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Analysis of Oligoethylene Oligoamines

LEIF BERGSTEDT and GUNNAR WIDMARK

Institute of Analytical Chemistry, University of Stockholm, S-104 05 Stockholm 50, Sweden

Oligoethylene oligoamines as their commercial products DETA, TETA, TEPA, and PEHA have been analysed by gas chromatography, whereby 3, 7, 12, and 20 fractions, respectively, have been recorded. With the exception of two missing structures of PEHA, this is in accordance with the number of isomers expected.

By the aid of mass spectra collected when using a combination instrument, GC/MS, and logarithmic retention data of all the fractions, two main series of compounds have been found, one of aliphatic amines and one of their piperazine derivatives. Branched compounds form sub-series, and to all the individual constituents found, structures have been suggested on the basis of experimental findings.

Polyethylene polyamines are commercial products of increasing technical usage, and possess properties of particular scientific interest. Although most commonly manufactured by polymerisation of ethylene imine by methods resembling those converting ethylene oxide into polyglycols, the structural range of variation is much greater in the case of the polyamines. Not only polymers of different degrees of branching may occur, but also those containing piperazine rings. Moreover, in the absence of a reagent such as ethylene diamine, derivatives containing an ethylene imine ring will be formed.

Since the polymers of ethylene imine with high molecular weights are too difficult to separate into individual isomers, this structural study has been limited to cover the oligomers containing 2 to 5 units of ethylene. These oligomers are commercially available, and the technical products are denoted by the abbreviations DETA, TETA, TEPA, and PEHA, which give the numbers of ethylene and amino groups, respectively.

For these oligomers a number of structural alternatives may be given. DETA exists in only one form, but both TETA and TEPA form a straight and a branched isomer; in the case of PEHA four structural alternatives are possible. However, taking the possible formation of a piperazine ring into account, independent of the way in which this ring is formed, 12 additional isomers have to be looked for. Thus, a total of 21 compounds can be expected to be present in the samples of this study, assuming higher oligomers being excluded due to careful distillation.

The separation by gas chromatography of oligoethylene oligoamines has been reported by some authors [1,2] but the chromatograms published do not indicate separation of any isomers. Nor do any successful attempts appear to have been made for structural analysis of the effluents leaving the gas chromatograph, or of the fractions collected after thin-layer chromatography. Recently, Spell [3] has published infrared spectra obtained from some samples within this class of compounds. These samples were purified on a large scale.

In the present work, the gas chromatographic separation was trimmed until 20 peaks were gained from a commercial sample of PEHA. Samples of TEPA, TETA, and DETA have given 12, 7, and 3 peaks, respectively. Including a first peak of low-boiling materials, the numbers of peaks found for DETA, TETA, and TEPA are in accordance with the discussion given above. However, a total number of 22 peaks were expected to be seen in chromatograms of PEHA; thus, two structural isomers of PEHA have not been found.

With the aid of a mass spectrometer coupled to a gas chromatograph, (LKB-9000) interpretable mass spectra have been obtained from all these separated fractions. It has also been found possible to group the mass spectrometric information to fit well into the pattern of linear log-retention relations of the gas chromatograms.

Finally, we wish to underline that we are primarily interested in the structure of the amines as they leave the gas chromatograph. Possible rearrangement of the amines during the passage through the column has not been investigated. Due to sorption and/or partial decompositions most likely occurring at the present gas chromatographic conditions, we desist from making quantitative interpretations.

EXPERIMENTAL

Materials and standards. Crude pentaethylene hexamine, PEHA, (Fluka); tetraethylene pentamine, TEPA, (Dow); triethylene tetramine, TETA, (Kebo); diethylene triamine, DETA, (Kebo) were used as the investigation objects. Of the compounds found to be present in these technical products, only *N*-(2-aminoethyl)-piperazine (Schuchardt) and ethylene imine (Kebo) were available commercially in a reasonable state of purity (> 95 %).

Gas chromatography. Although it is usually recommended that, *prior* to gas chromatographic analysis, amines should be converted into less polar derivatives, including, *e.g.* carbamates and sulfonates,[4] we have found the oligoamines investigated to be effectively separated as free amines on the alkalized column described below. Of the derivatives investigated, not even the trifluoroacetamides (TFA derivatives) [5] were found to pass the column in an acceptable manner when methylsilicone (SF-96) or nitrilesilicone (XF-1150) were used as stationary phases.

In order to be able to analyse the free amines, three stationary phases were examined, all utilized in mixtures with KOH: Versamid 900, Carbowax 20 M, and Apiezon-L. The latter was found to be superior to the others, especially with regard to later peaks of TEPA and PEHA. The presence of KOH was found necessary in order to avoid tailing. A solution of 10 % KOH in methanol was used for alkalization of Chromosorb W-HMDS, 60—80 mesh, and after evaporation of the methanol, Apiezon-L in petroleum ether was added to give a final 20 % loading (w/w).

All-glass columns which fitted into the combination instrument LKB 9000 were used throughout this investigation. In order to be able to trim the separation outside this expensive instrument, a separate gas chromatograph was constructed at this lab. which

could accept the column used. Thus, the column was attached to the mass spectrometer only when acceptable separations were achieved, as recorded on a flame ionisation detector. Column dimension: 275 × 0.2 cm i.d. glass tubing; carrier gas flow 33 ml/min nitrogen; recorded chart speed 10 mm/min.

At analysis of undiluted samples of the oligoamines, 0.1 to 0.2 μl were injected directly into the first part of the glass column. Both during trimming and at the final GC/MS analysis, the temperature of the column was maintained at 250°C; for PEHA 255°C. The injection block and the detector base were maintained at 280°C. After every injection of amine, a few 1 μl-injections of water were made to clean the interior from amine probably absorbed in the first part of the column. Although less intense, the chromatograms obtained after injections of water resembled those of actual analyses of amine.

Mass spectrometry. The mass spectra were measured by means of the combined gas chromatograph-mass spectrometer LKB 9000. The gas chromatographic part was run at the same temperature as mentioned above. The molecule separator temperature was 270°C and the ionization source temperature 270°C. The electron energy was 70 eV and the ionization current 60 μA. Recorded spectra were collected by a data acquisition system reported previously [6] and the spectra, background corrected and normalized, were printed and/or plotted out.

RESULTS AND DISCUSSION

The purpose of this investigation has been restricted to identification of the amines separated as they leave the gas chromatograph. In doing so it has not been found necessary to elaborate all the mass spectrometric data produced, and only few of the fraction ions have been interpreted in the traditional manner. Instead, the identification has been based on the patterns of fragmentation within the different series of homologues as being demonstrated by Tables 1 and 2. However, the further evidence used for each of the amines is discussed in some details below.

Fig. 1. Gas chromatogram of DETA. Temperature of analysis 250°C, for other conditions see experimental part. Formulas and mass spectra of fractions are given in Tables 1 and 2. Fraction 1 consists of an unresolved mixture.

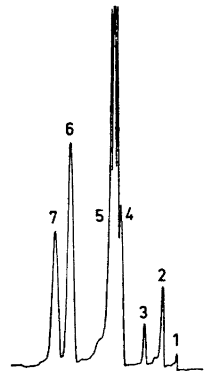


Fig. 2. Gas chromatogram of TETA, see further Fig. 1.

Table 1. Mass spectra of GC-fractions containing straight and branched amines. The intensities are given at the masses (*m/e*) where any intensity exceeds 5 % of its base peak.

GC-fraction No.	2	5	9	15	4	8	14	13
m/e	N-N-N	N-N-N-N	N-N-N-N-N	N-N-N-N-N-N	N-N-N | N	N-N-N-N | N	N-N-N-N-N | N	N-N-N-N-N | N
18	9.5	7.0	8.0	8.5	5	21.0	18.5	22.0
27	3.0	2.5	3.0	3.5	1	3.5	6.0	6.5
28	12.5	8.0	10.5	16.5	3.5	11.0	33.5	39.0
29	3.5	4.0	5.5	7.0	1	4.0	8.0	8.5
30	23.0	20.0	25.0	21.5	4	18.0	13.5	24.5
41	2.0	2.0	3.0	4.5	1	3.0	7.5	8.0
42	7.5	7.0	10.0	13.5	3	11.0	19.0	19.5
43	6.0	5.5	9.0	11.0	3.5	7.5	13.5	8.0
44	100.0	100.0	100.0	100.0	100	100.0	100.0	100.0
45	6.0	5.0	5.0	5.0	6	5.0	5.0	5.0
54				2.0				
55				3.0				
56	8.0[c]	18.5	31.5	3.55	22	22.0	42.0	42.5
57		5.0	9.5	11.0	4.5	5.0	12.5	14.5
58		5.5	14.5	25.0	12.5	18.5	31.0	30.5
59			2.5	4.5	2.5	3.0	6.0	6.0
61		10.0	9.5	6.5				
62			3.0	3.0				
68				3.0				
69				2.5				
70		6.5	18.0	22.5	18	16.0	29.0	30.0
71		2.5	10.5	10.5	4	5.0	13.0	12.5
72			2.0	8.0	2.5	1.5	7.0	7.0
73	51.0[b]	54.0	42.0	26.5	29.0	20.5	22.5	23.5
74	2.0	13.0	11.5	11.5	10.5	6.5	8.5	9.0
75			3.5	8.5			6.5	7.0
76				3.0				
82				1.5				
83			2.0	5.5			7.5	9.5
84		2.0	4.5	9.0	4		12.0	12.5
85		6.5	19.0	29.0	8.5	16.5	33.5	31.5
86	4.5	6.0	11.0	12.5	3		13.0	11.5
87		5.5	25.0	40.5	18	32.0	44.5	42.5
88			11.5	17.5	5.5	8.5	18.5	17.0
89				3.0				
97				8.0			12.5	13.0
98				7.5			11.5	12.5
99		14.0[c]	55.0	78.0	60[c]	58.0	79.5	68.5
104	3.0[a]							

Table 1. Continued.

111			7.5			9.5	10.5
112			7.5			11.5	11.5
113			9.5			14.0	13.5
116	22.0[b]	45.0[d]	30.0	98.5[b]	37.5[d]	28.5	21.5
117	6.0	2.5	2.0		3.0	1.5	1.0
118		2.5	1.5		3.0	1.5	
125			3.0			6.0	6.5
126			7.0			8.0	8.0
127			6.0			7.0	7.5
128			4.5			5.5	5.0
129		2.0					
130		1.5	6.5				
142		2.0[c]	9.0		5.0[c]	12.5	13.0
147	2.0[a]						
159		6.0[b]	23.5[d]		13.5[b]	22.5[d]	25.5[d]
185			1.0[c]			2.5[c]	3.0[c]
190		2.5[a]					
202			3.5[b]			4.5[b]	3.0[b]

[a] M+1. [b] M−30. [c] M−47. [d] M−73.

The gas chromatograms of DETA, TETA, TEPA, and PEHA are shown in Figs. 1–4. As can be seen from these chromatograms, peaks coincide in the same retention times. This holds also true for chromatograms of PEHA when correcting for the higher temperature, 255°C instead of 250°C.

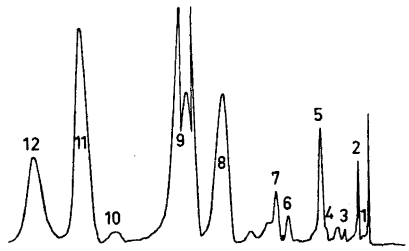


Fig. 3. Gas chromatogram of TEPA, see further Fig. 1.

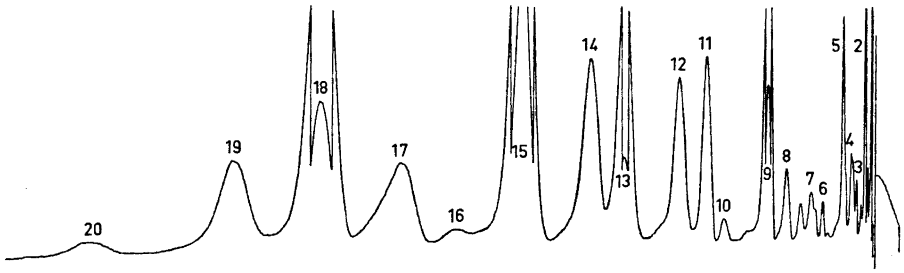


Fig. 4. Gas chromatogram of PEHA. Temperature of analysis 255°C; see further Fig. 1.

Table 2. Mass spectra of GC-fractions containing piperazine derivatives. The intensities are given at the masses (*m/e*) where any intensity exceeds 5 % of its base peak.

GC-fraction	3	7	12	19	10	17	20	6	11	18	16
m/e	N<⟩N-N	N<⟩N-N-N	N<⟩N-N-N-N	N<⟩N-N-N-N-N	N<⟩N-N-N —N	N<⟩N-N-N-N —N	N<⟩N-N-N-N —N	N-N<⟩N-N	N-N<⟩N-N-N	N-N<⟩N-N-N-N	N-N<⟩N-N-N —N
18	10.0	7.0	15.0	12.0	8.0	16.5	28	11.5	21.0	13.5	30.0
27	5.0	3.0	3.5	5.0	3.0	6.5	4.0	5.5	6.5	7.0	2.0
28	23.5	13.5	15.5	33.0	24.5	35.0	11.5	19.0	24.0	34.0	11.5
29	8.0	6.0	6.0	8.5	4.5	9.5	6.0	7.0	10.0	10.5	3.5
30	20.0	12.0	14.5	20.0	26.0	25.5	10.0	30.0	32.5	32.0	14.0
41	6.5	3.5	4.5	7.0	4.0	8.0	3.0	7.5	9.0	9.5	2.0
42	16.0	10.5	14.0	21.0	13.0	23.5	13.0	30.5	37.0	36.5	12.5
43	11.0	7.0	8.5	12.5	8.5	15.0	8.0	14.0	17.0	19.0	3.5
44	30.5	35.5	42.0	63.0	33.0	87.5	41.0	62.0	98.0	100.0	40.0
45	1.5	2.0	2.5	4.0	1.5	4.5	2.0	3.5	6.0	6.0	1.5
54	2.5										
55	7.0	4.0	4.0	6.5		7.5		9.5	12.5	14.5	
56	66.0	43.0	38.0	48.0	10	47.0	18.0	31.0	52.0	60.5	16.0
57	10.0	6.5	8.0	13.5	4	14.0	15.0	9.0	14.5	19.0	15.0
58	8.0	23.5	24.5	29.0	22	32.5	20.0	19.5	28.5	37.0	15.0
59		3.0	3.5	5.5		6.0		2.0	3.0	5.5	
61							11.0				10.0
68	1.5										
69	2.5										
70	27.0	22.0	25.0	34.0	12	33.5	19.0	31.0	53.0	59.0	17.5
71	3.0	3.5	6.5	11.5	3	16.5	18.0	7.0	15.0	16.0	15.0
72	2 5	2.0	3.0	7.5	2	9.5	10.0	3.5	7.0	11.5	15.5
73	4.0	10.5	12.5	17.0	4.5	24.5	26.0	9.0	24.5	23.5	25.0
74	1.0	2.5	3.5	6.5	1.0	9.0		2.0	6.0	9.0	
75				5.0		7.0				4.0	
82	1.5						9.0	8.0	10.5	10.5	8.0
83	9.5	4.5	7.5	10.0		10.0	18.0	9.0	16.0	20.0	15.0
84	12.5	9.0	10.5	16.0	14	16.5	20.0	13.5	15.5	22.0	20.0

85	4.0	5.5	12.5	27.5	21.5	31.5	38.0	11.5	30.0	16.5	28.0
86	1.0	3.0	3.5	11.0		11.5	18.0	4.5	10.0	18.5	12.5
87	13.0	8.5	8.0	26.0	5	36.5	38.0	9.5	18.0	35.5	26.5
88	3.5	1.5	2.5	9.0		16.0		1.5	4.0	14.0	
97	2.0	4.0	13.0	22.0	5.0	22.0	28.0	54.0	69.5	57.5	31.5
98	2.5	4.0	11.0	19.5		21.5	24.0	95.0	100.0	60.5	26.0
99	100.0[b]	100.0	100.0	100.0	100.0	100.0	100.0	37.5[d]	81.5	98.0	82.0
100	14.0	12.0	15.0	20.0	18.5	28.5	21.0	8.5	16.0	25.0	16.5
101				19.0		19.5	28.0		18.5	47.5	26.0
102										13.0	
111		3.0	8.5	16.5	37	26.5	23.0	6.5	17.0	26.0	17.5
112	6.0	11.5	28.5	21.0	13.5	25.0	27.0	12.0	23.0	22.0	21.0
113	4.5	5.0	17.0	32.5		28.5	40.0	14.5	58.0	81.0	26.0
114						9.5	12.0		25.5	16.5	10.0
116				15.0		33.5				37.5	
117				13.0							
125			3.5	9.0		7.0	20.0	19.0[c]	24.0	34.0	19.5
126			4.5	11.5		16.0	21.0	3.5	12.0	22.5	16.5
127			4.0	12.5		12.0	31.0	11.0	17.5	24.5	21.0
128				6.5	60	8.5	14.0			12.0	16.5
129	1.0				37		10.0				10.0
130	0.5[a]		5.0				11.0		11.5		11.0
142		7.0[b]	17.5[d]	26.0	18[d]	24.0	37.0	100.0[b]	100.0[d]	75.0	100.0
155		1.0	2.0	6.0	58	4.0		8.0	10.0	26.0	14.0
159				18.5	25	21.5	39.0			14.5	25.0
173								0.5[a]			
185			2.5[b]	11.5[b]	13[b]	6.0[d]	14.5[d]		12.5[b]	29.0[d]	11.0[d]
198						1.5			5	4.5	
211							10.0[c]				6.0[c]
216									1.5[a]		
228				2.0[b]		4.5[b]	8.0[b]			5.0[b]	5.0[b]

[a] M+1. [b] M−30. [c] M−47. [d] M−73.

DETA. For the lowest fraction, DETA, there is in addition to the main peak (2), of diethylene triamine, only one other large peak (3), and after comparing its mass spectrum and retention time with those of the reference material, the fraction 3 was identified as *N*-(2-aminoethyl)-piperazine. Fraction 1 is in all the chromatograms only a small peak, obviously formed by a mixture of low-boiling materials not resolved at the high temperature of the present GC-analysis.

Unfortunately, *N*-(2-aminoethyl)-piperazine was the only pure piperazine compound available as a reference substance. For the products TETA, TEPA, and PEHA, the identification must therefore be based only on similarities in mass spectra of lower homologues and on variation of retention time with molecular weight and substance class. However, the similarities were found to be obvious.

From the mass spectrum of diethylene triamine, it can be seen that the major fragment is formed by cleavage, giving the ethylene iminium ion $(C_2H_6N)^+$. Other important fragments are $[M-[\text{-}CH_2\text{-}NH_2]]^+$, $m/e=73$, and $[\text{-}CH_2\text{-}NH_2]^+$, $m/e=30$. The molecular ion is not detectable, instead there is a small intensity at M+1, $m/e=104$, due to a protonization typical also for monoamines.[7]

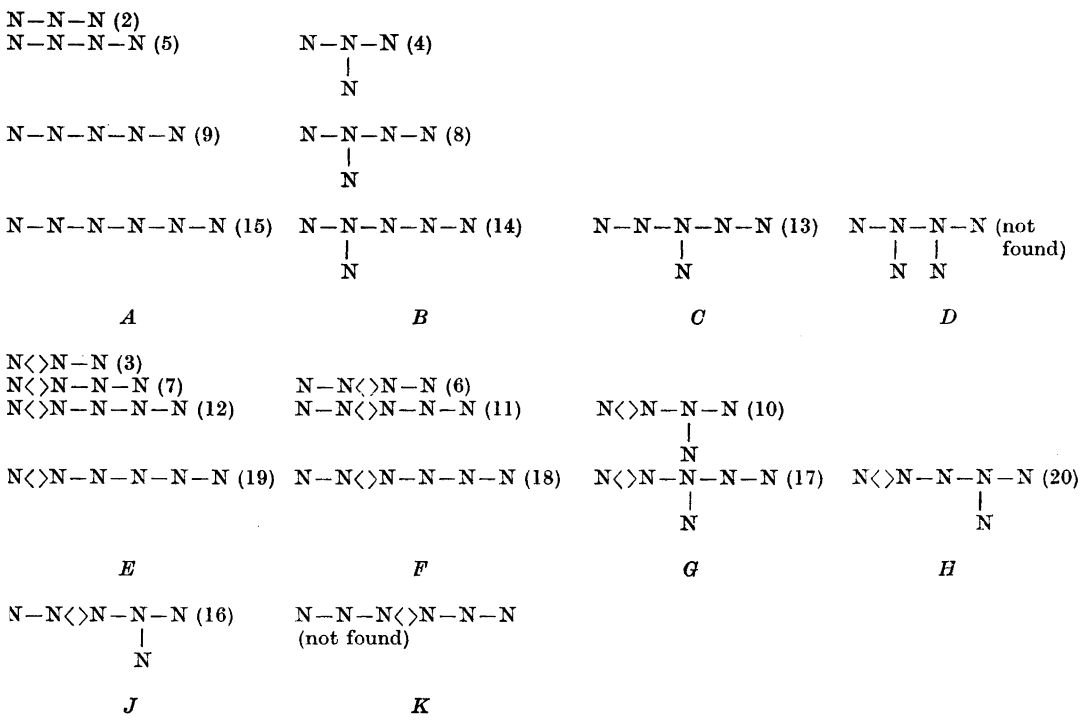
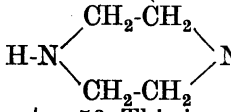


Fig. 5. Homologue series of oligoethylene oligoamines and their piperazine derivatives. Letters refer to the individual homologue series; numbers refer to fractions of the gas chromatograms; *cf.* Tables 1 and 2.

For *N*-(2-aminoethyl)-piperazine, the dominant fragment is due to



$m/e = 99$. Another important fragment is found at $m/e = 56$. This is most probably due to a ring cleavage, described by Saunders and Williams [8] but in the case of *N*-(2-aminoethyl)-piperazine with a CH_2-group attached to the N-atom. The product is thus the methylene derivative, $(C_3H_6N)^+$, of the ethylene iminium ion.

TETA. The chromatogram of TETA shows four additional peaks compared with that of DETA. According to the scheme in Fig. 5, four isomers are also possible in the formation process of ethylene amines and piperazine derivatives when four nitrogen atoms are available. The mass spectrum of the fraction forming peak 5 resembles that of peak 2, see Table 1, and also peaks 3 and 7 have similar mass spectra. This indicates that fraction 5 is of the straight aliphatic structure N–N–N–N and No. 7 is correspondingly a piperazine derivative, N⟨⟩N–N–N.* The fraction of peak 4 gives a high intensity at $m/e = 116$ corresponding to a loss of $[-CH_2-NH_2]$ which is reasonable for a branched compound, that is in this case N–N(–N)–N.

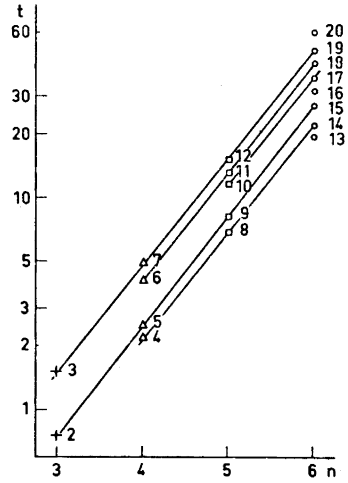


Fig. 6. Logarithmic plot of retention times (t, min) *versus* the number (n) of nitrogen atoms of constituents of PEHA as separated by gas chromatography; for fraction numbers see Tables 1 and 2.

For peak 6, the remaining alternative is then N–N⟨⟩N–N which is also confirmed by the mass spectrum where one dominant fragment is at $m/e = 98$, presumably the *N*-(2-aminoethyl)-ethylene iminium ion $(C_4H_{10}N_2)^+$.

TEPA. The mass spectrum obtained at peak 9 indicates the presence of a straight-chained tetra-ethylene pentamine. A logarithmic plot of retention

* Here and in the following we, for the sake of brevity, use a bar between two N-atoms to indicate an ethylene group. Piperazine rings are mostly given in the simplified form N⟨⟩N.

times *versus* the number of nitrogen atoms also shows a straight-line dependence between peaks 2, 5, and 9, see Fig. 6. A similar relation is also valid for fractions 3, 7, and 12 which means that 12 should be N⟨⟩N−N−N−N. In Fig. 5 these two series are marked A and E.

Of the remaining structural alternatives of TEPA, see Fig. 5, it is not difficult by comparison between the mass spectra of fractions 4 and 8 and between fractions 6 and 11 to identify 8 as N−N−N(−N)−N and 11 as N−N⟨⟩N−N−N. It only remains for the structure N⟨⟩N−N(−N)−N to be related to peak 10, which is confirmed by the mass spectrum, because intensity at $m/e=99$ indicates that the piperazine ring is substituted only at one N-atom. Also a higher intensity compared with that of fraction 12 at $m/e=185$ is consistent with branching.

PEHA. The mass spectrum of fraction No. 15 together with the retention time plot of Fig. 6 indicates that the structure is N−N−N−N−N−N. By correlation, fraction 19 when compared with 3, 7, and 12 can be identified as N⟨⟩N−N−N−N−N; similarly, 18 when compared with 6 and 11 can be identified as N−N⟨⟩N−N−N−N, and thus being the last member of the series F.

Fractions 13 and 14 show mass spectra of similar character, suggesting the alternatives N−N(−N)−N−N−N or N−N−N(−N)−N−N. Both structures can be regarded as higher homologues of N−N(−N)−N and N−N−N(−N)−N. If the variation in retention time is comparable to that of ordinary hydrocarbons, take for example 2-methyl-propane, 2-methyl-butane, 2-methyl-pentane, and 3-methyl-pentane (see Ref. 9), the structure N−N(−N)−N−N−N can be assigned to peak 14 and N−N−N(−N)−N−N to peak 13, the latter forming the only member of series C.

Of the remaining fractions, 17 and 20 have similar mass spectra resembling that of peak 10. This means that the piperazine ring is substituted only at one N-atom, but that the attached chain is branched. However, as N⟨⟩N−N(−N)−N is a lower homologue of N⟨⟩N−N(−N)−N−N this structure ought to be adopted for fraction 17 considering the slope of the line joining 10 and 17 in Fig. 6, series G in Fig. 5. This leaves the structure N⟨⟩N−N−N(−N)−N to fraction 20.

Fraction 16 has a dominant intensity at $m/e=142$. If this is due to the ion $[N-N\langle\rangle N-]^+$, the only possible remaining structure is N−N⟨⟩N−N(−N)−N. No fractions have been found corresponding to the structures D and K of Fig. 5.

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