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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Delman, A. D. , Stein, A. A. and Simms, B. B.(1967) 'Synthesis and Thermal Stability of Structurally Related Aromatic Schiff Bases and Acid Amides', *Journal of Macromolecular Science, Part A*, 1: 1, 147 – 178

To link to this Article: DOI: 10.1080/10601326708053922

URL: <http://dx.doi.org/10.1080/10601326708053922>

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Synthesis and Thermal Stability of Structurally Related Aromatic Schiff Bases and Acid Amides*

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BROOKLYN, NEW YORK

Synopsis

A wide variety of structurally related Schiff base and acid amide compounds and low-molecular-weight polymers were synthesized. The comparative thermal stabilities of the products in air were investigated by thermogravimetric analysis. Several of the Schiff bases prepared from aromatic diamine compounds and terephthalaldehyde exhibit unusually good resistance to decomposition by heat. The influence of chemical structure on thermal stability is shown, and the important factors that may serve as a guide for the tailor-making of high-molecular-weight polymers with superior heat resistance are discussed.

The material presented in this paper is an outgrowth of recent studies at the U.S. Naval Applied Science Laboratory to develop organic polymers that exhibit electrical semiconductance properties at elevated temperatures. As a result of this work a variety of Schiff bases and other structurally related substances were prepared.

Among the substances discussed herein are several that are probably identical with, or similar to, products reported earlier by other investigators. For example, Davydov and coworkers (1) described the formation of yellow and brown poly-Schiff bases from the reaction of *p*-phenylenediamine with terephthalaldehyde

* Presented at the Symposium on High Temperature Polymers, Western Regional Meeting of American Chemical Society, Los Angeles, Calif., Nov. 18-20, 1965. *Note:* The opinions or assertions contained in this paper are the private ones of the authors and are not to be construed as official or reflecting the views of the naval service at large.

and glyoxal, respectively. Amorphous yellow polyazines were synthesized from terephthalaldehyde and hydrazine or hydrazine sulfate (2-4). Akitt et al. (5) interacted glyoxal with *p*-phenylenediamine and *o*-phenylenediamine to produce orange-red and yellow-brown Schiff bases, respectively. Polyamide substances prepared from terephthaloyl chloride and *m*-phenylenediamine or *p*-phenylenediamine are described (6,7). Magat (8) reported the synthesis of a polyamide from the reaction of *p*-benzidine and terephthaloyl chloride.

Although these and similar products have received a good deal of attention, information concerning their relative resistance to decomposition by heat is not readily obtained. In this paper the results of thermoanalytical investigations of such materials are compared and related to the chemical structure factors contributing to stability.

EXPERIMENTAL

Preparation of Schiff Bases

In general, 0.05 mole of the diamine compound and 0.05 mole of terephthalaldehyde or glyoxal (30% aqueous solution) were refluxed overnight with 100 ml of benzene, while water was continuously removed. The reaction mixture was allowed to cool to room temperature and filtered. The residue was washed several times with benzene, Soxhlet-extracted for 24 hr with about 300 ml of various solvents suitable for removing unreacted products, and dried for 1 hr at 110°C. Terephthalaldehyde and *p*-phenylenediamine were similarly treated in the presence of 2 ml of concentrated sulfuric acid. The procedure described by Marvel and Hill (2) was used for preparing the product made from hydrazine sulfate and terephthalaldehyde. In the case of the reaction of 4,4'-stilbenediamine hydrochloride and terephthalaldehyde a mixture consisting of 0.05 mole of the acid salt of the diamine, 100 ml of water, 160 ml of ethyl alcohol, and 50 ml of pyridine or 0.05 mole of sodium carbonate was stirred for several minutes at high speed in a Waring blender, 0.05 mole of the dialdehyde was added, and stirring was continued for 1 hr. The mixture was filtered and the residue was dried, successively Soxhlet-extracted overnight with water, and then toluene, and dried for 1 hr at 110°C.

Preparation of Amide Products

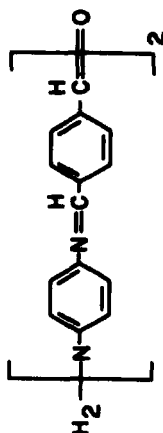
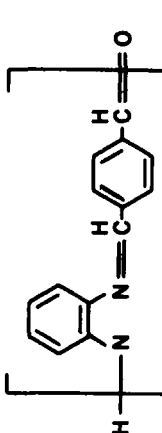
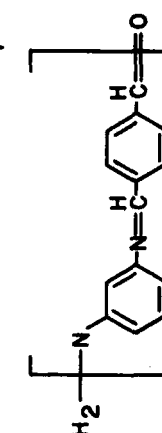
To a moderately stirred mixture of 0.05 mole of the diamine compound, 100 ml of benzene, and 50 ml of pyridine in a Waring blender was rapidly added a solution of 0.05 mole of terephthaloyl chloride in 150 ml of benzene. The mixture was stirred at high speed for several minutes and filtered, and the residue was washed free from soluble salts with water and dried at 110°C. The product was then Soxhlet-extracted for several days with dimethyl formamide and dried at 110°C. The product made from terephthaloyl chloride and *p*-phenylenediamine was similarly prepared by the addition of 0.05 mole of the acid chloride compound dissolved in 300 ml of trichloroethylene, while the condensation of the acid chloride compound and hydrazine sulfate was conducted in the presence of 0.15 mole of sodium carbonate as the acid acceptor. The reaction mixtures were worked up as before.

Treatment of Poly-Schiff Bases

Specimens of poly(3-aminobenzaldehyde) and poly(4-aminobenzaldehyde) were purchased from the Aldrich Chemical Co., Inc., Milwaukee, Wisconsin. A mixture of 20.0 g of poly(3-aminobenzaldehyde) and 100 ml of benzene was refluxed overnight, and 0.6 ml of water of condensation was collected. The mixture was filtered to produce 9.5 g of residue, which was dried and extracted for 24 hr with toluene to yield 8.1 g of insoluble product. A 22.7-g sample of poly(4-aminobenzaldehyde) was extracted for several days with water to produce 17.6 g of dried insoluble residue. The residue was refluxed overnight with 100 ml of benzene, 0.02 ml of water of condensation was collected, and the mixture was separated by filtration. The insoluble component was dried at 110°C to yield 13.8 g of product.

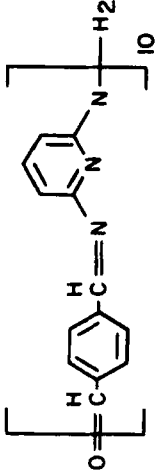
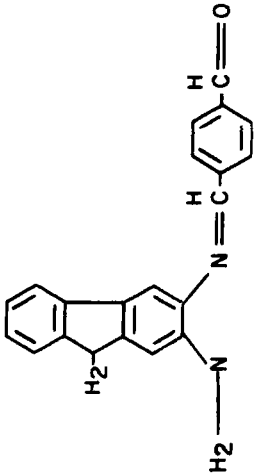
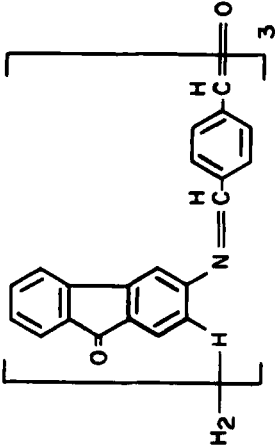
The colors, yields, uncorrected melting points, microanalytical results, and suggested chemical structures of all of the products are compiled in Tables 1 to 4. The general insolubility of the materials in common organic solvents precluded measurements of their molecular weights. Instead, estimations were made from elemental analysis data.

TABLE 1
Reaction Products from Terephthalaldehyde and Diamines

Specimen	Product	Diamine	Color	Yield, %	M.P., °C ^a	Carbon, %		Hydrogen, %		Nitrogen, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
I		<i>p</i> -Phenylenediamine (addn. of 2 ml concd. H ₂ SO ₄)	Orange	91.6	> 300	78.14	78.39	5.12	5.18	13.02	13.47
II		<i>o</i> -Phenylenediamine	Yellow	76.0	283-287	79.81	79.58	4.99	5.38	13.30	13.56
III		<i>m</i> -Phenylenediamine	Light yellow	43.5	> 300	79.25	79.16	5.50	5.03	12.56	13.21

IV	<p><i>p</i>-Benzidine</p>	Mustard yellow	88.8	> 300	83.33	83.53	5.09	5.37	9.72	9.32
V	<p>1,5-Diaminonaphthalene</p>	Yellow green	89.0	> 300	82.92	82.94	4.80	5.01	10.75	10.90
VI	<p>2,4-Diaminazobenzene</p>	Rust	48.9	> 300	75.24	74.38	4.70	4.83	17.53	17.58

TABLE 1 (Continued)

Specimen	Product	Diamine	Color	Yield, %	M.p., °C ⁿ	Carbon, %		Hydrogen, %		Nitrogen, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
VII		2,6-Diaminopyridine	Orange	71.6	Darkens 270-275	74.71	74.88	4.41	4.27	20.11	20.23
VIII		2,3-Diaminofluorene	Red	59.7	> 300	80.77	79.62	5.13	5.22	8.97	10.67
IX		2,3-Diamino-9-fluorene	Red	61.7	> 300	79.95	80.25	4.34	4.03	8.92	9.23

X	4,4'-Stilbenediamine hydrochloride	Orange	91.2	> 300	80.98	81.27	5.52	5.13	8.59	8.90
XI	Hydrazine sulfate	Greenish yellow	78.5	> 300	73.64	73.87	4.60	5.11	19.52	19.54
XII	1,5-Diaminoanthraquinone	Maroon	84.2	Decompd. 225-230	76.52	75.68	3.76	4.46	8.12	8.26

TABLE 1 (Continued)

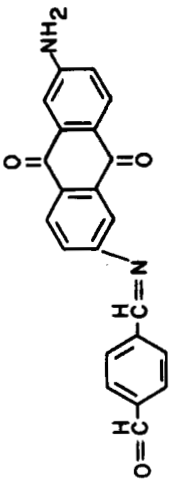
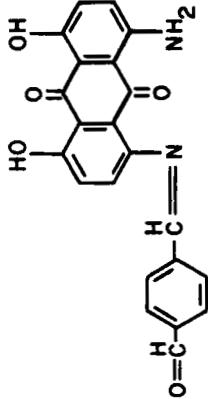
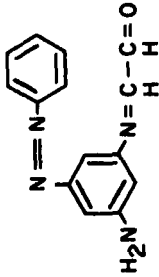
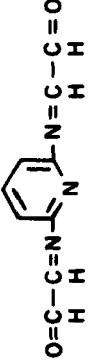

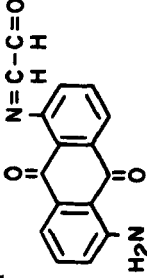
Specimen	Product	Diamine	Color	Yield, %	M.p., °C°	Carbon, %		Hydrogen, %		Nitrogen, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
XIII		2,6-Diaminoanthraquinone	Black	55.3	>300	74.58	74.93	3.95	3.48	7.91	7.71
XIV		1,8-Diamino-4,5-dihydroxyanthraquinone	Dark blue	41.5	>300	67.02	66.39	3.90	3.63	7.25	7.63

TABLE 2
Reaction Products from Glyoxal and Diamines

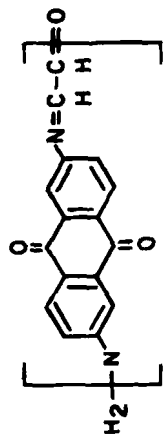
Specimen	Product	Diamine	Color	Yield, %	M.p., °C ^a	Carbon, %		Hydrogen, %		Nitrogen, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
XV		<i>p</i> -Phenylenediamine	Chocolate	74.5	>300	63.83	63.71	4.26	5.53	14.89	15.14
XVI		<i>o</i> -Phenylenediamine	Dark brown	24.5	162-4	63.83	63.20	4.26	4.93	14.89	15.15
XVII		<i>m</i> -Phenylenediamine	Dark brown	57.4	>300	63.83	63.70	4.26	3.94	14.89	13.81
XVIII		<i>p</i> -Benzidine	Chocolate	83.8	>300	75.00	73.65	5.36	5.53	12.50	12.32
XIX		1,5-Diaminonaphthalene	Dark brown	75.9	>300	72.73	72.60	5.05	4.54	14.14	13.83

^a Uncorrected.

TABLE 2 (Continued)

Specimen	Product	Diamine	Color	Yield, %	M.p., °C ^a	Carbon, %		Hydrogen, %		Nitrogen, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
XX		2,4-Diaminobenzene	Chocolate	61.9	>300	66.87	66.03	4.76	4.62	22.22	21.42
XXI		2,6-Diaminopyridine	Chocolate	38.1	>300	57.14	57.66	3.70	3.82	22.22	23.50
XXII		4,4'-Stilbenediamino hydrochloride	Red-brown	90.9	>300	76.80	75.49	5.60	5.33	11.20	11.34
XXIII		1,5-Diaminoanthraquinone	Red-brown	93.5	Decomp. 254-6	69.06	68.75	3.60	3.08	10.07	10.06

XXIV 2,6-Diaminoanthraquinone Dark purple 98.5 > 300 72.18 71.99 3.26 2.95 10.53 10.49



XXV 1,8-Diamino-4,5-dihydroxy-anthraquinone Dark purple 64.0 > 300 61.71 60.59 2.86 2.53 8.00 8.19

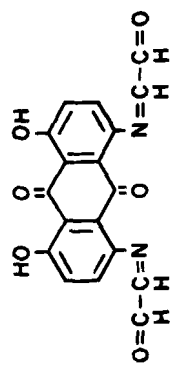


TABLE 3
Reaction Products from Terephthaloyl Chloride and Diamines

Specimen	Product	Diamine	Color	Yield, %	M.p., °C.	Carbon, %		Hydrogen, %		Nitrogen, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
XXVI		<i>p</i> -Phenylenediamine	Beige	84.4	>300	68.02	67.69	4.45	4.92	11.34	11.38
XXVII		<i>o</i> -Phenylenediamine	Beige	90.02	Discolor 255-260	69.26	69.13	4.14	4.83	10.54	10.57
XXVIII		<i>p</i> -Benzidine	Grey green	70.3	>300	74.30	73.22	4.64	4.86	8.67	8.52
XXIX		Hydrazine sulfate	Yellow green	82.6	>300	56.14	55.74	4.09	4.58	16.37	16.55

XXX

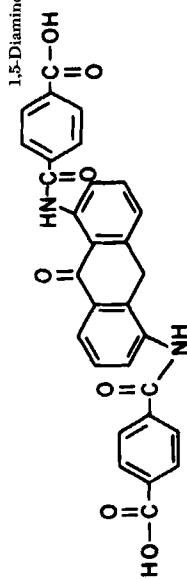
Orange
brown

74.3

> 300

67.42 67.19 3.37 4.24

5.24 5.53



XXXI

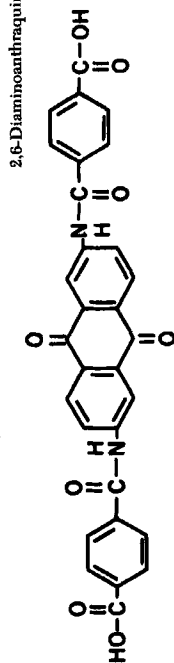
Black

46.7

> 300

69.50 69.12 3.47 3.89

5.41 5.18



XXXII

Black

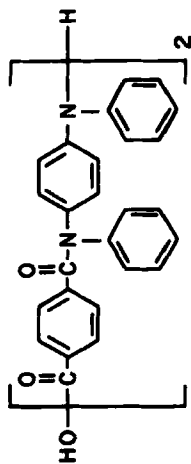
19.9

> 300

76.20 77.92 4.76 5.06

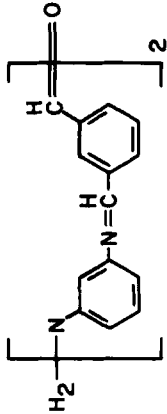
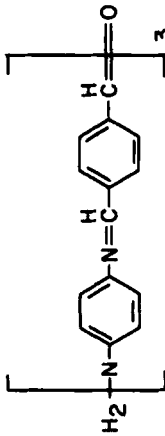
7.02 7.37

N,N'-Diphenyl-*p*-phenyl-enediamine



^a Uncorrected.

TABLE 4
Products from 3-Amino- and 4-Aminobenzaldehyde Polymers

Specimen	Product	Color	Yield, %	M.p., °C*	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
XXXIII		Light beige	48.2	> 300	78.14	78.08	5.12	5.16	13.02	12.45
XXXIV		Orange	62.5	> 300	79.25	79.54	5.03	5.35	13.21	13.15

* Uncorrected.

TABLE 5
Infrared Absorptions of Reaction Products (μ)

Reaction product no.	NH _{str}	OH _{str}	C=O (Aldehyde str)	COO— _{str}	CONH— _{str}	CON< _{str}	C=N (ring str)	C=C (ring str)	C=C/C=N (ring str)
I	2.99							6.28	
	3.07	—	5.87	—	—	—	6.18	6.63	—
II	3.01							6.27	
	3.07	—	5.87	—	—	—	6.17	6.67	—
III	2.98							6.32	
	3.14	—	5.86	—	—	—	6.13	6.62	—
IV	2.96							6.27	
	3.04	—	5.87	—	—	—	6.16	6.73	—
V	2.87							6.30	
	2.95	—	5.85	—	—	—	6.15	6.60	—
VI	2.90							6.25	
	2.98	—	5.87	—	—	—	6.14	6.35	—
VII	3.02							6.67	
	3.07	—	5.93	—	—	—	6.18	—	6.30
									6.35
									6.72
VIII	2.87							6.32	
	2.97	—	5.87	—	—	—	6.15	6.72	—
IX	2.91							6.30	
	3.03	—	5.91	—	—	—	6.15	6.68	—
X	—	—	5.87	—	—	—	6.16	6.38	—
								6.58	—
XI	—	—	5.87	—	—	—	6.13	6.28	—
								6.63	—
XII	2.93							6.28	
	3.04	—	5.87	—	—	—	6.12	6.64	—
XIII	2.98							6.27	
	3.10	—	5.87	—	—	—	6.12	6.37	—
								6.55	—
XIV	3.03							6.33	
	3.07		5.86	—	—	—	6.10	6.58	—
XV	—	—	5.87	—	—	—	6.08	6.27	—
								6.62	—
XVI	—	—	5.75	—	—	—	—	6.27	—
			5.90	—	—	—	6.13	6.67	—
XVII	—	—	5.77	—	—	—	6.10	6.33	—
								6.58	—
XVIII	2.96		5.75	—	—	—	—	6.25	—
	3.04	—	5.97	—	—	—	6.10	6.62	—
XIX	2.90		5.75	—	—	—	—	6.28	—
	2.97	—	5.87	—	—	—	6.13	6.57	—
XX	2.90		5.78	—	—	—	—	6.37	—
	2.98	—	5.88	—	—	—	6.10	6.58	—
XXI	—	—	5.78	—	—	—	—	—	6.00
									6.33
									6.37
XXII	2.90		5.77	—	—	—	—	6.38	—
	3.00	—	5.90	—	—	—	6.11	6.58	—
XXIII	2.93							6.33	
	3.03	—	5.75	—	—	—	6.12	6.64	—

TABLE 5 (Continued)

Reaction product no.	NH _{str}	OH _{str}	C=O (Aldehyde str)	COO— _{str}	CONH— _{str}	CON< _{str}	C=N (ring str)	C=C (ring str)	C=C/C=N (ring str)
XXIV	2.97		5.72					6.37	
	3.10	—	5.90	—	—	—	6.11	6.63	—
XXV	—	2.93	5.77	—	—	—	6.12	6.58	—
			5.88					6.22	
XXVI	3.02	3.78	—	5.92	6.06	—	—	6.58	—
					6.47	—	—	6.23	—
XXVII	—	3.10	—	5.93	6.04	—	—	6.54	—
					6.54	—	—	6.27	—
XXVIII	3.02	Very Broad	—	5.92	6.04	—	—	6.65	—
					6.57	—	—	6.28	—
XXIX	3.18	2.94	—	5.92	6.05	—	—	6.68	—
					6.60	—	—	6.30	—
XXX	—	—	—	5.80	6.08	—	—	6.65	—
					6.54	—	—	6.31	—
XXXI	2.93	3.04	—	5.95	6.11	—	—	6.60	—
					6.56	—	—	6.27	—
XXXII	—	3.76	—	5.82	6.04	—	—	6.70	—
					6.63	6.06	—	6.22	—
XXXIII	2.93	—	5.91	—	—	—	6.12	6.33	—
								6.32	—
XXXIV	2.98	—	—	—	—	—	6.15	6.63	—
	2.98								
	3.03	—	5.92	—	—	—	6.15	6.63	—

Infrared Spectra

The spectra from Nujol suspensions of the products were recorded in the region of 2.5 to 15.0 μ with a Perkin-Elmer model 21 double-beam spectrometer equipped with sodium chloride optics. Pertinent absorption frequencies and concordant band assignments are listed in Table 5.

Thermal Stability Measurements

The relative order of resistance of the materials to thermal decomposition was assessed by thermogravimetric analysis (TGA). About 200 mg of sample was heated in a Kanthal wire-wound furnace (9) at 180°C/hr in the presence of air, until the weight loss remained constant. Temperatures and weight losses were recorded with an Ainsworth model BYR-AU-A semimicro recording balance. The thermograms of the materials are presented in Figs. 1 to 18.

RESULTS

Synthesis of Materials

A wide variety of Schiff bases and structurally related amides have been produced in this investigation. In general, low-molecular-weight polymers were obtained by the condensation of the diamine compounds with terephthalaldehyde. Mono-Schiff bases were made from terephthalaldehyde and 2,6-diaminoanthraquinone or 1,8-diamino-4,5-dihydroxyanthraquinone.

The reaction of glyoxal with the diamine compounds produced mono- and di-Schiff bases, except for the condensation with 2,6-diaminoanthraquinone, in which case a low-molecular-weight polymer was formed.

Low-molecular-weight polymers were made from the reaction of terephthaloyl chloride and all the diamine compounds, except for 1,5- and 2,6-diaminoanthraquinone, which produced diamides.

The water of condensation collected during the heat treatment of poly(3-aminobenzaldehyde) and poly(4-aminobenzaldehyde) and analysis of the infrared spectra of the products suggest that the original materials were converted to low-molecular-weight Schiff-base polymers.

Infrared Spectra

A characteristic difference was observed when the spectra from the Schiff bases were compared with those made from their corresponding reactants. The N—H bending vibrations (6.11 to 6.23 μ) of the parent diamines were completely or partially replaced with sharper C=N stretching bands (6.08 to 6.18 μ). The spectra from poly(3-aminobenzaldehyde) and poly(4-aminobenzaldehyde) show C=N_{str.} absorption modes at 6.12 and 6.15 μ , respectively. Positive assignment of the C=N_{str.} bands from the spectra of the Schiff bases prepared from 2,6-diaminopyridine is complicated by superposition of the vibrations with C=C ring frequencies. Each of the Schiff bases shows aldehydic carbonyl stretching frequencies (5.72 to 5.91 μ). In addition, several of the products exhibit weak N—H stretching bands (2.85 to 3.15 μ). This suggests that the chain ends of the low-molecular-weight

polymers are comprised of carbonyl and, in some instances, amine groups. The remainder of the absorption bands in the spectra are consistent with the proposed chemical structures of the products.

The spectra made from the products obtained by reaction of the diamine compounds and terephthaloyl chloride show amide I (6.06 to 6.11 μ) and amide II (6.47 to 6.63 μ) absorption bands which replace the N—H bending modes (6.11 to 6.23 μ) in the spectra of the amine reactants. All of the materials give spectra that contain a carbonyl stretching band from 5.80 to 5.95 μ . Several of these appear as shoulders of the stronger amide I vibrations. Several products exhibit medium or weak N—H_{str.} bands (2.93 to 3.18 μ). Other absorption bands present in the spectra conform with the suggested structures for the reaction products.

Thermal Stability

The thermal behavior of the products prepared from terephthalaldehyde and phenylenediamine compounds is shown in Fig. 1. These data indicate that the products undergo little weight loss when heated to about 400°C. The substance in which the C=N linkages are in *ortho* or *para* position on the benzene ring are more resistant to decomposition by heat than the *meta*-substituted product.

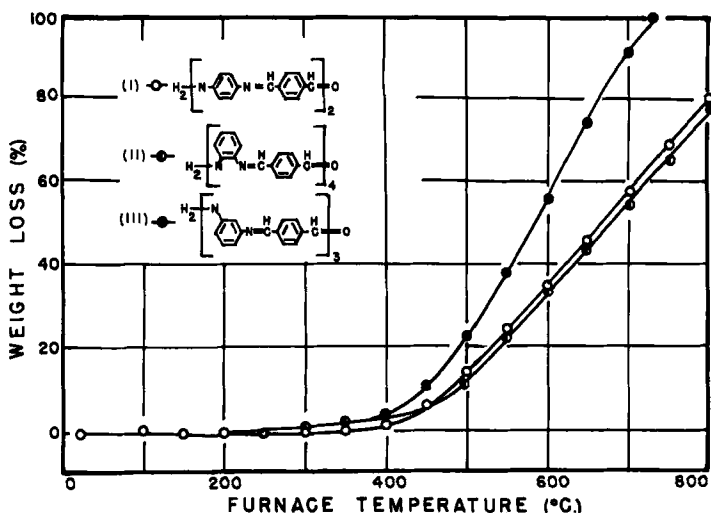


FIG. 1. TGA thermograms of I, II, and III.

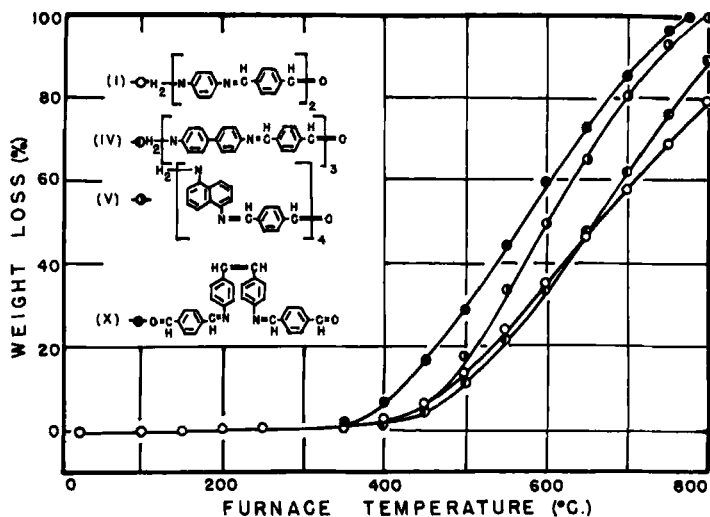


FIG. 2. TGA thermograms of I, IV, V, and X.

Figure 2 shows the effects of C=N linkage separation by various chemical groups on the resistance of products prepared from terephthalaldehyde to thermal decomposition. These data indicate that replacement of the *para*-substituted benzene ring with a *para*-substituted biphenyl group produces a slight increase in thermal

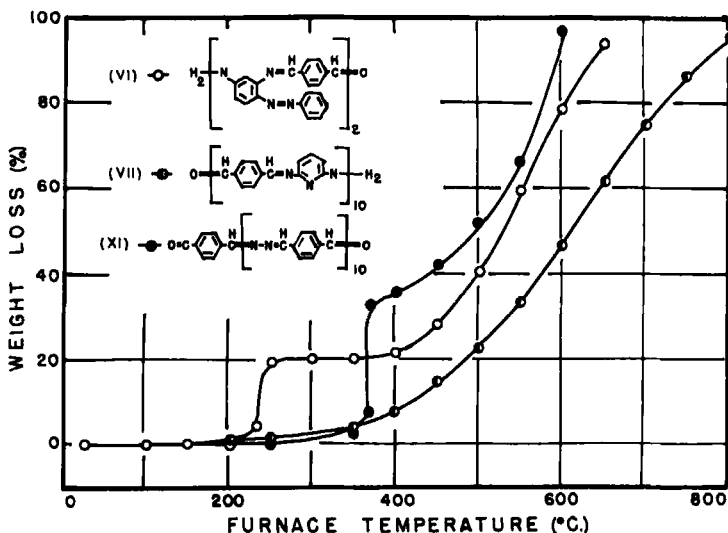


FIG. 3. TGA thermograms of VI, VII, and XI.

stability of the Schiff base product up to about 650°C. In decreasing order the 1,5-substituted naphthalene and *trans*-stilbene groups provide less heat resistance than the *para*-substituted benzene ring.

The thermograms shown in Fig. 3 indicate that the product synthesized from terephthalaldehyde and 2,6-diaminopyridine exhibits superior resistance to thermal decomposition over the substances derived from reactions of the dialdehyde with 2,4-diaminobenzene or hydrazine sulfate. All of the products are less heat-stable than the analogous material synthesized from *p*-phenylenediamine.

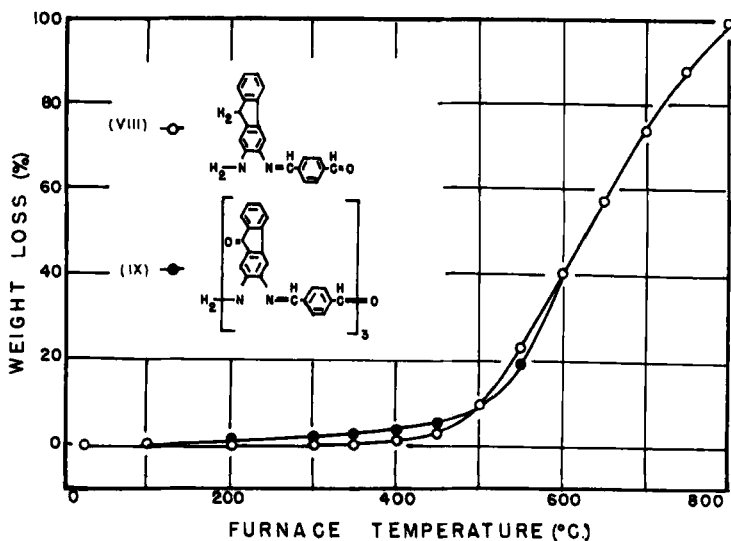


FIG. 4. TGA thermograms of VIII and IX.

Figure 4 presents the thermograms of materials synthesized from terephthalaldehyde and 2,3-diaminofluorene or 2,3-diamino-9-fluorenone. The excellent resistance of these products to thermal decomposition may be attributed to their high degree of aromaticity. The very close similarity of the thermograms produced by these materials suggests that their heat stabilities are not significantly influenced by the CH_2 and $\text{C}=\text{O}$ ring-substituent groups.

Thermograms of products obtained from terephthalaldehyde and diaminoanthraquinone derivatives are shown in Fig. 5. The substance prepared from 1,5-diaminoanthraquinone exhibits definite superiority in thermal resistance over the materials syn-

thesized from 2,6-diaminoanthraquinone and 1,8-diamino-4,5-dihydroxyanthraquinone. The heat stabilities of the latter two materials are similar. All of the products prepared from the anthraquinone derivatives are less heat-stable than the substance made from *p*-phenylenediamine. It appears from these data and the results obtained from the product derived from 1,5-diaminonaphthalene that condensed aromatic rings generally contribute less to the thermal resistance of Schiff-base materials than the phenyl ring or two benzene rings linked together as in biphenyl.

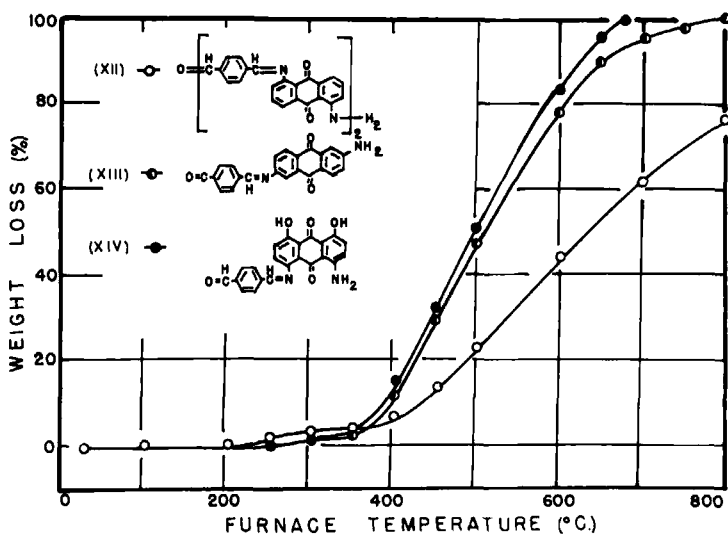


FIG. 5. TGA thermograms of XII, XIII, and XIV.

The thermograms of materials obtained from reaction of glyoxal and phenylenediamine compounds are presented in Fig. 6. In general, these materials exhibit less resistance to decomposition by thermal energy than those prepared from the same diamine compounds and terephthalaldehyde. This again shows the protective influence that the benzene ring has on the heat resistance of such products. In this series of compounds the product prepared from *m*-phenylenediamine is more heat-stable than the substances made from the other phenylenediamine isomers.

Figure 7 compares the thermograms from the products made by reaction of glyoxal with benzidine, 1,5-diaminonaphthalene, or 4,4'-stilbenediamine hydrochloride with that obtained from the

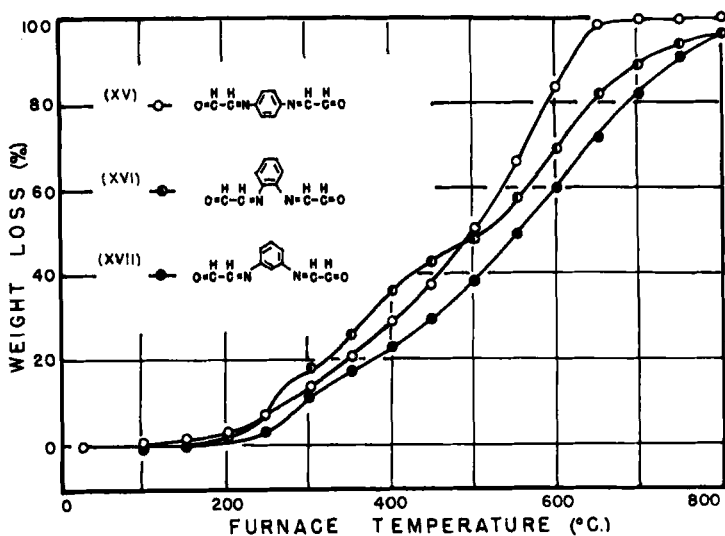


FIG. 6. TGA thermograms of XV, XVI, and XVII.

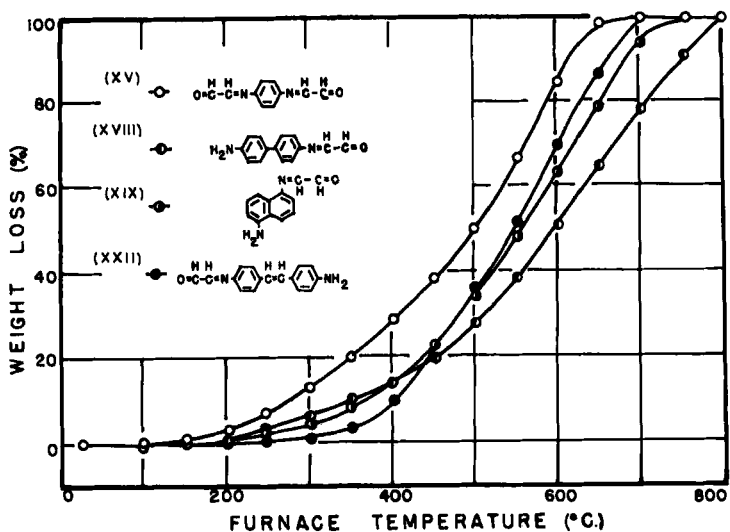


FIG. 7. TGA thermograms of XV, XVIII, XIX, and XXII.

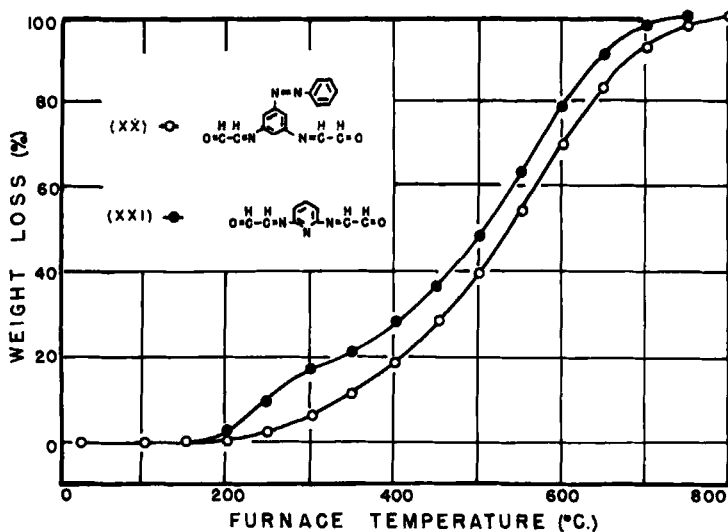


FIG. 8. TGA thermograms of XX and XXI.

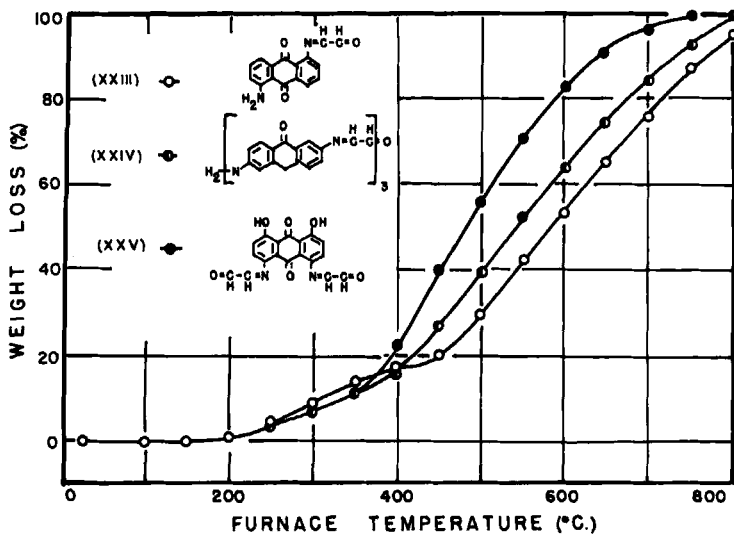


FIG. 9. TGA thermograms of XXIII, XXIV, and XXV.

same dialdehyde and *p*-phenylenediamine. These data show that the relative order of heat stability of these materials is similar to that of products prepared from corresponding diamine compounds and terephthalaldehyde.

The thermograms of the substances obtained from the reaction of glyoxal with 2,4-diaminoazobenzene or 2,6-diaminopyridine are shown in Fig. 8. The relative thermal resistance of these products are in converse order to that shown by corresponding materials prepared from these diamine compounds and terephthalaldehyde.

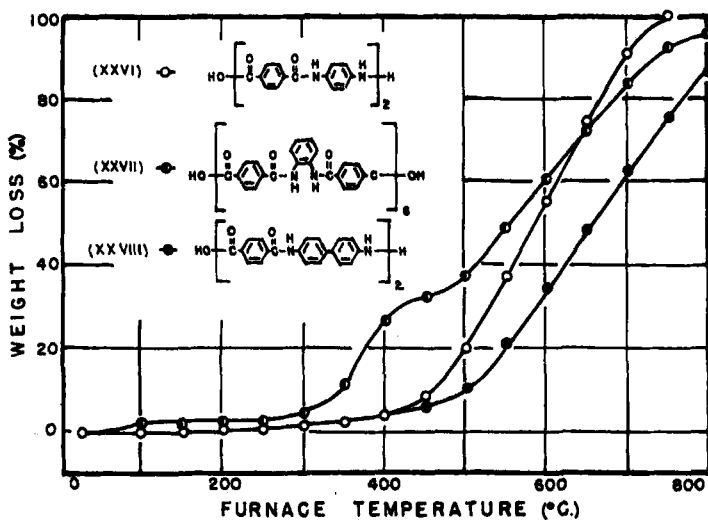


FIG. 10. TGA thermograms of XXVI, XXVII, and XXVIII.

Figure 9 presents the thermograms made from the reaction products of glyoxal with various anthraquinone derivatives. In terms of their relative resistance to thermal decomposition the results parallel those obtained from the products of the reactions of the same diamines and terephthalaldehyde.

The pyrolytic stabilities of the acid amide products synthesized by reaction of terephthaloyl chloride and phenylenediamine compounds or benzidine are shown in Fig. 10. These data show that the benzidine-derived substance is much more heat-resistant than the products made from the phenylenediamine compounds. This conforms with the results obtained with similar products made from the diamine and terephthalaldehyde or glyoxal. The material

made from *p*-phenylenediamine is more thermally stable than the substance prepared from *o*-phenylenediamine.

Figure 11 presents another example of the influence of aromatic rings on the heat resistance of structurally related products. The thermograms indicate that the material prepared from terephthaloyl chloride and hydrazine sulfate is the least stable of these products. The substance made from *p*-phenylenediamine, in which a benzene ring separates the nitrogen atoms, is much more resistant to pyrolysis. Resistance to thermal attack is apparently further

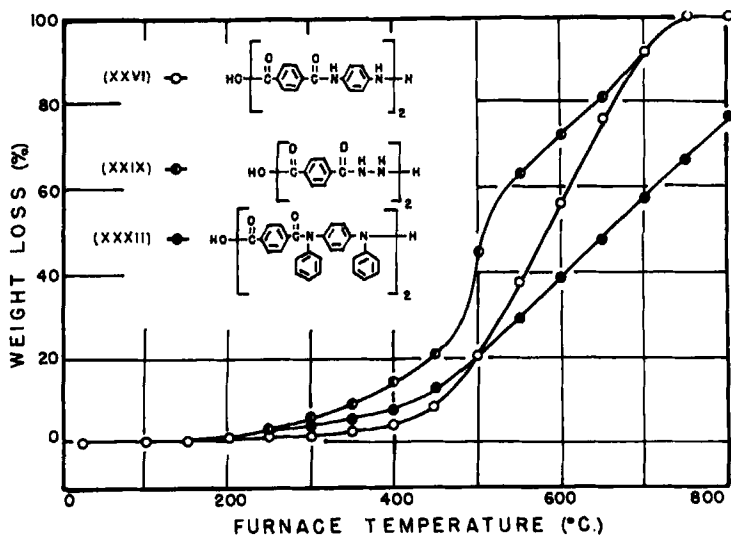


FIG. 11. TGA thermograms of XXVI, XXIX, and XXXII.

enhanced by replacing the N—H hydrogens with benzene rings, as is indicated by the thermogram of the product made from *N,N'*-diphenyl-*p*-phenylenediamine.

The thermograms of the materials prepared from diaminoanthraquinone compounds and terephthaloyl chloride are shown in Fig. 12. The order for the heat stabilities of these products is identical with that exhibited by similar substances made from these diamine compounds and terephthalaldehyde or glyoxal.

Figure 13 shows the thermograms obtained from the poly-(3-aminobenzaldehyde) and poly(4-aminobenzaldehyde) products. The *meta*-substituted material is more heat-stable than the *para*-substituted substance. These findings conform with the rela-

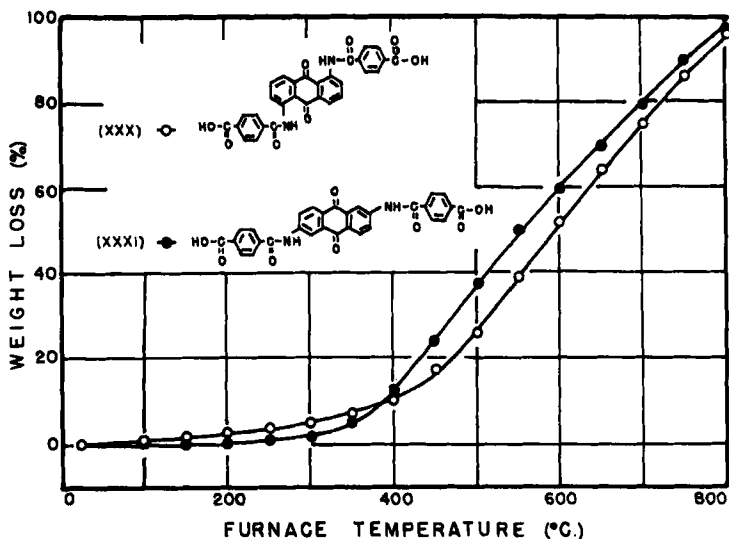


FIG. 12. TGA thermograms of XXX and XXXI.

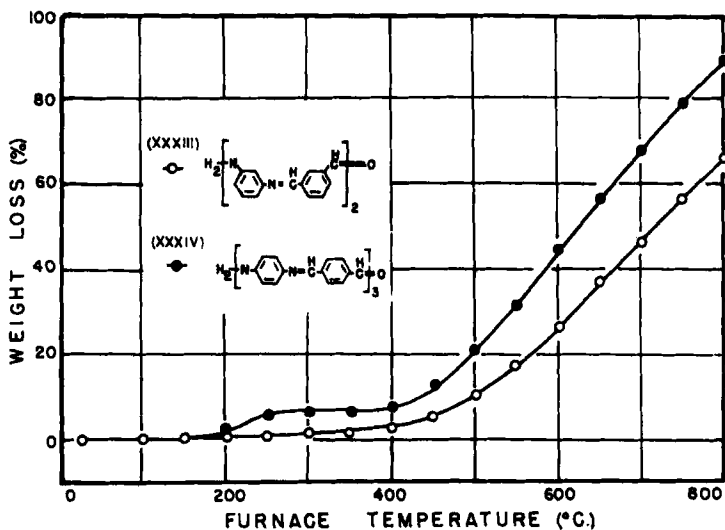


FIG. 13. TGA thermograms of XXXIII and XXXIV.

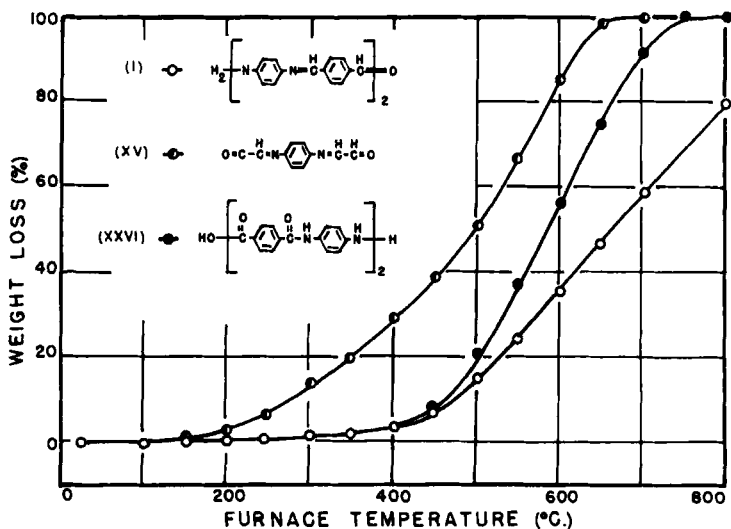


FIG. 14. TGA thermograms of I, XV, and XXVI.

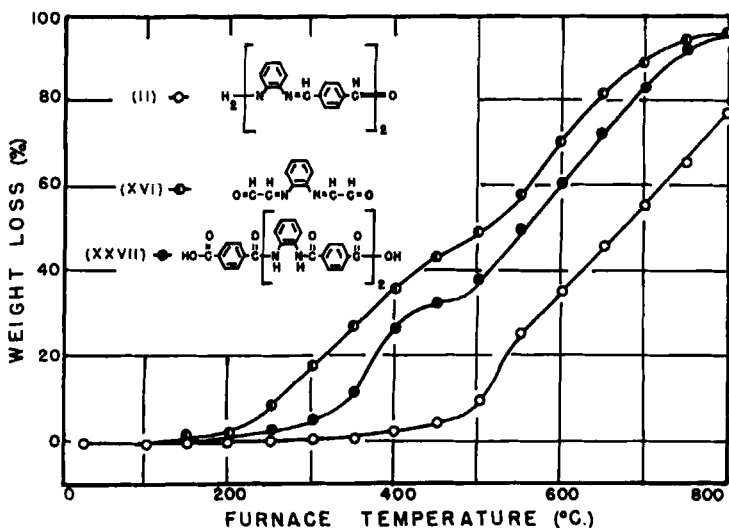


FIG. 15. TGA thermograms of II, XVI, and XXVII.

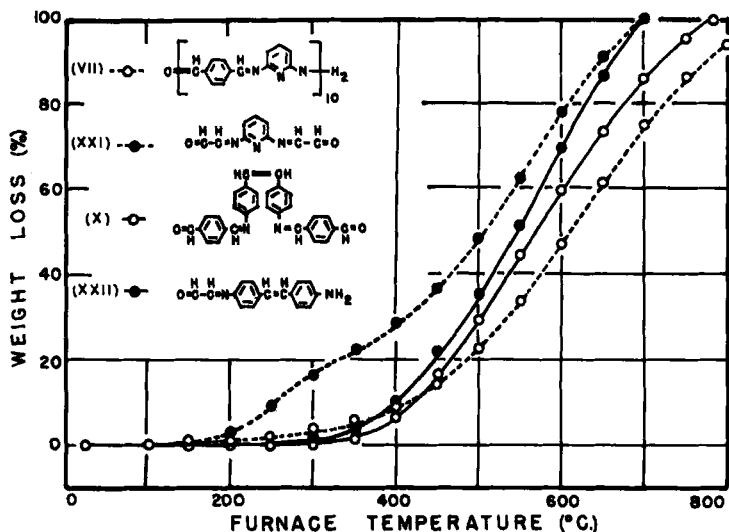


FIG. 16. TGA thermograms of VII, XXI, X, and XXII.

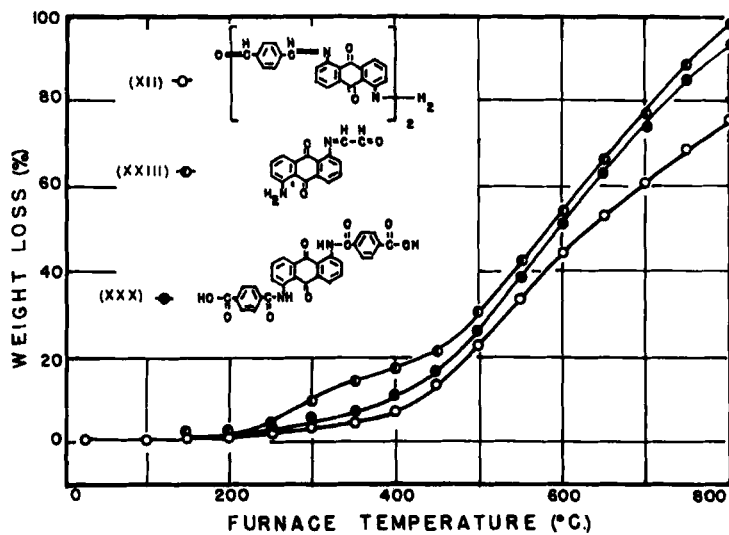


FIG. 17. TGA thermograms of XII, XXIII, and XXX.

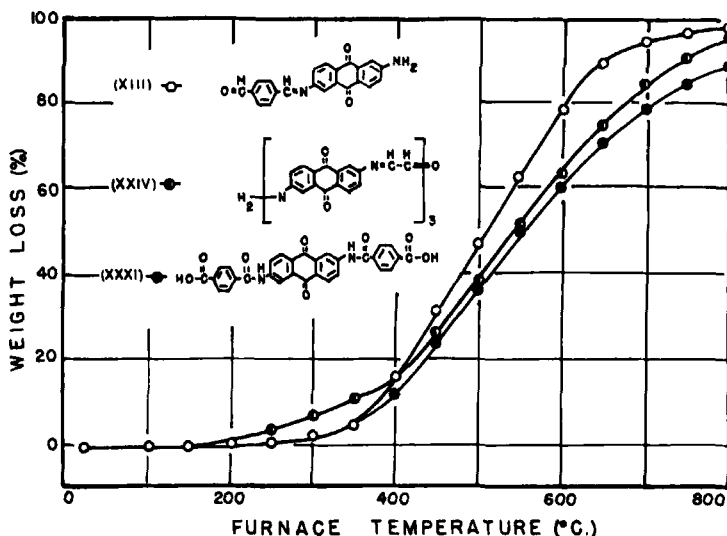


FIG. 18. TGA thermograms of XIII, XXIV, and XXXI.

tive order of heat resistance shown by the products made from glyoxal and the phenylenediamines.

Figures 14 through 18 present a comparison of the heat stabilities of various products made by reaction of the same diamine compound with terephthalaldehyde, glyoxal, or terephthaloyl chloride. In general, these data indicate that the Schiff-base products are more heat-stable than acid amide substances prepared from the corresponding diamine compound. This suggests that the $N=CH$ linkage provides greater stabilization to heat degradation than the $O=C-NH$ group. The stabilizing influence of the benzene ring is indicated once again by the consistently superior resistance of substances prepared from the diamine compounds and terephthalaldehyde over that shown by products made from corresponding diamines and glyoxal.

CONCLUSIONS AND DISCUSSION

A number of general observations have been made from this study: The fully aromatic Schiff-base materials examined were found to be consistently more heat-stable than the acid amide products, which were, in turn, generally superior in this respect to

corresponding Schiff-base substances that also contained alkyl groups.

The thermal behavior of the products investigated also appears to be influenced by the position and number of substituent groups on the ring structure: products with substituent groups around a benzene ring in *meta* position generally were more heat-stable than analogous materials with *ortho*- or *para*-substituted groups. For the derivatives prepared from the diaminoanthraquinones the materials containing substituent groups in 1,5 position consistently were superior in thermal resistance to corresponding products with substituents in 2,6 position. As the number of substituent groups around the ring system increased, the heat stability decreased. The latter observation conforms with the findings of Fabuss et al. (10), who determined that the thermal decomposition temperature of organic compounds decreases with an increase in the number of substituent groups on the ring.

The nature of the ring system also appears to exert an effect on thermal resistance. The materials with biphenylene groups showed a higher decomposition temperature than similar products with phenylene, naphthalene, stilbene, or pyridine units. According to Wheland (11), the sp^2 - sp^2 hybridization of the single C—C bond between the benzene rings of the biphenylene group provides increased stability to the molecule.

These studies also show that the products which contain fused-ring systems, such as naphthalene and anthraquinone, are less heat-stable than corresponding substances with the more simple benzene rings joined together, as in biphenyl. Comparable results have been reported by Johns and co-workers (12), who determined that polyaromatics have lower decomposition temperatures than benzene and suggests that the lower stability of the polyphenyls might be due to steric-hindrance factors.

Comparison of the heat stabilities of the acid amides prepared in this study shows that the resistance of such products is improved by replacing N—H hydrogens with N-phenyl bond. The improved stability of the products modified in this manner may be attributed not only to the increased aromatic character of the molecule but also to the elimination of N—H bonds which can serve as low-energy decomposition paths. Blake et al. (13) observed that blocking this path by replacing N—H hydrogens in N,N'-diphenyl-*p*-phenylenediamine raised the decomposition point substantially.

However, complete substitution of N—H hydrogen atoms in high-molecular-weight acid amide chains may not be necessary to attain improved heat resistance. Bartlett (14) suggests that there may be a limit to the number of phenyl groups that can effectively contribute to the stability of molecules; introduction of phenyl rings in excess of this limiting number may not necessarily produce a corresponding increase of the decomposition temperature.

Our studies also suggest that products with N—N or N=N bonding may exhibit lower heat resistance than similar materials without such bonding.

These studies have been concerned primarily with the influence of molecular structure on the thermal stability of a variety of aromatic Schiff bases and other structurally related organic substances to provide an insight into some of the more significant factors that can effect the pyrolytic decomposition of such relatively simple molecules. This information, together with results gathered from other studies concerning the mechanism of thermal degradation of more complex polymeric systems containing such structures should provide a basis for the selection of functional groups for use in tailor-making polymers with high thermal stability for particular end-item applications.

Acknowledgment

The authors are indebted to Dr. L. P. Herin for many of the experimental phases of this study.

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Received by editor January 14, 1966

Submitted for publication September 6, 1966