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IIT Research Institute
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Prepared for
U.S. Department of Energy
Assistant Secretary For Fossil Energy

W. D. Peters, Project Manager
Bartlesville Project Office
P.O. Box 1398
Bartlesville, OK 74005

Prepared by
IIT Research Institute
National Institute for Petroleum and Energy Research
P. O. Box 2128
Bartlesville, OK 74005
918-336-2400

ABSTRACT

An analytical method which distinguishes between primary, secondary and tertiary amines has been developed. Trifluoroacetic anhydride, with 4-pyrrolidinopyridine as a catalyst, is used to form di- and mono-trifluoroacylated derivatives of primary and secondary aromatic amines, respectively. Tertiary aromatic amines such as quinoline do not react. GC/MS is then used to analyze the derivatized samples. Retention indices and response factors (relative to 4-fluoroaniline) are reported for >50 pure compounds known or expected to be present in fossil fuel base fractions. Also, results from the analysis of base fractions from mildly hydrotreated SRC II coal liquids and petroleum-derived light cycle oils will be reported.

ACKNOWLEDGEMENT

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INTRODUCTION

Aromatic amines are of interest to the refiner because they are produced during the conversion of the heavy ends of petroleum to distillate fuels (1,2). Synthetic crudes from coal and shale oil also contain aromatic amines. In coal liquids, primary polyaromatic amines have been implicated as the most mutagenic compound class present (3).

Until recently, aromatic amines were difficult to differentiate in fuels using GC/MS because of the similarity of electron impact fragmentation patterns of underivatized primary, secondary, and tertiary amines. During the late 1960's, an improved analysis of these compounds as trifluoroacetamide derivatives was reported by Saxby et al. (4-6). Since then, several researchers have reported using acetylation and trifluoroacetylation to distinguish between primary and tertiary aromatic amines in gasoline (7), creosote oil (8) and coal liquids (9-12). Later et al. used an analogous derivatization with pentafluoropropionic anhydride to detect primary aromatic amines in an SRC II coal liquid (13,14), and Bartle et al. adducted anilines with hexafluoroacetone for analysis via ^{19}F nuclear magnetic resonance spectroscopy (15).

In these acetylations, one acetyl or trifluoroacetyl group was substituted onto both primary and secondary amines, such as anilines or partially hydrogenated azaarenes. Tertiary aromatic amines, i.e., azaarenes such as naphthenopyridines or quinolines, did not react. The increased mass and easily distinguished fragment ions of the derivatized compounds, as well as shifts in their GC retention times, were used to aid in their identification using GC/MS.

However, monotrifluoroacetylation does not distinguish between primary and secondary amines which are isomass. For example, aminoindans, which are primary amines, will have the same mass (229) as methyl indoline and 1,2,3,4- tetrahydroquinoline after derivatization. The differentiation of primary and secondary amines is important when developing improved processes for the upgrading of heavy ends of petroleum. Research on the hydrodenitrogenation (HDN) of heavy crude feedstocks would benefit from improved analytical techniques which would allow better monitoring of the concentration of aromatic amine intermediates (16).

For these reasons, an analytical method which distinguishes between primary, secondary, and tertiary aromatic amines has been developed. Rigorous reaction conditions are used to form di- and mono-trifluoroacetylated derivatives of primary and secondary amines, respectively. GC/MS is then used to analyze the derivatized base concentrate. The method has been applied to the analysis of a mildly upgraded SRC II coal liquid and preliminary results are reported here.

EXPERIMENTAL

Fuel Fractionation

The history of the raw and hydroprocessed SRC II coal liquid is described elsewhere (17). The feed (HT-9) and a mildly upgraded product (HT-8) were distilled to produce 200-325° C distillate fractions, acid-base-neutral separations were performed (18), and bases were subfractionated into 7 fractions (19). The whole base fraction accounted for 7.9 percent of feed and 14.1 percent of the hydrotreated (980 SCF/bbl H_2 consumption, 325° C, NiMo catalyst, 1.0 LHSV) 200-325° C distillate (2).

Chemical Derivatization

Standard blends of 6-8 pure compounds, retention index markers (4-fluorophenol, 1-naphthol, and 9-phenanthrol), and an internal standard (4-fluoroaniline) were prepared in dichloromethane (5 mg/mL/component). Concentrations of 50 mg/ml for base fractions, with 5 mg/mL internal standard and retention index markers, were typical. Aliquots (0.2 mL) of the above mixtures were combined with 0.5 mL catalyst (0.8 M 4-dimethylaminopyridine (DMAP) or 4-pyrrolidinopyridine (PPY) in dichloromethane) and 0.4 mL trifluoroacetic anhydride in a 5 mL heavy wall glass reaction vial (Supelco, Bellefonte, PA, cat. 3-3299) fitted with a Teflon cap (ibid., cat. 3-3303). Samples were held at 60° C for 10 minutes, and rapidly cooled. Hexane (2.0 mL) was added, samples were shaken well, and chilled at 0° C to facilitate precipitation of the catalyst as its trifluoroacetate salt. The supernatant was analyzed within 5 hours.

GC/MS

A Kratos (Ramsey, NJ) MS-80 GC/MS system consisting of a Carlo Erba model 4162 temperature programmed GC, modified in-house with a Hewlett-Packard cool-on-column inlet, capillary direct interface, EI source, MS-80 magnetic scan mass spectrometer and Data General Nova 4-based DS-55 data system was used for all analyses. Samples (0.2 to 0.4µl) were injected, and the column (Restek Corp., Bellefonte, PA, RTX-1 fused silica, 105 m, 0.25 mm I. D., 0.5 µm film) was held 2 minutes at 30° C, programmed at 20° C/min to 70° C, then 2° C/min to 320° C, and held 10 minutes.

Other instrumental conditions were: GC/MS interface 310° C, He column flow 1 mL/min, column head pressure 3.0 Kg/cm^2; mass spectral conditions - 70 eV ionizing voltage, 1,000 resolution, 0.5 sec/decade scan rate, source pressure 10^{-5} torr, and source temperature 300° C.

Retention Indices

The retention indices were calculated using acetylated 4-fluorophenol, 1-naphthol, and 9-phenanthrol as reference compounds as shown in Eq. 1, below:

$$\text{Eq. 1} \qquad I_X = 100\left[I_N + \frac{t_{(x)} - t_{(N)}}{t_{(N+1)} - t_{(N)}}\right]$$

I_x is the retention index and $t_{(x)}$ is the retention time of each acetylated amine derivative, and $t_{(N)}$ and $t_{(N+1)}$ are the retention times of the acetylated reference compounds whose elution times bracket each amine. I_N for 1-fluorophenol is 1, 1-naphthol is 2, and 9-phenanthrol is 3, with N representing the number of aromatic rings present in each reference compound.

Although it is customary to use retention index reference compounds with the same functionality as the compounds examined, phenols were used here for two reasons. First, these same reference compounds were used to calculated a large body of retention indices reported earlier for trifluoroacetylated hydroxyaromatics (20). Use of the same reference compounds will allow a common basis of comparison of trifluoroacetylated fuel components. Secondly, 2- and 3-ring trifluoroacetylated hydroxyaromatics are stable at GC temperatures which cause breakdown of the equivalent 2- and 3-ring diamides. If desired, the $I_{(x)}$ values reported here can be converted to values based on aromatic amines as reference compounds.

Relative Response Factors

Relative response factors (RRF) were calculated according to Eq. 2, below:

$$\text{Eq. 2} \qquad RRF = (A_X/A_S)(W_S/W_X)$$

where A = area percent, based on the GC/MS total ion current, and W = weight, x = derivatized aromatic amine, and s = derivatized standard (4-fluoroaniline).

RESULTS AND DISCUSSION

Derivatization Reactions

Table 1 lists the compounds derivatized to form amides along with their retention indices (I_X) and their total ion current responses relative to that of 4-fluoroaniline (RRF). The compounds are listed in their underivatized form, grouped into primary, secondary, and tertiary amines.

In general, primary aromatic amines such as anilines and aminoindans are reacted twice to form di-trifluoroacetamides (diamides); secondary amines such as N-alkylanilines, 1,2,3,4-tetrahydroquinolines, indolines, and carbazoles, react once to form monotrifluoroacetamides (mono-amides); and tertiary amines such as quinolines and 2,3-cyclohexenopyridines (5,6,7,8-tetrahydroquinolines) do not react.

A catalyst is necessary during the reaction (21, 22). Initially, DMAP was used as a catalyst, but PPY was found to provide more complete trifluoroacetylation of some compounds. Reaction conditions were optimized using 2,6-diethylaniline, which is a sterically hindered primary amine, and N,N-diethylaniline, which is a tertiary amine that undergoes ring acetylation at the ortho and para positions. Catalyst and reagent concentrations and reaction time (10 minutes) were held constant and the reaction temperature was varied. At room temperature, 58 percent of the 2,6-diethylaniline was converted to the diamide derivative, with the balance in the monoamide form. At both 50 and 60° C, it was 100 percent converted to the diamide form.

Of the six tertiary amines examined so far, 3 formed ring-acylated derivatives. It was initially hoped to avoid ring acetylation of N,N-dialkylanilines using mild reaction conditions, but, at room temperature, N,N-diethylaniline was completely converted to the mono-ring-acylated form, with 92 percent addition at the para- and 8 percent at the ortho-position. No evidence for the addition of more than one trifluoroacetyl group to the ring was found at either 50 or 60° C when the supernatant was analyzed within 4 hours storage at 0° C. The appearance of "over-reaction" peaks was noted after 6 hours storage, however, so subsequent samples were analyzed within 5 hours of derivatization and storage.

One of the other two tertiary amines which formed ring-acylated derivatives (2,3-cyclopentenopyridine), added 2 trifluoroacetyl groups to the saturated ring. The percentage of the derivative formed was quite reproducible, however, as shown by a RRF standard deviation of 6 percent. 2,3-cyclohexenopyridine (5,6,7,8-tetrahydroquinoline) and its alkyl-substituted homologs did not form derivatives.

The percentage of each aromatic amine which reacted to form the expected derivative is shown in Table 1, column 2. Twenty five of the 31 primary aromatic amines formed only diamides. Those cases of incomplete conversion were generally of two types. The first includes compounds such as methylbenzylamines, where the relatively low acidity of the amine hydrogens makes their displacement difficult. The second type involves higher boiling aromatic diamides, which appear to thermally decompose above a column elution temperature of about 200° C.

Derivatization Reproducibility

Each blend of aromatic amines and internal standards was derivatized 3 times, and each reaction mixture was analyzed twice, with no more than 5 hours between GC/MS injections. As shown in Table 1, replicate response factors from the 6 runs on each blend typically varied less than ±10 percent. Since this variation included contributions from both GC injections and mass spectral measurements, the reproducibility of replicate reactions was undoubtedly higher than 90 percent in most cases.

The few examples where RRF standard deviations varied more than ±10 percent were caused either by derivative decomposition on-column or by the tailing of underivatized tertiary amines such as quinoline (±24.7 percent) or N,N-dimethylbenzylamine (±27.7 percent) on the capillary column.

Mass Spectral Fragmentation Patterns

Trifluoroacetyl derivatives of primary aromatic amines typically show strong molecular ions and distinctive mass fragmentation patterns. Characteristic $[M-69]^+$ and $[M-97]^+$ ions are present in mass spectra of almost all aromatic amine derivatives, but the $[M-97]^+$ ion is usually more prominent for amide derivatives, and $[M-69]^+$ more intense for carbon-acylated compounds. Spectra of 2-n-alkylanilines usually show a fragment at $[M-18]^+$, corresponding to loss of H_2O. The major fragment in 4-n-alkylaniline derivatives corresponds to benzylic cleavage of the n-alkyl group. Addition of the trifluoroacetyl group(s) often markedly changes the fragmentation pathway of the derivative compared to the parent compound (21).

Figure 1 shows the spectra of 4 underivatized isomeric aromatic amine compounds of interest in HDN studies; 2,3-cyclohexenopyridine (a), 1,2,3,4-tetrahydroquinoline (b), 1,2,3,4-tetrahydroisoquinoline (c) and 5-aminoindan (d). Three of the spectra (a, b, and d) are virtually indistinguishable, and the fourth (c) differs only by the presence of a prominent m/z 104 fragment. Derivatization, however, enables differentiation of all four compounds, since, as shown in Figure 2, (a) remains unchanged, while (b) and (c) form monoamides and (d) forms a diamide. The two

monoamides can be easily differentiated by a fragment at $[M-15]^+$, present in the spectrum of (c), but absent in (b). The spectrum of the diamide (d) shows a molecular ion at m/z 325, 96 mass units higher than that of (b) and (c), and 192 units higher than (a). These spectra illustrate the marked improvement in ease of compound identification after trifluoroacetylation.

SRC II Coal Liquid

The main aromatic amine compound types identified so far in SRC II 200-325° C base fractions are shown in Figure 3. For the hydrotreated fractions, these include: Fraction 4 - anilines and 1,2,3,4-tetrahydroquinolines; Fraction 5 - the bulk of the anilines, from C1 through C6, and 4-aminoindan and its alkyl homologs; Fraction 6 - homologues of quinoline and 2,3-cyclohexenopyridines, 5-aminoindan, indoline, an unidentified naphthenoquinoline type, and small amounts of alkylanilines, and Fraction 7 - *t*-decahydroquinoline and its alkylhomologues.

Fraction 6 from the feed material (about 70 percent of the total basic nitrogen in the distillate, by weight) consists primarily of azaarenes, with large amounts of quinolines, and some partially hydrogenated nitrogen compounds also present.

The following tentative conclusions may be drawn from data collected so far: First, more decahydroquinolines than 1,2,3,4-tetrahydroquinolines (by weight) are present in the hydrotreated material, as predicted by Steele, et al. (16). Secondly, there are more 2-substituted anilines, particularly 2-ethyl and 2-propyl-, than other isomers, an indication of their production from ring-opening of larger compounds. In general, hydrogenation of the nitrogen-containing aromatic rings in azaarenes occurs preferentially over that of other rings. Compounds such as aminoindans may be derived from partially hydrotreated azaarenes, such as 1,2,3,4-tetrahydroquinolines, via rearrangement, or via some other source.

CONCLUSIONS

Most primary, secondary, and tertiary aromatic amines in fuels boiling below 350° C may be differentiated by the formation of trifluoroacetyl derivatives, which are eluted and identified using GC/MS. Replicate response factors of the derivatives, based on the GC/MS total ion current, typically vary less than ± 10 percent.

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TABLE 1

GC Retention Indices and MS Response Factors of Trifluoroacetylated Amine Compounds

CHEMICAL NAME	% Reacted	I_x	Response RRF	Response %σ[6]
PRIMARY AROMATIC AMINES[1]				
4-fluoroaniline	100	125.65	1.00	-
aniline	100	130.16	1.29	5.2
2-methylaniline	100	142.16	1.16	9.5
3-methylaniline	100	146.64	1.15	9.0
4-methylaniline	100	150.59	1.05	6.8
2,6-dimethylaniline	100	156.32	1.10	4.9
2-ethylaniline	100	158.18	1.03	4.8
2,5-dimethylaniline	100	158.46	1.03	5.2
3,5-dimethylaniline	100	162.66	1.04	5.1
2,4-dimethylaniline	100	162.78	1.14	4.5
2-isopropylaniline	100	165.44	1.01	2.1
2,3-dimethylaniline	100	165.51	1.06	4.6
4-ethylaniline	100	168.24	1.05	3.7
3,4-dimethylaniline	100	172.33	1.00	4.8
2-propylaniline	100	173.48	0.92	5.2
2,4,6-trimethylaniline	100	176.29	1.07	5.8
2,4,5-trimethylaniline	100	183.29	1.01	2.6
4-propylaniline	100	185.61	1.08	2.7
2,6-diisopropylaniline	100	201.02	0.98	7.0
4-n-butylaniline	100	204.48	0.83	5.3
4-nonylaniline, monoamide	92	317.08	1.19	12.9
4-nonylaniline[5]	8	290.53	0.10	76.0
4-decylaniline	31	305.75	0.47	62.7
benzylamine	100	152.73	0.99	6.3
4-methylbenzylamine	92	172.84	0.99	5.8
2-methylbenzylamine	95	173.09	1.12	6.9
(2-aminoethyl)benzene	93	173.26	1.15	3.6
5-aminoindan	100	202.02	0.89	5.1
1-amino-5,6,7,8-tetrahydronaphthalene	100	213.38	0.95	2.2
2-aminonaphthalene, monoamide[4]	42	258.22	0.49	20.2
2-aminonaphthalene	36	225.83	-	-
9-aminophenanthrene, monoamide	100	340.21	1.22	27.0
2-aminobiphenyl	100	233.33	1.03	10.9
SECONDARY AROMATIC AMINES[2]				
t-decahydroquinoline	100	214.42	1.15	5.2
N-ethylaniline	100	171.90	0.96	4.4
N-butylaniline	100	207.53	1.03	5.9
1,2,3,4-tetrahydroquinoline	100	219.70	0.97	8.2
1,2,3,4-tetrahydroisoquinoline	100	227.96	0.93	2.5
indoline	100	210.31	0.80	8.8
diphenylamine	100	254.43	1.01	5.1
N-phenyl-1-naphthylamine[4]	60	329.78	0.64	5.5
TERTIARY AROMATIC AMINES[3]				
N,N-dimethylaniline, para derivitive	90	229.71	0.80	4.8
N,N-diethylaniline, para derivitive	92	255.67	1.01	9.1
N,N-dimethylbenzylamine	0	147.77	0.59	27.7
2,3-cyclohexenopyridine	0	178.42	0.53	4.4
quinoline	0	180.89	0.73	24.7
2,3-cyclopentenopyridine	100	212.67	0.81	6.5

[1] di-(trifluoroacetamides), except as noted
[2] mono-(trifluoroacetamides), except as noted
[3] derivatized compounds are all ring-acylated
[4] RRF average of 4 determinations
[5] RRF average of 5 determinations
[6] Relative standard deviation of RRF

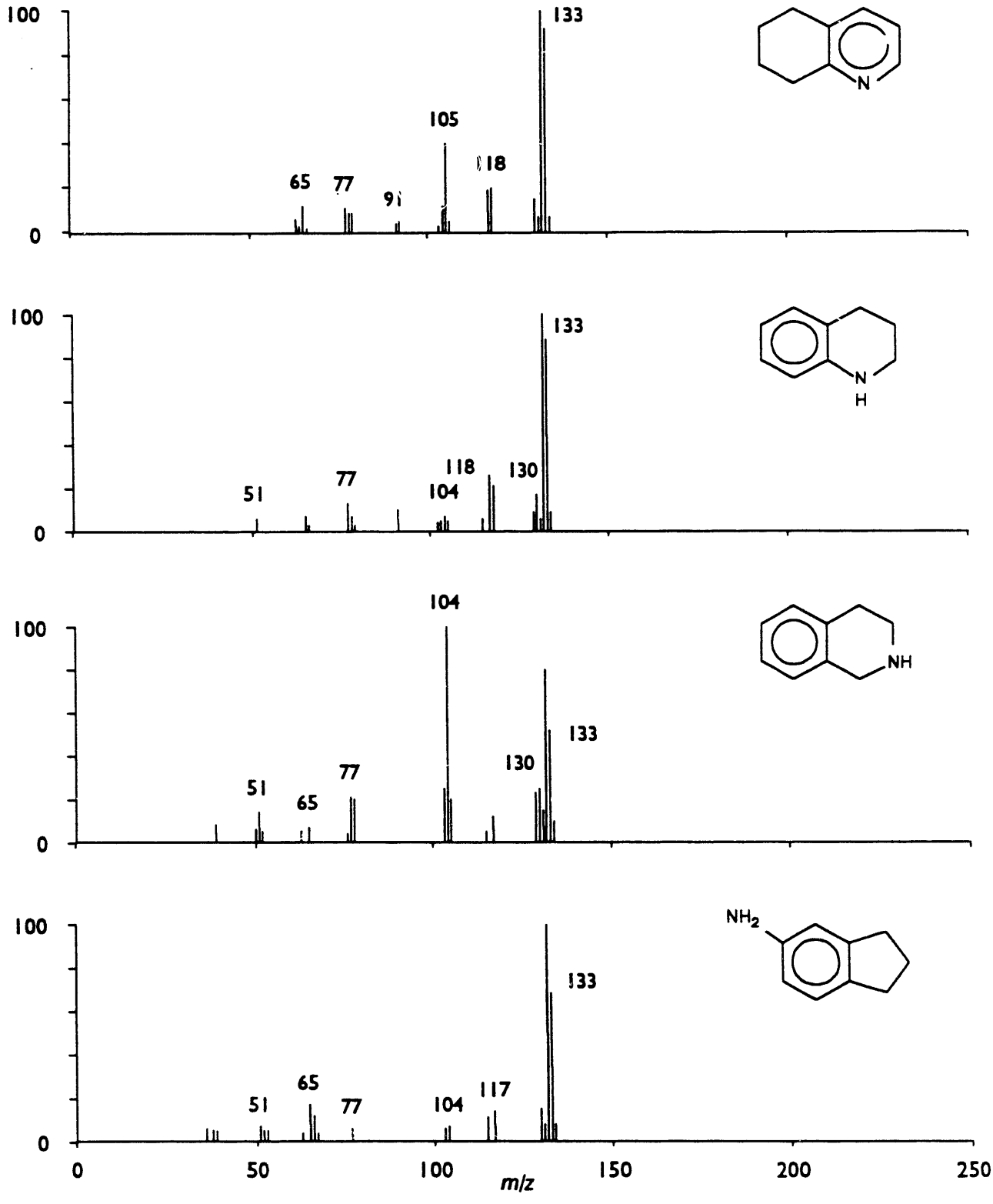

Figure 1. Mass Spectra of Hydrodenitrogenation Intermediates.
(Twenty Most Prominent Ions)

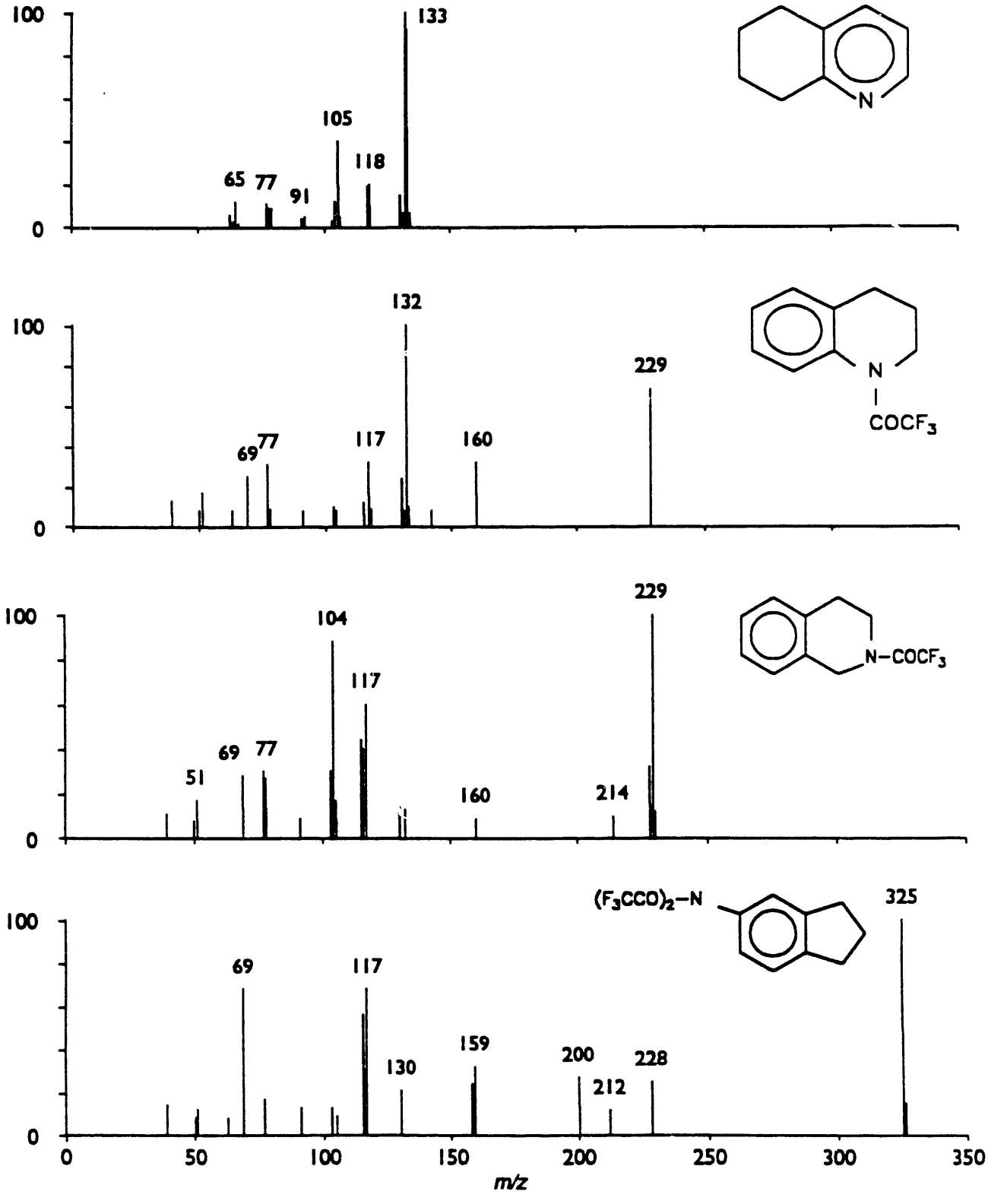

Figure 2. Mass Spectra of Hydrodenitrogenation Intermediates Derivatized to form Mono- or Di-trifluoroacetamides.
(Twenty Most Prominent Ions)

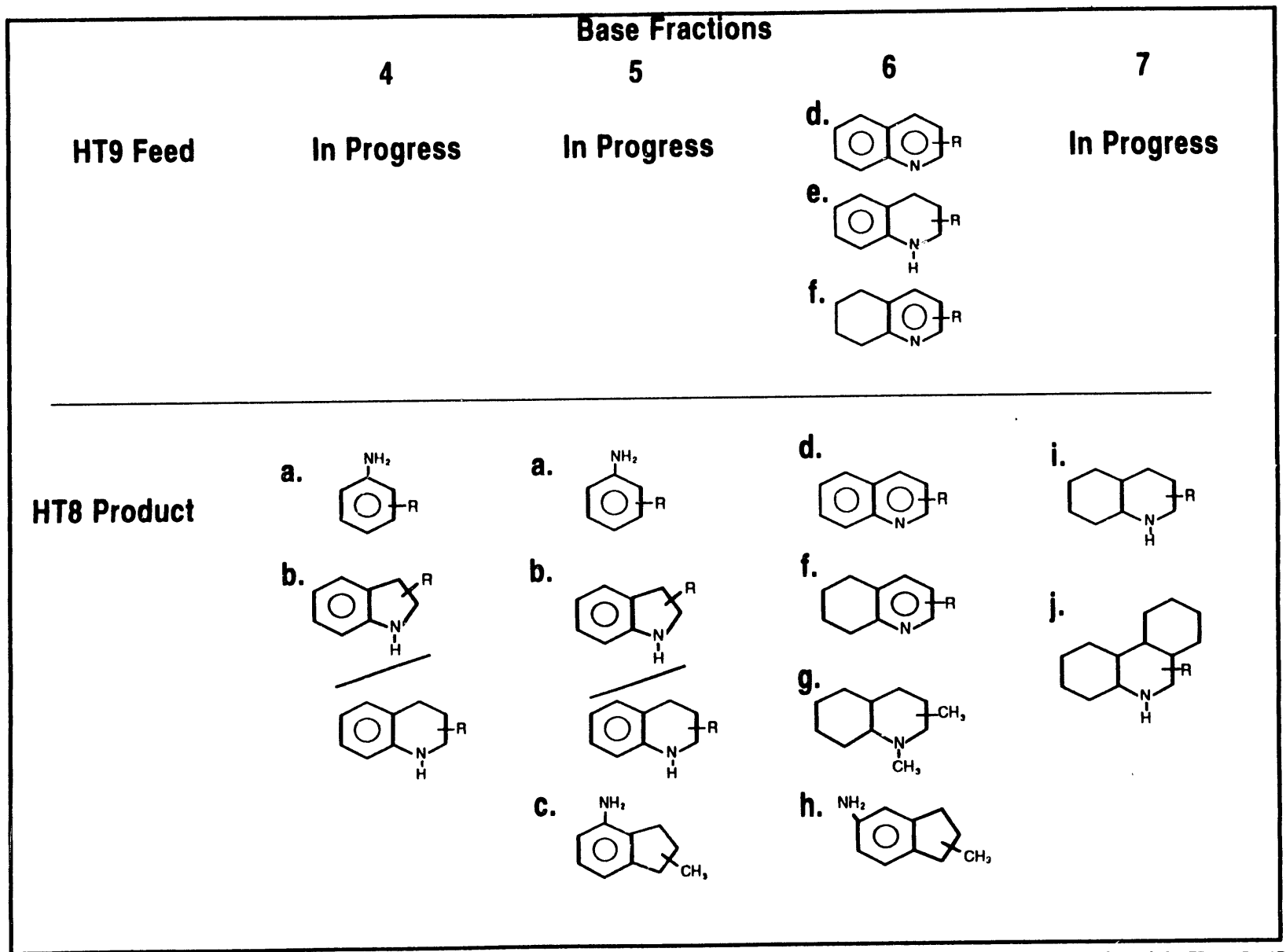

Figure 3. Aromatic Amine Compound Types in an SRC II 200-325° C Coal Liquid Feed (HT9) and Lightly Hydrotreated Product (HT8): a. anilines, b. indolines/1,2,3,4-tetrahydroquinolines, c. 4-aminoindans, d. quinolines, e. 1,2,3,4-tetrahydroquinolines, f. 2,3-cyclohexenopyridines, g. N-alkyldecahydroquinoline, h. 5-aminoindans, i. decahydroquinolines, and j. tetradecahydrophenanthridines.

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