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LITERATURE CITED

(1) Barnes, R.S., Fainman, M.Z., *Lubrication Eng.* **13**, 545 (1957).
(2) Berlow, E., Barth, R.H., Snow, J.E., "The Pentaerythritols," Reinhold, New York, 1958.
(3) Blake, E., Edwards, J., Hammann, W., Wright Air Development Center, **Tech. Rept. 54-532**, 76 (1955).
(4) Cohen, G., Murphy, C.M., O'Rear, J.G., Ravner, H., Zisman, W.A., *Ind. Eng. Chem.* **45**, 1766 (1953).
(5) Heyden Newport Chemical Corp., New York, **Tech. Bull. PE 3-55, PE 2**, 1956.
(6) Larsen, R.G., Bondi, A., *Ind. Eng. Chem.* **42**, 2421 (1950).
(7) Mahoney, L.C., Kevlin, W.M., Barnum, E.R., Sax, K.J., Armed Serv. Tech. Inform. Agency Doc. No. **AD 130925**, 1957.
(8) Mahoney, L.C., Kevlin, W.M., Barnum, E.R., Sax, K.J., Saari, W.S., Williams, P.H., Armed Serv. Tech. Inform. Agency Doc. No. **155862**, 1958.
(9) Murphy, C.M., Ravner, H., *Ind. Eng. Chem.* **44**, 1607 (1952).
(10) Murphy, C.M., Zisman, W.A., *Ibid.*, **42**, 2415 (1950).
(11) Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, Tech. Memo. **WCRT 56-164**, 1956.

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# Preparation and Properties of Some *N*-Aryl Hydroxamic Acids

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*N*-Phenylbenzohydroxamic acid, introduced by Shome (*13*) as reagent superior to cupferron, has found extensive analytical applications (*2, 10-12*). A recent search (*15*) for analogous reagents with more desirable analytical characteristics produced several hydroxamic acids

$$\begin{array}{l} R_1\text{—N—OH} \\ \quad\quad | \\ R_2\text{—C=O} \end{array}$$

in which $R_1$ and $R_2$ are substituted by aryl, furyl, thienyl, etc. Preparation and properties of these substituted hydroxamic acids are presented here. Spectral properties in ultraviolet and visible regions, solubility in water and organic solvents, and storage qualities important for characterization and analytical application of hydroxamic acids are described. Of the 22 hydroxamic acids described here eight were previously prepared by other workers, but some of their properties are recorded for the first time.

The general methods employed in the synthesis of hydroxamic acids are outlined by Yale (*17*) in a well documented review article. We prepared these by reacting *N*-aryl hydroxylamines with acid chlorides at low temperatures in an ether solution buffered with pyridine (*15*). Both mono- and di-substituted derivatives are formed showing, thereby, that both of the hydrogen atoms of *N*-aryl hydroxylamine are attacked. Mono-derivatives are soluble in ammonia and are separated from the di-derivatives by taking advantage of this property.

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## EXPERIMENTAL

**Materials and Apparatus.** All hydroxamic acids were recrystallized from mixtures of benzene and petroleum ether at least two times and were vacuum dried. For preparing standard solutions, a small quantity of each hydroxamic acid was weighed on a Mettler microbalance and was dissolved in spectroscopic grade of 95% ethyl alcohol or glass-distilled water. Graduated apparatus of standard calibration was used for measurements.

Ultraviolet and visible absorption spectra of the hydroxamic acids were scanned on a Beckman Model DK-2 ratio recording spectrophotometer using two 10-mm. matched silica cells. The absorption measurements, made at constant wavelength for the calculation of molar absorptivity, $\epsilon$, were performed on an Unicam SP 500 spectrophotometer. Molar absorptivity is expressed in units of liters per mole cm.

**Preparation.** *N*-Phenylhydroxylamine (*5*), *N*-1-naphthylhydroxylamine (*14*), and *N*-*p*-tolylhydroxylamine (*15*) were freshly prepared and crystallized from a mixture of benzene and petroleum ether before use.

All acid chlorides used in this study were prepared by the action of thionyl chloride on the corresponding acids. An excess of thionyl chloride was employed and the reaction mixture heated on the steam bath for 1 to 2 hours, after which the excess of thionyl chloride was distilled off and the acid chloride obtained by distillation under reduced pressure. The boiling points and the yields of these acid chlorides were in agreement with literature values (*16*).

**Procedure for Synthesis.** One molar proportion of *N*-arylhydroxylamine was dissolved in liberal excess of cold diethyl ether and the solution stirred mechanically with external

cooling to bring the temperature to 0° or less. To this, 1.1 to 1.2 moles of pyridine (or if necessary more of it), and 0.9 mole of appropriate acid chloride (if the acid chloride is solid, a solution of it in anhydrous diethyl ether) were added dropwise from two dropping funnels during the course of an hour or more. The reaction mixture was always kept basic. Usually a granular, orange-yellow precipitate was obtained, but in a few cases a brownish sticky material was formed. The ethereal mother liquor was decanted and the ether removed under vacuum at room temperature. Any solid material thus obtained was combined with the bulk of the product which was successively treated with ice-cold $2N$ hydrochloric acid to remove the excess pyridine, and then washed several times with ice-cold water. The material was thoroughly triturated in a porcelain mortar with an excess of saturated solution of sodium hydrogen carbonate to remove the acidic impurities. The solution was filtered, and the solid was washed with water and treated several times with cold liquor ammonia (sp. gr. 0.88). The filtered ammoniacal solution, which was generally yellow or green, was added dropwise to a solution of $6N$ hydrochloric acid containing some crushed ice to yield the hydroxamic acid which was filtered, washed with water, and dried. The product was crystallized from dilute ethyl alcohol (10–20%) or from a mixture of benzene and petroleum ether (the latter being preferred), generally without the use of charcoal. During crystallization, heat treatment for prolonged period was avoided.

**Solubilities.** Exploratory studies demonstrated that all hydroxamic acids had positive temperature coefficients for solubility; hence, for preparing saturated solutions, an approach to equilibrium was made by supersaturation (8).

Saturated solutions were prepared by shaking very fine suspensions of excess hydroxamic acid in 50 to 100 ml. of water for 2 days at a temperature about 5° higher than that at which the solubility was to be determined, then allowed to stand in a thermostat for 1 day. The excess solid was removed. An aliquot of the filtrate was diluted to a convenient concentration to measure the absorbance at suitable wavelengths. The solubility was then calculated from the known molar absorptivity.

All measurements were made at least twice.

## DISCUSSION

Most of the reactions proceeded as expected with 40–60% yield. The ortho- and meta-substituted derivatives were difficult to prepare. They readily changed into oily form during neutralization of their ammonia extracts with hydrochloric acid. Crystalline products could, however, be obtained in unsatisfactory yields by the slow evaporation of solutions of the oily products in ethyl alcohol under vacuum.

The physical properties of hydroxamic acids are given in Table I. Most of them are white; nitro-substituted derivatives are yellow, and cinnamic acid derivatives are pale green. They are stable toward heat, light, and air and can be stored for an indefinite period without deterioration. Their aqueous, alcoholic, and chloroform solutions, too, are stable and can be kept for several weeks if stored

Table I. Properties of Hydroxamic Acids

| Hydroxamic Acid | Formula | M.P., °C. | Aqueous Soly., Mg./Liter 25° C. | U.V. Spectra in 95% Ethyl Alcohol | | Calcd. | | | Found | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $\lambda_{max}$ (mμ) | $10^{-3}\epsilon$ | C | H | N | C | H | N | |
| *N*-Phenylbenzo- | $C_{13}H_{11}NO_2$ | 121. | 400 | 268 | 8.9 | | | | | | | *3, 4, 7, 13* |
| *N*-*p*-Tolylbenzo- | $C_{14}H_{13}NO_2$ | 111 | 250[c] | 270[a] | 9.8 | 73.99 | 5.77 | 6.16 | 73.90 | 5.57 | 6.20 | *6* |
| *N*-Phenylcinnamo- | $C_{15}H_{13}NO_2$ | 162 | 4 | 292[d] | 22.6 | 75.30 | 5.48 | 5.85 | 75.45 | 5.60 | 6.00 | *9* |
| *N*-*p*-Tolylcinnamo- | $C_{16}H_{15}NO_2$ | 159 | 3 | 290[e] | 21.8 | 75.87 | 5.97 | 5.53 | 75.80 | 6.10 | 5.50 | None |
| *N*-Phenyl-2-theno- | $C_{11}H_9NO_2S$ | 98 | 510 | 254[f] | 12.9 | 60.26 | 4.13 | 6.38 | 60.50 | 4.15 | 6.50[g] | *1, 15* |
| | | | | 285 | 15.3 | | | | | | | |
| *N*-*p*-Tolyl-2-furo- | $C_{12}H_{11}NO_2S$ | 125.5 | 80 | 252[h] | 10.0 | 61.78 | 4.75 | 6.00 | 61.70 | 4.80 | 5.95[i] | *15* |
| | | | | 286 | 12.8 | | | | | | | |
| *N*-Phenyl-2-furo- | $C_{11}H_9NO_3$ | 135 | 510 | 284[j] | 14.9 | 65.02 | 4.46 | 6.89 | 65.10 | 4.49 | 6.96 | *1, 7* |
| *N*-*p*-Tolyl-2-furo- | $C_{12}H_{11}NO_3$ | 142 | 150 | 285[k] | 14.2 | 66.35 | 5.10 | 6.45 | 66.45 | 4.98 | 6.40 | None |
| *N*-Phenyl-1-naphtho- | $C_{17}H_{13}NO_2$ | 131 | 50[c] | 283[l] | 10.9 | 77.55 | 4.98 | 5.32 | 77.70 | 5.10 | 5.45 | *7* |
| *N*-1-Naphthylbenzo- | $C_{17}H_{13}NO_2$ | 165 | 13[c] | 289[a] | 8.7 | 77.55 | 4.98 | 5.32 | 77.28 | 4.90 | 5.40 | *7* |
| *N*-*p*-Tolyl-1-naphtho- | $C_{18}H_{15}NO_2$ | 138 | 14[c] | 283[e] | 10.6 | 77.96 | 5.45 | 5.05 | 78.25 | 5.36 | 4.95 | None |
| *N*-Phenyl-*o*-methylbenzo- | $C_{14}H_{13}NO_2$ | 81 | ... | 257[a] | 9.6 | 73.99 | 5.77 | 6.16 | 74.10 | 6.10 | 5.95 | None |
| *N*-Phenyl-*p*-methylbenzo- | $C_{14}H_{13}NO_2$ | 116. | ... | 270[a] | 9.7 | 73.99 | 5.77 | 6.16 | 74.10 | 5.56 | 5.94 | None |
| *N*-Phenyl-3,5-dinitrobenzo- | $C_{13}H_9N_3O_6$ | 133 | 70 | 235[e] | 23.7 | 51.49 | 2.99 | 13.86 | 51.65 | 3.00 | 14.10 | *7* |
| *N*-Phenyl-*o*-nitrobenzo- | $C_{13}H_{10}N_2O_4$ | 148 | 270[c] | 254[e] | 16.6 | 60.46 | 3.90 | 10.85 | 60.80 | 3.70 | 11.20 | None |
| *N*-Phenyl-*m*-nitrobenzo- | $C_{13}H_{10}N_2O_4$ | 117 | ... | 262[e] | 15.0 | 60.46 | 3.90 | 10.85 | 60.65 | 4.00 | 10.80 | None |
| *N*-Phenyl-*p*-nitrobenzo- | $C_{13}H_{10}N_2O_4$ | 168 | 40 | 251[a] | 14.4 | 60.46 | 3.90 | 10.85 | 60.65 | 3.95 | 10.93 | None |
| *N*-*p*-Tolyl-*p*-nitrobenzo | $C_{14}H_{12}N_2O_4$ | 153 | 40[c] | 252[e] | 15.1 | 61.76 | 4.44 | 10.29 | 61.90 | 4.49 | 10.60 | None |
| *N*-Phenyl-*o*-chlorobenzo- | $C_{13}H_{10}NO_2Cl$ | 106 | 265[c] | 258[a] | 10.3 | 63.04 | 4.07 | 5.66[m] | 63.25 | 4.15 | 5.60 | None |
| *N*-Phenyl-*p*-chlorobenzo- | $C_{13}H_{10}NO_2Cl$ | 153 | 30[c] | 270[a] | 10.6 | 63.04 | 4.07 | 5.66[n] | 62.86 | 4.13 | 5.73 | None |
| *N*-*p*-Tolyl-*p*-chlorobenzo- | $C_{14}H_{12}NO_2Cl$ | 166 | 8 | 270[a] | 10.4 | 64.25 | 4.62 | 5.35[o] | 64.56 | 4.63 | 5.41 | None |
| *N*-Phenyl-*m*-bromobenzo- | $C_{13}H_{10}NO_2Br$ | 85.5 | 180[c] | 271[a] | 9.1 | 53.45 | 3.43 | 4.80[p] | 53.50 | 3.50 | 5.03 | None |

[a] In aqueous solution absorption is general. [b] In chloroform, $\lambda_{max}$ = 271 mμ; $\epsilon$ = 7,900. [c] At 35° C. [d] In aqueous saturated solution, $\lambda_{max}$ = 286 mμ; $\epsilon$ could not be determined because of insolubility of compound. [e] In aqueous solutions the band becomes very broad and is displaced to shorter wavelengths. [f] In aqueous solution, $\lambda_{max}$ = 253 and 280 mμ; $\epsilon$ = 11,400 and 12,400. In chloroform, $\lambda_{max}$ = 284 mμ; $\epsilon$ = 9,100. Other band was not observed because of strong absorption of chloroform at shorter wavelengths. [g] Calcd: S, 14.62. Found: S, 14.50. [h] In aqueous solution, $\lambda_{max}$ = 250 and 279 mμ; $\epsilon$ = 9,100 and 10,200. [i] Calcd: S, 13.74. Found: S, 13.90. [j] In aqueous solution, $\lambda_{max}$ = 270 mμ; $\epsilon$ = 14,900. In chloroform $\lambda_{max}$ = 284 mμ; $\epsilon$ = 9,500. [k] In aqueous solution, $\lambda_{max}$ = 270 mμ; $\epsilon$ = 14,900. [l] In aqueous solution, $\lambda_{max}$ = 283 mμ; $\epsilon$ = 10,700. [m] Calcd: Cl, 14.32. Found: Cl, 14.50. [n] Calcd: Cl, 14.32. Found: Cl, 14.25. [o] Calcd: Cl, 13.55. Found: Cl, 13.40. [p] Calcd: Br, 27.35. Found: Br, 27.20.

in amber bottles. This is a very desirable property from the viewpoint of analytical applications. All hydroxamic acids described are slightly soluble in water, but are soluble in organic solvents such as benzene, diethyl ether, chloroform, carbon tetrachloride, *o*-dichlorobenzene, and ethyl alcohol and also in ammonia, alkali hydroxides and sodium carbonate. Solubility data for only a few compounds are available in literature. Values for solubility of *N*-phenylbenzohydroxamic acid, *N*-phenyl-1-naphthohydroxamic acid, and *N*-phenyl-3,5-dinitrobenzohydroxamic acid reported here are in general agreement with the values reported by earlier workers (*3*, *7*), but there is an unaccountable disagreement in the values for *N*-phenyl-2-furohydroxamic acid and *N*-1-naphthylbenzohydroxamic acid.

Spectral data for only one compound, *N*-phenylbenzohydroxamic acid, are available in literature (*3*, *4*). There is a general agreement between the values reported here and by earlier workers. The position and intensity of absorption bands of hydroxamic acids are often affected by the solvents used for preparing their solutions. In general, the well defined bands observed in 95% ethyl alcohol solutions either disappear or show a hypsochromic shift, if water is used as solvent. This solvent effect is shown for a few representative compounds in Figure 1. The solvent effect (Table I and Figure 1) should not be overlooked when measuring the hydroxamic acid concentration of a solution using the spectroscopic method. Relevant calibration curves should be prepared at convenient wavelengths for each solvent. In the solubility measurements reported here, wherever the aqueous insolubility of a hydroxamic acid required the use of water-ethyl alcohol mixtures for the preparation of its standard solution, either proper corrections for the solvent effect were applied, or both sample and standard solutions were so prepared that at the time of final measurement of absorbance they had identical composition of solvents.

None of the colored hydroxamic acids shows an absorption maximum in the visible region of spectrum; the absorption is of a general character and falls off rapidly at longer wavelengths.

All the compounds give the characteristic color test of hydroxamic acids with ferric chloride.

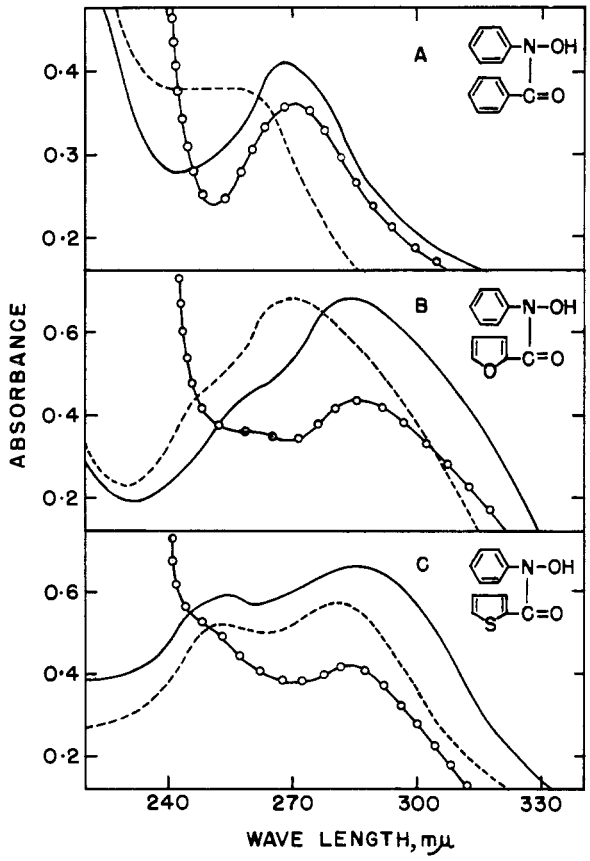


Figure 1. Effect of solvent on the ultraviolet absorption spectra of hydroxamic acids

A. *N*-Phenylbenzohydroxamic acid
B. *N*-Phenyl-2-furohydroxamic acid
C. *N*-Phenyl-2-thenohydroxamic acid
—— $4.57 \times 10^{-5}$ M of each acid in ethyl alcohol
---- in water
·–·–· in chloroform


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## LITERATURE CITED


(1) Armour, C.A., Ryan, D.E., *Can. J. Chem.* **35**, 1454 (1957).
(2) Brandt, W.W., *Record Chem. Progr.* **21**, 159 (1960).
(3) Dyrssen, D., *Acta Chem. Scand.* **10**, 353 (1956).
(4) Grammaticakis, P., *Bull. Soc. Chim. France* **1951**, p. 965.
(5) Kamm, O., Marvell, C.S., "Organic Syntheses," Vol. 1, p. 445, Gilman, H., Blatt, A.H., ed., Wiley, New York, 1946.
(6) Lukashevich, V.O., *Ann.* **521**, 198 (1935).
(7) Lutwick, G.D., Ryan, D.E., *Can. J. Chem.* **32**, 949 (1954).
(8) Mader, W.J., Vold, R.D., Vold, M.J., "Technique of Organic Chemistry," Vol. I, Part I, p. 655, Weissberger, A., ed., Interscience, New York, 1959.
(9) Majumdar, A.K., Mukherjee, A.K., *Anal. Chim. Acta.* **22**, 514 (1960).
(10) Priyadarshini, U., Tandon, S.G., *Chem. Ind. London* **1960**, p. 931.
(11) Priyadarshini, U., Tandon, S.G., *Anal. Chem.* **33**, 435 (1961).
(12) Ryan, D.E., *Analyst* **85**, 569 (1960).
(13) Shome, S.C., *Ibid.*, **75**, 27 (1950).
(14) Smith, G.F., "Cupferron and Neo-Cupferron," p. 11, G.F. Smith Chemical Co., Columbus, Ohio, 1938.
(15) Tandon, S.G., Bhattacharya, S.C., *Anal. Chem.* **33**, 1267 (1961).
(16) Wagner, R.B., Zook, H.D., "Synthetic Organic Chemistry," p. 546, Wiley, New York, 1953.
(17) Yale, H.L., *Chem. Revs.* **33**, 209 (1943).



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