazone, which could not be obtained by the above method, was prepared by the reaction of the corresponding azine with a 5-fold molar excess of 85% hydrazine hydrate. This method had been used previously[24] for the synthesis of *m*-methoxybenzaldehyde hydrazone. When the reaction was applied to anisaldehyde azine,[24] however, reaction appeared to take place, as evidenced by the gradual disappearance of the solid azine (and its characteristic yellow color), but after evaporation of the ether extracts of the reaction mixture, only azine was obtained. This experiment was repeated in the present work because it was felt that the azine obtained in the ether extract must have been formed from the desired hydrazone after extraction. The azine is relatively insoluble in ether. As traces of either acid or oxidizing agents will rapidly convert hydrazones of this type (see below under *Stability of Hydrazones*) to azines, the ether was washed with 10% sodium hydroxide, dried, and passed down an alumina column to remove peroxides. When this ether was used for extraction of the reaction mixture, a pale yellow liquid was obtained after evaporation of the solvent *in vacuo.* When exposed to air the product rapidly deposited *p*-anisaldehyde azine as a yellow powder. It was completely converted to the azine on attempted distillation. The spectrum was therefore determined without purification or analysis of the material. The general shape of the spectrum, as well as the mode of synthesis and facile conversion to the azine leave little doubt that the liquid product was anisaldehyde hydrazone. *p*-Dimethylaminobenzaldehyde hydrazone could not be obtained even by the latter method.

Methylhydrazones and dimethylhydrazones. These compounds were all prepared by the reaction of an ethanolic solution of the appropriate aldehyde with a molar excess of the hydrazine. A few drops of acetic acid were added, the mixture was heated to boiling, water was added until the solution became turbid, and the mixture was chilled. The crystals were filtered and recrystallized from ethanol-wate-mixtures. *p*-Dimethylaminobenzaldehyde dimethylhydrazone melted at 72–73° (lit.[25] m.p. 74–75°). *p*-Nitrobenzaldehyde dimethylhydrazone melted at 112–113° (lit.[25] m.p. 112°). *p*-Anisaldehyde dimethylhydrazone was distilled, b.p. 123–124° (2.4 mm.) (lit.[25] b.p. 120° (3 mm.).

Semicarbazones were prepared by a standard method.[26]

Stability of hydrazones. Hydrazones with electron-withdrawing groups in the *para* position were only slowly decomposed when exposed to moisture or air. Stability increased as methyl groups were introduced on the terminal nitrogen. The melting point and spectrum of *p*-nitrobenzaldehyde dimethylhydrazone were unchanged after standing overnight in an open beaker. The *p*-nitro derivatives were the most stable, as had been noted by Curtius and Lublin[23] for the simple hydrazones of *o*-, *m*-, and *p*-nitrobenzaldehyde. In 95% ethanol, λ_{max} of a 1.30×10^{-4} *M* solution of *p*-nitrobenzaldehyde hydrazone remained constant at 237 and 343 mμ during 12 hr., and the absorbancy at the higher peak decreased from 1.62 to 1.45. During the same interval, λ max of a 1.03×10^{-4} *M* solution of *p*-cyanobenzaldehyde hydrazone decreased from 306 to 302 and the second primary band at 226 mμ changed to a barely discernible shoulder; the absorbancy of the first primary band decreased from 2.08 to 1.90 during this period.

Hydrazones with electron-donating groups on the ring were extremely unstable, rapidly undergoing oxidation and/or hydrolysis when exposed to air. To save time in determining spectra, concentrations of the hydrazones and methylhydrazones were not determined. The dimethylhydrazones were more stable and their concentrations were determined.

Acknowledgment. The author expresses his appreciation to Dr. David Todd of the Worcester Foundation for Experimental Biology for permission to use his original data for the absorption spectra of the benzaldehyde hydrazones.[2]

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[22] Melting points and boiling points are uncorrected. Spectra were obtained with a Cary Model 11 recording spectrophotometer, using silica cells of 1 cm. light path. Properties and analyses of new compounds are listed in Table II.

[23] T. Curtius and A. Lublin, *Ber.*, **33,** 2460 (1900).

[24] H. Franzen and T. Eichler, *J. prakt. Chem.*, [2], **82,** 241 (1910).

[25] R. H. Wiley, S. C. Slaymaker, and H. Kraus, *J. Org. Chem.*, **22,** 204 (1957).

[26] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, Fourth Ed., John Wiley & Sons, Inc., New York, 1956, p. 218.