

## Near Ultraviolet Absorption Spectra of Melamine and Some Related Compounds

George W. Costa, Robert C. Hirt, and D. J. Salley

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of the lifetime on the temperature. If the amplitudes increase only slightly with  $T$  in the range covered, the curves of  $1/\tau$  against  $T$  will appear to be linear. In the present case, the range of  $T$  may be too small to allow decision between a truly linear curve and an exponential curve which is linear only in a first approximation.

The variations in *slope* of the  $1/\tau-T$  curves of Fig. 1 are not easily explained, however, by a thermal quenching mechanism. The latter mechanism depends essentially on microscopic properties of the crystal, which are confined to distances of a few molecular diameters for true molecular vibrations. It appears that values of these properties should be the same in every crystal, which requires that the slopes of the  $1/\tau-T$  curves should all be the same. This is clearly not the case. On the other hand, if thermal quenching arises from low frequency lattice vibrations of large amplitude, so that waves extend through large aggregates, then there is nothing to distinguish this mechanism from the exciton picture except a change in descriptive notation.

From the preceding discussion it appears that the exciton picture is capable of giving a qualitative explanation of the observed results on the lifetime in solid acetone. The possibility of thermal quenching is not excluded, but is considered inadequate as a basis of explanation of the curves of Fig. 1.

### Observation on Solid Biacetyl

The decay of the fluorescence of solid biacetyl at 78°K, when irradiated with wave-lengths in the region 4350Å, was found to be non-exponential at high exciting intensities. At lower exciting intensities, the decays became non-exponential as the temperature increased. At those intensities where the decays of fluorescence of biacetyl at 78°K appeared to be exponential, the average of the observed lifetimes was  $1.26 \times 10^{-3}$  sec. Thus the theory developed above for the temperature dependence of the lifetime of fluorescence in solid acetone cannot be applied even qualitatively to biacetyl because of the non-exponential nature of the decays.

A single experiment was done in which solid biacetyl at 78°K was irradiated with wave-lengths in the region 2500Å. Absorption of light of this wave-length excites the biacetyl molecules to a electronic energy level different from that reached on absorption of 4350Å. The lifetime under these conditions was found to be unchanged however, indicating that in both cases, the fluorescence transition is the same. The large difference in energy between the two upper electronic states must be lost in a time small compared with the time resolving power of our oscillograph, ( $10^{-5}$  sec.) since no time lag was observed between excitation and fluorescence.

## Near Ultraviolet Absorption Spectra of Melamine and Some Related Compounds

GEORGE W. COSTA,\* ROBERT C. HIRT, AND D. J. SALLEY

*Stamford Research Laboratories, American Cyanamid Company, Stamford, Connecticut*

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An absorption band of low intensity has been found in the 2800 to 3400Å region for solutions of melamine, trimethylol melamine, trimethyl ether of trimethylol melamine, hexamethylol melamine, and cyanuric chloride. The band has also been observed in gaseous melamine at elevated temperatures. The band is believed to be due to a singlet-triplet transition, rather than analogous to the 2600Å absorption system of benzene.

MELAMINE is usually considered to have a symmetrical "amino" structure containing three conjugated double bonds<sup>1</sup> analogous to those in benzene. General empirical observation suggests that such a system should show an absorption band in the region of 2500 to 3400Å, and indeed Maccoll<sup>2</sup> has predicted that symmetrical triazine ( $C_3N_3H_3$ ) should exhibit a band near 3700Å. In addition, considerations of the symmetry of the molecule suggest that a forbidden electronic transition would be involved and hence that the absorption would be relatively weak. Two earlier

articles<sup>3,4</sup> on the ultraviolet absorption spectra of melamine and related compounds were not concerned with these aspects but with the absorption in the 2350Å region. Consequently, a search of the longer wave-length region has been made for solutions of melamine and some related compounds and for melamine vapor.

### EXPERIMENTAL

Melamine, trimethylol melamine, hexamethylol melamine, the trimethyl ether of trimethylol melamine, and cyanuric chloride, all prepared by various members of these Laboratories, were recrystallized, resublimed,

\* Present address: Department of Chemistry, Northeastern University, Boston, Massachusetts.

<sup>1</sup> E. H. Hughes, J. Am. Chem. Soc. **63**, 1737 (1941).

<sup>2</sup> A. Maccoll, J. Chem. Soc., 670-672 (1946).

<sup>3</sup> Dixon, Woodberry, and Costa, J. Am. Chem. Soc. **69**, 599 (1947).

<sup>4</sup> I. M. Klotz and T. Askounis, J. Am. Chem. Soc. **69**, 801 (1947).

or otherwise treated in an effort to obtain the highest possible purity. For melamine and cyanuric chloride these efforts undoubtedly succeeded in producing a very pure material, but they may not have succeeded entirely for the other compounds which are somewhat unstable and which are initially obtained in admixture with other closely related compounds. Aqueous solutions were made of all but cyanuric chloride; this latter was examined in cyclohexane. Ethylene glycol was also used as a solvent for melamine. Since the absorption was weak in the region examined, relatively concentrated solutions were employed. Cell lengths (5 to 100 mm) and solution concentrations (0.2 percent to 3.5 percent) were so chosen that in all cases the observed absorbances (optical densities) were within the range of 0.1 to 0.8, where a precision of  $\pm 1$  percent could be obtained.

In the case of melamine, the solubility<sup>5</sup> in water at room temperature was not sufficient to allow adequate absorption with the cell length available. Consequently, it was examined in a nearly saturated solution at about 75°C in an electrically heated cell, or as a solution supersaturated at room temperature. In the latter, the solution could be held as long as an hour before crystallization set in.

A Beckman spectrophotometer, Model DUV, accommodating 5 to 100 mm length cells and using a

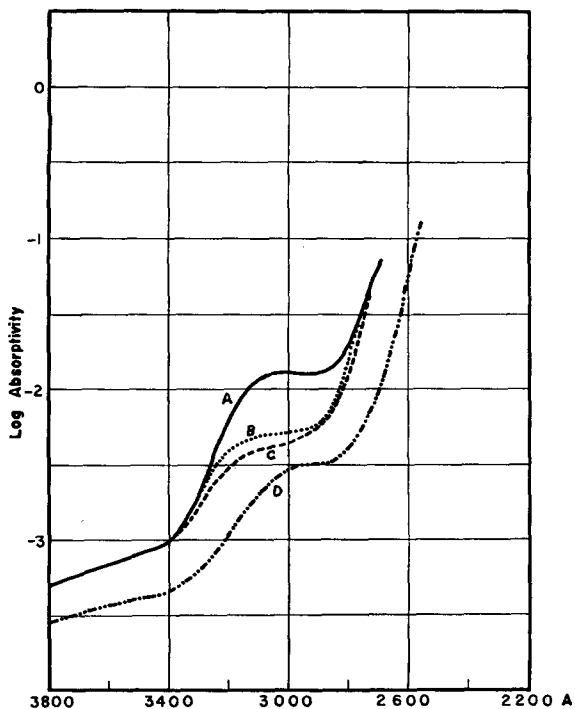


FIG. 1. Near ultraviolet absorption spectra of: A—Trimethyl ether of trimethylol melamine; B—Hexamethylol melamine; C—Trimethylol melamine; D—Melamine.

<sup>5</sup> Chapman, Averell, and Harris, *Ind. and Eng. Chem.* **35**, 137 (1943).

TABLE I. Near ultraviolet bands.

Compound	pH	Band wave-length, Å	Absorptivity	
			Specific	Molar
Melamine, recrystallized	1.4	2950	0.0103	1.3
Melamine, recrystallized	8.4	2950	0.0021	0.26
Melamine, recrystallized	11.7	2950	0.0079	1.0
Melamine, resublimed, 3×	1.5	2950	0.0092	1.2
Melamine, resublimed, 3×	8.0	2950	0.0031	0.39
Trimethylol melamine	0.8	3000	0.0160	3.5
Trimethylol melamine	7.9	3000	0.0046	1.0
Trimethylol melamine	11.4	3000	0.0050	1.1
Trimethyl ether of trimethylol melamine	1.3	2980	0.056	14.2
Trimethyl ether of trimethylol melamine	8.6	2980	0.013	3.3
Trimethyl ether of trimethylol melamine	11.7	2980	0.014	3.6
Hexamethylol melamine	8.0	3100	0.0047	1.3
Cyanuric chloride	(c-hexane)	3400	0.0009	0.17

water-cooled hydrogen lamp of high intensity,<sup>6</sup> was employed for most of the measurements on solutions, but some examinations were also made with a Cary automatic recording spectrophotometer.<sup>7</sup>

For photographing the vapor spectrum of melamine, a Hilger medium quartz spectrograph with a water-cooled Nestor hydrogen lamp and Eastman Kodak Type III-O plates were used. A 50 mm vapor cell was equipped with quartz windows and was enclosed in a small electrically heated furnace having quartz windows. The temperature inside the furnace was measured with a thermocouple. The vapor was maintained at about 198°C and 243°C to obtain a concentration sufficiently high to give satisfactory spectrograms in less than a hour of exposure. The plates were traced on a Leeds and Northrup recording microphotometer. The absorbance (optical density) values obtained from the tracings were corrected by use of H and D curves for the emulsion at various wave-lengths; they were also corrected for the variation in intensity of the hydrogen lamp with wave-length, which was obtained from a microphotometer tracing of the hydrogen lamp spectrum, photographed on the same plate.

## RESULTS

The ultraviolet absorption spectra were expressed as the logarithm of the absorptivity *versus* wave-length, using Beer's law in the form:

$$\log_{10} I_0/I = A = a \cdot b \cdot c,$$

where  $I_0$  is the intensity of the incident light,  $I$  is the intensity of the transmitted light,  $A$  is the absorbance (optical density),  $a$  is the absorptivity (specific extinction),  $b$  is the cell thickness in mm,  $c$  is the concentration in g/100 ml.

<sup>6</sup> The lamp was of the type described by A. J. Allen and R. G. Franklin, *J. Opt. Soc. Am.* **29**, 453 (1939) and was obtained from A. G. Nestor of the Bartol Foundation.

<sup>7</sup> We are indebted to Drs. R. H. Kienle and G. L. Buc of the Calco Chemical Division of this Company for the use of this instrument.

A weak, unresolved band or shoulder was displayed by all the compounds in the region of 2800 to 3400Å. Figure 1 shows the spectra for aqueous solutions of melamine (supersaturated solution), trimethylol melamine, hexamethylol melamine, and the trimethyl ether of trimethylol melamine. Curves similar to these were obtained for melamine in water at 75°C and in ethylene glycol at room temperature. No fine structure was found in these bands even with the Cary instrument. The intensity of the band was very low, with absorptivity values in the range 0.001 to 0.1, as shown in Table I. The effect of *pH* changes was to enhance the band at either low or high *pH* values as is evident in Table I. For the compounds tested, Beer's law was obeyed within the limit of experimental error in the concentration range of 0.2 to 3.5 percent; changes in both cell thickness and concentration were made in verification of this behavior.

Cyanuric chloride in cyclohexane solution displayed a low intensity band near 3400Å, as shown in Fig. 3. This band, like the band near 2500Å, appeared to be partially resolved into two bands.

The spectrum of melamine vapor also showed a shoulder band appearing at 3100 to 3200Å, similar to that in the solution spectra at 2900 to 3000Å. This is shown in Fig. 4. Measurable absorption could be found from the microphotometer tracings as far as 3400Å and there was strong absorption below 2450Å. Since

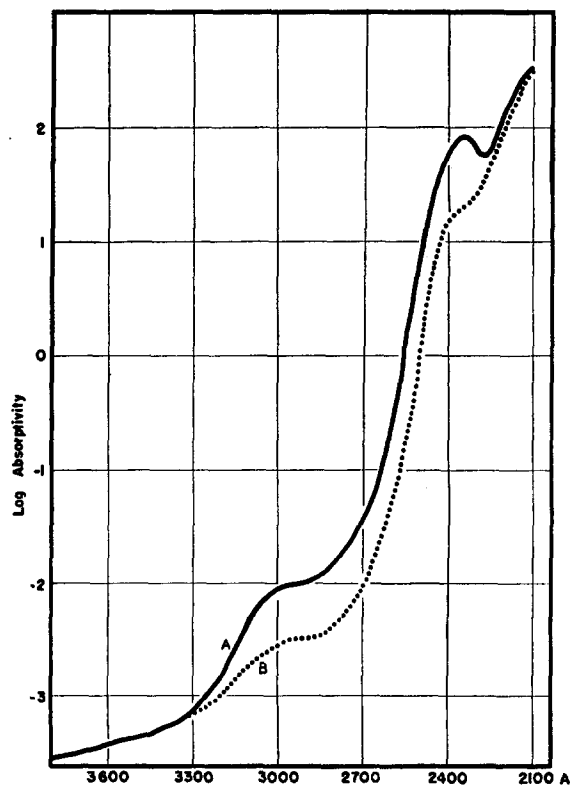


FIG. 2. Ultraviolet absorption spectra of melamine: A— at *pH* 1.4; B..... at *pH* 8.4.

the absorption in the near ultraviolet range was of primary interest, the strong absorption below 2450Å was not investigated at this time. No fine structure was observed.

## DISCUSSION

Although the bands observed in the 2800 to 3400Å region are of very low intensity, their reality appears unquestionable. The intensity of the band for samples of melamine obtained from various sources and subjected to repeated purification did not change, showing that it did not arise from an impurity. The facts that Beer's law is obeyed at high concentrations and that the band is observed in organic solvents means that it

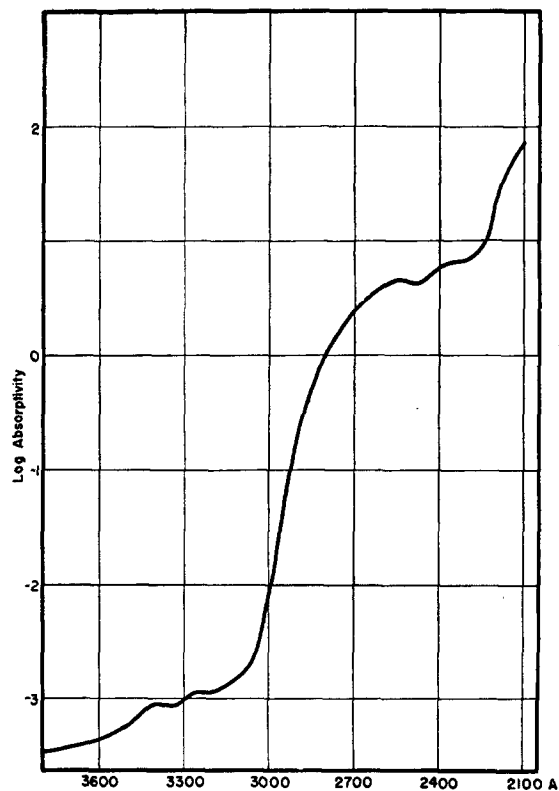


FIG. 3. Cyanuric chloride in cyclohexane.

cannot be attributed to the presence of ions or solvated molecules. The enhancement by *pH* changes indicates, however, that the ions so formed have a somewhat higher absorptivity than that of the neutral molecule. Finally the appearance of the band in the vapor phase indicates that it is characteristic of the melamine molecule.

It would appear that the band is due to an electronic transition arising from the triazine nucleus of the molecule, and two alternative suggestions may be offered at this time concerning the nature of this transition. The proposal which stimulated the investigation of the 2500 to 3400Å region was that a band corresponding to the 2600Å absorption of benzene

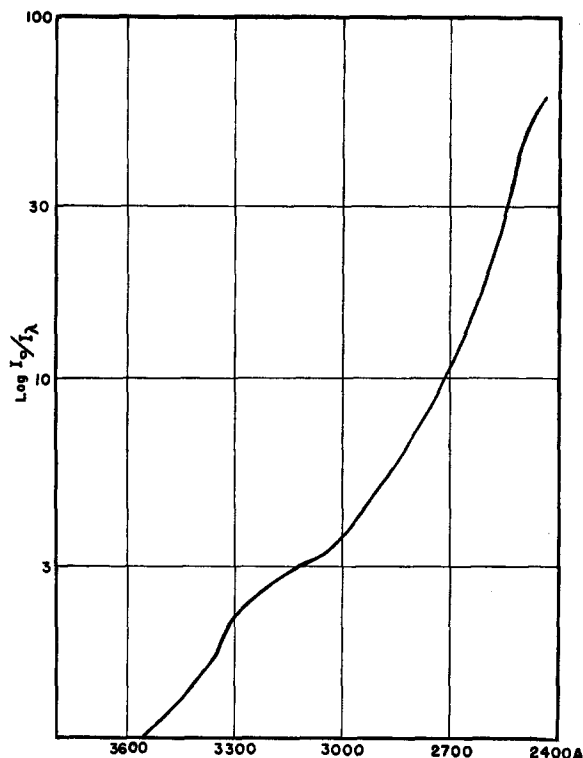


FIG. 4. Melamine vapor at 243°C.

and its derivatives should exist for melamine. That the band should be weak in intensity was expected from the fact that the trigonal symmetry of the "amino" or "normal" structure of the melamine molecule places it in the  $D_{3h}$  symmetry point group (neglecting the hydrogen atoms). Symmetry considerations for molecules belonging to this point group show that the transition analogous to the 2600Å ( $^1A_{1g} \rightarrow ^1B_{2u}$ ) benzene transition is forbidden electronically. This has been demonstrated in the cases of 1,3,5-trichlorobenzene and 1,3,5-trimethylbenzene.<sup>8</sup> However, the intensity of the observed band in melamine is roughly  $10^{-3}$  that for benzene. This large intensity difference argues against this explanation, for it is unlikely that such a transition should be any *more* forbidden in melamine than in benzene.

The alternative suggestion is that a singlet-triplet transition is involved. Benzene has very weak absorption bands near 3400Å<sup>9,10</sup> arising from a symmetry-forbidden, singlet-triplet transition ( $^1A_{1g} \rightarrow ^3B_{1u}$ ); this has been discussed in detail by Kasha<sup>11</sup> and by Shull.<sup>12</sup> The intensity of this benzene absorption, however, is

<sup>8</sup> H. Sponer, Chem. Rev. 41, 281 (1947).

<sup>9</sup> A. L. Sklar, J. Chem. Phys. 5, 669 (1937).

<sup>10</sup> G. N. Lewis and M. Kasha, J. Am. Chem. Soc. 66, 2100 (1944), and 67, 994 (1945).

<sup>11</sup> M. Kasha, Chem. Rev. 41, 401 (1947).

<sup>12</sup> H. Shull, J. Chem. Phys. 17, 295 (1949).

about  $10^{-2}$  that of the melamine band. Another singlet-triplet transition ( $^1A_{1g} \rightarrow ^3E_u$ ) in benzene (though not observed probably due to the overlapping of the 2600Å absorption) was expected by Roothaan and Mulliken<sup>13</sup> to have an intensity  $10^3$  stronger than the  $^3B_{1u}$  and thus about  $10^2$  weaker than the  $^1B_{2u}$  transition. This expected intensity for the benzene band is thus about the observed intensity of the melamine band. If then, the 2950Å melamine absorption arises from a singlet-triplet transition, the strong absorption of the triazines in the 2200–2500Å region<sup>3,4</sup> (Fig. 2) may be considered as corresponding to the 2600Å region bands of benzene and substituted benzenes.<sup>14</sup>

Cyanuric chloride can exist only in the "normal" form<sup>4</sup> and hence is also a planar, trigonally symmetrical molecule belonging in the symmetry point group  $D_{3h}$ . The low intensity band near 3400Å is thought to correspond to that of melamine at 2950Å, and that near 2500Å to that of melamine near 2350Å. The differences near 2500Å between the cyanuric chloride spectrum shown on Fig. 3 and that reported by Klotz<sup>4</sup> are believed to be due to the different solvents used. The presence of this weak band in cyanuric chloride spectra argues against explanations involving ions or contributions from the amino nitrogen atoms.

A choice between the two alternative explanations at this time would be in favor of the singlet-triplet hypothesis. Both of these explanations attribute the absorption to electronic transitions arising from symmetrical, benzene-like structures in these triazines. The increase in molar absorptivity in the weak band from melamine to trimethylol melamine to the trimethyl ether of trimethylol melamine is consistent with the reduction in symmetry due to the additional atoms, although admittedly but little can be said with regard to the configuration of the latter two compounds. The similarity of the melamine and cyanuric chloride spectra, together with the correlation between melamine and benzene spectra, support the opinion that melamine itself in aqueous solution has the symmetrical amino structure.<sup>4</sup> Further investigations on the ultraviolet absorption spectra of melamine and related compounds, especially unsymmetrically substituted triazines, are being pursued here in the hope that new evidence on the structure of these compounds and the origin of their spectra may result.

#### ACKNOWLEDGMENT

We are grateful to Dr. R. F. Stamm and Dr. F. Halverson for many helpful suggestions and discussions, and to Mrs. D. M. Sousa for aid with the experimental work.

<sup>13</sup> C. C. J. Roothaan and R. S. Mulliken, J. Chem. Phys. 16, 118 (1948).

<sup>14</sup> R. C. Hirt and J. P. Howe, J. Chem. Phys. 16, 480 (1948).