Magnetochemical Study of Cyanuric Acid, Melamine, and Some Derivatives

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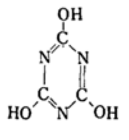
(Received March 28, 1958)

The structure of highly symmetrical heterocyclic rings which appear in cyanuric acid and melamine has been the subject of much interest. Their structures in the solid state were established from X-ray studies. The former molecule[1] was found to be in the carbonyl form II and the latter[2] in the amide form V. Magnetic susceptibilities and anisotropies of cyanuric ring compounds have been examined by several investigators, but their conclusions as to the structure of cyanuric acid were conflicting. Pascal[3] concluded that the magnitude of the diamagnetic susceptibility favors form I, however, Maruha[4] suggested that its structure is a resonance hybrid of form II and the zwitter-ionic forms III and IV. On the other hand, Lonsdale[5] found that the cyanuric acid molecule has anisotropy of the same order as those of melamine and cyanuric triazide and she favored form I. Besides, the recorded values for cyanuric acid disagreed considerably as shown in Table I. Therefore, a more detailed examination of the diamagnetic susceptibilities of cyanuric acid and melamine, including also their derivatives which have no tautomeric forms, was undertaken.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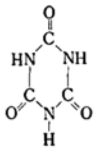
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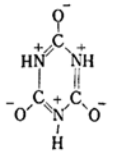
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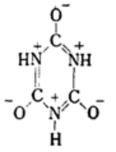
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Experimental

Materials.—Cyanuric chloride, commercial product, recrystallized from benzene, m.p. 146°C. Trimethyl cyanurate[6c], m.p. 135°C. Triphenyl cyanurate[6d], m.p. 230~231°C. Hexaethylmelamine[6b], b.p. 147~148°C/2.5 mmHg. Melamine, commercial product, recrystallized from water and sublimed in vacuo. Trimethylolmelamine, commercial product, dried in vacuo. 2,4-Dianilino-6-chloro-*s*-triazine[6a], sublimed in vacuo, m.p. 199°C. 2,4-Dianilino-6-methoxy-*s*-triazine[6c] sublimed in vacuo, m.p. 168°C. Melamine hydrochloride, prepared by dehydration in vacuo from hemihydrate. Cyanuric acid, supplied by Nippon Carbide Ind. Co., recrystallized from water repeatedly and sublimed in vacuo.

Magnetic measurements — The susceptibility measurements were carried out using a Gouy balance as previously described[7].

Results and Discussion

In Table I specific and molar susceptibilities together with other recorded values of the latter quantity are presented for

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[1] E. H. Wiebenga, *J. Am. Chem. Soc.*, **74**, 6156 (1952).

[2] E. W. Hughes, ibid., **63**, 1737 (1941).

[3] P. Pascal, *Compt. rend.*, **176**, 1887 (1923).

[4] J. Maruha, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **71**, 627 (1950).

[5] K. Lonsdale, *Proc. Roy. Soc.*, **A177**, 272 (1941).

[6] J. T. Thurston et al., *J. Am. Chem. Soc.*, **73**, 2981, 2984, 2986, 2990 (1951).

[7] H. Akamatu and Y. Matsunaga, This Bulletin, **26**, 364 (1953).

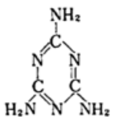
TABLE I

DIAMAGNETIC SUSCEPTIBILITIES OF CYANURIC ACID, MELAMINE, AND THEIR DERIVATIVES

	Substance	Suscept. $(-\chi)$	Molar Suscept. $(-\chi_M)$ Obs.	Calc.	Lit.
I	Cyanuric chloride	0.435	80.2	82.1	81.1[10]
	Trimethyl cyanurate	0.525	89.9	89.9	—
	Triphenyl cyanurate	0.576	205.9	205.1	—
	Hexaethylmelamine	0.675	198.8	197.9	—
II	Melamine	0.502	63.3	60.8	65.2[11], 61.7[12]
	Trimethylolmelamine	0.519	112.2	110.2	—
	2,4-Dianilino-6-chloro-*s*-triazine	0.558	166.7	165.8	—
	2,4-Dianilino-6-methoxy-*s*-triazine	0.586	172.5	168.5	—
	Melamine hydrochloride	0.538	87.5	84.9	—
	Cyanuric acid	0.422	54.5	52.6	63.2[3], 50.5[4], 61.5[13]

ten compounds. The first group consists of four compounds which have no tautomeric form. On the basis of these experimental values we estimated the constant for unsubstituted triazine at -36.5[8] on the assumption that the magnetic contribution of substituents is just the same as in the case of derivatives of benzene. The molar susceptibilities in the fourth column were evaluated on the same assumption. Pascal[3] gave -36.5 for the contribution of the triazine ring and -1.85 for the correction term. Our values which must be compared with these two are -27.7 and $+6.95$. It must be noted that our values are in serious disagreement with Pascal's, but our correction term is close to those for the pyrimidine ring $(+6.5)$ and for the pyrazine ring $(+9)$ given by Pacault[9].

The agreement between the experimental and the calculated values in the case of the first group is satisfactory; however, it should be noted that in the second group the former values are appreciably and consistently more diamagnetic. The substances in the latter group have the amino nitrogen on which one or two hydrogen atoms remain, so they have the possibility of being in another form, the imide structure (for example, the form VIII of melamine). But from X-ray and spectroscopic studies[14,15], it seems to be unreasonable that the increase of diamagnetism is due to the structural change to the imide form.



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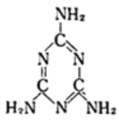

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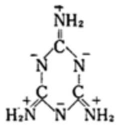

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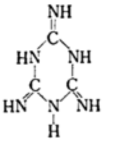

(VIII)

The contribution of the *zwitter*-ionic forms seems to be rather important in the melamine molecule. To explain the C-N bond lengths the three structures V, VI and VII must contribute nearly equally[2]. The conjugation between amino group and aromatic nucleus diminishes considerably in the derivatives of benzene, when the hydrogen atoms attached to the amino nitrogen are completely substituted by alkyl groups[16]. By analogy, it would seem that the increase of diamagnetism appearing in the substances in the second group relates to the extraordinarily large contribution of ionic structures.

We shall examine more quantitatively the magnitude of molar susceptibilities of these heterocyclic compounds. The value for the Kekulé-like form of unsubstituted triazine is estimated at -19.6 by Gray and Cruickshank's method[17]. If this value is equal to the isotropic contribution of the ring as is usual in aromatic nuclei, the molar anisotropy must be about -50. This is too large if we compare it with -30 reported by Lonsdale[18] for the molar anisotropy of

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[8] All values of susceptibility are in c. g. s. units and are multiplied by 10^6 throughout this paper.

[9] A. Pacault, *Ann. chim.*, (12), **1**, 527 (1946).

[10] J. Farquharson, *Trans. Faraday Soc.*, **32**, 219 (1936).

[11] I. E. Knaggs and K. Lonsdale, *Proc. Roy. Soc.*, **A177**, 140 (1940).

[12] J. Ploquin and C. Vergneau-Souvray, *Compt. rend.*, **234**, 97 (1952).

[13] S. K. Siddhanta and P. Ray, *J. Indian Chem. Soc.*, **20**, 359 (1943).

[14] I. M. Klotz and T. Askounis, *J. Am. Chem. Soc.*, **69**, 801 (1947).

[15] M. J. S. Dewar and L. Paoloni, *Trans. Faraday Soc.*, **53**, 261 (1957).

[16] G. W. Wheland, "Resonance in Organic Chemistry", John Wiley & Sons, Inc., New York, (1955), p. 99-100.

[17] F. W. Gray and J. H. Cruickshank, *Trans. Faraday Soc.*, **31**, 1491 (1935).

[18] K. Lonsdale, *Z. Krist.*, **95**, 471 (1936).

cyanuric chloride. Such a discrepancy becomes more remarkable in the case of melamine. The calculated value for the form V or VI is −45.6 and the anisotropy given by the combination with the experimental molar susceptibility is equal to −53. On the other hand, Knaggs and Lonsdale's observed values are −58.1 for the isotropic contribution and −21 for the anisotropy. These disagreements suggest that the real isotropic contribution of a triazine ring is more diamagnetic than the calculated one and the resonance with the zwitter-ionic form brings about a marked increase of the isotropic diamagnetism.

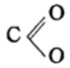
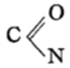
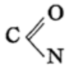
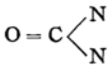
As to cyanuric acid, the calculated value, obtained by assuming the presence of a triazine ring, is near the experimental one. However, this agreement cannot be considered as conclusive evidence for form I since we can say that the value of the molar susceptibility also favors the carbonyl form as discussed in the following paragraph.

The structure of urea is closely similar to part of the carbonyl form of cyanuric acid. With this compound the resonance energy is relatively large. This fact suggests that resonance with the zwitter-ionic structures is important in this case too. The diamagnetism of urea was examined in detail by Clow[19]. The experimental values are in serious disagreement with the calculated ones for the carbamide structure especially in the case of urea itself and the monosubstituted derivatives. Therefore, it is no wonder that Gray and Cruickshank's method gives such unreasonable estimates as −39.3 for the isotropic contribution of the carbonyl form of cyanuric acid and −45.6 for the molar anisotropy.

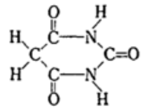
Since Pascal determined his first constants, it has been well known that the magnetic contributions of oxygen and nitrogen atoms depend markedly on their surroundings. He gave many group constants in his second system of the additivity rule[20]. Some of them are cited in Table II. Using the constant for the amide group with substituent, we obtain −47.5 for the isotropic diamagnetism of the carbonyl form II and −21 for the molar anisotropy. The latter value is in good agreement with −24 given by Lonsdale[5]. The molecule of cyanuric acid contains a triazine ring only in the zwitter-ionic forms III and IV; hence the large anisotropy suggests that the contribution of these structures to a resonance hybrid is very important. This view is consistent with the evidence from other sources.

TABLE II

PASCAL'S CONSTANTS IN HIS SECOND SYSTEM

Group		Constant ($-\chi_M$)
C=O		8.1
		15.15
	(amide without substituent)	15.70
	(amide with substituent)	13.83
	(urea)	25.5

Recently Sato[21] measured the susceptibilities of barbituric acid (IX) and its many derivatives. Using the constants for the oxygen atoms in alcohol (−4.61) or the carboxyl group (−3.36) instead of that in ketone (+1.72), his calculated values were found to be in rather good agreement with the experimental ones. However, if we apply his procedure to cyanuric acid, the calculated values are −51.7 to −55.5 for the isotropic contribution of the carbonyl form and nearly zero to −8.4 for the molar anisotropy. This estimated anisotropy is in poor agreement with that reported by Lonsdale. The procedure which was applied successfully to the case of barbituric acid seems to be unreliable for cyanuric acid.



(IX)

Summary

The magnetic susceptibilities of melamine, cyanuric acid, and eight of their derivatives were measured by the Gouy method. On the basis of the molar susceptibilities of the four compounds which have no tautomeric form, the constant for triazine was estimated at −36.5. It appeared that Gray and

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[19] A. Clow, *Trans. Faraday Soc.*, **33**, 381 (1937); **34**, 457 (1938).

[20] J. Hoarau, A. Pacault and P. Pascal, *Cahier de physique*, No. 74, p. 30 (1955).

[21] Y. Sato, *Bull. Res. Inst. Non-Aqueous Solns. Tohoku Univ.*, **6**, 1 (1956).

Cruickshank's method gives too small an estimate for the isotropic part of the molar susceptibility in all cases and resonance with the zwitter-ionic structures brings about an increase of the isotropic diamagnetic contribution. With regard to cyanuric acid, the magnitude of the molar susceptibility seemed to be not inconsistent with the form containing a triazine ring. However, using Pascal's second additivity rule we found that both the magnitude of the isotropic diamagnetism and that of the molar anisotropy favor the carbonyl form.

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