361. *The Apparent Dipole Moment of Hexamethylenetetramine in Chloroform Solution.*

By R. J. W. Le Fèvre and G. J. Rayner.

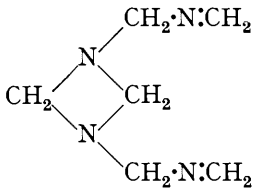
Although Duden and Scharff's formula (1895) for hexamethylenetetramine—in which the four nitrogen atoms are situated at the apices of a regular tetrahedron—has been shown to be compatible with *X*-ray examinations of the *solid* (Gonell and Mark; Dickinson and Raymond; 1923) and with electron-diffraction studies of the *vapour* (Hampson and Stosick, 1938), it is not reconciled easily with many of the chemical reactions of this substance in *solution*.

Dipole-moment measurements now described suggest that the tetramine molecule dissolved in chloroform is non-polar, and therefore has a symmetrical structure. Some physical evidence is thus provided permitting the Duden–Scharff model for the dissolved state, as well as the solid and the gaseous. Raman displacements are recorded for solutions of hexamine in both water and chloroform.

The Formula of Hexamethylenetetramine.—This apparently monoacid base crystallises in colourless rhombohedra, dissolves extensively in water but less in chloroform and alcohol, and is insoluble in ether and the usual non-polar solvents. It sublimes or melts at a high temperature, 280—300°, which exceeds the m. p. of many quaternary ammonium salts and is unexpected for a molecule where electrovalencies are not likely to be operative. The chemical properties do not provide unequivocal evidence: it can take up directly 2 or 4 atoms of bromine or iodine (Horton, *Ber.*, 1888, **21**, 2000; Legler, *ibid.*, 1885, **18**, 3350) and will combine with only one molecule of alkyl halide or a half molecule of alkylene dihalide (Wohl, *Ber.*, 1886, **19**, 1843; Delépine, *Bull. Soc. Chim.*, 1897, **17**, 293); yet with

nitrous acid it yields trimethylenetrinitrosoamine, or with nitric acid, trimethylenetrinitroamine.

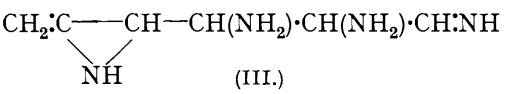
Various formulæ have been suggested, each covering certain of the chemical reactions: (I) (Guareschi, " Alkaloide," Berlin, 1896, p. 620); (II) (Lösekann, *Chem. Zentr.*, 1890, **14**, 1409; Grassi and Motta, *Gazzetta*, 1899, **29**, i, 33); (III) (Cohn, *J. pr. Chem.*, 1897, **56**, 345); (IV) (van't Hoff; cf. Delépine, *Ann. Chim.*, 1898, **15**, 523); (V) (Duden and Scharff, *Annalen*, 1895, **288**, 218). The problem has never been settled finally, and in 1935 the formula (VI) was proposed by Dominikiewicz (*Arch. Chem. Farm.*, **2**, 78) to meet the needs of certain acylation reactions; the modern interpretation of (VI) is referred to on p. 1923.



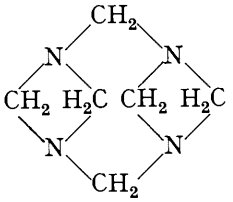
(I.)

$N(CH_2{\cdot}N{:}CH_2)_3$

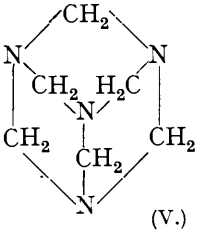
(II.)



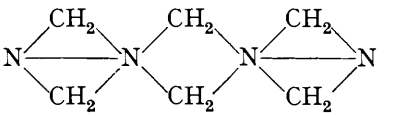
(III.)



(IV.)



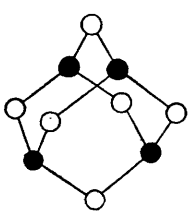
(V.)



(VI.)

Formula (V) when erected in three dimensions is a symmetrical structure (Fig. 1) in which the four nitrogen atoms are situated with their centres at the apices of a regular tetrahedron and the six carbon atoms at the points of a regular octahedron. Such a distribution of atoms is reported to be congruent with *X*-ray data for crystalline hexamine (Dickinson and Raymond, *J. Amer. Chem. Soc.*, 1923, **45**, 22; Gonell and Mark, *Z. physikal. Chem.*, 1923, **107**, 181) and with an electron-diffraction study of vapourised hexamine (Hampson and Stosick, *J. Amer. Chem. Soc.*, 1938, **60**, 1814). Consequently, other formulæ seem less likely to be correct, although in the dissolved state the possibility of structural modification occurring by solvation must not be forgotten.

FIG. 1.



Present Work.—Chloroform, in a mixture containing it, and provided no combination takes place (as in the examples of Earp and Glasstone, J., 1935, 1709), has a polarisation which is practically independent of concentration or state (Le Fèvre and Le Fèvre, J., 1935, 1747), a fact which allows its polarisation contribution to a solution to be calculated for different concentrations by the usual mixture rules. Its suitability as a medium for dipole-moment determination is, however, diminished by uncertainties regarding its polarising effects on the solute molecules. Known experimental data illustrate this; *e.g.*, benzene ($[R_L]_D$, 26 c.c.) in chloroform has a polarisation of 28 c.c. (Le Fèvre and Le Fèvre, J., 1936, 487) and as a gas 27 c.c. (McAlpine and Smyth, *J. Amer. Chem. Soc.*, 1933, **55**, 453); on the other hand, *p*-dinitrobenzene ($[R_L]_D$, 39 c.c.) has a polarisation of 34—39 c.c. in chloroform (Le Fèvre and Le Fèvre, J., 1935, 957; Jenkins, J., 1936, 862) but one of 46·5 c.c. in the vapour state (Coop and Sutton, this vol., p. 1269).

Nevertheless, noting that with both benzene and its *p*-dinitro-derivative the measurements in chloroform led to correct conclusions regarding molecular structure, we thought it worth while to obtain the data now to be recorded for hexamine.

The following table summarises the dielectric polarisation measurements: w_1 is the

weight fraction, ε the dielectric constant at *ca.* 1200 kc., d the density and p_{12} the specific polarisation of the solution.

Hexamethylenetetramine in Chloroform.

$100w_1$.	ϵ.	$d_{4°}^{t°}$.	p.	$100w_1$.	ϵ.	$d_{4°}^{t°}$.	p.
	Temp. 25°.				Temp. 35°.		
0	4·7240*	1·47899	0·37447	0	4·5520*	1·46060	0·37116
1·2805	4·6909	1·47663	0·37357	2·8550	4·4826	1·45610	0·36894
2·2267	4·6640	1·47493	0·37278	3·2520	4·4755	1·45606	0·36861
2·5010	4·6552	1·47440	0·37251	4·6200	4·4411	1·45290	0·36770
2·8550	4·6417	1·47360	0·37208				
3·2520	4·6312	1·47325	0·37169		Temp. 45°.		
4·3370	4·6006	1·47107	0·37082	0	4·3950*	1·44190	0·36818
4·6200	4·5887	1·47010	0·37050	2·8550	4·3353	1·43810	0·36608
				3·2520	4·3252	1·43744	0·36572

* From Ball (J., 1930, 595).

From these data, the total polarisations at infinite dilution have been calculated as $M(\mathrm{d}p_{12}/\mathrm{d}w_1 + p_2)$, where M is the molecular weight of hexamine (140·2) and $\mathrm{d}p_{12}/\mathrm{d}w_1$ is the quotient $\Sigma(p_{12} - p_2)/\Sigma w_1$.

Total Polarisations at Infinite Dilution.

Temp.	25°	35°	45°
$\mathrm{d}p_{12}/\mathrm{d}w_1$	−0·082	−0·077	−0·075
${}_{\infty}P_1$, c.c.	41·0	41·2	41·0

The molecular refraction of hexamine does not appear to have been previously determined; the necessary observations relating to solutions in (*a*) chloroform and (*b*) water are therefore recorded.

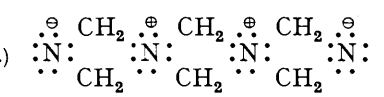
Molecular Refraction of Hexamethylenetetramine.

$100w_1$.	$d_{4°}^{t°}$.	$n_D^{25°}$.	r_{12}.	$[R_L]_D$.	$100w_1$.	$d_{4°}^{t°}$.	$n_D^{25°}$.	r_{12}.	$[R_L]_D$.
	(a) *Chloroform as solvent*, t = 25°.					(b) *Water as solvent*, t = 18°.			
0	1·47899	1·44310	0·17929	—	0	0·99862	1·33307*	0·20602	—
1·2805	1·47663	1·44582	0·18053	38·7	4·4444	1·00825	1·34063	0·20824	35·9
2·2267	1·47493	1·44723	0·18124	37·4	5·6238	1·01081	1·34244	0·20872	35·6
2·5010	1·47440	1·44757	0·18143	37·1	7·1011	1·01405	1·34503	0·20947	35·7
4·3370	1·47107	1·45012	0·18273	36·2	8·1899	1·01652	1·34693	0·21000	35·7

* Schreiner (*Z. physikal. Chem.*, 1928, **133**, 423) gives $n_D^{12°}$ 1·33308.

These results are somewhat lower than that calculated, *viz.*, 39·7 c.c. (from $CH_2 = 4·26$, tertiary N = 3·00; Eisenlohr, *Z. physikal. Chem.*, 1910, **75**, 605; Brühl, *ibid.*, 1912, **79**, 1; 1895, **16**, 479), and the measurements in chloroform show an unusual concentration dependence. For the estimation of the dipole moment, some allowance must be made for the atomic polarisation; if, following Sugden (*Trans. Faraday Soc.*, 1934, **30**, 734), we assume for this large molecule what is true for many substances, that the atomic and electronic polarisation sum is 1·05 × $[R_L]_D$, then,* if $[R_L]_D$ is taken as 39 c.c., this distortion polarisation is evidently of the same order as the experimentally observed total polarisations, *i.e.*, hexamethylenetetramine has a moment approaching zero.

Discussion.—Only formulæ (IV), (V), and (VI) are likely to correspond to the required non-polar molecules, since they alone possess the necessary symmetry, but our result cannot decide between these beyond indicating the improbability of (VI). This must presumably be a quadrapole with two kationic charges situated on the two inner, and two anionic charges on the two outer, nitrogen atoms, the complete structure having the four nitrogens collinear. This is illustrated in the adjoining electronic formula (VII). Such an arrangement with opposed dipoles would most probably cause anomalous polarisation effects (similar to those

(VII.) 

* Such an approximation is probably safe in the present instance since it adequately covers the case of trimethylamine as a vapour (Le Fèvre and Russell, *Nature*, 1938, **142**, 617).

shown by, *e.g.*, *p*-benzoquinone in benzene; J., 1935, 1698) which the quantitative treatments of Jenkins (J., 1936, 910), Bauer (*J. Chem. Physics*, 1936, **4**, 458), and Frank and Sutton (*Trans. Faraday Soc.*, 1937, **33**, 1307) show to vary as the *square* of the individual moments concerned (cf. however, the most recent treatment of this problem; Coop and Sutton, *loc. cit.*). In the case of benzoquinone, with two >C=O link moments of 2—3 D., an anomalous orientation polarisation of *ca.* 10 c.c. has been observed. Since hexamine is 1·5 times as large as benzoquinone and, on the basis of (VI), would have two exceedingly great dipoles (5—10 D. ?) not less flexibly held than the C=O groups of benzoquinone, it can be safely concluded that the present measurements show such anomalies to be absent. Formulæ (IV) and (V) therefore remain.

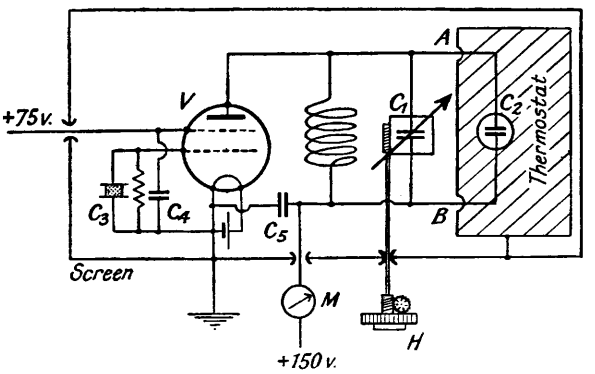
Of these, the latter is favoured by the Raman spectra of hexamethylenetetramine in either water or chloroform solutions. Mr. C. R. Bailey has directed our attention to the fact that a tertiary nitrogen atom, in this spectroscopy, is often very like a methylene group. Accordingly, it is satisfactory to find that the two sets of Raman displacements now recorded agree closely with the published descriptions of the same properties of *cyclo*hexane (Kohlrausch and Stockmair, *Z. physikal. Chem.*, 1936, *B*, **31**, 382); from this we infer that hexamine contains six-membered rings only, so that (IV)—with two four rings, and one eight ring—is less probably correct.

Incidentally, the Raman spectra are of interest in suggesting that the solute is essentially the same in *both* the solvents used; this is a conclusion which, in view of the various reactions effected by reagents in aqueous solution which seem to be incompatible with Duden and Scharff's structure (V), definitely required to be established.

Experimental.

Apparatus.—The dielectric-constant measurements were obtained with the help of an apparatus different from that used in previous work in this department. It is based directly on one of the two standard forms of the Pearce quartz-maintained oscillator in which the grid of a triode is connected to the earthed side of the filament through a small condenser, the dielectric of which is a section of a quartz crystal, shunted by a high resistance of several megohms, while the anode circuit contains inductance and capacity and is tuned. If a current meter is

Fig. 2.



inserted in the anode H.T. lead, a fairly sudden change in reading will be observed when the anode circuit is tuned through the natural frequency of the quartz. If now a condenser, whose dielectric can be varied, is connected in parallel to the variable condenser, a comparison of capacities, giving dielectric constants, is possible because the *total capacity*, being always constant for a given setting of the current meter at the inflexion point, will require that capacity increases in one condenser shall be compensated for by decreases in the other and *vice versa*. Owing probably to their lower inter-electrode capacities, screened-grid valves and especially pentodes have been found to give far steeper and sharper current–capacity curves than ordinary triodes. In the present apparatus, shown diagrammatically in Fig. 2, a valve of the former type has been employed.

Components used. Valve (*V*) Mullard PM 12, 2v, screened grid; inductance (*L*), 31 turns

of 22 s.w.g. d.c.c. copper wire on an 8·3 cm. (diam.) former. The condenser C_1 is an approximately 250 μμF. variable semi-circular plate instrument fitted with a worm-geared extension handle terminating in a graduated drum head (*ca.* 4″ diam.) and revolution counter (*H*). The capacity of this condenser was proportional to the setting of the moving vanes over the central three-fifths of the scale; accordingly its use has been restricted to within this limit, and readings simply taken in units of " turns of the rotating head " (*H*). These could easily be set with a 5 milliamp. meter for *M* to less than 1/200 of a turn, while the available part of the scale was covered in 35—40 turns. The condenser C_2 was of the Sayce–Briscoe type (J., 1925, **127**, 315), slightly modified to permit complete immersion in the thermostat and having long side arms to enable it to be filled and emptied by air pressure or suction without any alteration of its position being necessary. The whole apparatus was surrounded by an earthed zinc-gauze screen.

The Raman Spectra.—These were investigated by Mr. T. I. Williams, using the experimental arrangement described by Angus, Ingold, and Leckie (J., 1936, 925). The exposure times were 24—48 hours; the errors in the lines below probably do not exceed 6 cm.$^{-1}$. In the following table the observed displacements are given in cm.$^{-1}$ (exciting sources: 4358 and 4047 A. mercury lines); the figures in parentheses are the visually estimated intensities. The plates were similar when either water or chloroform was used as solvent.

326 (1)	678 (2)	1340 (2)	1920 (½)	2949 (1)
449 (1)	777 (½)	1368 (2)	2750 (½)	2981 (½)
504 (2)	813 (4)	1446 (1)	2890 (2)	3161 (1)
551 (1)	1044 (2)	1846 (½)	2922 (3)	

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