

Citation:

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somewhat smaller, and thus give rise to the dark core in some chromospheric lines.

In explaining further particulars regarding the appearance of chromospheric lines one will have to reckon with the fact, that the refracting power of the solar atmosphere is not symmetrical on both sides of an absorption line (cf. fig. 8, plate I, Proc. Roy. Acad. XII, p. 283), but on an average greater with R-light than with V-light. That asymmetry is in general greater with weak lines than with stronger ones, and must increase when we pass from the red end of the spectrum to the violet end, if the presumption proves correct, that the refracting power $R_0\Delta_0$ of the solar atmosphere for waves not belonging to a region of the spectrum where anomalous dispersion prevails, gradually increases from the red to the violet.

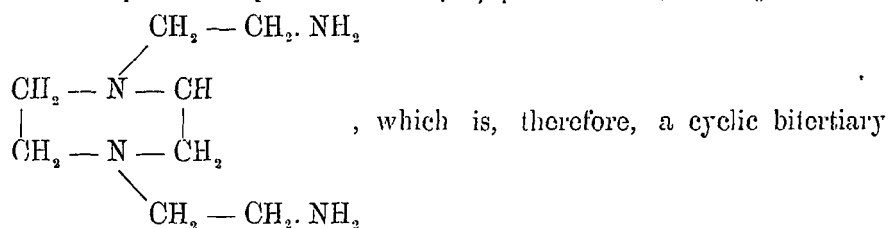
Chemistry. — “*On derivatives of piperazine.*” By Prof. FRANCHIMONT and Dr. E. KRAMER.

In October 1908 Dr. W. A. VAN DORP JR. made known the results of his research on piperazine derivatives. Among other things he had found that by the action of two mols. of formaldehyde and two mols. of hydrogen cyanide on piperazine, *piperazino N(di) acetonitrile* was obtained. From this nitrile, which in aqueous solutions gives no compounds with acids, he prepared the corresponding amide *piperazino N(di) acetamide*, which did combine with acids such as hydrogen chloride (2 mols.), and *piperazino N(di) acetic acid*, which also yielded compounds with acids. He did not succeed in preparing esters of this acid owing to the insolubility of the hydrochloride compound of the acid in alcohol.

We have now succeeded in obtaining the esters of this acid by starting from the compound of the acid with sulphuric acid; this compound contains one mol. of sulphuric acid and two mols. of water to each mol. of *piperazino N(di) acetic acid*. It was heated with an excess of sulphuric acid and alcohol and thus yielded the sulphuric acid compound of the ester, which is crystalline and soluble in water; on treatment with bases, or carbonates under a layer of ether or benzene, the sulphuric acid is abstracted. The *methyl ester* of *piperazino N(di) acetic acid* then consists of a colourless, crystallised substance m.p. 63°, soluble in water, also in ether and benzene. The *ethyl ester* m.p. 47°.5, is also crystalline and readily soluble in water, alcohol, ether, and ligroin and very readily so in benzene and chloroform. Being tertiary amines, both

not only combine with acids but also with methyl iodide but of this they only absorb one molecule; these compounds yield beautiful crystals, that of the methyl ester melts at 144° — 145° , that of the ethyl ester at 143° .

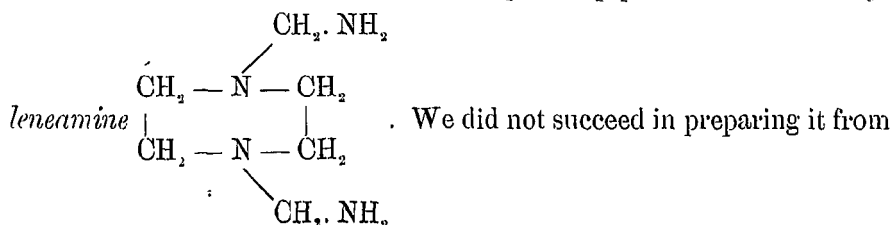
About a year ago I obtained, by the reduction of *piperazino N(di) acetonitrile* with sodium and alcohol a beautifully crystallised amine, which gave the carbylamine reaction and of which the hydrochloride and the hydroplatinichloride compounds pointed, on analysis, to the compound expected, namely *piperazino N(di) ethyleneamine*



amine, and also twice a primary amine, a combination which, as far as I am aware, is not as yet known and is being further investigated by us.

It yields with water a crystallised compound m. p. 63° (the anhydrous compound melts at 40° — 41°), which is hygroscopic and gives a white precipitate with NESSLER's reagent. With four mols. of hydrogen chloride a compound is formed which is very soluble in water and yields beautiful anhydrous crystals, which are non-hygroscopic.

Beautiful compounds are also formed with four mols. of picric acid and with four mols. of oxalic acid. When recrystallised from boiling water, the first forms golden yellow lustrous scales, the second colourless crystals sparingly soluble in cold water. With two mols. of picryl chloride it yields a picryl derivative which is very sparingly soluble in the usual organic solvents but may be recrystallised from pyridine, and then forms brownish-yellow crystals; the compound is decomposed on heating at about 238° . A benzoyl derivative was also obtained, of which more later on. As this amine behaved strangely in some respects we thought it desirable to study one of its homologues also, by way of comparison, and chose in the first place the lower compound *piperazino N(di) methyleneamine*



piperazino N(di) acetamide by applying HOFMANN's original method or the modified process and therefore chose another way, namely, the reduction of the corresponding nitrile with sodium and alcohol. This nitrile was still unknown, although we were acquainted with the co-related amide the dicarbamino-piperazine or piperazino N₂di carbonylamide (piperazyldi-urea) and the esters of the correlated acid dicarboxyalkyl-piperazine (piperazyldiurethane). The sought nitrile is N(di) cyanopiperazine or *piperazino N(di) formonitrile*. It was prepared from bromocyanogen and piperazine in aqueous solution with addition of alkali. It is sparingly soluble in cold water, but more readily so than its homologue, and insoluble in ether. It crystallises from alcohol in leaflets m.p. 168°, which shine like mother of pearl; from water it is deposited in long flat crystals with a strong lustre resembling in form the well known Gypsum troins. This nitrile, like its homologue gives, in benzene solution, a white hygroscopic precipitate with dry hydrogen chloride, which is no doubt a combination with HCl.

It does not combine with methyl iodide and (unlike its homologue) not with benzene either. In water, no compound is formed with oxalic acid.

By reduction of this nitrile with sodium and alcohol we have obtained the desired-amine, which crystallises beautifully with water. The compounds with hydrogen chloride, picric acid and oxalic acid have been prepared, and also the picryl and benzoyl derivative and will be described later on in the "Recueil des Travaux chimiques."

We may state here, however, that the amine is not decomposed on boiling with dilute sulphuric acid; in any case it does not yield ammonia and formaldehyde as might have been expected from a derivative of methylenediamine (which it certainly is).

Physics. — "*Some remarks suggested by a paper by Messrs. TIMMERMANS and KOHNSTAMM.*" By Mr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ.)

In these Proceedings Vol. XII, p. 234 in a paper by Messrs. TIMMERMANS and KOHNSTAMM some remarks occur in reference to my former papers on plaitpoint lines etc., which remarks, in my opinion, rest on a misunderstanding.

I hope later on to collect the papers published by me on the subject mentioned in a book, but I may be allowed already now briefly to refute Messrs. T. and K.'s ideas concerning the results obtained by me theoretically.