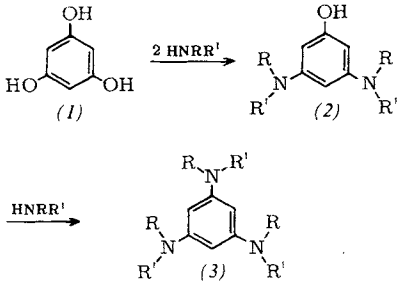
COMMUNICATIONS

N-Persubstituted 3,5-Diaminophenols and 1,3,5-Benzenetriamines and their Protonation

By *F. Effenberger* and *R. Niess*[*]

N-Persubstituted 3,5-diaminophenols *(2)* and 1,3,5-benzenetriamines *(3)* have not been described previously. We have prepared aminobenzenes *(2)* and *(3)* by heating phloroglucinol *(1)* with secondary amines in an autoclave[1].



The reactions are carried out with an excess of amine (phloroglucinol : amine = 1:4), the molar ratio *(2)*:*(3)* obtained depending solely on the reaction temperature. The products can be purified by fractional distillation or recrystallization.

Amine used	Temp. (°C)	*(2)* Yield (%)	*(2)* M.p. (°C) (b.p., °C/mm)	*(3)* Yield (%)	*(3)* M.p. (°C) (b.p., °C/mm)
Pyrrolidine	20	100	174–185	–	
	180–200	–		95	179–181
Piperidine	180–200	98	154–156	–	
	280–300	–		40	184
Morpholine	180–200	91	185–187	–	
	280–300	–		37	308–312
Dimethylamine	130–150	68	(148/0.008)	22	
	220	14		69	(131/0.01)

With mineral acids the benzenetriamines *(3)* form definite salts containing 1, 2, or 3 moles of acid.

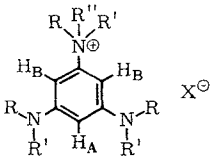
Depending on the substituents R and R', stable *N*- or *C*-protonation products, *(4)* and *(5)* respectively, are formed on monoprotonation. *N*-protonation of tripiperidinobenzene [*(3)*, R and R' = $(CH_2)_5$] for example leads to the formation of *(4)*, whilst with tripyrrolidinobenzene [*(3)*, R and R' = $(CH_2)_4$] a crystalline compound of the type *(5)* is produced. (Physical properties: *e.g. (5)*, X = BF_4, yellow needles. m. p. 254–257 °C).

Assignment of structure was based on ^{1}H–NMR-spectroscopic data. The ^{1}H–NMR spectrum of tripyrrolidinobenzene hydroiodide [*(5)*, R and R' = $(CH_2)_4$, X = I] in $CDCl_3$ showd H_B as a singlet at τ = 5.17 and H_A as a singlet at τ = 6.20 (relative intensities 1:1).

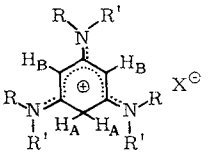
Particular structural characteristics can be gleaned from the ^{1}H–NMR spectra of tripiperidinobenzene monoperchlorate [*(4)*, R and R' = $(CH_2)_5$, X = ClO_4]. In polar solvents (*e.g.* $(CD_3)_2CO$ or $(CD_3)_2SO$) the three nuclear protons appear as a singlet at τ = 3.6, whilst the proton attached to the nitrogen (whose presence can be seen only on integration) indicates rapid proton exchange among the amino groups. On the other hand, in $CDCl_3$ this proton is fixed on an amino function and the signals of the three nuclear protons are widely separated in the spectrum (1 H at τ = 2.10 [N–H], 2 H at τ = 3.38 and 1 H at τ = 4.63). A *meta* coupling of the ring protons H_A and H_B was not observed. The comparable *N*-methyl compound [*(6)*, R and R' = $(CH_2)_5$, X = ClO_4], however, shows only a small amount of splitting of the nuclear protons (τ-values centered at 3.5) and a distinct *meta* coupling (J_{AB} = 2 Hz).

We conclude from the NMR spectra that there is a strong electronic disturbance of the aromatic π-electron system in tripiperidinobenzene monoperchlorate. An alternative to the benzenoid structure *(4)* is a valence isomer with a "Dewar structure"; although this would certainly agree with the NMR spectrum, we have no other evidence to support this structure.

Further investigations, in particular X-ray structural analysis of the tripiperidinobenzene monoperchlorate, are in progress.



(4), R'' = H
(6), R'' = CH_3



(5)

Received: August 11th, 1966; revised Sept. 9th, 1966 [Z 320 IE]
German version: Angew. Chem. *78*, 1100 (1967)

[*] Dr. F. Effenberger and R. Niess
Institut für Organ. Chemie
der Techn. Hochschule
Azenbergstr. 14/16
7 Stuttgart (Germany)

[1] The preparation of the aminobenzenes was reported at the *Chemiedozententagung* in Würzburg on April 29th, 1966.