[CONTRIBUTION FROM THE BIOCHEMICAL RESEARCH DIVISION, U. S. ARMY CHEMICAL WARFARE LABORATORIES]

Ultraviolet Absorption Spectra of Some Hydroxamic Acids and Hydroxamic Acid Derivatives

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Ultraviolet absorption spectra of several hydroxamic acids and hydroxamic acid derivatives were determined and correlated. An attempt has been made to describe the structure of benzohydroxamic acid anion on the basis of the spectral data.

In connection with studies involving a series of *p*-substituted benzohydroxamic acids, it was deemed desirable to obtain ultraviolet absorption spectra of these materials in acid and alkaline solution. The compounds studied, their absorption maxima (λ) and their molar extinction coefficients (ϵ) are given in Table I. The unexpected behavior of the anion with respect to its acid, prompted us to investigate the spectra of other hydroxamic acids. The data on the second group of acids are presented in Table II.

The similarity in the λ_{max} of acids I and IX, the latter of which can exist only in the keto form, and the dissimilarity between I and XIV, the latter of which can exist only in the enol form, suggests that benzohydroxamic acid (I) exists predominantly at the keto state (Fig. 1). Mathis came to the

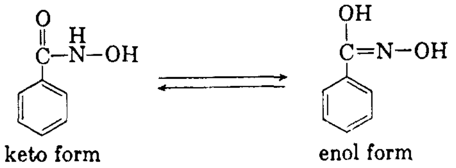
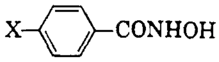


Figure 1

TABLE I

WAVE LENGTHS OF MAXIMUM ABSORPTION AND MOLAR EXTINCTION COEFFICIENTS FOR SERIES



		Acid[a]		Anion[b]			
	Compound	λ_{max} (Mμ)	ϵ_{max}	λ_{1max} (Mμ)	ϵ_{1max}	λ_{2max} (Mμ)	ϵ_{2max}
I	X=H	227	8,750	215	9,510	268	5,350
II	CH_3	232	11,800	224	10,350	267	6,650
III	OCH_3	253	18,250	236	10,600	264	9,460
IV	NH_2[c]	220	8,260			272	12,350
V	Cl	237	13,800	227	11,600	272	6,150
VI	F	230	8,530	219	8,390	265	5,600
VII	CN	236	16,500	232	16,400	291	6,160
VIII	NO_2[d]	268	11,180				

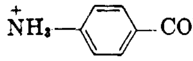
[a] Determined in 0.1*N* HCl. [b] Determined in 0.005*N* NaOH. [c] Compound IV exists as  $\overset{+}{N}H_3$—C$_6$H$_4$—CONHOH in acid solution. [d] Decomposes in base.

TABLE II

WAVE LENGTHS OF MAXIMUM ABSORPTION AND MOLAR EXTINCTION COEFFICIENTS OF SEVERAL HYDROXAMIC ACIDS AND DERIVATIVES

		Acid[a]		Anion[b]	
	Compound	λ_{max} (Mμ)	ϵ_{max}	λ_{max} (Mμ)	ϵ_{max}
IX	$C_6H_5CONCH_3OH$	228	10,000	220	9,250
X	$C_6H_5CONHOCH_3$[c]	223	11,000	257	5,150
XI	$CH_3CH{=}CH{-}CONHOH$	211	13,000	263	7,200
XII	$CH_3{-}(CH{=}CH)_2{-}CONHOH$	262	29,500	255	20,000
XIII	$CH_3{-}(CH{=}CH)_2{-}COOH$	256	25,200	254	25,100
XIV	$C_6H_5(C{=}NOH)OC_2H_5$[d]	238	8,520	265	8,020
XV	*p*-$CH_3OC_6H_4CONCH_3OH$	248	11,600	235	10,600

[a] Determined in 0.1*N* HCl. [b] Determined in 0.005*N* NaOH. [c] Determined in ethyl alcohol and at *p*H 13 in water. [d] Determined at *p*H 6.7 and 13. The *p*K$_a$ of XIV is *ca.* 11.

same conclusions through infrared analysis of various hydroxamic acids and oximes.[1]

The absorption maxima of all the *p*-substituted benzohydroxamic acids shown in Table I (except *p*-aminobenzhydroxamic acid cation) are displaced toward longer wave lengths with respect to benzohydroxamic acid. The shifts shown by compounds II, III, IV, V, and VIII are qualitatively similar to those observed with *p*-substituted derivatives in the benzoic acid series.[2] The *p*-fluoro group appears to exert a slight bathochromic shift.

Benzohydroxamic acid anion and the anions of its *p*-substituted derivatives exhibit two absorption maxima, one, bathochromic, the other, hypsochromic to that of the corresponding hydroxamic acids. *p*-Aminobenzohydroxamic acid anion is an exception showing only a bathochromic shift.

In contrast to the *p*-substituted benzohydroxamic acid anions which give two absorption bands, the anions of *N*-methylbenzohydroxamic acid (IX), *O*-methylbenzohydroxamic acid (X) and ethylsynbenzhydroximic acid (XIV) exhibit only one absorption band. The anion of *N*-methylbenzohydroxamic acid is hypsochromic with respect to its conjugate acid; *O*-methylbenzohydroxamic acid anion, bathochromic to its conjugate acid. Tautomerism is prohibited in IX and its anion leading to absorption behavior analogous to benzoic acid–benzoate ion while such is not the case with X. Ethylsynbenzhydroximic acid anion is bathochromic with respect to its acid form.

Benzohydroxamic acid anion is capable of existing in several forms (Fig. 2). A, B, and C represent various possible structures. If we assume that internally hydrogen bonded structures of B and C do not contribute appreciably to the excited state of the anion, then replacing a hydrogen in the hydroxamate group by an alkyl group in B and C should give spectra which are representative of B and C. Similarly, replacing the hydrogen on the nitrogen atom of structure A with a methyl group should give a spectral curve representative of A. Thus *N*-methylbenzohydroxamic acid anion should give an absorption curve typical of A, ethylsynbenzhydroximic acid anion would represent B and *O*-methylbenzohydroxamic acid anion would be characteristic of C.

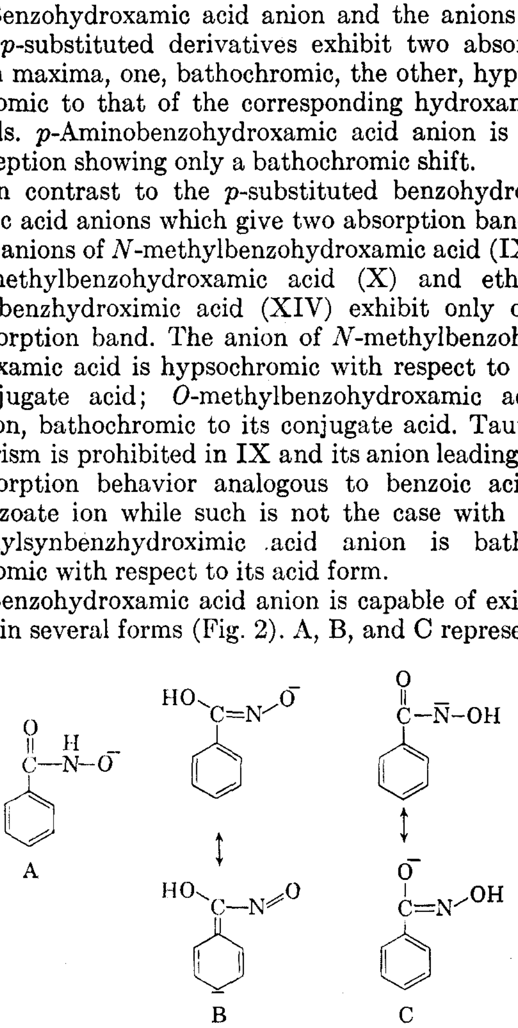


Figure 2

Since the anions of these three compounds (IX, X, and XIV) all exhibit only one absorption band, while benzohydroxamic acid anion and its *para*- substituted derivatives exhibit two bands, it seems plausible that benzohydroxamic acid anion contains contributions from at least two and possibly three forms, one of which is form A and the other is either form B or C or both. Thus, the bathochromic shift exhibited by benzohydroxamic acid anion is probably due to structures B or C or both, contributing to the excited state of the molecule. The hypsochromic shift is probably due to the contribution of structure A.[3]

It is interesting to note that the 268 mμ absorption band of benzohydroxamic acid anion is hardly affected by introduction into the *para*-position of a methyl, methoxyl, chloro, amino or fluoro group. It is likewise noteworthy that no reasonable resonance structures involving participation of the benzene ring, the *para*- substituent and the hydroxamate group can be readily represented for these substances. Introduction of the electron attracting cyano group in the para position readily displaces the 268 mμ band to 291 mμ as the possibilities for conjugation of this group with the benzene ring and the hydroximate group are now greatly enhanced (Fig. 3).

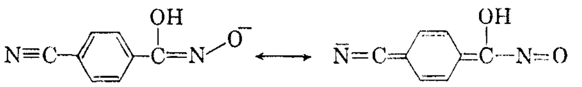


Figure 3

Two olefinic hydroxamic acids, *trans*-crotonohydroxamic acid (XI) and sorbohydroxamic acid (XII) were also studied. The anion of the former gave a bathochromic shift with respect to its acid form. It is possible that crotonohydroxamic acid anion has a band which is also hypsochromic, however if it does exist, this band would be expected in the vacuum ultraviolet region. Sorbohydroxamic acid anion was hypsochromic with respect to its conjugate acid. A broad shoulder appeared in the region of 277 mμ to 293 mμ which could well be the manifestation of a bathochromic band. The 255 mμ band of this anion is not due to the formation of sorbic acid anion which absorbs at 254 mμ. A colorimetric study of the hydrolysis of sorbohydroxamic acid indicated that this substance was stable in the *p*H range of 11 to 13.[4]

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(1) M. F. Mathis, *Compt. rend.*, **232**, 505 (1951).

(2) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

(3) Through an infrared study of the potassium salt of benzohydroxamic acid, Mathis (ref. 1) concludes that the anion has the structure of A only. His conclusion is based upon the absence of a band indicative of the OH bond and, an absorption of the molecule at 3.0μ, which he attributes to the NH bond.

(4) Determined by the disappearance of sorbohydroxamic acid analyzed as its ferric chloride complex; S. Hestrin, *J. Biol. Chem.*, **180**, 249 (1949).

EXPERIMENTAL

Compounds investigated. Most of the hydroxamic acids used in this study were prepared by procedures already described in the literature.[5]

N-Methyl benzohydroxamic acid and its *p*-methoxy derivatives were prepared by the reaction of benzoyl and anisoyl chloride, respectively, with *N*-methylhydroxylamine. *N*-Methylbenzohydroxamic acid was a colorless liquid which boiled at 103–105° at 0.6 mm.

Anal. Calcd. for $C_8H_9NO_2$: C, 63.5; H, 5.95; N, 9.3. Found: C, 63.1; H, 6.1; N, 9.7.

p-Methoxy-*N*-methylbenzohydroxamic acid melted at 108°.

Anal. Calcd. for $C_9H_{11}NO_3$: C, 59.7; H, 6.1. Found: C, 60.2; H, 6.2.

trans-Crotonohydroxamic acid was synthesized from crotyl chloride and hydroxylamine and melted at 116°.

Anal. Calcd. for $C_4H_7NO_2$: C, 47.5; H, 6.9. Found: C, 47.4; H, 6.9.

Spectra. The ultraviolet absorption spectra were determined by means of a Beckman Quartz DU Photoelectric spectrophotometer or a Cary Spectrophotometer. Solutions of the hydroxamic acids (*ca.* 5.8×10^{-5} molar) were made up in 0.1*N* hydrochloric acid and 0.005*N* sodium hydroxide except as noted in Tables I and II. To minimize decomposition of the hydroxamic acids, the solution was made alkaline just prior to use.

Acknowledgment. The author wishes to express gratitude to Mr. Omer O. Owens for preparing some of the compounds used in this investigation. The author also wishes to thank the Analytical Research Branch of these Laboratories for the use of their Cary recording spectrophotometer.

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(5) Benzohydroxamic acid—W. B. Renfrew and C. R. Hauser, *J. Am. Chem. Soc.*, **59**, 2312 (1957); *p*-substituted benzohydroxamic acids—B. E. Hackley, Jr., R. E. Plapinger, M. Stolberg, and T. Wagner-Jauregg, *J. Am. Chem. Soc.*, **77**, 3651 (1955); ethylsynbenzhydroximic acid—E. Eiseler, *Ann.*, **175**, 328 (1875) and O. Gurke, *Ann.*, **205**, 285 (1905); sorbohydroxamic acid—G. M. Steinberg and J. Bolger, *J. Org. Chem.*, **21**, 660 (1956); and *O*-methylbenzohydroxamic acid—W. Lossen, *Ann.*, **281**, 186 (1894).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Rearrangement of *N*-Phenylbenzimidoyl γ-Ethylallyl Ether

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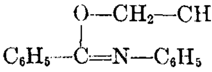
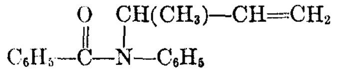
Thermal rearrangement of *N*-phenylbenzimidoyl γ-ethylallyl ether leads to the formation of *N*-ethylvinylcarbinyl benzanilide. Thus, migration of the γ-ethylallyl group from the oxygen to nitrogen occurs with inversion. At somewhat higher temperatures this initial pyrolysis product rearranges to *o*-benzamido-γ-ethylallylbenzene. This nitrogen to carbon migration also proceeds with inversion.

Relatively few *N*-phenylbenzimidoyl allyl ethers have been rearranged. Mumm and Möller[2] demonstrated that *N*-phenylbenzimidoyl γ-methylallyl ether (I) rearranges with inversion to produce *N*-α-methylallyl benzanilide (II). In order to obtain further information concerning the similarity of this transformation and the Claisen rearrangement, Lauer and Lockwood[3] studied the pyrolysis of *N*-phenylbenzimidoyl γ,γ-dimethylallyl ether, III. No normal rearrangement product had been obtained in the case of the γ,γ-dimethylallyl ether of ethyl *p*-hydroxybenzoate[4] and likewise, no shift of the γ,γ-dimethylallyl group from oxygen to nitrogen occurred in the case of *N*-phenylbenzimidoyl γ,γ-dimethylallyl ether. Instead, the migrating γ,γ-dimethylallyl group became attached to the aromatic nucleus without inversion, and the structural change was represented as follows:



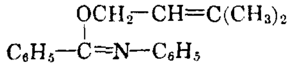
$C_6H_5-\overset{\overset{\displaystyle O-CH_2-CH=CHCH_3}{|}}{C}=N-C_6H_5$

I



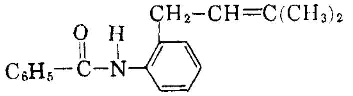
$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle CH(CH_3)-CH=CH_2}{|}}{N}-C_6H_5$

II



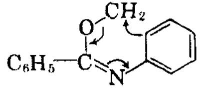
$C_6H_5-\overset{\overset{\displaystyle OCH_2-CH=C(CH_3)_2}{|}}{C}=N-C_6H_5$

III



IV

This process can be viewed as a double inversion; the first step involving migration from oxygen to nitrogen and the second from nitrogen to carbon. A first step of this kind might be expected to be hindered by steric factors. No normal migration of the γ,γ-dimethylallyl group with inversion occurs in the Claisen rearrangement and therefore by analogy such a step might be considered to be unlikely. A single six-membered cyclic transition state of type A, which would not require oxygen to nitrogen migration with inversion, can be postulated.



A

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(1) From the Ph.D. Thesis of C. S. Benton submitted in August 1957.

(2) O. Mumm and F. Möller, *Ber.*, **70**, 2214 (1937).

(3) W. M. Lauer and R. G. Lockwood, *J. Am. Chem. Soc.*, **76**, 3974 (1954).

(4) W. M. Lauer and O. Moe, *J. Am. Chem. Soc.*, **65**, 289 (1943).