1-(4-Chlorophenyl)-4-(2-hydroxyethyl)-piperazine.—A slight excess over 0.1 mole (4.405 g.) of ethylene oxide was introduced near the bottom of a solution of 19.66 g. (0.1 mole) of 1-(4-chlorophenyl)-piperazine in 100 ml. of methanol in a manner that did not permit boiling. No external heating of the ethylene oxide was necessary. After addition of the ethylene oxide had been completed the mixture was stirred several hours at room temperature, and finally the methanol was evaporated on the steam-bath. The residue was solid after cooling, and recrystallization from heptane gave 19.5 g. (or 81.2% yield) of 1-(4-chlorophenyl)-4-(2-hydroxyethyl)-piperazine.

Acknowledgment.—During the period in which this research was conducted Thomas H. Wicker, Jr., held a Parke, Davis & Company research fellowship. The authors wish to express their appreciation for this research grant.

GAINESVILLE, FLORIDA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Ultraviolet Absorption Spectra of Substituted Aminotriazines

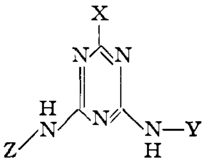
BY C. G. OVERBERGER AND SEYMOUR L. SHAPIRO[1]

RECEIVED DECEMBER 7, 1953

The ultraviolet absorption spectra for a representative number of aminotriazines have been obtained and the results compared with known spectra. The data are interpreted on the basis of individual structure and current theory.

In three previous papers,[2] the synthesis and properties of a number of substituted aminotriazines has been reported. It was of interest to establish the relationship between their structure and their ultraviolet absorption spectra.

The general structure of the compounds reported here may be represented by A. A summary of the published spectra for related compounds is given in Table I.

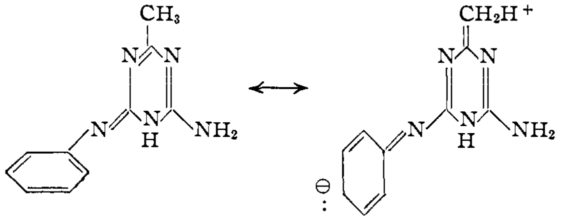


A

The spectra of compounds obtained in this work are reported in Table II.

Substitution of an anilino group for an amino group (1 and I) results in a considerable increase in the intensity of absorption and a significant bathochromic shift of the maximum band. A comparison of compounds 1 and 2 indicates that there is a hyperchromic and hypsochromic effect when the phenyl group is attached directly to the triazine ring. The introduction of a phenyl group on a triazine (compare 1 and 2) shows no bathochromic effect.

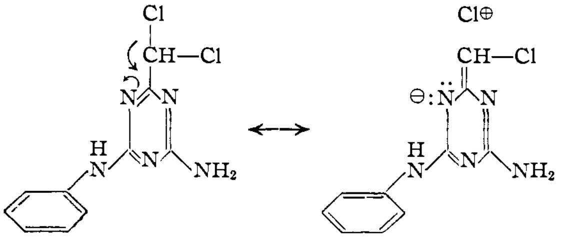
O'Shaughnessy and Rodebush[3] found in a study of the absorption spectra of substituted biphenyls, that *para* methyl substituents gave significant bathochromic shifts and increased absorption at the maximum. Inspection of the data for compounds 1 and 7 shows that, in the formoguanamine structure, the substitution of methyl for hydrogen results in very little change of spectra. On the other hand, when IV and VIII are compared with I, there are pronounced spectral changes with bathochromic shifts and increased intensities. The relatively low absorption of 11 and 12 and the insignificant contribution of a methyl group in 7 as compared to 1 indicate that the phenyl group is probably involved in the excited state as indicated



The availability of only two hydrogens on the α-carbon atom in VIII compared to IV is indicated by the lower intensities for VIII. The introduction of a p-bromo group on the phenyl ring results in a bathochromic shift and increased intensities. (Compare III and I and IX and VIII.) This is probably due to excited states in which the bromine atom is contributing to the stabilization of the above electron distributions.[4]

If halogen is placed on the α-carbon atom as in V, VI, VII and X, a pronounced hypsochromic shift is obtained. The order of intensity of absorption is 3Cl > Br = 2Cl > Cl. Thus one bromine and two chlorines result in an intensity similar to the unsubstituted methyl group (Fig. 1).

This is of interest since the excited states involving electron release from the halogen may play a significant role.



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(1) A portion of a thesis by Seymour L. Shapiro submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

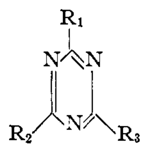
(2) (a) C. G. Overberger and S. L. Shapiro, THIS JOURNAL, **76**, 93 (1954); (b) S. L. Shapiro and C. G. Overberger, *ibid.*, **76**, 97 (1954); (c) C. G. Overberger and S. L. Shapiro, *ibid.*, **76**, 1061 (1954).

(3) M. T. O'Shaughnessy and W. H. Rodebush, *ibid.*, **62**, 2906 (1940). For a discussion of bathochromic shifts resulting from methyl substitution in conjugated systems, see V. A. Crawford, *J. Chem. Soc.*, 2061 (1953).

(4) L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947).

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA FOR DIAMINOTRIAZINES

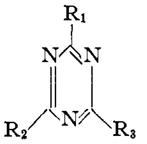


					Min.		Max.	
	R_1	R_2	R_3	Solvent	λ, mμ	$\epsilon \times 10^{-3}$	λ, mμ	$\epsilon \times 10^{-3}$
1	H	Amino	Amino[a]	Ethanol	242	2.8	248–253	2.9
2	Phenyl	Amino	Amino[a]	Ethanol			249	25.0
3	Phenyl	Amino	Amino[b,c]	Ethanol	228	16.0[d]	244	18.6
4	Phenyl	Amino	Amino[b]	0.01 *N* NaOH	228	16.5[d]	247	19.2
5	Phenyl	Amino	Amino[b]	0.01 *N* HCl	228	9.0[d]	255–261	16.2
6	*p*-Chlorobenzyl	Amino	Amino[a]	Ethanol	248	3.1	259	4.0
7	Methyl	Amino	Amino[e]	Water	238	2.4[d]	252–256	3.2[d]
8	Amino	Amino	Amino[f]	Water, *p*H 7.03			236	2.5[d]
9	Amino	Amino	Amino[f]	HCl, *p*H 1.01[g]	227	7.8[d]	236	9.7[d]
10	Methyl	*p*-Chloranilino	Amino	0.01 *N* HCl	230[d]	10.4[d]	272	14.15
11	Methyl	Methyl	Methyl	Ethanol[h]			256	0.79
12	Ethyl	Ethyl	Ethyl	Ethanol[h]			259	0.68

[a] P. B. Russell, G. H. Hitchings, B. H. Chase and J. Walker, THIS JOURNAL, **74**, 5403 (1952). [b] Reference 7. [c] As the monohydrochloride, monohydrate. [d] Estimated from graph. [e] Guanamines, American Cyanamid Co., New York, 1951, p. 4. [f] Reference 5. [g] N. N. Crounse, *J. Org. Chem.*, **16**, 492 (1951). [h] T. L. Cairns, A. W. Larchar and B. C. McKusick, THIS JOURNAL, **74**, 5633 (1952).

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA OF AMINO ANILINO-*s*-TRIAZINES



					Min.		Max.	
	R_1	R_2	R_3	Solvent	λ, mμ	$\epsilon \times 10^{-3}$	λ, mμ	$\epsilon \times 10^{-3}$
I	H	Amino	Anilino	CH_3OH	232	6.89	261	12.55
II	H	Amino	Anilino	1 *N* HCl			250	11.4
III	H	Amino	*p*-Br-anilino	CH_3OH	236	7.17	278	22.65
IV	CH_3	Amino	Anilino	CH_3OH	235	12.40	271	20.38
V	CH_2Cl	Amino	Anilino	CH_3OH	232	11.23	257	18.95
VI	$CHCl_2$	Amino	Anilino	CH_3OH	232	11.35	255	20.81
VII	CCl_3	Amino	Anilino	CH_3OH	232	13.4	253	25.43
VIII	C_2H_5	Amino	Anilino	CH_3OH	232	9.78	271	18.81
IX	C_2H_5	Amino	*p*-Br-anilino	CH_3OH	236	9.39	277	25.98
X	$CBrHCH_3$	Amino	Anilino	CH_3OH	232	9.99	256	20.00
XI	$CH{=}CH_2$	Amino	Anilino	CH_3OH	239	14.49	255	22.50
XII	$CH_2CH_2OCH_3$	Amino	Anilino	CH_3OH	235	8.89	270	18.91
XIII	XII·acetic acid			CH_3OH	235	9.08	270	18.70
XIV	XII·trichloroacetic acid			CH_3OH	235	12.18	272	20.35
XV	XII·heptafluorobutyric acid			CH_3OH	235	8.22	269	17.81
XVI	XII·HCl			CH_3OH	234	7.49	269	15.75
XVII	XII			1 *N* HCl	242	11.0	263	12.15
XVIII	$CH_2CH_2OC_2H_5$	Amino	Anilino	CH_3OH	235	9.55	269	18.70
XIX	CH_2CH_2O-*n*-C_3H_7	Amino	Anilino	CH_3OH	233	10.68	265	18.78
XX	CH_2CH_2OH	Amino	Anilino	CH_3OH	233	9.90	265	17.79
XXI	COO^-	Amino	Anilino[a]	CH_3OH	234	10.88	258	20.25
XXII	COOMe	Amino	Anilino	CH_3OH	235	10.8	257	21.6
XXIII	COOEt	Amino	Anilino	CH_3OH	235	10.7	256	21.8
XXIV	COOPr	Amino	Anilino	CH_3OH	235	11.3	256	22.4
XXV	$CONHNH_2$	Amino	Anilino	CH_3OH	231	11.5	254	21.8
XXVI	$CH_2CH_2OCH_3$	$NHCOCH_3$	Anilino	CH_3OH	248	14.12	227 270	23.19 22.16
XXVII	H	$NHCOCH_3$	Anilino	CH_3OH	241	11.8	265	16.5
XXVIII	OH	Amino	Anilino[b]	CH_3OH	232	12.6	265	22.2
XXIX	$OCOCH_3$	Amino	Anilino[c]	CH_3OH	224	11.1	243	15.7

[a] As diethylaminoethyl alcohol salt. [b] As hydrochloride $2H_2O$. [c] Position of CH_3CO– group not unequivocally established.

Since the effect is hypsochromic, the transition probability for the electron cloud does not extend to any extent through the phenyl ring. Such contributions become especially significant as the

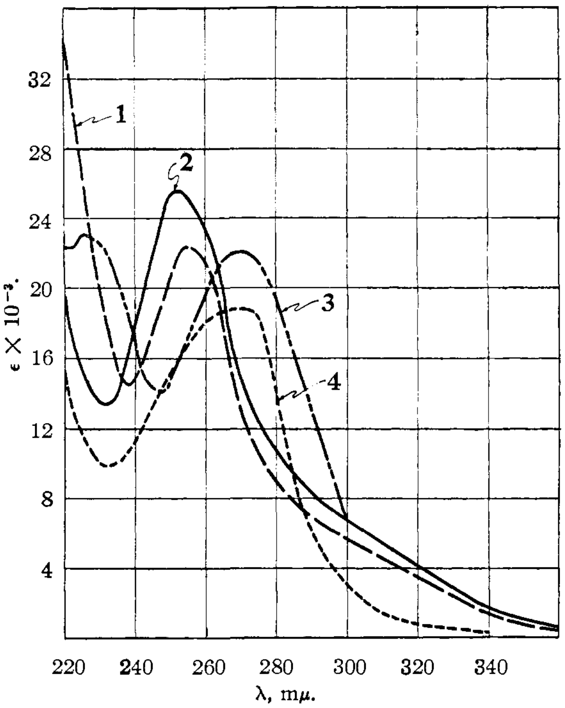


Fig. 1.—Ultraviolet absorption spectra of representative triazines: 1, R = $CH{=}CH_2$, R_2 = C_6H_5NH, R_3 = NH_2, XI, Table II; 2, R_1 = CCl_3, R_2 = C_6H_5NH, R_3 = NH_2, VII, Table II; 3, R_1 = $CH_2{-}CH_2OCH_3$, R_2 = C_6H_5NH, R_3 = $NHCOCH_3$, XXVI, Table III; 4, R_1 = $CH_2{-}CH_3$, R_2 = C_6H_5NH, R_3 = NH_2, VIII, Table II.

number of halogen atoms increases. The positive nature of the halogen is in accord[2b] with its susceptibility to reduction with iodide ion and its inertness and stability. From Fig. 1, curve 2, it is seen that a shoulder is occurring about 285 mμ, a longer wave length for the trichloro compound, and this may be due to the weaker but longer electronic path through the phenyl ring. As will be stated subsequently, the vinyl compound has a similar spectrum.

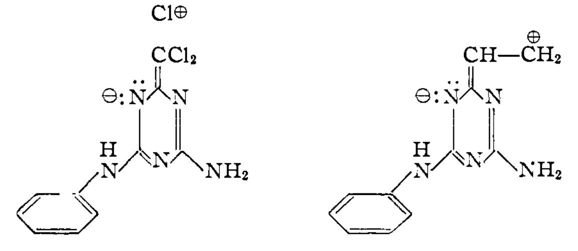
The absorption spectra of the compounds XXI through XXV are similar as expected. In XXI, the carboxyl group may be in the form of its anion.

If compounds XII, XVIII, XIX and XX are compared with VIII, there is essentially no difference in the intensity of absorption but there is a slight hypochromic shift

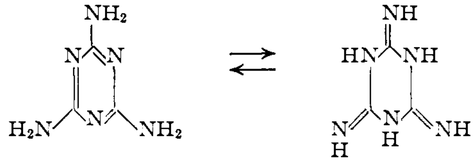
$$\underset{271}{-CH_2\text{-}CH_3} > \underset{270}{-CH_2\text{-}CH_2\text{-}O\text{-}CH_3} > \underset{269}{-CH_2\text{-}CH_2\text{-}OC_2H_5} >$$

$$\underset{265}{-CH_2\text{-}CH_2\text{-}O\text{-}C_3H_7\text{-}n} > \underset{265}{CH_2\text{-}CH_2\text{-}OH}$$

A consideration of the vinyl compound XI shows a bathochromic and hyperchromic effect relative to the strong triazine absorption at 235 mμ established by Klotz[5] and is reasonably accounted for by conjugation of the double bond with the triazine nucleus. From Fig. 1, curve 1, a shoulder is occurring at *ca.* 285 mμ, similar to the trichloro compound. The hypsochromic shift, compared with the ethyl derivative, is probably due to excited states which involve electron release from the vinyl group. This is in accord with the ability of 2-vinylpyridine to add nucleophilic reagents[6] and is consistent with the electron attracting power of the triazine ring. This is of special interest since vinyl groups attached to a carbon aromatic ring system usually give bathochromic effects.



Klotz and Askounis[5] have concluded on the basis of the absorption spectra of melamine that it is largely in the triamine form in solution



In strong acid (compare 8 and 9), there is a pronounced hyperchromic effect. This was attributed to the formation of a conjugate acid of the triazine and the destruction of the symmetry of the molecule. The reduced symmetry by increasing the dipole strength would increase the transition probability and hence the intensity of absorption. Inspection of the data for XIII, XV and XVI shows a decrease in the absorption intensity at the maximum as the strength of the acid forming the salt is increased. The effect is more pronounced with XVII. Comparisons with the band of maximum

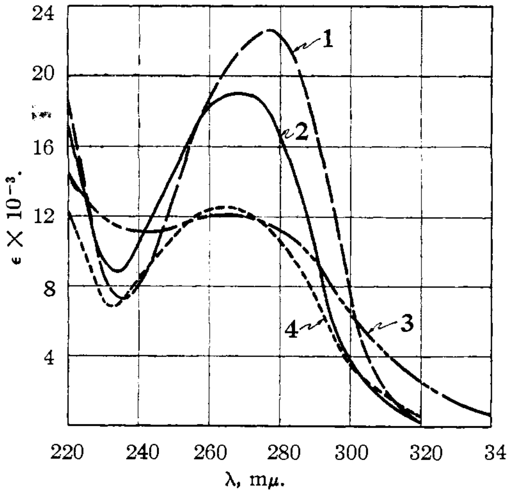


Fig. 2.—Ultraviolet absorption spectra of representative triazines: 1, R_1 = H, R_2 = p-BrC_6H_4NH, R_3 = NH_2, III, Table II; 2, R_1 = $CH_2{-}CH_2OCH_3$, R_2 = C_6H_5NH, R_3 = NH_2, XII, Table II; 3, R_1 = $CH_2{-}CH_2OCH_3$, R_2 = C_6H_5NH, R_3 = NH_2 in 1 *N* HCl, XVII, Table II; 4, R_1 = H, R_2 = C_6H_5NH, R_3 = NH_2, I, Table II.

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(5) J. M. Klotz and T. Askounis, THIS JOURNAL, **69**, 801 (1947).

(6) (a) W. E. Doering and P. A. N. Weil, *ibid.*, **69**, 2461 (1947); (b) M. H. Wilt and R. Levine, *ibid.*, **75**, 1368 (1953).

absorption shows a hypochromic and hypsochromic effect in 1 *N* hydrochloric acid (Fig. 2).

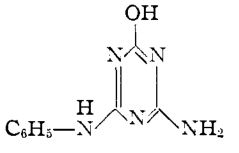
These effects are in accord with the suggestion that there is an increasing tendency for the triazine to be present in the conjugate acid form. The cationoid state results in a decrease of absorption in our unsymmetrical system.

A similar effect is observed on comparing II and I and Nachod and Steck[7] also observed a hypochromic effect in 0.01 *N* hydrochloric acid as compared to the neutral solution as shown in 3 and 5. A similar effect[4] has been noted with the unsymmetrical amine, aniline and its conjugate acid although there is a pronounced hypsochromic effect on going to the salt in this case.[4,8]

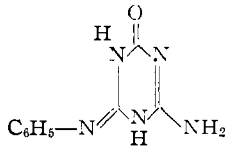
Consideration of structure XXVI shows the marked influence of acetylation on the spectrum. There is very little relationship to be seen between XXVI and XII, the parent product. There has been a large increase in intensity and a new type of absorption and it would appear that a new chromophore has been introduced (Fig. 1). For brevity, diagrams showing possible electronic paths are omitted.

The acetylation of I to yield XXVII does not give the extensive changes in the spectrum of the parent product as noted in the previously described acetylated product. There are, however, some marked bathochromic and hyperchromic effects.

The substitution of hydrogen by hydroxyl attached to the triazine ring as in XXVIII yields essentially a hyperchromic effect. Since the compound was examined as the hydrochloride, it is likely that the form most nearly representing the structure is B instead of a tautomeric structure such as C



B



C

Acetylation of XXVIII yielded a monoacetate XXIX which in view of its resultant hypochromic and hypsochromic effect compared to the spectrum of compound XXVIII is believed to reflect O-acetylation.

While the instrument used in this study was incapable of resolution of bands beyond 220 mμ, it is of interest to note that the minima reported of virtually all of the diaminotriazine compounds in this series was in the vicinity of 232 to 238 mμ reflecting a decrease in absorption from a maximum in the far ultraviolet. Hirt and Salley,[9] in a recent study of simple diaminotriazine, also indicate a minimum at about 237 mμ for their compounds with the maximum still not resolvable at about 200 mμ. It would appear, therefore, that extension of the ultraviolet study of the diaminotriazines in the neighborhood of 200 mμ would yield pertinent information particularly relevant to the triazine ring system.

The spectra were all determined with a model DU Beckman spectrophotometer using 1-cm. cells.

Acknowledgment.—We are grateful to Dr. Louis Freedman of the U. S. Vitamin Corporation for his generosity in allowing one of us to use the facilities of their laboratories. We are also grateful to Dr. E. I. Becker of the Polytechnic Institute of Brooklyn for helpful discussions.

BROOKLYN, NEW YORK

[7] F. C. Nachod and E. A. Steck, THIS JOURNAL, **70**, 2819 (1948).

[8] See also E. J. Modest and H. Kangur, Abstracts of 124th A.C.S. Meeting, page 26-O for a similar effect with 1,2-dihydro-*s*-triazines.

[9] R. C. Hirt and D. J. Salley, *J. Chem. Phys.*, **21**, 1181 (1953).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION, LABORATORY OF ADVANCED RESEARCH, REMINGTON RAND, INC.]

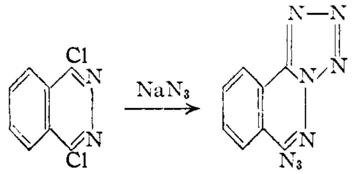
Azidopyrimidines[1]

BY FREDERIC R. BENSON, LAWRENCE W. HARTZEL AND ELIZABETH A. OTTEN

RECEIVED DECEMBER 3, 1953

Attempts have been made to prepare ditetrazolo[a,c]pyrimidines; reactions designed to lead to this ring system have produced instead the isomeric 2,4-diazido pyrimidines. Evidence favoring the diazide structure of these compounds has been secured from their behavior toward hydrolysis, from heating at high temperature, and from their ultraviolet absorption spectra.

The preparation of ring systems containing two tetrazole groups fused to a single ring has been studied by Stollé and Storch.[2] These investigators attempted to obtain such compounds by the reaction of sodium azide with dichloroquinazoline, dichloroquinoxaline and dichlorophthalazine. In all cases it was found possible to effect ring closure with the formation of a tetrazole ring in only one position, a mixed tetrazolo–azido compound being obtained.



More recently, Andrisano[3] has described the preparation of 6-furylditetrazolo[a,c]pyrimidine from 6-furyl-2,4-dihydrazinopyrimidine and nitrous acid. Proof of structure of this compound was not given. Alternative structure possibilities for this compound include 2,4-diazido-6-furylpyrimidine or the two

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[1] This work was performed under a subcontract from Arthur D. Little, Inc., by Remington Rand, Inc., in connection with an Army Ordnance Corps project. This article has been approved for publication by the Public Information Division, National Military Establishment.

[2] R. Stollé and H. Storch, *J. prakt. Chem.*, **135**, 128 (1932).

[3] R. Andrisano, *Boll. sci. facolta chim. ind. univ. Bologna*, **5**, 48 (1944–1947); *C. A.*, **44**, 3904i (1950).