only nickel (76.48%) and phosphorus (23.58%) to be present in the atomic ratio of Ni/P of 1.711. This is in keeping with the findings of Hutter[9] who states that nickel phosphates of atomic ratios of Ni/P of (a) 1.49, ortho; (b) 1.02, pyro; and (c) 0.50, meta, are all reduced with hydrogen to dinickel phosphide with the reduction of the nickel orthophosphate starting at 450°.

Results

Table I indicates the optimum furnace temperature to be approximately 374°, where $NiP_{0.585}$ catalyzes a 96.9 weight % yield of aniline. Table II

TABLE I

EFFECT OF FURNACE TEMPERATURE ON CATALYST EFFICIENCY

Weight of $NiP_{0.584}$ catalyst, 11.4 g.; average feed rate of nitrobenzene, 10 millimoles, hr.$^{-1}$, g. $NiP_{0.584}{}^{-1}$; average mole ratio of $H_2/C_6H_5NO_2$ in the feed, 13.

Furnace block temp., ±5°C.	Catalyst efficiency (weight % aniline)
335	93.7
360	95.6
374	96.9
400	96.2
421	95.3

TABLE II

EFFECT OF MOLE RATIO OF HYDROGEN TO NITROBENZENE IN THE FEED UPON CATALYST EFFICIENCY

Weight of $NiP_{0.584}$ catalyst, 11.4 g.; average feed rate of nitrobenzene, 11 millimoles, hr.$^{-1}$ g. $NiP_{0.584}{}^{-1}$; average furnace temperature, 380°.

Mole ratio $H_2/C_6H_5NO_2$	Catalyst efficiency (weight % aniline)
11.3	96.9
23.0	95.1
25.0	94.9
31.6	92.5

indicates that dilution of the feed stream with hydrogen beyond the mole ratio of hydrogen to nitrobenzene of 11.3 adversely affects the yield of aniline. Under the following rather broad condition $NiP_{0.584}$ catalyst effected yields in excess of 95 weight % aniline: pressure, atmospheric; furnace temperature, 350 to 420°; feed rate of nitroben-zene, 10 millimoles per hour per gram of $NiP_{0.584}$ catalyst; and mole ratio of hydrogen to nitrobenzene in the feed stream, 11 to 23.

Discussion

Rooley, Rohrer and Brown[5] found that both nickel molybdate and nickel chromate when reduced in hydrogen formed catalysts containing significant amounts of nickel metal, and Rohrer, King and Brown[4] discovered the same to be true for reduced nickel vanadate catalyst. However, the following evidence indicates that nickel phosphate is reduced in hydrogen according to the reaction

$$8Ni_3(PO_4)_2 + 64H_2 = 12Ni_2P + P_4 + 64H_2O$$
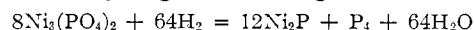
to form dinickel phosphide catalyst containing no metallic nickel. 1. The method of preparation of Ni_2P was that of Hutter[9] and Rose.[18] 2. The thirteen strongest lines in the X-ray powder diffraction pattern of the catalyst correspond to those for Ni_2P.[16,17] 3. The insolubility of the catalyst in hydrochloric acid, its solubility in nitric acid to give nickel and phosphate ions, and its gray-black color correspond to the properties of Ni_2P prepared and described by Biltz and Heimbrecht.[16] 4. Insufficient metallic nickel is present in the catalyst to give a test for the nickel ion in the hydrochloric acid solubility test. 5. It would be extremely difficult to account for the rate at which aniline was produced by this catalyst if the catalytic activity were due only to an immeasurably small trace of metallic nickel possibly present. 6. When metallic nickel is prepared as a catalyst for this reaction the optimum operating temperature is 192°[19] or lower,[20] depending upon the method of preparing the catalyst, whereas the optimum operating temperature for Ni_2P is 374.° 7. There is a slight excess of phosphorus over the stoichiometric Ni_2P, i.e., $Ni_2P_{1.169}$.

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(18) H. Rose, *Pogg. Ann.*, **24**, 232 (1832).

(19) O. W. Brown and C. O. Henke, *J. Phys. Chem.*, **26**, 161 (1922).

(20) Unpublished data from this Laboratory.

The Stability of Metal Chelates of Compounds Related to Anthranilic Acid

BY ALLEN YOUNG[1] AND THOMAS R. SWEET

RECEIVED SEPTEMBER 10, 1957

The acidity constants of anthranilic acid, N-methylanthranilic acid, 2,2'-iminodibenzoic acid, 2,2'-hydrazodibenzoic acid, N,N'-methylenedianthranilic acid, N,N'-trimethylenedianthranilic acid, N-(2-aminoethyl)-anthranilic acid, α-amino-o-toluic acid, α-carboxy-o-anisic acid, N-(carboxymethyl)-anthranilic acid, and N,N-bis-(carboxymethyl), anthranilic acid were determined in 1:1 volume water–dioxane and the stabilities of the chelate compounds of cobalt, nickel, copper, zinc and cadmium with each of these acids were obtained. The variations in the constants were related to the properties of the metal ions and the structural differences in the ligand molecules.

The acidity constants of anthranilic acid and some related compounds and the apparent formation constants for chelation of these substances with the divalent cations of cobalt, nickel, copper, zinc and cadmium in 1:1 volume water–dioxane have

(1) Abstracted in part from the doctoral dissertation of Allen Young, March, 1957.

been studied. The method that was used is similar to that previously described for substituted anthranilic acids[2] and N,N'-ethylenedianthranilic acid.[3]

(2) W. F. Harris and T. R. Sweet, *J. Phys. Chem.*, **60**, 509 (1956).

(3) T. R. Sweet and W. F. Harris, *ibid.*, **61**, 694 (1957).

Experimental

Reagents.—Metal nitrate solutions were prepared and standardized by the method described in an earlier publication.[4] The dioxane was purified by the method suggested by Calvin and Wilson.[5]

Anthranilic acid and N-methylanthranilic acid were commercial products that were prepared for use by recrystallization from water.

2,2'-Iminodibenzoic acid was prepared by the procedure suggested by Ullmann and Hoz,[6] and their melting point of 294–295° was obtained.

2,2'-Hydrazodibenzoic acid was prepared by the reduction of o-nitrobenzoic acid as described by Sargent and Pedlow.[7] The product melted at 228°. Comparison of infrared spectra indicated that 4,4'-diamino-3,3'-dicarboxybiphenyl was not present in the product.

N,N'-Methylenedianthranilic acid was prepared by the procedure of Bischoff and Reinfeld.[8] The melting range of 150–158° with decomposition, reported by them, was observed.

N,N'-Trimethylenedianthranilic acid was prepared by a modification of the procedure of van Alphen.[9] The impure product was extracted with hot acetone. Recrystallization from acetic acid removed unreacted anthranilic acid which is much more soluble than the desired product. The melting point of the final product was 209°.

N-(2-Aminoethyl)-anthranilic acid was prepared by the reaction of o-chlorobenzoic acid with an excess of ethylenediamine. Anhydrous potassium carbonate (25.6 g.), 31.4 g. of o-chlorobenzoic acid, 32 ml. of ethylenediamine, 68 ml. of n-amyl alcohol and 0.3 g. of copper turnings were refluxed in a 500-ml. flask for five hours. The amyl alcohol and remaining ethylenediamine were then steam distilled out of the mixture. The hot aqueous solution was filtered. The filtrate was chilled in ice and the pH was lowered to 7.8 with cold 1:1 hydrochloric acid. The light yellow precipitate which appeared was filtered out. This precipitate was treated with 160 ml. of absolute alcohol to extract o-chlorobenzoic acid. It was then treated with hot 1:1 hydrochloric acid, in which the desired product is very soluble. The small amount of o-chlorobenzoic acid still present was filtered from the hot solution. Chilling the filtrate caused the product to crystallize out as the dihydrochloride. The product melted sharply at 245–246° with evolution of gas. *Anal.* Calcd.: Cl, 28.05; C, 43.00; H, 5.57; N, 11.07; equiv. wt., 84.4. Found: Cl, 28.08; C, 42.86; H, 5.59; N, 11.15; equiv. wt., 84.5.

α-Amino-o-toluic acid was prepared by the five-step synthesis: phthalic anhydride → phthalimide → phthalide → (o-carboxylphenyl-acetonitrile → α-amino-o-toluic acid. Procedures for each step were adapted from "Organic Syntheses." The product was isolated as the hydrochloride and melted at 217–218°. The same melting point was observed by Wegscheider and Glogau.[10]

α-Carboxy-o-anisic acid was prepared according to Meyer and Duczmal.[11] The observed melting point was 191–192.5°.

N-(Carboxymethyl)-anthranilic acid was prepared by the reaction of excess anthranilic acid with monochloroacetic acid. This reaction has been studied by Haller[12] and by Philips.[13] The product melted at 215–216°.

N,N-Bis-(carboxymethyl)-anthranilic acid was prepared by the reaction of excess monochloroacetic acid with anthranilic acid in the presence of base. The product melted at 210–212°.

Procedure.—The weighed reagent was added as a solid to 50 ml. of purified dioxane. Distilled water, nitric acid and metal nitrate solutions were added in this order. The total volume of the aqueous portions was 50 ml. The final volume was 98.7 ml. at 35°. These solutions were titrated with 0.2 N sodium hydroxide at 35°. The Beckman model

(4) W. F. Harris and T. R. Sweet, THIS JOURNAL, **77**, 2893 (1955).

(5) M. Calvin and K. W. Wilson, *ibid.*, **67**, 2003 (1945).

(6) F. Ullmann and H. Hoz, *Ann.*, **355**, 353 (1907).

(7) D. E. Sargent and G. W. Pedlow, Jr., U. S. Patent 2,570,866 (1951); *C. A.*, **46**, 4568 (1952).

(8) C. A. Bischoff and F. Reinfeld, *Ber.*, **36**, 41 (1903).

(9) J. van Alphen, *Rec. trav. chim.*, **61**, 493 (1942).

(10) R. Wegscheider and A. Glogau, *Monatsh.*, **24**, 915 (1903).

(11) R. Meyer and C. Duczmal, *Ber.*, **46**, 3366 (1913).

(12) H. L. Haller, *Ind. Eng. Chem.*, **14**, 1040 (1922).

(13) M. Philips, *ibid.*, **13**, 759 (1921).

G pH meter, equipped with a Beckman no. 1190-80 glass electrode and a saturated calomel cell, was standardized at 35° at pH 4.02 using Beckman no. 14044 buffer. Corrections were added to all meter readings obtained in the dioxane-water medium. These corrections ranged from 0.07 to 0.10 unit, depending upon the individual electrodes used, and were found by titration of nitric acid under the same conditions. Equivalent weights and acidity constants were determined from titrations made in the absence of divalent cations.

Calculations.—The acidity constants were calculated from pH titration curves. In general, when two constants for an acid were close, their values were calculated by applying convergence corrections[14] to the temporary values taken from the pH curve at the half-equivalence points. The values thus obtained were found to be in good agreement with values found by solving simultaneous equations and by Schwarzenbach's[15] graphical method.

Formation constants for the chelates of monobasic and dibasic acids were calculated by using equations that are given in previous publications.[2,3]

The equations that were used to calculate the formation constants for the metal chelates of the tribasic acids were

$$(R) = \frac{k_{a1}k_{a2}k_{a3}\{3C_R + (OH^-) + A - (Na^+) - (H^+)\}}{3(H^+)^3 + 2(H^+)^2 k_{a1} + (H^+)k_{a1}k_{a2}}$$

$$\bar{n} = \frac{C_R - \left\{ k_{a1}k_{a2}k_{a3} + (H^+)k_{a1}k_{a2} + (H^-)^2 k_{a1} + (H^+)^3 \right\} \frac{(R)}{k_{a1}k_{a2}k_{a3}}}{C_M}$$

where

C_R = total concentration of all ligand species
C_M = total concentration of all metal species
A = concentration of strong acid added

$k_{a1} = (H^+)(H_2R)/(H_3R)$; $k_{a2} = (H^+)(HR)/(H_2R)$

$k_{a3} = (H^+)(R)/(HR)$

$k_1 = (MR)/(M^{++})(R)$; $k_2 = (MR_2)/(MR)(R)$

For N-(2-aminoethyl)-anthranilic acid dihydrochloride, a tribasic acid having one strongly dissociated proton, (H_3R) is zero, and no strong acid was added. For this special case, the following equations for (R) and $\bar{n}$ were used

$$(R) = \frac{k_{a2}k_{a3}\{3C_R + (OH^-) - (Na^+) - (H^+)\}}{2(H^+)^2 + (H^+)k_{a2}}$$

$$\bar{n} = \frac{C_R - \{k_{a2}k_{a3} + (H^+)k_{a2} + (H^+)^2\} \frac{(R)}{k_{a2}k_{a3}}}{C_M}$$

Where 2:1 complexes were formed, temporary formation constants were taken from $\bar{n} - pR$ curves at $\bar{n} = \frac{1}{2}$ and $\bar{n} = 3/2$. Convergence corrections[14] were applied to these temporary values to give the correct values of log k_1 and log k_2.

Results and Discussion

The pK_a values of the acids in 50 volume per cent. dioxane are given in Table I and the logarithms of the formation constants of the metal chelates in 1:1 volume water–dioxane are shown in Table II. Metal concentrations from 0.5×10^{-3} to 1.2×10^{-3} molar, reagent concentrations near 5×10^{-3} molar, and nitric acid concentrations near 5×10^{-3} molar were used.

The order of stability of the 1:1 chelates of the twelve ligands is Co < Ni < Cu > Zn. This is the Irving–Williams order[16] which is generally observed.

The orders of stability of the 1:1 chelates of each of the ligands, N-methylanthranilic acid (I), 2,2'-

(14) L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, THIS JOURNAL, **75**, 457 (1953).

(15) G. Schwarzenbach, A. Willi and R. O. Bach, *Helv. Chim. Acta*, **30**, 1303 (1947).

(16) H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953); *Nature*, **162**, 746 (1948).

ACIDITY CONSTANTS IN 50 VOLUME % DIOXANE

Acid	pka_1	pka_2	pka_3
Anthranilic	6.6		
N-Methylanthranilic	6.68		
2,2'-Iminodibenzoic	6.05	7.02	
2,2'-Hydrazodibenzoic	5.99	6.80	
N,N'-Methylenedianthranilic	6.36	6.82	
N,N'-Trimethylenedianthranilic	6.45	7.17	
N,N'-Ethylenedianthranilic[3]	6.53	7.18	
N-(2-Aminoethyl)-anthranilic dihydrochloride	<2	5.54	9.45
α-Amino-o-toluic hydrochloride	4.17	10.16	
α-Carboxy-o-anisic	4.05	7.06	
N-(Carboxymethyl)-anthranilic	5.44	6.96	
N,N-Bis-(carboxymethyl)-anthranilic	4.49	5.30	8.53

in five the 1:1 chelates of cadmium are more stable, and in one case the constants are the same.

The addition of the methyl group to anthranilic acid to give N-methylanthranilic acid brings about two important changes as far as chelation is concerned. First, the electron-donating property of the methyl group should make the nitrogen atom a better electron donor which will tend to increase the size of the formation constants. Second, steric effects of the methyl group may be expected to make it more difficult for N-methylanthranilic acid ligands to fit around metal ions, as compared to the ability of anthranilic acid ligands. The results indicate that the two factors tend to offset each other for the chelates of nickel, cobalt and zinc. The first factor appears to be of more importance

TABLE II

LOGARITHMS OF APPARENT FORMATION CONSTANTS OF METAL CHELATES IN 50 VOLUME % DIOXANE AT 35°

Acid	Copper		Nickel		Cobalt		Zinc		Cadmium	
	1:1	2:1	1:1	2:1	1:1	2:1	1:1	2:1	1:1	2:1
Anthranilic	5.0	4.2	3.2	2.5	2.8	2.8	2.6	3.2	3.0	2.3
N-Methylanthranilic	4.4	3.7	3.0	2.6	3.0	2.6	3.3	2.5	3.3	2.7
2,2'-Iminodibenzoic	8.0		5.4		5.1		5.6		5.8	
2,2'-Hydrazodibenzoic	7.8		3.8		3.8		4.6		4.7	
N,N'-Methylenedianthranilic	7.4		3.8		3.5		3.8		4.4	
N,N'-Ethylenedianthranilic[3]	10.2		8.6		6.4		6.1		6.0	
N,N'-Trimethylenedianthranilic	8.1		5.4		5.0		5.2		5.3	
N-(2-Aminoethyl)-anthranilic	10.4	4.9	7.8	6.9	6.0	5.4	5.4	4.4	3.5	3.0
α-Amino-o-toluic	7.6	6.0	5.2	4.1	4.4	4.2	5.0	6.1	4.0	3.6
α-Carboxy-o-anisic	7.5		5.8		5.8		6.8		6.4	
N-(Carboxymethyl)-anthranilic	9.6	2.8	6.8	4.1	5.6	3.0	5.6	2.8	5.1	2.7
N,N-Bis-(carboxymethyl)-anthranilic	14.3		13.0		11.8		12.3		10.8	

iminodibenzoic acid (II), 2,2'-hydrazodibenzoic acid (III) and N,N'-methylenedianthranilic acid (IV) are: Cu > Cd > Zn > Ni > Co. For each of the five cations, the order is: II > III > IV > I.

The lower stabilities of the chelates of 2,2'-hydrazodibenzoic acid and N,N'-methylenedianthranilic acid as compared to those of 2,2'-iminodibenzoic acid probably are a result of increased steric hindrance and decreased flexibility of ligands and complexes. The structures of 2,2'-hydrazodibenzoic acid and N,N'-methylenedianthranilic acid appear quite unfavorable for the formation of chelates with nickel and cobalt.

The order Cu > Ni > Co > Zn > Cd which was found for N,N'-ethylenedianthranilic acid by Sweet and Harris[3] is observed in the present work for N-(2-aminoethyl)-anthranilic acid and N-(carboxymethyl)-anthranilic acid. For both N,N'-ethylenedianthranilic acid and N-(2-aminoethyl)-anthranilic acid the 1:1 complex of nickel is considerably more stable than that of cobalt. This is believed to be the result of a special favorability of the five-membered chelate ring containing an ethylenediamine structure for nickel.

A comparison of the formation constants of zinc and cadmium chelates supports the statements of Izatt, Fernelius and Block[17] that zinc and cadmium chelates generally have about the same order of stability and that one cannot predict with certainty which will be more stable with a particular ligand. In six cases the 1:1 chelates of zinc are more stable,

for cadmium, and the second of more importance for copper. It is reasonable to expect that the steric difficulties would be least for cadmium since it has the largest ionic radius.

The chelate effect, a term that was introduced by Schwarzenbach,[18] is a comparison of the stability of the chelates of ligands containing several donor groups with the stability of the chelates of simpler ligands. To make a valid comparison, the same number and types of donor groups must be included. In the present work, the log k values of N,N'-ethylenedianthranilic acid and N,N'-trimethylenedianthranilic acid are compared with the log k_1k_2 values of the 2:1 complexes of N-methylanthranilic acid. By definition

chelate effect = log $k_{\text{di-A.A.}}$ − log k_1k_2 N-CH₃A.A.

Table III shows the chelate effects of N,N'-ethylenedianthranilic acid. Copper, and especially nickel, show considerable increased stability with the dianthranilic acid. The ethylenediamine effect for nickel is again demonstrated. The chelate effects of N,N'-trimethylenedianthranilic acid are shown in Table IV. Here, the negative chelate effects indicate that the six-membered ring in the N,N'-trimethylenedianthranilic acid complexes is so unfavorable that the ligand has less tendency to form the quadridentate chelates than do two N-methylanthranilic acid bidentate ligands.

As compared to anthranilic acid, α-amino-o-toluic acid involves two major changes. The amino nitrogen becomes much more basic, and the chelate

(17) R. M. Izatt, W. C. Fernelius and B. P. Block, J. Phys. Chem., 59, 80 (1955).

(18) G. Schwarzenbach, Helv. Chim. Acta, 35, 2344 (1952).

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 pH values for α-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.

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

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

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

(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).

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.