MOLECULAR STRUCTURE AND GRAY AND CRUICKSHANK'S METHOD OF CALCULATING MOLECULAR DIAMAGNETISM. PART I. UREA AND SUBSTITUTED·UREAS

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The magnetic susceptibility values for urea and substituted ureas have been calculated according to Gray and Cruickshank's method on the basis of evidence furnished by X-ray study of the crystal structure of urea. It has been shown that the calculated value differs considerably from the experimental one. The structures considered by Clow and his method of calculating the susceptibility value have been criticised and proved to be untenable, and the agreement obtained between the calculated and the experimental values by him has thus been shown to have little or no significance.

In a previous communication (Siddhanta and Ray, *J. Indian Chem. Soc.*, 1943, 20, 359), the values of molecular susceptibilities of dicyandiamide, acetamide and cyanuric acid were carefully determined and the values were compared with those calculated by the method of Gray and Cruickshank (*Trans. Faraday Soc.*, 1935, 31, 1491) using resonating structures established by X-ray analysis of the crystals of the compounds. It was shown that the agreement of the calculated values with the experimental ones was not close enough to justify the adoption of the aforesaid method as a reliable tool for exploring molecular structure.

Remarkable agreement between experimental χ_u values and those calculated on the basis of the above-mentioned method has, however, been claimed by Gray and Cruickshank (*loc. cit.*) for benzene, naphthalene, carboxylic acids, water and hydrogen peroxide; and by Clow and co-workers (*Trans. Faraday Soc.*, 1937, 33, 381), for urea and its derivatives as well as for certain organic sulphur compounds besides several salts and esters of sulphates, sulphites, thiosulphates, etc. (*ibid.*, 1937, 33, 894; 1940, 36, 1018, 1029). From a consideration of the results set forth in the communication mentioned above (Siddhanta and Ray, *loc. cit.*), it is considered worthwhile to test the validity of these claims by a closer scrutiny of the evidences on which they are based.

In this paper, it is proposed to deal with urea and substituted ureas studied by Clow (*loc. cit.*). From a consideration of the X-ray analysis of urea by Wyckoff and Corey (*Z. Krist.*, 1934, 89, 462), Pauling has shown that the substance resonates between three structures I, IIa, and IIb of which (I) contributes 60% and (IIa) and (IIb) contribute 20% each to the normal state of the molecule ("The Nature of Chemical Bonds", 1940, p. 212).

$$\underset{(\text{I})}{\overset{H_2N}{\underset{H_2N}{\bigg\rangle}}C=O} \qquad \underset{(\text{IIa})}{\overset{H_2N}{\underset{H_2\overset{+}{N}}{\bigg\rangle}}C-\bar{O}} \qquad \underset{(\text{IIb})}{\overset{H_2\overset{+}{N}}{\underset{H_2N}{\bigg\rangle}}C-\bar{O}} \qquad \underset{(\text{III})}{\overset{H_2N}{\underset{H_2N}{\bigg\rangle}}\overset{+}{C}-\bar{O}}$$
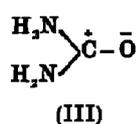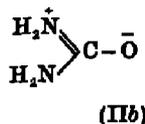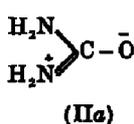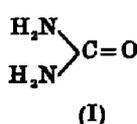
Viewed in the light of Gray and Cruickshank's method, structures (IIa) and (IIb) are identical. If the double bond is split up into a polarised single co-valent bond, as

suggested by Gray and Cruickshank, structure (III) would result from all the above cases. In Gray and Cruickshank's method of calculation, it is assumed that each double-bonded structure and the single co-valent structure, which arises from it by the splitting up of the double bond, contribute equally to the normal structure of the molecule; under these circumstances the resultant molecular susceptibility of the compound would be 3/10 due to (I), 1/5 due to (IIa and IIb) combined and $\frac{1}{2}$ due to III (case A). If, however, we ignore the structure (III), the resultant molecular susceptibility will be 3/5 due to (I) and 2/5 due IIa and to IIb combined (case B).

Structure IV shows the disposition of the H-bonds in the crystal of urea as shown by X-ray analysis. The direction of the arrow shows that the O atoms accept the H-bonds formed by the H atoms of the -NH$_2$ groups in urea. Each oxygen atom receives four H-bonds and all the H atoms in urea molecule are engaged in bond-formation. It may, however, be pointed out that in Gray and Cruick-shank's method of calculation, the oxygen atom in structure (I), having only two lone-pairs of electrons, can receive, according to these authors, two H-bonds in maximum, and similarly the O atoms in structures (II) and (III), having three lone-paris, can receive not more than three H-bonds. Hence in calculating the molecular susceptibility for the hydrogen-bonded structure, it has not been possible to make the calculation on the basis of four H-bonds per molecule of urea as found by X-ray analysis; the calculations have consequently been made for structure (I) assuming the presence of two H-bonds per molecule and for structures (II) and (III) assuming three H-bonds per molecule (i.e., taking the maximum number of H-bonds possible, according to Gray and Cruickshank's method, for the structure concerned). Table I summarises the results of calculation for the individual structures as well as for the cases A and B, with and without H-bonds.
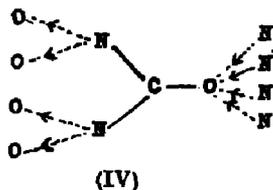
(IV)

TABLE I*

Exp. χ_M for urea = 33.60 (Pascal, *Ann. chim.*, 1912, 26, 355), 33.40 (Deveto, *Rend. Atti. Naz. Acad. Lincei*, 1932, 15, 973), 33.66 (Clow, *loc. cit.*).

Average χ_M value = 33.55.

Structure.	χ_M (Gray and without H-bonds.	Cruickshank) with H-bonds.	χ_M (Pascal).	Resonance contribution.
I	27.46	30.19	20.21 † ⎫ 27.13 ** ⎬	
II	25.48	28.19		
III	36.95	39.15		
Case A	31.82	34.48	. . . .	3/10(I)+1/5(II)+½(III)
Case B	26.67	29.80	. . . .	3/5(I)+2/5(II)

*All the susceptibility values used in this paper are to be multiplied by −10⁻⁶
†The two N atoms diamidic and the O atom ordinary double-bonded.
**The two N atoms open chain and the O atom ordinary double-bonded