View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1954 on http://pubs.rsc.org | doi:10.1039/JR9540004476
Downloaded by Brown University on 20 December 2012

Triethylenediamine (1 : 4-*Diaza*bicyclo[2 : 2 : 2]*octane*) *and Hexaethylenetetramine. Part II.* The Properties of* 1 : 2 : 2 : 4 : 5 : 5-*Hexamethylpiperazine.*

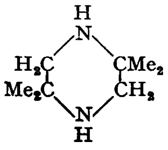
By Frederick G. Mann and Alwyn Senior.

[Reprint Order No. 5581.]

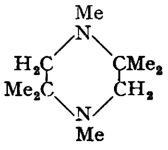
The above hexamethylpiperazine shows many of the normal properties of a 1 : 4-dialkylpiperazine, and will readily combine with 1 and 2 equivalents of many simple alkyl quaternising agents. But whereas 1 : 4-dimethylpiperazine readily combines with ethylene dibromide to give triethylenediamine dimethobromide, the hexamethylpiperazine reacts with this and other alkylene dibromides to give the dihydrobromide of the piperazine. The reasons for this striking difference in properties are briefly discussed.

We have investigated in considerable detail the combination of 1 : 4-dialkylpiperazines with ethylene, trimethylene, and *o*-xylylene dibromides to form polycyclic quaternary salts, and the various products to which these salts give rise on thermal decomposition. In the course of the dibromide work, we attempted unsuccessfully to combine 1 : 2 : 2 : 4 : 5 : 5-hexamethylpiperazine (II) with ethylene dibromide to give the dibromide (III; R = Me), which should have been susceptible to optical resolution : in view of the work on (II) recently described by McElvain and Bannister (*J. Amer. Chem. Soc.*, 1954, **76**, 1126), our more extensive results obtained with this base are now briefly recorded.

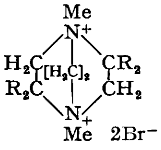
We have prepared 2 : 2 : 5 : 5-tetramethylpiperazine (I) by Conant and Aston's method (*ibid.*, 1928, **50**, 2783), whereby *iso*butyraldehyde is converted by ferricyanide oxidation into 2 : 5-dihydro-2 : 2 : 5 : 5-tetramethylpyrazine which on hydrogenation gives the piperazine (I); the latter, when methylated with formaldehyde in formic acid, gave 1 : 2 : 2 : 4 : 5 : 5-hexamethylpiperazine (II).



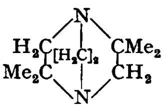
(I)



(II)



(III)



(IV)

This compound (II) has many of the normal properties of a 1 : 4-dialkylpiperazine : the tertiary amine groups combine with acids to form normal salts (of which several have been prepared for crystallographic examination) and, more particularly, undergo ready quaternisation with alkyl halides, and thus the mono-methobromide and -methiodide and the dimetho-bromide, -iodide, -(methyl sulphate) and -toluene-*p*-sulphonate have been isolated. In striking contrast, however, the compound (II) when heated with ethylene, trimethylene, and *o*-xylylene dibromides affords in all cases the dihydrobromide of (II), and cyclisation to compounds of type (III) could not be detected, although 1 : 4-dimethylpiperazine and ethylene dibromide readily combine to form triethylenediamine dimethobromide (III; R = H) (Mann and Mukherjee, *J.*, 1949, 2298). The only indication of quaternisation of (II) with an alkylene dibromide was obtained by exposing a mixture of (II) and ethylene dibromide to sunlight at room temperature for a week, when ethylenebis-(1 : 2 : 2 : 4 : 5 : 5-hexamethyl-1-piperazinium) dibromide (V; X = Br) was formed. This reaction with ethylene dibromide is strictly analogous to that shown by hexahydro-1 : 4-diphenyl-1 : 4-azarsine and -1 : 4-azaphosphine (Beeby and Mann, *J.*, 1951, 886 : Mann and Miller, *J.*, 1952, 3039).

McElvain and Bannister (*loc. cit.*) also obtained the dihydrobromide of (II) by the

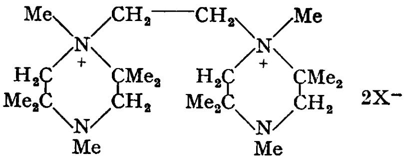
---

* Part I, *J.*, 1949, 2298.

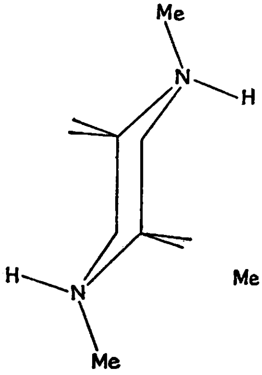
View Article Online

Published on 01 January 1954 on http://pubs.rsc.org | doi:10.1039/JR9540004476
Downloaded by Brown University on 20 December 2012

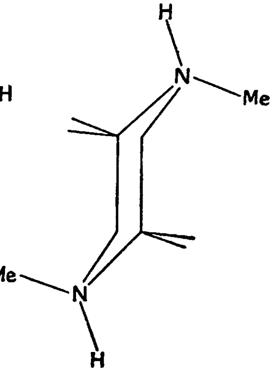
action of hot ethylene dibromide: they claim however to have obtained the dipicrate of the tertiary amine (IV) in 0·15% yield by the pyrolysis of 1-2′-bromoethyl-2 : 2 : 5 : 5-tetramethylpiperazine dihydrobromide.



(V)



(VI*A*)



(VI*B*)

The reason for this striking difference in behaviour of 1 : 4-dimethyl- and 1 : 2 : 2 : 4 : 5 : 5-hexamethyl-piperazine (II) towards alkylene dibromides remains uncertain. A plausible explanation is that 1 : 4-dimethylpiperazine exists as an equilibrium mixture of the Z and the C form, and that the latter form could readily give the above cyclisation, whereas in the hexamethylpiperazine (II) the two *gem*-dimethyl groups " lock " the molecule in the Z form, which clearly could not give this cyclisation. It is noteworthy that an *X*-ray crystal examination of hexamethylpiperazine dinitrate, carried out by Dr. W. Cochran in the Cavendish Laboratory of the University of Cambridge, shows that the molecule has a centre of symmetry, and therefore the cation must have the Z conformation with *trans*-*N*-Me groups, *i.e.*, (VI*A*) or (VI*B*): clearly however this conformation may not be retained by the cation in solution, or be that of the liquid base. [Incidentally, the orientation of the methyl groups in (II), although placed beyond reasonable doubt by various syntheses of (I), is thus independently confirmed.] Dr. J. Chatt, of the Butterwick Research Laboratories (Imperial Chemical Industries Limited), has kindly determined the dipole moments of the liquid bases, and finds that the dimethyl- and hexamethyl-piperazine in benzene solution have moments (μ) of 0·53 and 0·63 D respectively. The full significance of these results is also difficult to assess. Even if the hexamethylpiperazine were " locked " in the Z form, the oscillation of the *N*-methyl groups about the nitrogen atom [*i.e.*, between positions almost identical with those occupied by the *N*-Me and the *N*-H groups in the cations (VI*A*) and (VI*B*)] would produce a small but finite moment, as in *p*-dimethoxybenzene. In the dimethylpiperazine, this factor, in addition to the uncertain degree of equilibrium of two forms, prevents assessment of an expected value.

A model of the hexamethylpiperazine (II), constructed with the C conformation, shows no indication of steric hindrance of the nitrogen atoms, and this is confirmed by the model of the cation (III; R = Me), which is free from strain and obstruction. Although decisive evidence is lacking, it appears therefore that the abnormal behaviour of (II) is due to a locked Z conformation.

McElvain and Bannister (*loc. cit.*) suggest that the formation of a bridged diquaternary salt with ethylene dibromide is effectively prevented by the presence in the 1 : 4-disubstituted piperazine molecule of (*a*) a *gem*-dimethyl group adjacent to the nitrogen atoms, or (*b*) substituent groups larger than methyl groups in the 1 : 4-positions. This is not strictly true, however, for we find that 1 : 4-diethylpiperazine readily gives this reaction with ethylene dibromide.

EXPERIMENTAL

All compounds, unless otherwise stated, were colourless. The m. p.s of several salts varied greatly according to (*a*) the immersion temperature, noted as (I.T.), and (*b*) the use of an open or an evacuated sealed capillary tube, noted as (O.T.) and (E.T.) respectively; in these cases

View Article Online

Downloaded by Brown University on 20 December 2012
Published on 01 January 1954 on http://pubs.rsc.org | doi:10.1039/JR9540004476

the conditions are stated in full. M. p.s recorded without qualification were determined in an open tube heated from room temperature.

1 : 4-*Dimethylpiperazine*.—Pollard and Forsee (*J. Amer. Chem. Soc.*, 1935, **57**, 1788) claim to have prepared this base in 88% yield by the action of formaldehyde, zinc, and hydrochloric acid on piperazine, followed by ether-extraction. We find, however, that the marked volatility of the base in boiling ether causes low yields. The following method has therefore been employed. A mixture of piperazine (80 g.), formic acid (520 c.c.), and 40% formaldehyde (320 c.c.) was boiled under reflux for 10 hr., diluted with water (100 c.c.) and concentrated hydrochloric acid (100 c.c.), and considerably concentrated by distillation: the thoroughly chilled residue was basified with aqueous sodium hydroxide and distilled in steam. The distillate (*ca.* 70 c.c.) was made strongly alkaline by the addition of solid potassium hydroxide, and the dimethylpiperazine which separated was collected, dried again with the solid hydroxide, and distilled, having b. p. 130—132° (57 g., 54%).

It gave a dihydrochloride (from ethanol), m. p. 265—266° (effervescence) (Found: C, 38·4; H, 8·85; N, 14·75. Calc. for $C_6H_{14}N_2,2HCl$: C, 38·5; H, 8·6; N, 14·9%), a *dihydrobromide* (from ethanol), m. p. 248° (O.T.), 232—234° (E.T.) (Found: C, 25·9; H, 5·6; N, 10·2. $C_6H_{14}N_2,2HBr$ requires C, 26·1; H, 5·8; N, 10·15%), a dipicrate, yellow crystals which when washed with water, but not recrystallised, had m. p. 297° (vigorous decomp.) (Found: C, 38·1; H, 3·3; N, 19·9. Calc. for $C_6H_{14}N_2,2C_6H_3O_7N_3$: C, 37·9; H, 3·2; N, 19·65%), a *dimethobromide* (from the base with methyl bromide in a sealed tube at 100° for 4 hr.; crystallised from water), m. p. above 370° (O.T.), 345—347° (decomp.) (E.T.) from room temperature, 364° (decomp.) (E.T., I.T. 337°) (Found: C, 31·8; H, 6·4; N, 9·0. $C_8H_{20}N_2Br_2$ requires C, 31·6; H, 6·6; N, 9·2%), a *dimethopicrate* (washed with water but not recrystallised), m. p. 301—306° (O.T.), 295—300° (E.T.) from room temperature, and 311° (O.T.), 310° (E.T., I.T. 290°), all with vigorous decomp. (Found: C, 40·0; H, 4·2; N, 18·6. $C_{20}H_{24}O_{14}N_8$ requires C, 40·0; H, 4·0; N, 18·7%), and a dimethiodide (from water), m. p. 310° (decomp.) (I.T. 290°) (Found: C, 24·2; H, 5·1; N, 6·7. Calc. for $C_8H_{20}N_2I_2$: C, 24·1; H, 5·1; N, 7·0%).

2 : 2 : 5 : 5-*Tetramethylpiperazine* (I).—This base gave a dihydrochloride (from concentrated hydrochloric acid), m. p. >370° (O.T.) or (E.T.) (Found: C, 44·7; H, 9·1. Calc. for $C_8H_{18}N_2,2HCl$: C, 44·65; H, 9·3%), a dibenzoyl derivative, m. p. 274° (Found: C, 71·4; H, 7·9. Calc. for $C_{22}H_{26}O_2N_2,H_2O$: C, 71·7; H, 7·7%), and a dinitroso-derivative, m. p. 208—210° (from dilute acetic acid). For the first two of these derivatives McElvain and Pryde (*J. Amer. Chem. Soc.*, 1949, **71**, 326) give m. p. >310° and 273—276° respectively, and for the third Conant and Aston (*loc. cit.*) give m. p. 208—210°. We find, contrary to Drew and Head (*J.*, 1934, 49) and in accordance with McElvain and Pryde, that the dihydrochloride is almost completely insoluble in ethanol.

1 : 2 : 2 : 4 : 5 : 5-*Hexamethylpiperazine* (II).—This base, prepared from (I) as stated, was isolated initially in 95% yield as the dihydrochloride, which crystallised from ethanolic hydrochloric acid (Found: C, 49·5; H, 9·7; N, 11·4. Calc. for $C_{10}H_{22}N_2,2HCl$: C, 49·4; H, 9·9; N, 11·5%). The salt darkens at *ca.* 333° and sublimes at 375—385° (O.T.) from room temperature but sublimes at 352—360° (O.T., I.T. 327°) and 352—370° (E.T., I.T. 327°). McElvain and Bannister (*loc. cit.*) give m. p. >250°.

The free base, obtained from this salt by basification, ether-extraction, and distillation, had b. p. 70—71°/11 mm., m. p. 26—27° (Found: C, 70·75; H, 13·0; N, 16·65. Calc. for $C_{10}H_{22}N_2$: C, 70·6; H, 12·95; N, 16·5%). It gave the following salts.

The *dipicrate*, when recrystallised from dimethylformamide, washed with methanol, and dried at 50°/0·1 mm. for 6 hr., afforded yellow crystals, m. p. 275° (Found: C, 42·55; H, 4·1; N, 18·0. Calc. for $C_{10}H_{22}N_2,2C_6H_3O_7N_3$: C, 42·05; H, 4·5; N, 17·7%). McElvain and Bannister gave m. p. 264—265° (decomp.). The *diperchlorate* formed crystals from water (Found: N, 7·8. $C_{10}H_{22}N_2,2HClO_4$ requires N, 7·6%), decomposing violently at 262°. The *dichloroaurate*, recrystallised from water, gave yellow crystals, m. p. >370° (Found: C, 14·2; H, 3·0. $C_{10}H_{22}N_2,2HAuCl_4$ requires C, 14·1; H, 2·9%). The *dinitrate* was prepared by the addition of 50% nitric acid to the free base, and when recrystallised from methanol–dilute nitric acid gave crystals, m. p. 156° from room temperature, and 174° (O.T., I.T. 161°), 182° (E.T., I.T. 161°) (Found: C, 40·8; H, 8·1; N, 18·6. $C_{10}H_{22}N_2,2HNO_3$ requires C, 40·6; H, 8·2; N, 18·9%).

For the dinitrate Dr. Cochran reports " Oscillation of the photographs of the crystals taken with copper radiation (λ = 1·54 Å) show that they are monoclinic with a = 14·8, b = 6·4, c = 8·0 Å (±2%). Weissenberg photographs taken with the crystal rotated about each of the b and c axes in turn confirm these unit-cell dimensions, and give β = 96° ± 1°. They also show the systematic absences: ($0k0$) when k is odd; ($h0l$) when $h + l$ is odd. The space group is

View Article Online

Published on 01 January 1954 on http://pubs.rsc.org | doi:10.1039/JR9540004476
Downloaded by Brown University on 20 December 2012

therefore $P2_1/n$, which is a centrosymmetric space group. If there are two molecules per unit cell, the molecule must also be centrosymmetric.

"We have $d = 1{\cdot}66Mz/v$ where d = density, M = molecular weight (296·3), and $v = 14{\cdot}8 \times 6{\cdot}4 \times 8{\cdot}0 \times \sin 96° = 750$ Å^3.

"If we take $z = 2$, then $d = 1{\cdot}3$ g./c.c., but if $z = 4$, $d = 2{\cdot}6$ g./c.c. The latter value is impossible, the former very reasonable. The molecule is therefore centrosymmetric."

The *monomethobromide* was readily formed in a solution of the base in methyl bromide at 18°, and, recrystallised from methanol, had m. p. 309° (decomp. and partial sublimation) (Found: C, 49·6; H, 9·35; N, 10·4. $C_{11}H_{25}N_2Br$ requires C, 49·8; H, 9·5; N, 10·6%). The *dimethobromide* was formed when the above solution was heated in a sealed tube at 100° for 4 hr., and after crystallisation from methanol formed a *hemihydrate*, m. p. 300° (with sublimation) (Found: C, 39·4; H, 7·8; N, 7·6. $C_{12}H_{28}N_2Br_2,0{\cdot}5H_2O$ requires C, 39·0; H, 7·9; N, 7·6%). The monomethiodide was obtained by boiling a solution of the base in methanolic methyl iodide, and after crystallisation from methanol had m. p. 318° (decomp.) (O.T.) from room temperature and 317° (with sublimation) (E.T., I.T. 306°) (Found: C, 42·6; H, 8·1; N, 9·15. Calc. for $C_{11}H_{25}N_2I$: C, 42·3; H, 8·1; N, 9·0%). The dimethiodide, prepared as the dimethobromide, and dried at 60°/0·1 mm. for 6 hr., formed a *monohydrate*, crystals, m. p. 260—262° (much preliminary decomp.) from room temperature, and 258—262° (with slight preliminary decomp.) (I.T. 240°) (Found: C, 30·3; H, 6·3; N, 5·95. $C_{12}H_{28}N_2I_2,H_2O$ requires C, 30·5; H, 6·4; N, 5·9%); on exposure to air it formed a stable *tetrahydrate*, m. p. 261° (decomp.) (Found: C, 27·5; H, 6·6; N, 5·8. $C_{12}H_{28}N_2I_2,4H_2O$ requires C, 27·4; H, 6·9; N, 5·3%). McElvain and Bannister give m. p. 311—312° (decomp.) for both iodides.

The *dimethonitrate* was prepared by treating the iodide with aqueous silver nitrate, and afforded crystals of the *hemihydrate* from aqueous ethanol (Found: C, 43·2; H, 8·6; N, 17·0. $C_{12}H_{28}O_6N_4,0{\cdot}5H_2O$ requires C, 43·2; H, 8·8; N, 16·8%): it softened at 165° and melted *ca.* 310° (decomp.) (O.T.), at 148° (E.T.) from room temperature, and 152° (E.T., I.T. 140°). The *dimetho(methyl sulphate)* was obtained by boiling a methanolic solution of the base with dimethyl sulphate, and precipitating the salt with ethanol; recrystallisation from aqueous ethanol and then drying at 60°/0·1 mm. for 5 hr. gave the hygroscopic *monohydrate*, m. p. 264° (decomp.) from room temperature, 258° (decomp.) (I.T. 244°) (Found: C, 38·5; H, 8·3. $C_{14}H_{34}O_8N_2S_2,H_2O$ requires C, 38·1; H, 8·3%). The *dimethotoluene*-p-*sulphonate*, similarly prepared, formed crystals, m. p. 311° (decomp.), from methanol (Found: C, 57·7; H, 8·0; N, 5·1. $C_{26}H_{42}O_6N_2S_2$ requires C, 57·5; H, 7·8; N, 5·2%).

Reaction of the Piperazine (II) *with Alkylene Dibromides.*—(1) *Ethylene dibromide.* A mixture of (II) (0·4 g.) and the dibromide (0·2 c.c., 1 mol.) was slowly heated in a sealed tube to 160—170°, and there maintained for 6 hr. A filtered aqueous extract of the product was evaporated to dryness, and the residue (m. p. 343°), when recrystallised from 48% hydrobromic acid, afforded the piperazine dihydrobromide (Found: C, 36·2; H, 7·5; N, 8·5. Calc. for $C_{10}H_{22}N_2,2HBr$: C, 36·2; H, 7·3; N, 8·4%), m. p. 358°, unchanged by a sample prepared directly from (II). It gave the dipicrate, m. p. 272° (decomp.) alone and mixed (Found: C, 42·6, 42·8; H, 4·9, 4·8; N, 17·5, 17·5%). The same result was obtained when the above mixture was heated at 100°, but no reaction apparently occurred when the mixture was heated at 60° for 5 days.

The mixture in a tube, when set aside however for 1 week with daily exposure to sunlight, gave a crystalline deposit, which when recrystallised from 48% hydrobromic acid afforded the monohydrated *ethylenebis-*(1 : 2 : 2 : 4 : 5 : 5-*hexamethyl-*1-*piperazinium bromide*) *dihydrobromide* (V; X = Br), m. p. >370° (O.T.), 354° (E.T.) (Found: C, 37·0; H, 7·15; N, 7·6. $C_{22}H_{48}N_4Br_2,2HBr,H_2O$ requires C, 37·3; H, 7·4; N, 7·9%). The same compound was obtained when the deposit was recrystallised from methanol–ether and then methanol. This dihydrobromide gave the yellow monohydrated *dipicrate* of the bis(piperazinium picrate) (V; X = $C_6H_2O_7N_3$), m. p. 270° (decomp., preliminary softening) (from acetone) (Found: C, 42·2; H, 4·6; N, 17·3. $C_{34}H_{52}O_{14}N_{10},2C_6H_3O_7N_3,H_2O$ requires C, 42·5; H, 4·65; N, 17·2%).

(2) *Trimethylene dibromide.* A mixture of the piperazine (II) (0·8 g.) and the dibromide (0·48 c.c., 1 mol.) was heated in a sealed tube at 150° for 4 hr. The cold product was extracted with methanol, and the residue, when recrystallised from aqueous ethanol, afforded the dihydrobromide of (II) (Found: C, 36·6; H, 7·5%), m. p. 358°, alone and mixed. The extract contained a solid, precipitated with ether, but insufficient for investigation.

(3) o-*Xylylene dibromide.* A mixture of the piperazine (II) (1·6 g.) and the dibromide (2·5 g., 1 mol.), when similarly heated at 140° for 6 hr., was unchanged. An identical mixture, heated at 150—160° for 8 hr., gave a product which, recrystallised as in (2), gave the dihydro-

View Article Online

Published on 01 January 1954 on http://pubs.rsc.org | doi:10.1039/JR9540004476
Downloaded by Brown University on 20 December 2012

bromide of (II) (Found: C, 35·9; H, 7·5; N, 8·4%), which furnished the dipicrate, m. p. 274° (decomp.) (Found: C, 42·3; H, 5·0; N, 17·6%).

1 : 4-*Diethylpiperazine*.—This was prepared by Pollard and Forsee's method (*loc. cit.*), whose account lacks important detail. A solution of piperazine (20 g.) in water (100 c.c.) containing concentrated hydrochloric acid (40 c.c.) was cooled to 10°, and freshly distilled acetaldehyde (24 g.) then added, the temperature being kept below 20°. An excess of powdered zinc was then rapidly added and, after the initial brisk reaction, the mixture was heated under reflux at 70° for 8 hr., and then cooled, strongly basified with potassium hydroxide, filtered, and extracted with ether. The dried extract on distillation gave diethylpiperazine, b. p. 71°/18 mm., 172—176°/760 mm. (Found: N, 19·4. Calc. for $C_8H_{18}N_2$: N, 19·7%). The low yield (30%) is due to the formation of a considerable proportion of higher-boiling material.

Reduction of 1 : 4-diacetylpiperazine with lithium aluminium hydride gave 1 : 4-diethylpiperazine, b. p. 75—77°/25 mm., in 24% yield and was more laborious.

The diethylpiperazine for characterisation was heated with an excess of methyl bromide at 100° for 6 hr., and furnished the *dimethobromide*, m. p. 304—305° (decomp.), from methanol (Found: C, 36·5; H, 7·7; N, 8·1. $C_{10}H_{24}Br_2N_2$ requires C, 36·2; H, 7·3; N, 8·4%); it gave a yellow *dimethopicrate*, m. p. 290° (decomp.) (from acetone) (Found: C, 41·8; H, 4·5; N, 18·1. $C_{22}H_{28}O_{14}N_8$ requires C, 42·05; H, 4·5; N, 17·8%).

A mixture of 1 : 4-diethylpiperazine (1 g.) and ethylene dibromide (1·32 g., 1 mol.) was heated at 100° for 4 hr., and the product when recrystallised from ethanol afforded the highly deliquescent triethylenediamine diethobromide, m. p. 238—241°; it was therefore converted into the yellow *diethopicrate*, which, crystallised from acetone, had m. p. 295° (decomp.) from room temperature, 298° (decomp.) (I.T. 2·85°) (Found: C, 42·3; H, 3·95; H, 17·65. $C_{22}H_{26}O_{14}N_8$ requires C, 42·2; H, 4·2; N, 17·9%). A mixture of this picrate with the above dimethopicrate had m. p. 282—285° (decomp.) (I.T. 260°).

The properties of this diethobromide and of analogous salts obtained from other alkylene dibromides, and particularly their behaviour on thermal decomposition, will be described in a later communication.

Dipole Moments of 1 : 4-*Dimethyl*- and 1 : 2 : 2 : 4 : 5 : 5-*Hexamethyl-piperazines*.—Carefully dried and purified samples were used. Dr. Chatt reports: " Solutions of the piperazines in benzene were investigated using yellow light (λ 5880 Å) at 25°. The results are set out using the notation and method of evaluation of Everard, Hill, and Sutton (*Trans. Faraday Soc.*, 1950, **46**, 417).

1 : 4-*Dimethylpiperazine*.

ω	α	β	γ	$_TP$	$_EP$	$_oP$	μ
0·0336 0·0213 0·0116	0·0000	0·1796	−0·0504	45·062	39·373	5·688	0·53

1 : 2 : 2 : 4 : 5 : 5-*Hexamethylpiperazine* (II).

ω	α	β	γ	$_TP$	$_EP$	$_oP$	μ
0·0374 0·0246 0·0087	0·0144	0·2322	−0·0443	70·328	62·347	7·981	0·63

" Although there was a little spread of the values used to obtain α, β, and γ, the measurements (see Table) allowed an accuracy of ±0·01 D. Uncertainty in the value of the atom polarisation, however, means that the absolute accuracy may not be so high. Special precautions were taken to exclude moisture and carbon dioxide, and little error might be expected from such impurities."

We gratefully acknowledge the help we have received from Dr. W. Cochran and Dr. J. Chatt, and a grant provided by the Department of Scientific and Industrial Research (A. S.).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, July* 22*nd*, 1954.]