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g of bromine remained. Filtration yielded 469 g of colorless crystalline product, mp 168–172 °C. Evaporation of the filtrate gave 60 g of additional product. Recrystallization from methanol gave mp 170–172.5 °C (lit. (*6*) 164 °C).

Resolution. All procedures in the formation of the *d*-tartrate salts were performed at ice temperatures. To a stirred cold mixture of **4** (29.8 g, 0.1 mol) in 180 mL of H_2O and 125 mL of ether was added a cold solution of NaOH (4.4 g, 0.11 mol) in 40 mL of H_2O. After separation of the ether layer, the aqueous layer was extracted with three portions of cold ether (100-mL total). The combined ether solution was washed once with cold H_2O and added to a cold solution of *d*-tartaric acid (15.1 g of 99.7%, 0.1 mol) in 175 mL of methanol. Filtration of the resulting precipitate yielded 32.4 g of colorless crystalline material, $[\alpha]^{22}_{\mathrm{D}}$ +10.7° (*c* 1.0, H_2O). The material was recrystallized from methanol (temperature below 60 °C): first crop (room temperature), 13 g, $[\alpha]^{22}_{\mathrm{D}}$ −2.5°; second crop (0 °C), 4 g, $[\alpha]^{22}_{\mathrm{D}}$ +9°; third crop (solvent reduction), 12 g, $[\alpha]^{22}_{\mathrm{D}}$ +24°.

Several recrystallizations of the levorotary first-crop material from methanol (temperature < 60 °C) gave the (−) *d*-tartrate salt of mono-2,3-dibromopropylamine [**(−)-5**], $[\alpha]^{24}_{\mathrm{D}}$ −12.8° (*c* 0.939, H_2O).

Several recrystallizations of the third-crop material (dextrorotary) from H_2O (temperature < 60 °C) gave the (+) *d*-tartrate salt of mono-2,3-dibromopropylamine [**(+)-5**], $[\alpha]^{24}_{\mathrm{D}}$ +34.8° (*c* 0.939, H_2O) (lit. (*6*) $[\alpha]_{\mathrm{D}}$ 31°).

(+)-2,3-Dibromo-1-propanol [**(+)-1**]. To a cold solution of the (+) *d*-tartrate salt **(+)-5** (5.5 g, 0.015 mol) in 40 mL of H_2O containing 0.77 g of H_2SO_4 was added with stirring a solution of $NaNO_2$ (1.25 g of 97%, 0.0175 mol) in 10 mL of H_2O over a period of 6 min. Stirring of the cold mixture was continued for 30 min and the mixture was then allowed to stand at room temperature overnight. Usual workup, after adding 0.5 g of urea, gave 2.4 g of light yellow liquid, $[\alpha]^{22}_{\mathrm{D}}$ +12.6° (*c* 1.253, MeOH). Comparison of the NMR spectrum with that of reference 2,3-dibromo-1-propanol showed an extraneous doublet (J = 6 Hz) at δ 3.6, indicative of contamination with some 1,3-dibromo-2-propanol. GLC analysis showed 87% of the major primary alcohol and 13% of the secondary.

Chromatographic separation was performed on dry packed columns of silica gel or neutral aluminum oxide (deactivated with 8% H_2O) using mixtures of hexane, benzene, and ether. The secondary alcohol eluted first on the silica gel while the primary was first on the aluminum oxide. There was considerable retention on aluminum oxide which varied with degree of deactivation. Fractions were analyzed by NMR or GLC. Distillation of combined best fractions from several runs (0.395 g), using a micro cold finger apparatus, at 3 mm (oil bath temperature gradually raised to 90 °C) gave 0.301 g of colorless liquid (99.5% primary alcohol by GLC), $[\alpha]^{26}_{\mathrm{D}}$ +13.8° (*c* 1.004, MeOH).

(−)-2,3-Dibromo-1-propanol [**(−)-1**]. The levorotary enantiomer was obtained from the (−) *d*-tartrate salt **(−)-5** by the procedure described above for the dextrorotary enantiomer. Distillation of 0.36 g of combined chromatography fractions yielded 0.19 g of colorless liquid (98.8% primary alcohol by GLC), $[\alpha]^{29}_{\mathrm{D}}$ −12.6° (*c* 1.076, MeOH).

Separation of the primary and secondary alcohols was also accomplished by preparative GLC. The compounds so obtained were analyzed by mass spectrometry. Both 2,3-dibromo-1-propanol and 1,3-dibromo-2-propanol gave low-intensity (~2% of height of the base peak) molecular ions at m/z 216, 218, and 220 in an approximate ratio of 1:2:1 corresponding to the abundance of the various bromine isotopes. Corresponding low-intensity ion fragments due to loss of the hydroxyl radical were observed at m/z 199, 201, and 203. The spectra for the two structural isomers differed markedly in the intensities of other fragment ions. Whereas 2,3-dibromo-1-propanol produced intense (80–90% of the height of the base peak) fragment ions from the loss of a bromine radical and HBr, 1,3-dibromo-2-propanol produced weakly intense ions at m/z 136, 137, 138, and 139 (17–20% of the height of the base peak). Furthermore, the base peaks for the primary alcohol were at m/z 106 and 108, corresponding to the loss of HBr plus H_2CO, whereas the base peaks for the secondary alcohol were at m/z 123 and 125, corresponding to the loss of the bromomethylene radical.

Acknowledgment

We thank Mr. William Howald for his assistance in obtaining the mass spectra.

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Received for review April 12, 1982. Accepted July 23, 1982. A grant from the National Institute of Environmental Health Sciences to S.D.N., ES 02728, is gratefully acknowledged. Mr. William Howald is supported by the NIH Division of Research Resources Grant RR 09082.

Preparation of New *N*-[α-(Benzylidenamino)benzyl]benzamides and *N*,*N*′-Benzylidenebis(benzamides)

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Several benzylamines were oxidized with buffered potassium permanganate to give complex iminobenzamides. These products were then aroylated with acid chlorides to give bis(benzamides).

In connection with the earlier work concerning the novel oxidation of benzylamines to give complex iminobenzamides (*1–3*), several new examples of the reaction are now reported (Table I). These iminobenzamides, and others, were transformed into complex bis(benzamides) by treatment with a variety of aromatic acid chlorides (Table II).

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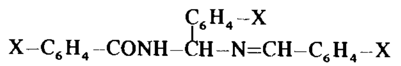
0021-9568/82/1727-0475$01.25/0

Table I. Complex Iminobenzamide Oxidation Products

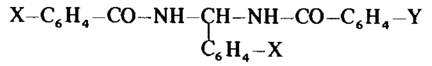


$X-C_6H_4-CONH-\underset{}{\overset{C_6H_4-X}{\overset{|}{C}}}H-N=CH-C_6H_4-X$

compd no.	parent benzylamine	X	empirical formula of oxidation product[a]	yield, %	mp,[b] °C	¹H NMR,[e,f] δ
1	benzylamine	H	$C_{21}H_{18}N_2O$[c]	55	145–148	6.97–8.17 (m, ArH and methine), 8.53 (s, –CH=N–)
2	2-methylbenzylamine	2-CH$_3$	$C_{24}H_{24}N_2O$	79	118–120	2.23–2.77 (ArCH$_3$[g]), 6.87–8.23 (m, ArH and methine), 8.53 (s,[h] –CH=N–)
3	2-chlorobenzylamine	2-Cl	$C_{21}H_{15}Cl_3N_2O$[d]	82	143–145	6.93–8.33 (m, ArH and methine), 9.03 (s,[h] –CH=N–)
4	2-fluorobenzylamine	2-F	$C_{21}H_{15}F_3N_2O$[i]	64	133–135	6.73–8.50 (m, ArH and methine), 8.83 (s,[h] –CH=N–)
5	4-methylbenzylamine	4-CH$_3$	$C_{24}H_{20}N_2O$[c]	74	125–129	2.33 (s, ArCH$_3$[g]), 6.83–8.07 (ArH and methine), 8.43 (s, –CH=N–)

[a] Elemental analyses for C, H, and N in agreement with theoretical values obtained and submitted for review. They were performed by Robertson's Microanalytical Laboratory, 73 West End Avenue, Florham Park, NJ 07932. [b] All melting points were obtained in a Thomas-Hoover melting-point apparatus in open capillary tubes. All samples were recrystallized from ethanol-water. [c] Data from preliminary study; see ref *3*. [d] This compound is included for completeness. [e] Proton magnetic resonance spectra were obtained from a Varian Associates EM 300X nuclear magnetic resonance spectrometer, and chemical shifts (δ) are recorded downfield from an internal tetramethylsilane (Me_4Si) standard. The compounds are suspended in $CDCl_3$ and enough dimethyl sulfoxide (Me_2SO-d_6) is added to effect solution. [f] Amide (NH) absorptions are not usually discernible. [g] The range/chemical shift for nearly isochronous or isochronous absorptions is recorded. [h] Broad; some splitting indicated or NH. [i] Mass spectrum, *m/e* 368 (M). Other characteristic fragmentations and rearrangements are as follows (*m/e*, ion (relative intensity, %)): 246, $C_{14}H_{10}F_2NO$ (46); 139, C_7H_6FNO (42); 123, C_7H_4FO and/or C_7H_6FN (100).

Table II. Complex Bis(benzamides)



$X-C_6H_4-CO-NH-\underset{C_6H_4-X}{\underset{|}{C}}H-NH-CO-C_6H_4-Y$

compd no.	parent iminobenzamide[a]	acid chloride	X	Y	empirical formula of product[b,c]	yield, %	mp,[d] °C	¹H NMR,[e] δ
1	1	benzoyl chloride	H	H	$C_{21}H_{18}N_2O_2$	67	231–232	6.80–7.80 (m, ArH and methine), 8.40–9.10 (m, NH[f])
2	1	4-fluorobenzoyl chloride	H	4-F	$C_{21}H_{17}FN_2O_2$	76	204–205	6.60–8.30 (m, ArH and methine), 8.43–8.80 (m, NH)
3	1	4-methylbenzoyl chloride	H	4-CH$_3$	$C_{22}H_{20}N_2O_2$	74	189–191	2.37 (s, ArCH$_3$[g]), 6.70–8.10 (ArH and methine), 8.40–8.93 (m, NH)
4	1	4-chlorobenzoyl chloride	H	4-Cl	$C_{21}H_{17}ClN_2O_2$	78	176–178	6.98–8.15 (m, ArH and methine), 8.62–8.92 (m, NH)
5	2	benzoyl chloride	2-CH$_3$	H	$C_{22}H_{20}N_2O_2$	81	216–220	2.28–2.67 (ArCH$_3$[g]), 6.42–8.82 (m, ArH, methine, and NH)
6	1	3-fluorobenzoyl chloride	H	3-F	$C_{21}H_{17}FN_2O_2$	71	222–224	6.83–8.17 (m, ArH and methine), 8.47–9.37 (m, NH)
7	1	3-chlorobenzoyl chloride	H	3-Cl	$C_{21}H_{17}ClN_2O_2$	72	157–159	6.83–8.27 (m, ArH and methine[h])
8	1	2-fluorobenzoyl chloride	H	2-F	$C_{21}H_{17}FN_2O_2$	81	194–195	6.77–9.43 (m, ArH, methine, and NH)
9	1	2-methylbenzoyl chloride	H	2-CH$_3$	$C_{22}H_{20}N_2O_2$	76	212–214	2.40 (s, ArCH$_3$[g]), 6.70–8.13 (m, ArH and methine), 8.37–9.10 (m, NH)
10	2	4-chlorobenzoyl chloride	2-CH$_3$	4-Cl	$C_{23}H_{21}ClN_2O_2$	79	203–206	2.13–2.57 (ArCH$_3$[g]), 6.70–8.10 (ArH and methine), 8.33–8.83 (m, NH)
11	2	4-fluorobenzoyl chloride	2-CH$_3$	4-F	$C_{23}H_{21}FN_2O_2$	75	186–189	2.42–2.50 (ArCH$_3$[g]), 6.75–8.08 (ArH and methine), 8.25–9.15 (m, NH)
12	4	benzoyl chloride	2-Cl	H	$C_{21}H_{16}F_2N_2O_2$	84	198–200	6.50–9.20 (m, ArH, methine, and NH)
13	6	benzoyl chloride	4-CH$_3$	H	$C_{23}H_{22}N_2O_2$	76	203–204	2.12–2.52 (ArCH$_3$[g]), 6.78–8.08 (ArH and methine), 8.35–8.85 (m, NH)
14	6	4-chlorobenzoyl chloride	4-CH$_3$	4-Cl	$C_{23}H_{21}ClN_2O_2$	86	218–220	2.30 (s, ArCH$_3$[g]), 6.70–8.13 (ArH and methine), 8.27–9.20 (m, NH)
15	6	4-fluorobenzoyl chloride	4-CH$_3$	4-F	$C_{23}H_{21}FN_2O_2$[i]	82	229–231	2.38–2.60 (ArCH$_3$[g]), 6.63–8.10 (m, ArH and methine), 8.38–9.23 (m, NH)

[a] Number of parent iminobenzamide in Table I. [b] Elemental analyses for C, H, and N in agreement with theoretical values obtained and submitted for review. They were performed by Robertson's Microanalytical Laboratory, 73 West End Avenue, Florham Park, NJ 07932. [c] All products were recrystallized from ethanol-water. [d] Melting points were obtained in a Thomas-Hoover melting-point apparatus in open capillary tubes. [e] Proton magnetic resonance spectra were obtained from a Varian Associates EM-300X nuclear magnetic resonance spectrometer, and chemical shifts (δ) are reported downfield from an internal tetramethylsilane (Me_4Si) standard. The compounds were suspended in $CDCl_3$ and enough dimethyl sulfoxide (Me_2SO-d_6) was added to effect solution. [f] Usually discernible, and when there were no solubility problems, exchange with D_2O was observed. [g] Nearly isochronous or isochronous absorptions. [h] NH not discernible. [i] Mass spectrum, *m/e* 376 (M). Other characteristic fragmentations and rearrangements are as follows (*m/e*, ion (relative intensity, %)): 257, $C_{15}H_{14}FN_2O$ (100); 253, $C_{16}H_{17}N_2O$ (41); 237, $C_{16}H_{15}NO$ (6); 225, $C_{15}H_{17}N_2$ (30); 139, C_7H_6FNO (7); 135, C_8H_9NO (14); 123, C_7H_4FO (27); 119, C_8H_7O (34); and 105, C_7H_5O (8).

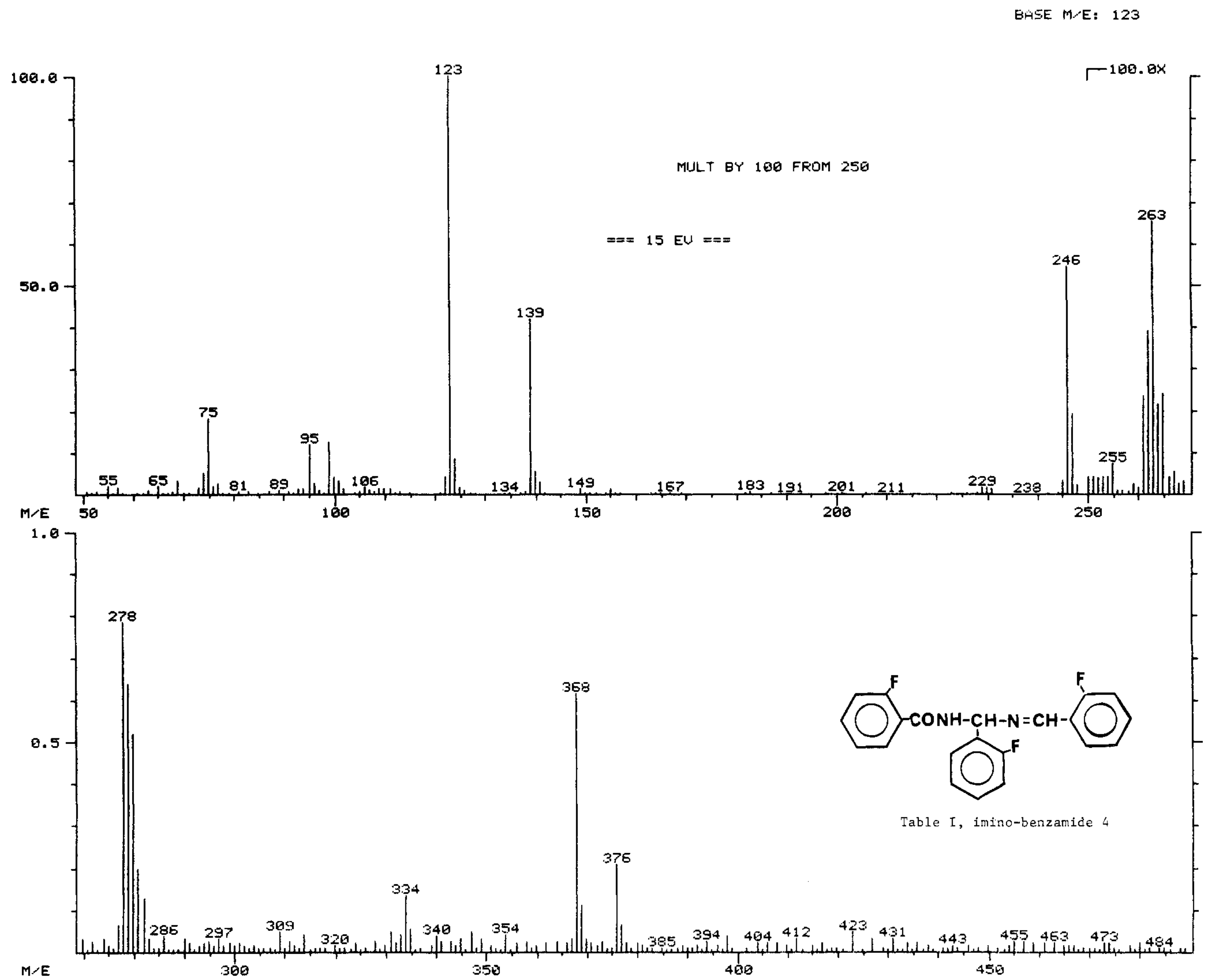
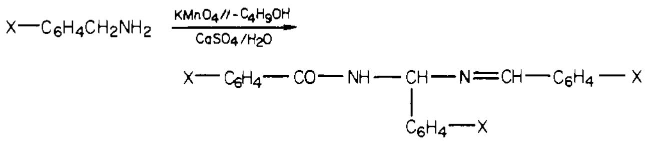


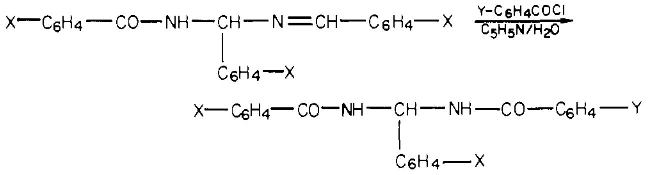
Figure 1. Mass spectra of iminobenzamide 4.

The oxidation of the benzylamines was effected in aqueous *tert*-butyl alcohol buffered by calcium sulfate, which caused precipitation of calcium hydroxide as the organic product was formed. The structures of these unusual iminobenzamides have been established previously, in a preliminary study (*3*), by elemental analysis, absorption spectra, and acid hydrolysis to give substituted benzaldehydes (2 equiv), substituted benzamides (1 equiv), and ammonia. The new iminobenzamides gave satisfactory elemental analyses and infrared spectra. Each material prepared displayed absorptions at ca. 3330 (NH), 1640 (C=O), and 1615 (C=N) cm^{-1}. In addition, proton magnetic resonance spectra displayed aromatic, methyl (where applicable), and imine (—CH=N—) resonances (Table I).



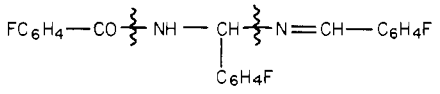
$$X{-}C_6H_4CH_2NH_2 \xrightarrow[CaSO_4/H_2O]{KMnO_4//\text{-}C_4H_9OH} X{-}C_6H_4{-}CO{-}NH{-}\underset{\displaystyle C_6H_4{-}X}{CH}{-}N{=}CH{-}C_6H_4{-}X$$

When these iminobenzamides were treated with a variety of aroyl chlorides in pyridine, unusual bis(benzamides) were formed (Table II). These new compounds were also characterized by infrared spectra (3333 cm^{-1} for NH and 1667 cm^{-1} for C=O), proton magnetic resonance (for ArH, methyl when applicable, and NH), and elemental analyses.



$$X{-}C_6H_4{-}CO{-}NH{-}\underset{\displaystyle C_6H_4{-}X}{CH}{-}N{=}CH{-}C_6H_4{-}X \xrightarrow[C_5H_5N/H_2O]{Y\text{-}C_6H_4COCl} X{-}C_6H_4{-}CO{-}NH{-}\underset{\displaystyle C_6H_4{-}X}{CH}{-}NH{-}CO{-}C_6H_4{-}Y$$

Several representative compounds (Tables I and II) were given mass-spectral analysis. In general, the compounds easily fragmented; however, mass spectra of iminobenzamide 4 (Table I, Figure 1) taken at 15 eV did display a molecular ion at *m/e* 368 and other informative fragmentations/rearrangements. The base peak, *m/e* 123, could result from simple fragmentation of the amide carbon-nitrogen bond or from an ion resulting from rearrangement ($FC_6H_4CH{=}NH$). Another rearrangement could account for the ion noted at *m/e* 139 ($FC_6H_4CONH_2$). Interestingly, a spectrum of this compound obtained at 70 eV contained an ion, *m/e* 109, which could be assigned to a benzyl- or tropylium-type ion. Bis(benzamide) **15** (15 eV)



$$FC_6H_4{-}CO \wr NH{-}\underset{\displaystyle C_6H_4F}{CH} \wr N{=}CH{-}C_6H_4F$$

iminobenzamide 4

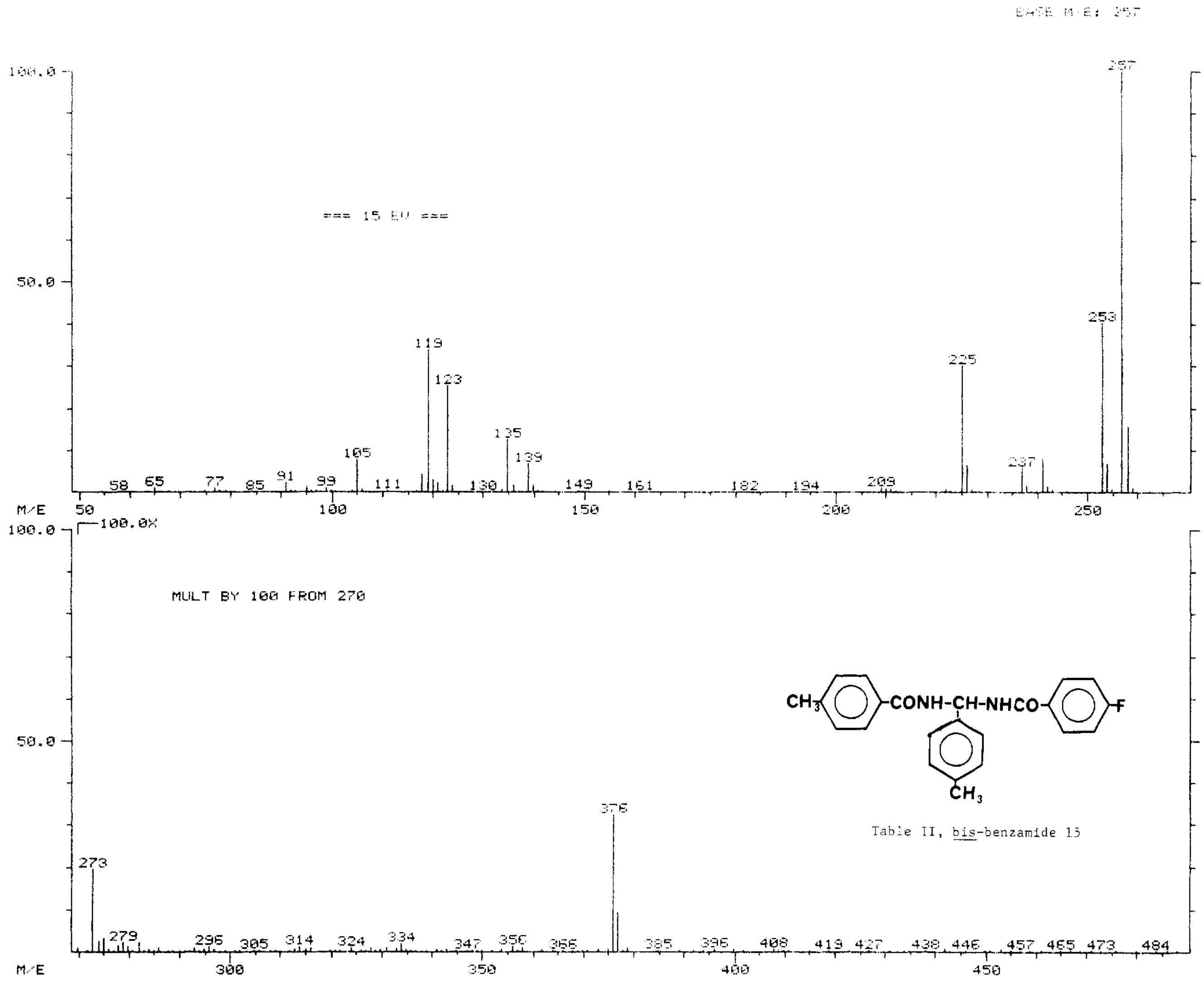
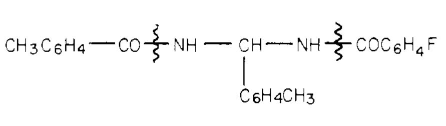


Figure 2. Mass spectra of bis(benzamide) **15**.

(Table II, Figure 2) also displayed a molecular ion at *m/e* 376 and several simple fragmentations (amide carbon–nitrogen bonds) to give ions at *m/e* 119 ($CH_3C_6H_4CO$), *m/e* 123 (FC_6H_4CO), *m/e* 257 ($CH_3C_6H_4CH(NH)NHCOC_6H_4F$), and *m/e* 253 ($CH_3CONHCH(NH)C_6H_4CH_3$). Rearrangements could also account for ions noted at *m/e* 237 ($CH_3C_6H_4CON{=}CHC_6H_4CH_3$), *m/e* 139 ($FC_6H_4C(OH){=}NH$ or $FC_6H_4CONH_2$), and *m/e* 135 ($CH_3C_6H_4C(OH){=}NH$ or $CH_3C_6H_4CONH_2$).



$$CH_3C_6H_4\text{—}CO\text{—}NH\text{—}\underset{\displaystyle C_6H_4CH_3}{\underset{|}{CH}}\text{—}NH\text{—}COC_6H_4F$$

bis(benzamide) 15

Experimental Procedures

See references cited and footnotes of Tables I and II. Mass spectra were obtained at the University of South Carolina by Michael D. Walla using a Finnigan 4021 GC–MS system with Incos data system.

Acknowledgment

The technical assistance of Willie Jefferson, Girlie Livingstone, Janet Collin, and Charlie Wright is appreciated. Dr. Stephen L. Morgan of the Department of Chemistry at the University of South Carolina is also acknowledged. Dr. George I. Robertson's rapid microanalytical services are also appreciated.

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Received for review July 23, 1981. Revised manuscript received June 14, 1982. Accepted July 21, 1982. This project was supported at Voorhees College by a Minority Biomedical Support grant (RR08141-03) from the Public Health Service. The mass spectrometer used was furnished by NSF-IFP grant No. 8011451.