

formation, and the amount of hormone dissolved increases with further increase in the concentration of the micellar substance. On greater dilution the hormone usually separates out sooner or later, and always when the critical concentration is approached. In this respect the various colloids differ considerably.

The association colloid solutions of the hormones give a small contact angle with lipid surfaces. They therefore easily wet the skin and the mucous membranes, penetrate them, and transport the solubilized hormone into the tissues and cells. In this manner it is thus possible to transfer considerable amounts of hormones into the organism. Some of these solutions can be introduced by subcutaneous or intravenous injection. The investigations concerned with the latter aspect are, however, still incomplete.

The investigations are being continued.

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1. F. Hoffmann-La Roche & Co. A.-G., Brit. Pat. 434 406 (1934), Ref. *C.A.* 1935 II 3950.
2. F. Hoffmann-La Roche & Co. A.-G., Brit. Pat. 522 834 (1940), Ref. *C.A.* 1942, 1142.
3. Friedrich, H, D.R.P. 696 594 (1940); Ref. *C.A.* 1941, 6067.
4. Lorenz, E., Shimkin, M. B., and Stewart, H. L. *J. Natl. Cancer Inst.* 1 (1940) 355.
5. Wiesner, B. P. H., and Milton, R. Brit. Pat. 515 566 (1939), Ref. *C.A.* (1941) 6067.
6. Stimmel, B. F. *Science* 98 (1943) 480.
7. Cantarow, A., Paschkis, K. E., Rakoff, A. E., and Hansen, L. P. *Endocrinology* 35 (1944) 129.
8. Ekwall, P., and Setälä, K. *Acta Chem. Scand.* 2 (1948) 733.

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The Molecular Structure of N,N'-dichloropiperazine

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Structure determinations of simple derivatives of piperazine are of interest in connection with problems related to cyclohexane and other substances containing six-membered rings. The presence of two nitrogen atoms in the ring makes the number of possible configurations attainable by a given molecule greater than it is in the corresponding cyclohexane derivative. In the case of the N,N'-dichloro compound *three* possible configurations based on the "chair" form of the ring have to be considered: the α,α , the α,ϵ and the ϵ,ϵ configuration¹.

We have measured the dipole moment of the substance in benzene solution, determined the unit cell and space group of the crystalline form and finally carried out an electron diffraction investigation of the vapour, based on the sector method.

Measurements of the dielectric constant of benzene solutions strongly indicate that the dipole moment is zero.

The crystals are monoclinic with the lattice constants:

$$a = 5.63 \text{ \AA}, b = 5.47 \text{ \AA}, c = 10.98 \text{ \AA}, \\ \beta = 94^\circ$$

The space group is $C_{2h}^5 - P2_1/c$. The unit cell contains *two* molecules and the molecules must therefore exhibit a center of symmetry in the crystalline state.

It is interesting to compare the crystallographic data with those found in the case of the 1,4-dibromocyclohexane of m. p. 112° and the corresponding diiodo-compound of m. p. 142° given in a paper published in 1932². There can be little doubt as to the isomorphism of these

substances and it seems probable that the corresponding 1,4-dichlorocyclohexane of m. p. 101° has a corresponding crystal structure. In the case of the diiodo-compound the position of the iodine atoms in the unit cell was determined in 1932, and the results of an electron diffraction investigation of the vapours of all three 1,4-dihalogenocyclohexanes in question published in 1938³ showed that even in the gaseous state the α,α configuration is the most stable one. In benzene solution the dipole moments are all zero⁴.

Before proceeding to a complete X-ray analysis of the crystals of N,N' -dichloropiperazine we have carried out an electron diffraction investigation of the vapour using the sector method. The $\frac{\sigma(r)}{r}$ -curve obtained (Fig. 1) leaves not doubt as to the correctness of the assumption that the molecular configuration corresponds very closely to that of the cyclohexane derivatives mentioned above. The position of the vertical arrows in Fig. 1 give the theoretical r -values and their height the weight factors of the inter-nuclear distances present in a molecule based on strictly tetrahedral angles and on bond distances of the expected lengths: C—C = 1.54 Å. C—N = 1.47 Å and N—Cl = 1.70 Å.

The weight factors employed are given as:

$$\frac{n Z_1 Z_2}{r}$$

n being the number of distances of a certain kind, Z_1 and Z_2 the atomic numbers

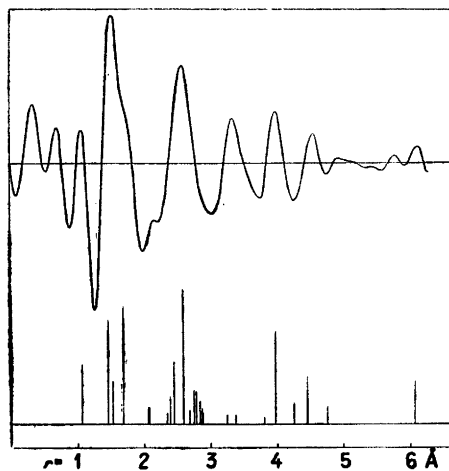


Fig. 1. $\frac{\sigma(r)}{r}$ -curve of N,N' -dichloropiperazine.

and r the atomic distance. More correct values of the weight factors may be evaluated when exact "normal curves" corresponding to given distances are at hand. So much may already be said, that the corrected values of the weight factors will explain the experimental $\frac{\sigma(r)}{r}$ -curve even better than those given in Fig. 1.

1. Hassel, O. *Research* (in publication).
2. Halmøy, E., and Hassel, O. *Z. physik. Chem. B* **16** (1932) 234.
3. Gudmundsen, J. G., and Hassel, O. *Z. physik. Chemi. B* **40** (1938) 326.
4. Halmøy, E., and Hassel, O. *Z. physik. Chem. B* **15** (1932) 472.

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