TABLE III

CHELATE EFFECT OF N,N'-ETHYLENEDIANTHRANILIC ACID

| | Copper | Nickel | Cobalt | Zinc | Cadmium |
|---|---|---|---|---|---|
| log $k$ for N,N'-ethylenedianthranilic acid[3] | 10.2 | 8.6 | 6.4 | 6.1 | 6.0 |
| log $k_1k_2$ for N-methylanthranilic acid | 8.1 | 5.6 | 5.6 | 5.8 | 6.0 |
| Chelate effect | +2.1 | +3.0 | +0.8 | +0.3 | 0.0 |

TABLE IV

CHELATE EFFECT OF N,N'-TRIMETHYLENEDIANTHRANILIC ACID

| | Copper | Nickel | Cobalt | Zinc | Cadmium |
|---|---|---|---|---|---|
| log $k$ for N,N'-trimethylenedianthranilic acid | 8.1 | 5.4 | 5.0 | 5.2 | 5.3 |
| log $k_1k_2$ for N-methylanthranilic acid | 8.1 | 5.6 | 5.6 | 5.8 | 6.0 |
| Chelate effect | 0.0 | −0.2 | −0.6 | −0.6 | −0.7 |

ring becomes seven-membered. The first change should result in increased stability of complexes; the second should have the opposite effect. The over-all result is a reversal in the positions of zinc and cadmium in the stability orders and a general increase in the size of the constants. This increase in the size of the constants is, however, more than offset by the increased proton affinity of the nitrogen. The result is that comparable values of $\bar{n}$ occur at much higher $p$H values for $\alpha$-amino-$o$-toluic acid than for anthranilic acid.

The effect of adding acetic acid groups to the nitrogen is seen in the series: anthranilic acid, N-(carboxymethyl)-anthranilic acid, and N,N-bis-(carboxymethyl)-anthranilic acid. For copper, nickel, cobalt and zinc the increase in $k$ from anthranilic acid to N,N-bis-(carboxymethyl)-anthranilic acid is between nine and ten units in the log, and for cadmium the increase is 7.8 units in the log. For copper, the increase between anthranilic acid and N-(carboxymethyl)-anthranilic acid is about the same as the increase between N-(carboxymethyl)-anthranilic acid and N,N-bis-(carboxymethyl)-anthranilic acid, but for the remaining four metal ions the increase in stability that results from the addition of the second acetic acid group is considerably larger than that resulting from the addition of the first. This indicates that copper, which has a strong tendency to form complexes of the square planar type, may have a dsp$^2$ configuration in the 1:1 anthranilic acid and N-(carboxymethyl)-anthranilic acid hydrated complexes and is forced into a tetrahedral sp$^3$ configuration with N,N-bis-(carboxymethyl)-anthranilic acid. The Hirschfelder model indicates that the donor groups of N,N-bis-(carboxymethyl)-anthranilic acid cannot be arranged to a square planar structure.

It is believed that the 1:1 complexes of N,N-bis-(carboxymethyl)-anthranilic acid are all tetrahedral and that bond angles are not a variable in determining the relative stabilities of the complexes. This is supported by the observation that the order of stability of the complexes of N,N-bis-(carboxymethyl)-anthranilic acid is the same as the order of the second ionization potentials of the five metals.

Constants are given in Table II for 2:1 complexes of N-(2-aminoethyl)-anthranilic acid and N-(carboxymethyl)-anthranilic acid. The formation of the 2:1 copper complexes is much less complete than the formation of the 1:1 copper complexes. This is in agreement with the assumption that a six coördinate sp$^3$d$^2$ configuration is not favored by copper as compared to the four coördinate dsp$^2$ configuration. An alternative explanation is that copper remains four-coördinate in forming the 2:1 complexes and the ligand acts as a bidentate with copper instead of a tridentate.

**Acknowledgment.**—We gratefully acknowledge financial aid to A. Y. in the form of a predoctoral Kettering Research Fellowship.

COLUMBUS, OHIO

---

[CONTRIBUTION FROM THE MONSANTO CHEMICAL CO., PLASTICS DIVISION]

# The Infrared Spectra of Some Derivatives of 1,3,5-Triazine

BY W. M. PADGETT II AND W. F. HAMNER

RECEIVED AUGUST 5, 1957

The infrared spectra from 2-16 μ of thirty-five derivatives of 1,3,5-triazine have been obtained, using solid samples dispersed in alkali halide disks. With the exception of cyanuric acid, which apparently associates with alkali halides,[8] all of the compounds gave identical spectra from pressed disks and from films sublimed onto rocksalt. Correlation of spectra and structures has led to the assignment of strong bands near 6.4 and 6.9 μ in the spectra of melamine derivatives to in-plane vibrations of the triazine ring, and of a weaker band near 12.25 μ to an out-of-plane ring vibration. Introduction of strongly electrophilic groups such as chlorine or positively-charged nitrogen onto the ring causes the out-of-plane ring band to shift toward longer wave lengths. Drastic alteration of the entire absorption pattern upon introduction of hydroxyl groups onto the ring provides evidence for tautomeric shifts in these compounds toward the corresponding "iso" or amido forms.

## Introduction

Several publications concerning the infrared spectra of 1,3,5-triazine and its derivatives have appeared in the last few years[1-3]; however, the spectra published have been too few in number to allow the assignment of bands characteristic of the substituted triazine ring system. Grundmann and his group[1] used the vibrational spectra of 1,3,5-triazine to support its ring configuration, assigned the major infrared bands at 6.4 and 7.1 μ to in-plane vibrations of the triazine ring atoms, and drew an analogy between the vibrational spectra of triazine and of benzene.

---

(1) J. Goubeau, E. L. Jahn, A. Kreutzberger and C. Grundmann, *J. Phys. Chem.*, **58**, 1078 (1954).

(2) A. Roosens, *Bull. soc. chim. Belg.*, **59**, 377 (1950).

(3) J. E. Lancaster and N. B. Colthup, *J. Chem. Phys.*, **22**, 1149 (1954).

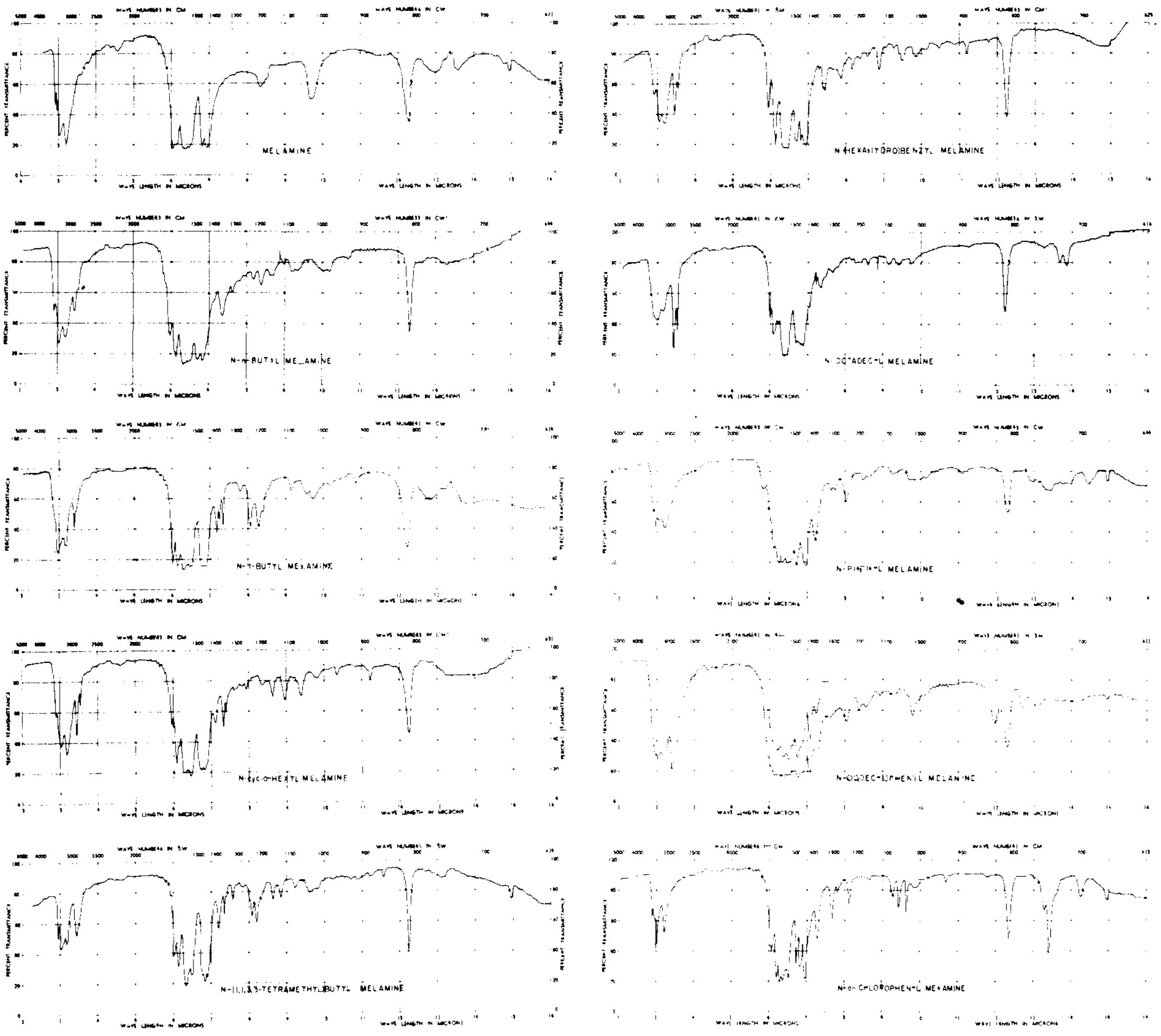

Fig. 1.—Infrared spectra of melamine and monosubstituted derivatives.

The present report on the infrared spectra of some 1,3,5-triazine derivatives is intended to present the spectra of a large series of such compounds, to correlate the spectra with compound structures and thereby to observe the effects of substitution of various functional groups on the triazine ring.

## Experimental Work

Since all but a few of the compounds investigated are sparingly soluble in solvents suitable for infrared work, they were studied as solids dispersed in KBr disks or sublimed onto NaCl plates. The KBr disk technique has been thoroughly described in other publications,[4,5] and was pursued in a very simple fashion, the sample and KBr being ground together for about a minute in a small mechanical ball mill, then pressed at 20,000 pounds in an evacuable die until a suitable disk was obtained. Background absorption at 2.9 μ due to water pick-up in the disks was less than 10%.

In the preparation of sublimed films, the finely divided sample was placed in the bottom of an evacuable glass tube, a rocksalt plate was suspended a few centimeters overhead, the tube was evacuated to less than 1 mm. pressure, and then the base of the tube was heated gently with a bunsen flame until a thin coat of powder had deposited onto the rocksalt. The films obtained, even when quite thick, were evenly deposited and lost little light by scattering. These films were used only as a check on the KBr disk spectra. Except where otherwise noted the spectra reproduced here are from the pressed disks.

The spectrometer was a Baird Associates model AB1 double beam instrument, equipped with standard sodium chloride optics. Wave length accuracy was within 0.02 μ as determined from a spectrum of polystyrene film.

## Discussion

In Fig. 1 are shown the infrared spectra of melamine (2,4,6-triamino-1,3,5-triazine) and some monosubstituted derivatives. The spectra are alike in their essential features, with three main regions of absorption: near 3 μ, between 6 and 7 μ, and just beyond 12 μ. The first region contains the N–H stretching absorptions (several maxima between 2.9 and 3.2 μ), and also the C–H stretching bands of the substituent group (3.4 to 3.6 μ). The second region is where the in-plane vibrations of the triazine ring as well as vibrations connected with the free amino groups are expected to absorb, and contains three or four large bands, the most outstanding of which is a strong, broad absorption at 6.4 μ. A comparison of these spectra and that of 1,3,5-triazine itself,[1] which contains

---

(4) U. Z. Schiedt and H. Reinwein, *Naturforschung*, **7B**, 270 (1952).

(5) M. M. Stimson and M. J. O'Donnell, This Journal, **74**, 1805 (1952).

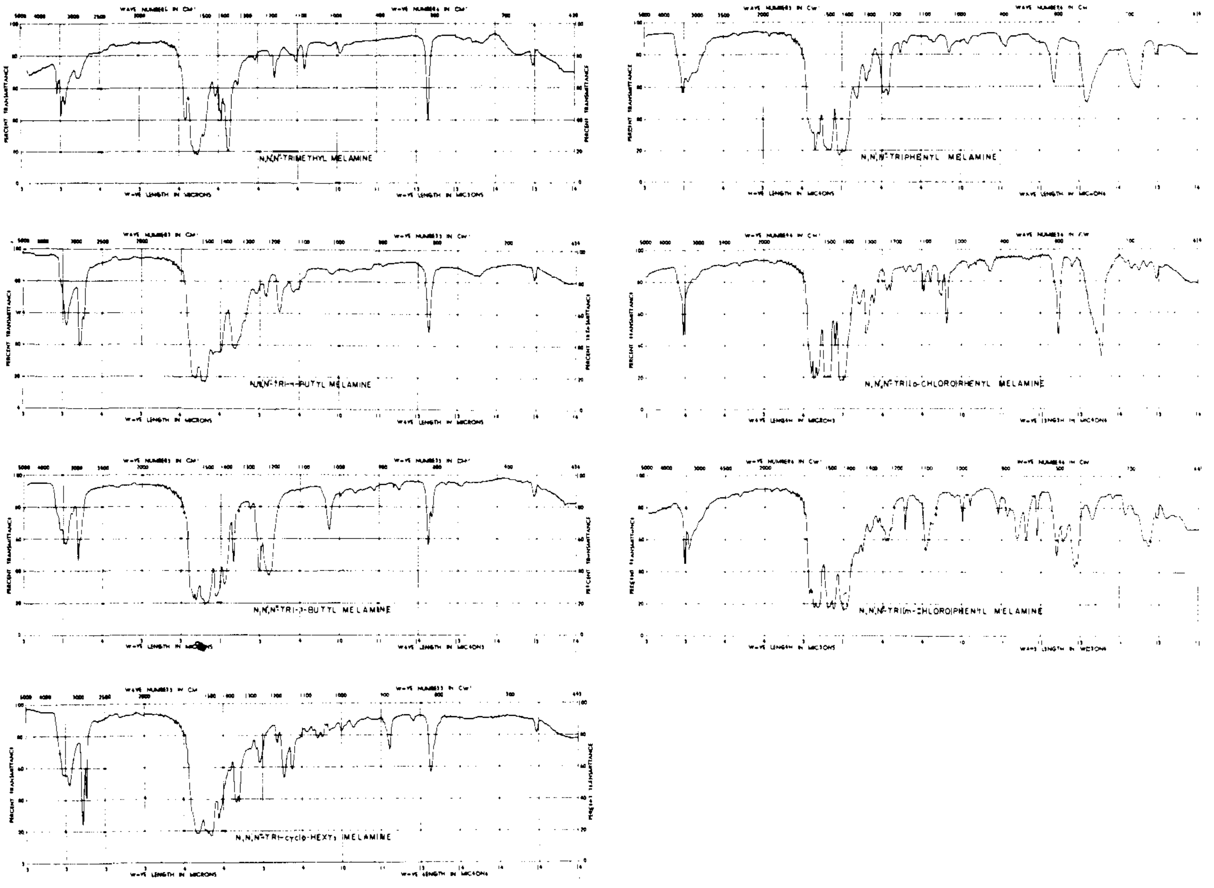

Fig. 2.—Spectra of N,N,'N''-trisubstituted melamines (NOTE: tri-*n*-butylmelamine is a viscous liquid, and was examined as a thin film spread on NaCl).

two strong "ring" bands at 6.4 and 7.1 μ leads to the assignment of the 6.4 μ band and at least part of the 6.7–6.9 μ absorption as stemming from in-plane vibrations of the triazine ring system. The somewhat weaker 5.9 to 6.1 μ absorption may then be logically assigned to the $NH_2$ group internal deformation vibrations. Whether the two bands at 6.7 and 6.9 μ in several of the spectra stem from separate normal vibrations or are the result of "splitting" of the ring mode has not been determined. At least one other type of absorption, methylene C–H deformation, can be expected in this region; however, the relatively low intensity of the C–H stretching bands near 3.4 μ indicates that the deformation absorption will be very weak. The same is true of the benzene ring bands expected in the spectra of the aryl melamines, since these are usually considerably weaker than the aromatic C–H deformation absorptions, and the latter occur only with medium intensity in the spectra shown here.

The third region of interest, that just beyond 12 μ, contains in particular a sharp, medium strength band at 12.25 μ, and provides one of the most interesting features in triazine spectra. This 12.25 μ band is extremely constant both in position and intensity in the spectra of melamine and its simple derivatives, but can be shifted to longer wave lengths by the interaction of strong electron-attracting groups with the triazine ring. The band has been assigned to an out-of-plane motion of the ring, corresponding to the lowest frequency $A_2''$ mode of triazine itself. It has been used previously[6,7] for the quantitative analysis of melamine in melamine–formaldehyde resins and is an excellent identifying mark for melamine-type compounds in general.

Figure 2 shows the spectra of seven NN'N''-trisubstituted melamines. The gross features of the spectra are similar to those of the monosubstituted compounds except for a larger contribution from the substituent groups due to the increase in their effective concentrations. The reduction in intensity of 6.1 μ peaks in the spectra of Fig. 2 is consistent with the conversion of all the amino groups to secondary amines, and supports the assignment of that band to N–H deformation absorption. Many of the medium-strength bands in the 7.5 to 12.0 μ region stem from skeletal vibrations in the substituents and correspond exactly to bands in the spectra of the corresponding primary alkyl or aryl amines. The 12.25 μ band is, once again, very constant in appearance; however, in the spectra of the three triaryl melamines, a slight shift to longer wave length is observed. The position of the in-place ring bands in the spectra of the

---

(6) "Infrared Spectra of Plastics and Resins," PB 111438, United States Dept. of Commerce, Office of Technical Services.

(7) Giovanna Torazza-Zerbi, *Chimica e industria* (*Milan*), **36**, 889 (1954).

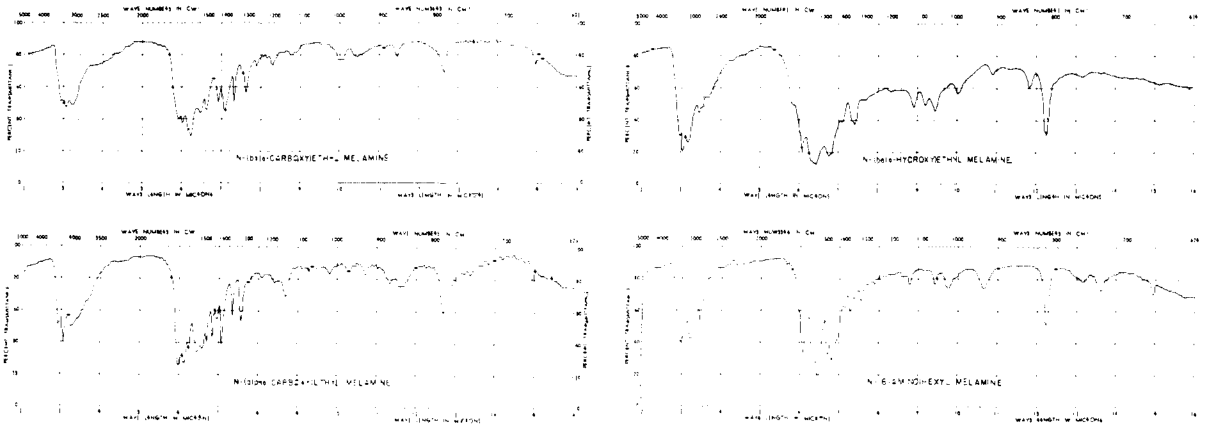

Fig. 3.—Spectra of monosubstituted melamines with functional groups attached to the hydrocarbon chain.

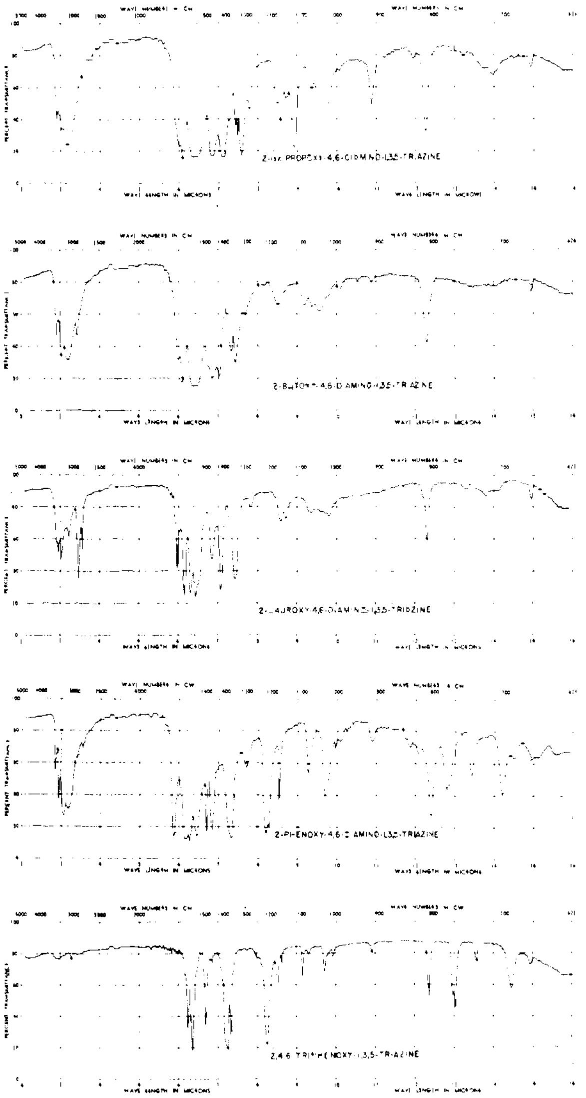

Fig. 4.—Spectra of several oxygen analogs to substituted melamines.

trisubstituted compounds is less certain than in those of the monosubstituted derivatives, especially in the case of the triaryl derivatives, where three strong bands centering at 6.3, 6.6–6.7 and 7.0 $\mu$ are observed. Although part of the structure of these bands undoubtedly is due to ring absorption of the phenyl groups, it is unlikely that this alone accounts for any of the three bands, judging from the relatively low intensity of the longer wave length "aromatic" absorption.

In Fig. 3 are given the spectra of four monosubstituted melamines containing functional groups attached to the hydrocarbon chain. It will be seen that the spectra of N-(6-amino)-hexylmelamine and N-($\beta$-hydroxy)-ethylmelamine conform to the pattern of other monosubstituted melamines, showing strongest absorption at 6.4 and 6.8 $\mu$, with a weaker NH deformation band (6.1 $\mu$) and the normal 12.25 $\mu$ "spike." Contribution to the spectra due to the functional groups themselves are almost completely masked by the very intense absorption of the melamine system. The carboxy-substituted melamines, on the other hand, deviate considerably from this melamine pattern, showing increased absorption near 6.0–6.2 $\mu$, fairly broad 3.3 $\mu$ absorption, and a shift of the out-of-plane ring band to 12.7 $\mu$. These alterations conform closely to what one would expect if the compounds exist as zwitterions, and the shift of the long wave length ring band may thus be said to reflect the alteration of the electron distribution in the ring by the proximity of the positively charged nitrogen of the zwitterion.

A similar effect can be observed in the spectra of compounds containing chlorine atoms connected directly to one or more of the ring carbon atoms. In Fig. 4 are shown the spectra of a number of such compounds and, apparently, in every case a shift of the long wave length ring band has occurred. The spectra of the di-*t*-butylamino and dicyclohexylamino derivatives exhibit the smallest effect in this respect, but a comparison of the precise wave lengths with those of Figs. 1 and 2 shows that a small shift has occurred with these two as well. The shortest wave length in-plane ring band appears fixed at 6.4 to 6.5 $\mu$ for the compounds containing only one chlorine substituent, but shifts to 6.7 $\mu$ in the spectrum of cyanuric chloride. The second ring band, falling at 7.7 $\mu$ for cyanuric chloride, has not been definitely assigned in the spectra of the monochloro compounds, and apparently is of very low intensity. These band shifts, especially

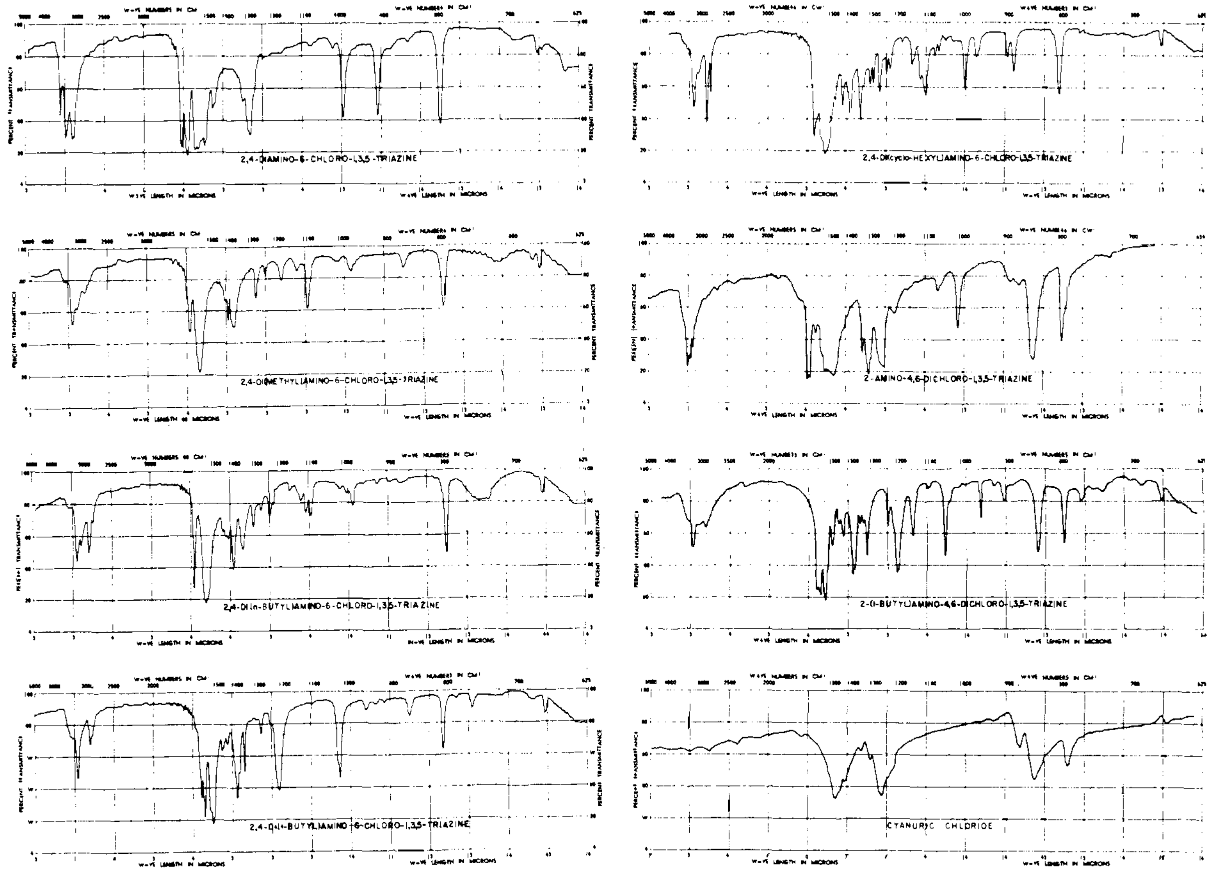

Fig. 5.—Spectra of some chlorotriazines.

that of the 12.25 μ band, are valuable identifying features of chlorotriazines, and are especially useful since a general method of synthesis of substituted melamines is reaction of a primary amine with the appropriate chlorotriazine.

Figure 5 gives the spectra of several 2-alkoxy-4,6-diamino-1,3,5-triazines, 2-phenoxy-4,6-diamino-1,3,5-triazine and 2,4,6-triphenoxy-1,3,5-triazine. It will be seen that these compounds are structurally very similar to the substituted melamines, one or more of the substituted nitrogen atoms having simply been replaced with oxygen atoms. This structural similarity is reflected in the spectra, which show the same general characteristics as observed for the substituted melamines. In addition, however, the three alkoxy compounds show strong absorption at 7.5–7.6 μ, not found in the spectra of monosubstituted melamines, and therefore attributable to the carbon–oxygen–carbon bridge. This band shifts to about 7.3 μ in the spectra of 2-phenoxy-4,6-amino-1,3,5-triazine and the triphenoxy homolog, and a second strong band appears near 8.2 μ just on the short wave length edge of the normal "aryl ether" region. Both of these are attributed to vibrations involving the ether linkage. The presence of the slightly shifted 12.25 μ band in the spectrum of 2,4,6-triphenoxy-1,3,5-triazine strongly supports its assignment as a ring mode in the spectra of the melamines.

None of the spectra in Figs. 1 through 5 are considered to provide evidence of shifts in tautomeric equilibrium toward "imino" or "iso" structures; in fact with the exception of the longer wave length in-plane ring-band, the bands observed show only such shifts in position and intensity as can be easily reconciled with inductive effects of the polar substituents on the ring. This is not the case, however, when hydroxyl groups are attached to the ring as, for instance with the compounds ammeline, ammelide and cyanuric acid. Figure 6 shows the infrared spectra obtained for these three compounds in KBr disks, and that of cyanuric acid as a film sublimed onto NaCl. The changes in solid state spectra of cyanuric acid have been reported earlier, and are attributed to complexing of the acid with alkali halides.[8] Neither ammeline nor ammelide exhibits the same sensitivity to environment. Bellamy[9] discusses the spectra of these compounds but draws no conclusions, due to insufficient data. He mentions the strong 1715 cm.$^{-1}$ (5.85 μ) absorption, which he would assign to carbonyl group stretching except that "thio-ammeline absorbs at 1695 cm.$^{-1}$ (5.9 μ) and in this case the absorption must be due to a displaced NH or ring vibration." On the other hand, the diffuse nature of the spectra, and the broad 3–4 μ absorption lead to the conclusion that strongly H-bonded hydroxyl groups are present at least in the ammeline structure, which

---

(8) W. M. Padgett, J. M. Talbert and W. F. Hamner, *J. Chem. Phys.*, **26**, 959 (1957).

(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

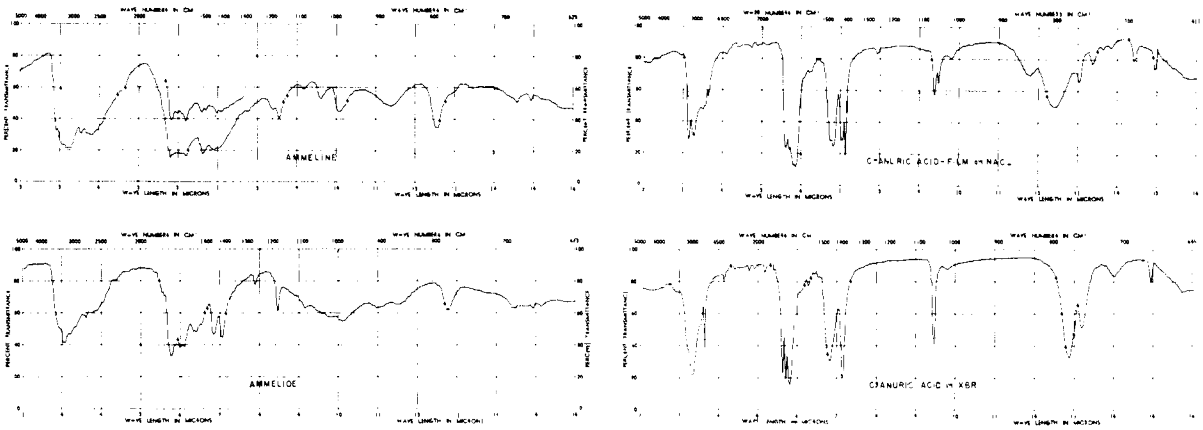

Fig. 6.—Spectra of ammeline, ammelide and cyanuric acid.

means the triazine ring conjugation would be conserved. With cyanuric acid the situation is much more certain, since the spectrum clearly supports other investigations[10,11] in showing cyanuric acid to favor the "iso" or amido form. In brief, although the spectra portray quite clearly the progression from the conjugated ring structure of melamine to the completely "iso" structure of cyanuric acid, it is difficult to say at what position the equilibrium lies in solid ammeline and ammelide. The spectrum of ammeline does, however, provide some evidence for conservation of the conjugated-ring form.

**Acknowledgment.**—The authors acknowledge with pleasure the contributions of W. R. Rolingson, F. M. Eddins and B. L. Williams who synthesized the majority of the compounds for this study, and of Jerry M. Talbert who prepared many of the alkali halide disks and aided in obtaining the spectra.

This work was reported in part at the Ohio State Symposium on molecular structure and spectroscopy, June, 1956.

TEXAS CITY, TEXAS

---

[10] E. H. Wiebenga, THIS JOURNAL, **74**, 6156 (1952).

[11] R. Newman and R. M. Badger, *ibid.*, **74**, 3545 (1952).

---

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

# Polarographic Reduction of Some Aromatic Aldehydes

BY ROBERT M. POWERS AND R. A. DAY, JR.

RECEIVED SEPTEMBER 16, 1957

The polarographic reduction of benzaldehyde and ten other aromatic aldehydes has been studied in buffered solutions in the *p*H range 1 to 13. A number of macroelectrolyses have been run at controlled potentials under varying experimental conditions. Products were isolated and the number of electrons consumed in the reduction process measured. The effect of substituents in the benzene nucleus on the second wave found in certain solutions of high *p*H is discussed. Further evidence is reported for the correlation between the separation of the two waves in basic media and the tendency of groups in the molecule to stabilize a free radical intermediate.

The polarographic reduction of benzaldehyde and many other aromatic aldehydes has been studied by numerous investigators,[1-7] and much of this work is summarized in two treatises on polarography.[8,9] The behavior of most of the simpler aromatic aldehydes as well as ketones is consistent with the mechanism summarizd by Ashworth[3] and Milner.[9] The influence of substituents in the benzene nucleus of benzaldehyde, however, often leads to variations in the normal pattern of behavior,[4] and other factors, such as type and concentration of buffer as well as the presence of certain electrolytes, may produce anomalous waves. Differences in behavior are most pronounced in strongly alkaline media where one, two and even three waves are sometimes observed with certain carbonyl compounds.[10]

The present work was undertaken to study the influence of certain nuclear substituents on the behavior of aromatic aldehydes. We were particularly interested in determining whether or not variations in behavior were consistent with the effects which one would predict from the structure of the aromatic molecule in terms of the mecha-

---

[1] M. Tokuoka, *Collection Czechoslov. Chem. Communs.*, **7**, 392 (1935).

[2] R. Pasternak, *Helv. Chim. Acta*, **31**, 753 (1948).

[3] M. Ashworth, *Collection Czechoslov. Chem. Communs.*, **13**, 229 (1948).

[4] I. A. Korshunov and L. N. Sazanova, *Zhur. Fiz. Khim.*, **23**, 202 (1949).

[5] H. J. Gardner, *Chemistry & Industry*, **29**, 819 (1951).

[6] R. N. Schmid and E. Heilbronner, *Helv. Chim. Acta*, **37**, 1453 (1954).

[7] L. Holleck and H. Marsen, *Z. Elektrochem.*, **57**, 301, 944 (1953).

[8] I. M. Kolthoff and J. J. Lingane, "Polarography," Second Ed., Vol. II, Interscience Publishers, Inc., New York, N. Y., 1952, p. 678.

[9] G. W. C. Milner, "The Principles and Applications of Polarography," Longmans, Green and Co., New York, N. Y., 1956, p. 501.

[10] R. A. Day, Jr., S. R. Milliken and W. D. Shults, THIS JOURNAL, **74**, 2741 (1952).