280. *The Methyleneimines: Determination of Parachor.*

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The methyleneimines resulting from the condensation of primary amines with formaldehyde were prepared pure in order that their parachors might be determined by the method of Sugden. Parachor determinations, using Sugden's constants, showed them to be cyclic trimethylenetriamines. The *iso*propyl and the *iso*butyl compound gave low parachor results. Calculation of the parachor by Mumford and Phillips's method showed that an increasing value must be given to the alkyl group attached to the nitrogen atom, rising to a maximum with the propyl derivative.

The condensation product of methylamine and formaldehyde was originally examined by Henry (*Bull. Acad. sci. Belge*, 1885, **26**, 200) who ascribed to it the formula $NMe{:}CH_2$.

As a result of the work of Brocher and Cambier (*Compt. rend.*, 1895, **120**, 449; see also Duden and Scharff, *Ber.*, 1895, **28**, 936), the cyclic formula $(NR{\cdot}CH_2)_3$ is now generally accepted for the products obtained by the condensation of the aliphatic primary amines with formaldehyde in the presence of alkalis. The property of these bases, particularly the lower members, of slow decomposition with liberation of formaldehyde, and their ready decomposition by dilute acids, but not by alkalis, suggest a possibility of the existence of an equilibrium of the type $(NR{\cdot}CH_2)_3 \rightleftharpoons 3NR{:}CH_2$.

This view is supported by the slow oxidation of the bases by air, or more rapidly by permanganate and hydrogen peroxide, to give small quantities of the corresponding *iso*cyanides, an oxidation which would not be expected to proceed if the base were wholly in the cyclic form. Ebullioscopic determinations, although in general favouring the cyclic formula, are invariably considerably below the theoretical.

In view of this uncertainty, it was deemed advisable to measure the parachors of the pure liquids. In addition, since Mumford and Phillips (J., 1929, 2112) were unable to confirm their view that " the differing strain in heterocyclic compounds might be expected to show in the deviation of their parachors from the normal " owing to lack of data, it seemed that the present series would exhibit such constitutive variations if real.

EXPERIMENTAL.

Preparation of the Bases.—All the bases used, except the *iso*propyl compound, have been previously described (J., 1931, 1490; 1932, 1353; 1935, 865).

*iso*Propylamine was prepared from acetone by reduction of its phenylhydrazone with sodium amalgam in alcohol–acetic acid solution, but the yield was much smaller than stated (Tafel, *Ber.*, 1886, **19**, 1926). The amine (1 mol.) was added slowly with cooling to formaldehyde (40%; 2½ mols.). Rise of temperature occurred with each addition, and the product which first formed dissolved. Finally, it formed an emulsion, and separated as an oily layer on the surface on the addition of excess alkali. It was left for 24 hrs. with intermittent shaking in order to complete the separation. The iso*propylmethyleneimine* was removed by extraction with ether, the extract dried (barium oxide), the ether removed, and the residue carefully distilled. It was obtained as a colourless oil, b. p. 220°, $d^{18°}$ 0·8961 [Found: N, 19·7; *M*, 196. $(C_4H_9N)_3$ requires N, 19·7%; *M*, 213].

Purification of the Bases.—The results obtained with the bases prepared as described above gave preliminary parachor values some 6 units below those calculated for the cyclic structure on the basis of Sugden's constants. Since the bases had been prepared some time previously and a distinct smell of *iso*cyanide was noticeable, they were redistilled from barium oxide, traces of a low-boiling product with a strong *iso*nitrile smell being removed. When low results were obtained in later determinations of a series, such products were always present in the base. The accuracy is thus affected by these traces of oxidation product, so great care was taken to obtain consistent results by distillation immediately before use, and also after a few readings were taken.

Parachor Determinations and Calculation.—The surface tension was measured by the method of maximum bubble pressure (J., 1922, **121**, 855; 1924, **125**, 27) with a cell of the Sugden type. The apparatus was calibrated by benzene, purified by freezing and fractionation. The diameter of the wide tube was 0·205 cm., and the cell constants ($A \times 10^3$) were : series I 7·033; series II 6·840; series III 6·811. The gauge contained a dilute solution of magenta in alcohol. The rate of bubbling was adjusted so as to give a clearly distinguishable rise to a strictly reproducible maximum in each case. The temperatures of the gauge and bubbler were varied independently. Density was measured by a pyknometer, of bulb capacity about 9·4 c.c., calibrated over a range of temperature by means of pure mercury, and checked by boiled-out water.

Parachors have been calculated from the formula $[P] = M\gamma^{\frac{1}{4}}/D$, in which the terms have their usual significance. The results are recorded in cols. 1—6 of the table, the subscript I referring to the open-chain structure $NR{:}CH_2$, and II referring to the ring structure $(NR{\cdot}CH_2)_3$.

DISCUSSION.

Examination of the differences based on Sugden's constants (cols. 7—10) makes it clear that the results are decidedly in favour of the cyclic structure for the compounds when the " calculated " values are derived from these constants. The small differences

						S.'s constants.				M. and P.'s constants.	
				$[P]$, obs.		$[P]$, calc.		Diff.		$[P]$, calc.	
R.	$d^{18°}$.	$\gamma^{18°}$.	M_{II}.	I.	II.	I.	II.	I.	II.	II.	Diff.
Me	0·9218	30·17	129·1	109·4	328·3	130·8	328·9	−21·4	− 0·6	339·5	−11·2
Et	0·8958	29·00	171·2	147·8	443·5	169·8	445·9	−22·0	− 2·3	459·5	−16·0
Pr	0·8799	28·71	213·2	187·0	560·9	208·8	562·9	−21·8	− 2·0	579·5	−18·6
Bu	0·8723	29·29	255·3	227·0	680·9	247·8	679·9	−20·8	+ 1·0	699·5	−18·6
Pr^{β}	0·8961	29·11	213·2	184·2	552·8	208·8	562·9	−24·6	−10·1	570·5	−17·7
Bu^{β}	0·8578	26·23	255·3	222·4	673·4	247·8	679·9	−25·4	− 6·5	690·5	−17·1

S = Sugden; M = Mumford and Phillips.

existing between observed and calculated values for the cyclic structure (cols. 6 and 8) do not appear to give any real evidence in favour of the existence of an equilibrium between the two forms in the pure liquids. The *iso*-compounds show the deviation from the normal which is usual in this type of compound.

When the parachors for the polymeric form are calculated on the basis of Mumford and Phillips's standards (col. 11), it is found that the differences in the last column are much greater than those in col. 10. An allowance of — 3·0 units is included in the calculation of the parachor for a branched chain, making a total allowance of — 9·0 units in each of the two *iso*-compounds examined. Since a normal value of 0·8 may be assigned to the six-membered ring in piperidine (Mumford and Phillips, *loc. cit.*), it was assumed that the same value would be applicable to the parent base, cyclic methyleneimine, $(NH{\cdot}CH_2)_3$, which has not yet been prepared

Consequently, it will be necessary to introduce a strain constant of — 3·0 units for each grouping in which hydrogen originally attached to nitrogen is replaced by an alkyl group, making a total of — 9 units for each compound. The differences recorded in the last column show a variation even after this correction, suggested by Mumford and Phillips, has been made. The difference is slight for the methyl derivative, but increases on ascending the series to a maximum with the *n*-propyl derivative.

Beck, Macbeth, and Pennycuick (J., 1932, 2258) proved that the monosubstituted malonic esters show a decrement which increases to a maximum with the butyl derivative. The decrement was even greater in the case of the disubstituted esters. They suggested that the constitutive effect might be attributed to the consequent decrease in the angle between two carboxyl groups, caused by the substitution of methylenic hydrogen by alkyl groups.

In the present cases we may assume that, in substituting the hydrogen attached to the nitrogen atom in the six-membered ring $(CH_2{\cdot}NH)_3$ by larger groups, these groups, as suggested by Ingold and Thorpe (J., 1921, **119**, 306), tend to reduce the valency angle in the ring, thus setting up a strain which increases in magnitude on ascending the series as far as the propyl derivative. It is not unreasonable to postulate a maximum with the propyl base, for it is readily seen that with this derivative the alkyl chain approaches most nearly to the hydrogens of the adjacent CH_2 groups within the ring, thus setting up a maximum strain : as expected, the *iso*-compounds with shorter chains should show a smaller decrement.

It is noteworthy that the maximum decrement of about 18 units approximates closely to that which might be assigned to a tritertiary amine.

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