L.—*Hexa-aminobenzene.*

By Bernhard Flürscheim and Eric Leighton Holmes.

When 2 : 4 : 6-trinitro-1 : 3 : 5-triaminobenzene was obtained for the first time by Jackson and Wing (*Amer. Chem. J.*, 1888, **10**, 282), these authors, as well as Palmer (*ibid.*, 1892, **14**, 378), attempted to reduce it to hexa-aminobenzene. But alcoholic ammonium sulphide led to decomposition; with tin or stannous chloride and hydrochloric acid, and with zinc dust and acetic acid, ammonia was invariably produced through the elimination of an amino-group, so that only a hydrochloride of penta-aminobenzene could be isolated. Jackson and Wing therefore concluded that hexa-aminobenzene, if actually formed, must be very unstable; and Palmer thought that " the results here noted appear to establish the fact that upon reduction of trinitrotriaminobenzene at least one nitro-group is replaced by hydrogen."

On theoretical grounds (see below) we were unable to agree with these deductions. If *salts* of hexa-aminobenzene were primarily produced, in which only some of the amino-groups would presumably be combined with the acid, then under the above experimental conditions these salts might conceivably be less stable than salts of penta-aminobenzene. But hexa-aminobenzene itself should certainly be more stable than penta-aminobenzene. If this view was correct, then it should be feasible to obtain hexa-aminobenzene, provided that every possibility of preliminary salt formation were excluded.

It has long been known that many mononitro-compounds can be reduced to amines by means of phenylhydrazine, and *m*-dinitrobenzene has been similarly reduced to *m*-phenylenediamine (Walther, *J. pr. Chem.*, 1896, **53**, 433), but polyamino-compounds do not appear to have been prepared by this method. We decided to try it, and the very first test-tube experiment, wherein trinitrotriaminobenzene was heated with phenylhydrazine, yielded *hexa-aminobenzene.* By a fortunate coincidence, phenylhydrazine is one of the very few solvents for trinitrotriaminobenzene, and it is the *only* organic substance in which hexa-aminobenzene has, so far, been found to be soluble. Accordingly, hexa-aminobenzene can be recrystallised from phenylhydrazine. Since the synthesis trinitrobenzene ⟶ 3 : 5-dinitroaniline ⟶ pentanitroaniline ⟶ trinitrotriaminobenzene ⟶ hexa-aminobenzene involves only a single, simple reaction for each stage, the yields being nearly quantitative in the third stage and reasonably good in the others, hexa-aminobenzene is fairly accessible.

Penta-aminobenzene had already been known in the form of its trihydrochloride (see above; also Barr, *Ber.*, 1888, **21**, 1547; Palmer and Jackson, *Amer. Chem. J.*, 1889, **11**, 448), but the free base could not be prepared therefrom. This is not surprising, since we found that a solution of free penta-aminobenzene in water decomposes almost instantaneously. We have now accomplished the synthesis of this base by heating 2 : 4 : 6-trinitro-1 : 3-diaminobenzene with phenylhydrazine. This new base is even more accessible than hexa-aminobenzene, since there are now only three stages, starting from a commercial product : *m*-nitroaniline ⟶ tetranitroaniline ⟶ trinitrodiaminobenzene ⟶ penta-aminobenzene, each stage again consisting of a single reaction.

In accordance with our anticipations, hexa-aminobenzene has been found to be distinctly more stable than penta-aminobenzene, not only in aqueous solution, but also as a solid. Both compounds share ready solubility in water and insolubility in the usual organic solvents. Both melt with decomposition, in air at temperatures which vary with the rates of heating (varying degrees of oxidation); the true melting-decomposition points are obtained in hydrogen, 247—248° for the hexa- and 228° for the penta-aminobenzene (heating at the rate of 5° per minute). Acetic anhydride transforms hexa-aminobenzene into its *hexa-acetyl* derivative. From an aqueous solution of the free base, picric acid precipitates a *tri-picrate*, and hydrochloric acid a *tetrahydrochloride*. The latter salt is characteristic for hexa-aminobenzene, since it is formed under various conditions; a higher hydrochloride could not be obtained even with hydrochloric acid saturated with hydrogen chloride at — 1·5°.

It is of theoretical interest to compare the phenylenediamines and all known polyamino-derivatives of benzene, of its homologues, and of anisole in their order of decreasing resistance to atmospheric oxidation. Compounds containing distinctly "negative" substituents, such as nitro- or halogeno-polyamino-derivatives, must, however, not be included, since such substituents have *per se* a stabilising effect towards oxidising agents (polar factor). In the following comparison, the relative stabilities of all the tri- and tetra-amino-compounds appear to follow from their descriptions in the literature.

Vicinal polyaminobenzenes : $1:2 > 1:2:3 > \left\{\begin{matrix}1:2:3:4\\1:2:3:4:5\end{matrix}\right. < 1:2:3:4:5:6$

Diaminobenzenes : $1:2 > 1:4 > 1:3$.

Triaminobenzenes : $1:2:3 > 1:2:4$.

Tetra-aminobenzenes : $1:2:3:4 > \left\{\begin{matrix}1:2:3:5\\1:2:4:5\end{matrix}\right.$.

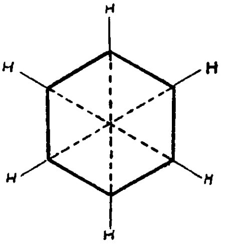
Non-vicinal polyaminobenzenes : $1:3 > 1:3:4 > \left\{\begin{matrix}1:2:3:5\\1:2:4:5\end{matrix}\right.$.

Triaminobenzenes and homologues : 1 : 2 : 3 approx. = 4-methyl-1 : 2 : 3; 1 : 3 : 4 approx. = 6-methyl-1 : 3 : 4; 2 : 6-dimethyl-1 : 3 : 5 approx. = 2 : 4 : 6-trimethyl-1 : 3 : 5.

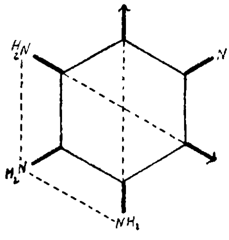
Tetra-aminobenzenes and homologues : 1 : 2 : 3 : 4 approx. = 5-methyl-1 : 2 : 3 : 4.

Triaminoanisoles and tetra-aminobenzenes : 1 : 2 : 3 : 4 approx. = 4-methoxy-1 : 2 : 3; 1 : 2 : 4 : 5 < 5-methoxy-1 : 2 : 4.

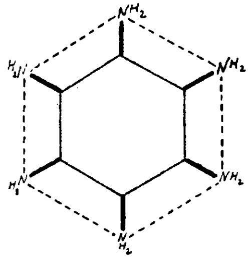
Clearly, (*a*) vicinal compounds are more stable than their isomerides; (*b*) vicinal as well as non-vicinal compounds become less stable as the number of amino-groups increases; (*c*) hexa-aminobenzene is the only case where, contrary to the latter rule, a further amino-group has enhanced the stability; (*d*) the introduction of methyl makes little difference; (*e*) the effect of a methoxy-group is somewhat, but not much inferior to the effect of a corresponding amino-group. It may be concluded that there is no marked purely steric protection against oxidation in these cases (*d*); that groups which make a large affinity demand on the nuclear atom with which they are linked thereby alter the stable affinity distribution in the ring, destroying its aromatic character and producing centres of increased unsaturation at other nuclear carbon atoms—an effect which increases with the affinity demand of the groups ($NH_2 > O{\cdot}CH_3$) (*e*) and with their number (*b*); that this effect is diminished when the affinity demand on nuclear carbon is reduced by residual bonds (neutralisation of residual affinity) between neighbouring groups (*a*); and that substitution of an amino-group for the last remaining hydrogen atom enhances the stability of the system (notwithstanding that the residual diagonal bonds of Werner's benzene formula which characterise aromatic stability have disappeared on account of the binding of this residual affinity by the nitrogen atoms), because neutralisation of residual affinity between neighbouring nitrogen atoms (as above) is now at a maximum and also because there are now no carbon atoms of increased unsaturation, but an entirely symmetrical, although non-aromatic affinity distribution has been achieved (*c*). These points find, to some extent, a graphical interpretation in the following formulæ, in which dashed lines denote residual bonds, and thicker lines (or thicker dashed lines) bonds (or residual bonds) with a higher affinity content; the arrows indicate enhanced free affinity.



Aromatic, stable.



Non-aromatic, uneven affinity distribution, unstable.



Non-aromatic, even affinity distribution, comparatively stable.

Experiments on the reaction of several other nitro-compounds with phenylhydrazine are dealt with in the experimental part (p. 336).

EXPERIMENTAL.

Preparation of Hexa-aminobenzene.—(a) *Attempted reduction of trinitrotriaminobenzene with stannous chloride in pyridine.* Since it seemed possible that stannous chloride might achieve the desired result in an anhydrous solvent, trinitrotriaminobenzene (1 part) and anhydrous stannous chloride (8 parts) were boiled with various proportions of pyridine and pyridine hydrochloride in air as well as in carbon dioxide, but without success.

(b) *Reduction of trinitrotriaminobenzene with phenylhydrazine.* Numerous experiments in which trinitrotriaminobenzene was heated with phenylhydrazine in air, carbon dioxide, or hydrogen showed that the nature of the gas made little difference—presumably owing to the rapid evolution of nitrogen during the reaction. It was found, however, that with increasing proportions of phenylhydrazine the yield of crude *hexa-aminobenzene* obtained became less, but its purity was enhanced. For instance, 1·2 g. of trinitrotriaminobenzene were heated in 6 c.c. of phenylhydrazine to 140° and kept at that temperature by external cooling until the gas evolution had ceased. Then another 5 c.c. of phenylhydrazine were added and the temperature was gradually raised to 200°. When the gas evolution had ceased, the mass was cooled : 0·380 g. of brown transparent crystals was obtained. On the other hand, when the second addition of phenylhydrazine was omitted, a 50% yield (by weight) of a less pure product was obtained. Similarly, 0·45 g. of the nitro-base, heated in 2·5 c.c. of phenylhydrazine in an atmosphere of carbon dioxide to 120°, kept at 120° for 40 minutes, then at 130° for 10 minutes, yielded, after cooling, dilution with benzene and filtration, as much as 0·266 g., but the product was black. The crude material was recrystallised from phenylhydrazine, one to three times according to its initial degree of purity, until it was obtained in small, light brown crystals, soluble in cold water without residue; the crystals were washed with benzene and brought to constant weight in a vacuum.

Properties of Hexa-aminobenzene.—It consists of small crystals—cubic octahedra, as Dr. I. E. Knaggs kindly ascertained for us—which, immediately after recrystallisation, always appear light brown in reflected light, even after seven recrystallisations. In the absence of traces of surface oxidation, it would presumably be colourless. It corresponds in this respect closely to 1 : 2 : 3-triaminobenzene (Salkowski, *Annalen*, 1872, **163**, 23), which retains the same colour, even after distillation, and appears to possess much the same stability towards atmospheric oxidation. In an atmosphere of hydrogen, hexa-aminobenzene melts with decomposition at 247—248°, after darkening from about 180° (rate of heating, 5° per minute). In air, the decomposition point, owing to oxidation, is the higher the more slowly the material is heated; at the rate of 30° per minute, the decomposition point is about 255°. Hexa-aminobenzene is moderately easily soluble in cold water and in phenylhydrazine, but insoluble in the usual organic solvents and in aniline, nitrobenzene, quinoline, benzyldiethylamine, dimethylaniline, pyridine, and amyl alcohol. On prolonged exposure to air, the material darkens; but this is merely due to surface oxidation, since after several days it still retains its crystalline aspect and remains almost completely soluble in water, leaving behind traces of a black oxidation product. In a partly evacuated tube at − 50° no darkening took place in 17 hours. Dr. Knaggs found that hexa-aminobenzene appeared pale yellow in transmitted light under a microscope; the colour persisted for weeks on exposure to air, with ultimate darkening at the edges of the octahedra. The colour of the aqueous solution is light yellow, darkening to brown within a few hours; the solution deposits a black solid after about 24 hours. Even crude hexa-aminobenzene (prepared according to the first of the three examples given) is almost totally soluble in cold water, but forms a light brown and less stable solution (Found: C, 42·55; H, 7·25; N, 50·35, 50·05. $C_6H_{12}N_6$ requires C, 42·85; H, 7·15; N, 50·0%).

Hexa-acetamidobenzene.—When 1·7 parts of hexa-aminobenzene were heated in an evaporating-dish on a water-bath with 20 parts (by vol.) of acetic anhydride, a vigorous reaction ensued, and the base went into solution; then a brownish substance separated. After 5 minutes this was drained on porous plate and recrystallised from aqueous acetic acid. Yield, 1·7 parts of minute white crystals, m. p. 356—357°, decomp. p. 363° (Found: C, 51·05; H, 5·85; N, 20·2. $C_{18}H_{24}O_6N_6$ requires C, 51·45; H, 5·7; N, 20·0%).

Hexa-aminobenzene Tetrahydrochloride.—This was precipitated, whatever the concentration and temperature, when an aqueous solution of the base was run into concentrated hydrochloric acid. (1) A solution of 0·2 g. in 3 c.c. of cold water was filtered (some remained undissolved) into 10 c.c. of concentrated hydrochloric acid with good stirring and ice-cooling. Needles separated which appeared colourless in suspension, but after drying between filter-paper and then to constant weight in a vacuum had a light greyish-brown colour. Yield, 0·10 g. (Found: Cl, 45·5%). (2) 0·270 G. of the base in 5 c.c. of water was filtered into 10 c.c. of concentrated hydrochloric acid with good stirring; the filter was then washed with a further 5 c.c. of water, which was run into a further 10 c.c. of the acid. The combined precipitates weighed 0·264 g. after being dried to constant weight in a vacuum (Found: N, 27·2; Cl, 45·0. $C_6H_{12}N_6,4HCl$ requires N, 26·75; Cl, 45·2%). (3) 0·15 G. of the base in 4 c.c. of water was run, drop by drop, into 10 c.c. of concentrated hydrochloric acid saturated with hydrogen chloride at − 15°, passage of the gas being continued during the addition of the solution of the base. The precipitate was dried to constant weight in a vacuum (Found: Cl, 45·7%).

Hexa-aminobenzene tetrahydrochloride shows no melting point, but darkens at about 240°. It is insoluble in hot alcohol, but soluble in water. The aqueous solution turns deep brown in about 5 hours, and deposits a black solid over-night. From a saturated aqueous solution of the salt, a rapid current of ammonia gas precipitates a black amorphous powder. The solid salt, exposed to the atmosphere, does not appear to attract moisture, but becomes a black mass within 3 days. When a saturated solution of the salt is added to a 50% aqueous solution of potassium hydroxide at room temperature, a base separates in straw-coloured needles. This base yields on acetylation crystals which do not melt at 385°.

Hexa-aminobenzene Tripicrate.—One part of hexa-aminobenzene dissolved in 100 parts of water was dropped into a solution of 7 parts of picric acid in 700 parts of water at 20°. The precipitate was dried in a vacuum, ground under benzene, and dried to constant weight in a vacuum. The compound formed a dark green, infusible powder. Yield, about 2 parts (Found: C, 33·4, 33·75; H, 3·35, 2·4; N, 24·75. $C_{24}H_{21}O_{21}N_{15}$ requires C, 33·7; H, 2·5; N, 24·6%).

Penta-aminobenzene.—The following mode of preparation is typical of several reductions: 1 G. of 2 : 4 : 6-trinitro-1 : 3-diaminobenzene was heated in 10 c.c. of phenylhydrazine in hydrogen. Gas began to be evolved at 120°; at 140° the reaction became so vigorous that cooling was required. Gradually 200° was reached, at which temperature the mass was kept until the gas evolution had ceased. On cooling and filtration, 0·17 g. of dark brown crystals was obtained. Recrystallisation from phenylhydrazine in hydrogen did not alter the colour (Found: C, 47·2; H, 7·5; N, 45·4. $C_6H_{11}N_5$ requires C, 47·05; H, 7·2; N, 45·75%).

Penta-aminobenzene, in an atmosphere of hydrogen, melts with decomposition at 228° (rate of heating, 5° per minute). It is insoluble in the usual organic solvents, but soluble in water.

2 : 4 : 6-*Trinitro*-1-*amino*-3 : 5-*dianilinobenzene.*—1·0 G. of pentanitroaniline in 5 c.c. of dry acetone was slowly added, with good shaking, to 3 c.c. of aniline dissolved in 5 c.c. of acetone. The red precipitate was filtered off, washed with acetone, and dried. Yield, 1·14 g. It was obtained from nitrobenzene in minute, light red crystals, m. p. 264° (decomp.). In most other solvents this *compound* is insoluble (Found: N, 20·7. $C_{18}H_{14}O_6N_6$ requires N, 20·5%).

When the preceding compound, 2 : 4 : 6-trinitrotoluene, 1 : 3 : 5-trinitrobenzene, picramide, or 3 : 5-dinitroaniline was heated in phenylhydrazine, evolution of gas took place but nothing definite could be isolated, except in the last two cases, in which solid products, which are being examined, were obtained.

We are greatly indebted to Sir W. H. Bragg and the Royal Institution for the facilities placed at our disposal at the Davy Faraday Laboratory.

THE ROYAL INSTITUTION, W. 1. [*Received, December 7th,* 1928.]