

## The Relative Thermal Stability of Polymer Model Compounds

DESMOND SHEEHAN, ALAN P. BENTZ, and JOHN C. PETROPOULOS

*Stamford Research Laboratories, American Cyanamid Company, Stamford, Connecticut*

### INTRODUCTION

In the past decade, research effort in the field of thermally stable polymers has increased enormously as a result of requirements imposed by missiles and high speed aircraft.

A typical approach to this problem is to utilize stable nuclei (e.g., such ring systems as borazine, phosphazine, ferrocene, benzene, triazine, or phthalocyanine) and search for methods to connect the nuclei with thermally stable linkages. A method was sought whereby the degree of thermal stability of the connecting linkages and the nuclei could be readily assessed from simple and easily synthesized model compounds before expending considerable effort in attempts to achieve a reasonable degree of polymerization.

Conveniently, it was found at this time that Hammann<sup>1</sup> of the Monsanto Chemical Company had developed a suitable method based on the early work of Smith and Menzies<sup>2</sup> for screening model compounds with respect to their relative thermal stabilities.

Our primary interest from the point of view of stable nuclei was in *s*-triazine derivatives. Research in this area leading to novel polymers and lubricants has become increasingly widespread in recent months, and one report<sup>3</sup> in particular describes a wide variety of triazine monomer and polymer syntheses, some of which already had been effected by one of the authors<sup>4</sup> elsewhere.

A few borazine derivatives were also examined, together with some bis(biphenyl) derivatives containing conventional linking groups such as ester, amide, and carbonate.

It would be presumptuous at this stage to suggest that the measurement of the arbitrary decomposition temperature which this study entails is a guarantee of comparable stability in the polymer system upon which any model might be based. However, it is hoped that a more detailed study of decomposition products of both the polymers and

representative models might prove that this one measurement of model decomposition temperature is sufficiently meaningful to permit the design of the more promising polymer systems to withstand high temperatures.

### RESULTS AND DISCUSSION

The method adapted for this investigation involved the measurement of an arbitrary decomposition temperature  $T_D$  of compounds with a structure comparable to that of the recurring unit in a polymer system. Hammann defines  $T_D$  as the temperature at which a compound decomposes to give an isothermal rate of pressure increase of 0.14 mm. Hg/sec.<sup>1</sup>

The measurements of  $T_D$  values were made under nitrogen in an isoteniscope as shown in Figure 1. The procedure is as follows.

A 3-g. portion of model compound is placed in the glass bulb. While the bulb is being evacuated, the sample is melted and allowed to resolidify to remove traces of volatile impurities. The bulb is then filled with nitrogen to a total pressure of 1 atm., and the sample heated to a temperature ( $T_1$ ) at which the first measurement is made. Expansion due to heating and the vapor pressure of the compound both contribute to an excess pressure which is vented. After equilibrating at  $T_1$  for several minutes, the system is isolated and further pressure increases (decomposition) are observed by means of a manometer-cathetometer arrangement. The change in pressure per run is less than 7 cm. Hg.

Data obtained at three or more temperatures are plotted as  $dp/dt$  versus  $1/T$  on semi-log paper. Such plots are usually linear, enabling the calculation of the precise temperature  $T_D$  at which  $dp/dt = 0.014$  mm. Hg/sec. (see Fig. 2).

The isoteniscope data plotted in this way may be used to obtain more information than the decomposition temperature ( $T_D$ ) alone. The slope of

TABLE I. Substituted Melamines

No.	Compound	m.p., °C.	Structure	$T_D$ , °C.
I	Hexaphenylmelamine	304-305		461
II	<i>N,N'</i> -Tetraphenylbenzoguanamine	246-247		446
III	Tris( <i>N</i> -phenyl- <i>N</i> -methyl)-melamine	121.5-122.5		429
IV	<i>N,N'</i> -Dimethyl- <i>N,N'</i> -diphenylbenzoguanamine	129-130		425
V	Hexamethylmelamine	171-174		>300 (distilled)
VI	<i>N,N'</i> -Tetramethylbenzoguanamine	105-106		>377 (distilled)
VII	Hexa- <i>n</i> -butyl-melamine	m.p. <0, b.p. ca. 160/0.1 mm.		341
VIII	Tripiperidinyl- <i>s</i> -triazine	211-213		>400 (sublimed)

(continued opposite page)

the line is related to the apparent activation energy of the decomposition. If the plot is made by use of the natural log of the rate of pressure increase, the activation energy ( $\Delta E$ ) is obtained directly by multiplying the slope by  $R$  (the gas constant) since

$$dp/dt = Ae^{-\Delta E/RT}$$

If both  $T_D$  and  $\Delta E$  are known, it is possible, with two assumptions, to calculate the relative frequency factors ( $A$ ) for the decomposition reaction. First, the standard decomposition rate which occurs at  $T_D$  is assigned an arbitrary value of unity. Now it is assumed for each substance tested that (1) the decomposition reaction leads to the same number of volatile fragments per mole, which is almost certainly correct within a factor of two or three, and (2) that the 3 g. used for the test contain the same number of mole-

cules in each case (again correct to about a factor of three).

The frequency factors in arbitrary units so calculated are, therefore, significant to about an order of magnitude, or  $\pm 1$  for  $\log A$ .

Examples of the correlation between a recurring unit in the polymer and a model compound might best be illustrated as follows:

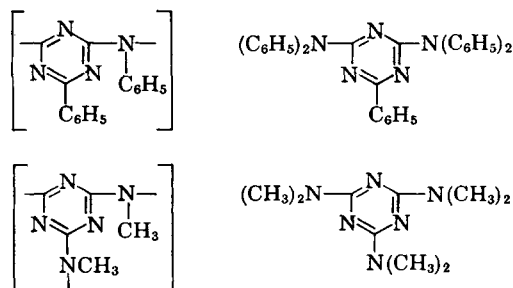


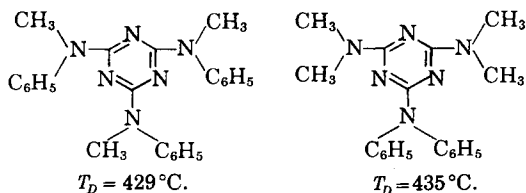
TABLE I. (continued)

No.	Compound	m.p., °C.	Structure	$T_D$ , °C.
IX	Triphenylmelamine	231–232.5		{ 307 <sup>a</sup> 378
X	<i>N,N'</i> -Diphenylbenzguanamine	212–213.5		{ 401 <sup>b</sup> 401
XI	2,4-Bis(dimethylamino)-6-diphenylamino- <i>s</i> -triazine	151–152		435
XII	2,4-Bis(diethylamino)-6-diphenylamino- <i>s</i> -triazine	91–93		397
XIII	2-Diphenylamino-4,6-bis(di- <i>n</i> -propylamino)- <i>s</i> -triazine	85–87		384
XIV	2,4-Bis(di- <i>n</i> -butylamino)-6-diphenylamino- <i>s</i> -triazine	48–49.5		364
XV	2-Diphenylamino-4,6-dipiperidinyl- <i>s</i> -triazine	164–165.5		433

<sup>a</sup> Represents the difference of one recrystallization without change in m.p. or infrared spectrum.

<sup>b</sup> Reproducible after further recrystallization.

In some instances the models tended to sublime or distill at elevated temperatures prior to decomposition. In some of these cases this problem was avoided by introducing heavy aromatic groups. As an example of this latter technique, hexamethylmelamine tends to distill at ca. 300°C. Two weighted models were prepared, which, when tested in the isoteniscope, gave reasonable agreement for the value of  $T_D$ :



Since the purpose of these measurements was to obtain a rapid estimate of structure-stability relationships, no attempt was made to determine the mechanisms of degradation. Nevertheless, it is readily seen that the results for each class of compound correlate fairly well and permit the conclusions given subsequently.

Following is a complete summary of results for the various classes of compounds tested. It should be noted that no special criteria of purity were used other than unchanged melting point with successive purifications. Higher values may be obtained with higher degrees of purity (see Table I).

### A. Substituted Melamines and Guanamines

The stability of amino-triazines increases according to the following order of substituents:  $-n\text{-C}_4\text{H}_9 < -n\text{-C}_3\text{H}_7 < -\text{C}_2\text{H}_5 < -\text{H} < -\text{CH}_3 < -\text{C}_6\text{H}_5$ .

The values for derivatives containing  $-\text{NC}_6\text{H}_5$  (446–461°C.),  $-\text{NCH}_3$  (425–435°C.) and  $-\text{NH}$  (378–401°C.) groups follows the order of the arylamines which were studied by Hammann<sup>1</sup> (shown in Table II).

The amidelike amino and methylamino triazine derivatives, however, are considerably more stable than the substituted arylamine analogs.

The differences among the alkyl substituents lead to the tentative suggestion that the lower degree of stability conferred by the higher alkyl groups might be due to interaction and/or increased

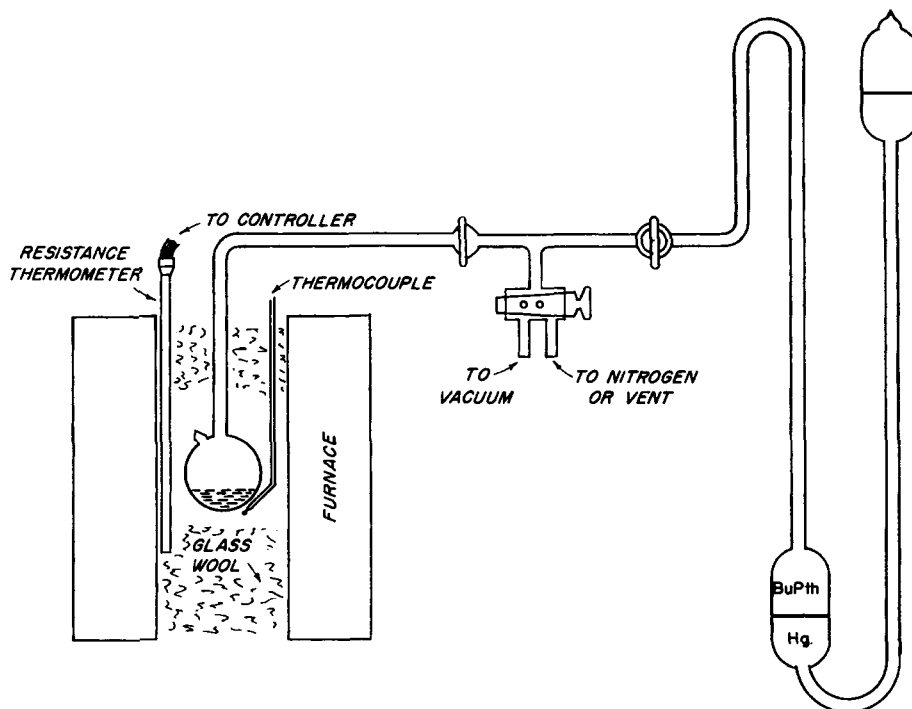


Fig. 1. Apparatus for determining decomposition temperature.

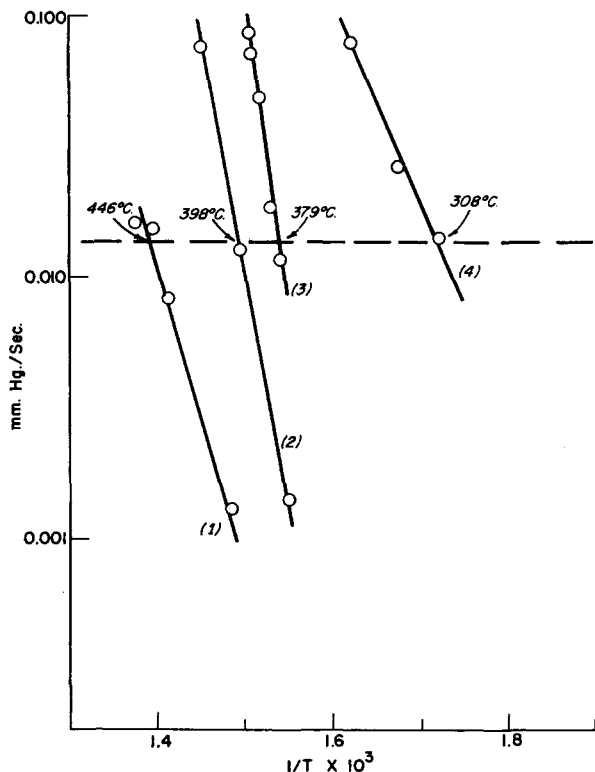
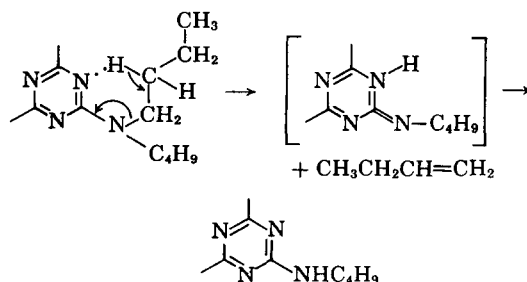


Fig. 2. Typical isoteniscope decomposition temperature plots: (1) *N,N'*-tetraphenylbenzoguaniamine (II); (2) 4-biphenyl-4-biphenylcarboxylate (XXXV); (3) bis(4-biphenyl) carbonate (XXXVI); (4) 2,4-diphenoxy-6-phenyl-*s*-triazine (XXIV).

collision frequency of an alkyl hydrogen with a ring nitrogen atom, somewhat analogous to the mechanism of pyrolytic degradation of aliphatic esters and amides:



It should be noted that the first step in this process, the formation of butylene, would be the decomposition associated with  $T_D$ .

Further credence is lent to this possibility by the behavior of the piperidine derivative, in which the cyclic alkyl groups are held rigidly in a position directed away from the triazine nucleus, preventing the interaction between alkyl hydrogens and ring nitrogens:

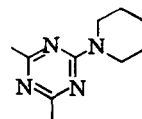


TABLE II  
Substituted Arylamines

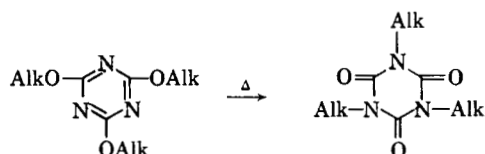
No.	Compound	$T_D$ , °C.
XVI		265
XVII		326
XVIII		458

It will be noted that the loss of symmetry involved in changing from a melamine to a benzoguanamine structure does not appear to incur any loss of stability.

The conclusion to be drawn then is that arylaminotriazines are the most promising structures in the series studied, and that methyl and certain

cycloalkyl substituents may also be sufficiently stable to warrant further interest.

The stability of all but the fluoroalkyl derivative in the series of normal cyanurates and benzoguanamide esters shown in Table III is surprisingly low. Studies of infrared spectra gave some information with regard to the mechanism of breakdown. The alkyl cyanurates are known to undergo a rearrangement at fairly low temperatures to the isocyanurate form thus:

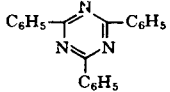
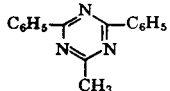


There is no evidence to suggest that such isomerization occurs in the breakdown process of the alkylthio or fluoroalkoxy compounds. In the aryl cyanurate series the possibility of complete isomerization prior to decomposition was shown to be

TABLE III  
Alkyl and Aryl Cyanurates and Benzoguanamide Esters

No.	Compound	m.p., °C.	Structure	$T_D$ , °C.
XIX	Tri- <i>n</i> -amyl cyanurate	Liquid; b.p. 218/0.75		Isomerizes ca. 200-250
XX	Tri- <i>n</i> -amyl thiocyanurate	b.p. 226/0.4 mm.		262
XXI	Tris(1H, 1H, 5H-octafluoropentyl)-cyanurate	b.p. ca. 160/0.1 mm.		394
XXII	Triphenyl cyanurate	235-236		231
XXIII	Triphenyl thiocyanurate	100-100.3		318
XXIV	2,4-Diphenoxy-6-phenyl- <i>s</i> -triazine	118-120		308
XXV	2,4-Bis(phenylthio)-6-phenyl- <i>s</i> -triazine	118-120		312
XXVI	Triphenylisocyanurate	279.5-280		377

TABLE IV  
 Alkyl and Aryl *s*-Triazines

No.	Compound	m.p., °C.	Structure	$T_D$ , °C.
XXVII	Triphenyl- <i>s</i> -triazine	233-235		>486 (distilled)
XXVIII	2,4-Diphenyl-6-methyl- <i>s</i> -triazine	111-112		>388 (distilled)

most unlikely, since triphenyl isocyanurate gave a value significantly higher than triphenyl cyanurate.

This last fact raises a point of special interest. Triphenyl isocyanurate might be considered a cyclic trimeric amide, and it is not surprising that the  $T_D$  value (377°C.) is comparable to that of the bis(phenyl) carboxamide (391°C.) discussed later. Since the normal aryl cyanurates do not apparently isomerize, they might be expected to give values comparable to aromatic esters, yet the aryl ester shown subsequently has a value 80°C. higher than the cyanurates.

The value for the fluoroalkyl cyanurate (394°C.) is particularly remarkable and apparently no isomerization occurs during decomposition. The

relatively high stability in this fluoroalkyl system may be due to the fact that no alkyl hydrogens are present to interact with the ring nitrogens.

Some caution must be exercised in any further discussion, since it is always possible that unusually low values may be due to a catalytic effect of the glass apparatus in the decomposition reaction. For the time being, however, we must conclude that cyanurates generally are considerably less stable than aminotriazines.

### C. Alkyl and Aryl *s*-Triazines

Only two compounds were examined, but one of these (XXVII) proved to be the most stable ( $T_D > 486$ ) triazine derivative tested (Table IV).

 TABLE V  
 Borazine Derivatives

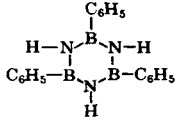
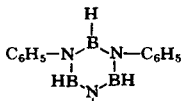
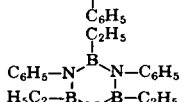
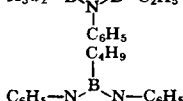
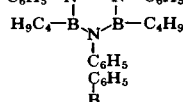
No.	Compound	m.p., °C.	Structure	$T_D$ , °C.
XXIX	<i>B</i> -Triphenylborazine	178-180		357
XXX	<i>N</i> -Triphenylborazine	160-161		344
XXXI	<i>B</i> -Triethyl- <i>N</i> -triphenylborazine	169-171		396
XXXII	<i>B</i> -Tri- <i>n</i> -butyl- <i>N</i> -triphenylborazine	129-132		344
XXXIII	Hexaphenylborazine	413-415		435 (Ref. 5)

TABLE VI  
 Biphenyl and Related Models

No.	Compound	m.p., °C.	R	$T_D$ , °C.
XXXIV	<i>p</i> -Quaterphenyl	311-312	—	ca. 508
XXXV	4-Biphenyl-4-biphenylcarboxylate	222-225.5		398
XXXVI	Bis(4-biphenyl) carbonate	193.5-195.5		379
XXXVII	<i>N</i> -4-biphenyl-4-biphenylcarboxamide	314-315		391
XXXVIII	Triphenylphosphine oxide	156		>450 (distilled)
XXXIX	Triphenyl phosphate	49-50		>423 (distilled)
XL	Tris(4-biphenyl)phosphate	140-141.5		452

This prompts the suggestion that with certain substituents, the triazine nucleus is of comparable stability to the benzene nucleus (cf. 1,3,5-triphenylbenzene  $T_D = 500^\circ\text{C}$ .<sup>5</sup>). The effect of alkyl groups has not been determined, but it may be forecast that, as in the case of the melamines, higher alkyl groups will tend to lower stability.

#### D. Borazine Derivatives

At the time that these model compounds were being studied, samples of borazine compounds became available as a result of other work in these laboratories. Since the stability determination was a fairly rapid procedure, it was considered advantageous to examine the borazine compounds for comparison with the triazine series.

Compounds containing B—H or N—H bonds in the borazine system proved relatively poor; likewise (as with the melamines), the *n*-butyl derivative is low (Table V). The *B*-triethyl-*N*-triphenyl compound is at least sufficiently high to warrant further interest in the homolog containing methyl instead of ethyl groups, and the completely phenylated structure is comparable to some of the melamines.

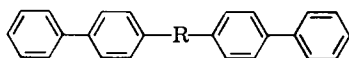
#### E. Biphenyl Derivatives and Related Models

A study of various conventional linking groups was made in order to provide information on their relative thermal stabilities for use either as linking groups in the main chain or as crosslinkages between linear polymers. Results are shown in Table VI.

TABLE VII

Structure	$T_D$ , °C.		
	R = H	R = CH <sub>3</sub>	R = C <sub>6</sub> H <sub>5</sub>
	265	326	458
	378	429	461
	357	—	435
	391	—	—

Polyphenylenes and polyphenyl ethers were known\* to have a high degree of thermal stability. *p*-Quaterphenyl as chosen as a standard for models of the type:



wherein the linkages could be studied without the interference of pyrolysis which occurs in aliphatic systems.

A decomposition temperature of 441°C. had been reported by Hamman<sup>1</sup> for quaterphenyl, but a commercial sample of quaterphenyl, after recrystallization, gave an extrapolated decomposition temperature value of 508°C. The ester and amide linkages were surprisingly stable (at least 60–80°C. higher than the most stable aliphatic analogs). Based on Hamman's comparison of diaryl amines and the evidence in these laboratories with phenylmelamines (see Table VII), one might, by analogy, expect that substituted amides would be more stable. Similar reasoning would suggest that the substituted urea linkages might be quite stable.

The phosphorus derivatives also gave very high values. Of special interest is the triphenylphosphine oxide as a model for a poly(phenylenephosphine oxide) structure.

\* Hamman's value<sup>1</sup> for a typical polyphenyl ether is 440°C.

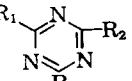
## EXPERIMENTAL

### 1. Triazine Derivatives

Almost all of these compounds can be prepared by standard procedures well documented in the literature.<sup>6-9</sup> Exceptions are as follows.

Certain 2,4-bis(dialkylamino)-6-diphenylamino-*s*-triazine syntheses were conveniently performed by the following typical modification.

Cyanuric chloride (36.8 g.) was dissolved in chloroform (500 ml.) in a 3-l. flask immersed in an ice bath. Di-*n*-propylamine (40 g.) was added at a rate maintaining the temperature below 25°C. The ice bath was removed and sodium hydroxide solution (800 ml., 0.5*N*) added to the reaction mixture rapidly, but not permitting the temperature to rise above 50°C. The chloroform layer was separated and evaporated on the steam bath, leaving the intermediate 2,4-bis(di-*n*-propylamino)-6-chloro-*s*-triazine as a pale brown oil. Without further purification this intermediate was mixed with diphenylamine (34 g.) in an open Erlenmeyer flask and heated directly on a hot plate over a period of 20 min. to a maximum temperature of 290°C. Hydrogen chloride was evolved during this heating period. The product crystallized on cooling and successive recrystallizations from large volumes of alcohol to ensure high purity afforded 7.6 g., m.p. 85–87°C. (crude product 60 g.).

TABLE VIII  
Analytical Results for New Compounds of the Type 

No.	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Empirical formula	Calculated			Found		
					C, %	H, %	N, %	C, %	H, %	N, %
I	–N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	–N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	–N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	C <sub>39</sub> N <sub>6</sub> H <sub>30</sub>	80.38	5.19	14.43	80.66	5.92	14.21
II	–N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	–N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	–C <sub>6</sub> H <sub>5</sub>	C <sub>33</sub> N <sub>6</sub> H <sub>26</sub>	80.65	5.10	—	80.58	5.54	—
III	–N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	–N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	–N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	C <sub>24</sub> N <sub>6</sub> H <sub>24</sub>	72.70	6.10	—	72.80	6.09	—
IV	–N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	–N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	–C <sub>6</sub> H <sub>5</sub>	C <sub>23</sub> N <sub>6</sub> H <sub>21</sub>	75.20	5.64	19.16	75.15	5.74	19.01
VI	–N(CH <sub>3</sub> ) <sub>2</sub>	–N(CH <sub>3</sub> ) <sub>2</sub>	–C <sub>6</sub> H <sub>5</sub>	C <sub>13</sub> N <sub>6</sub> H <sub>17</sub>	64.30	7.01	—	64.06	7.18	—
VII	–N( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	–N( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	–N( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	C <sub>27</sub> N <sub>6</sub> H <sub>54</sub>	70.07	11.76	—	69.74	11.60	—
VIII	–NC <sub>6</sub> H <sub>10</sub>	–NC <sub>6</sub> H <sub>10</sub>	–NC <sub>6</sub> H <sub>10</sub>	C <sub>18</sub> N <sub>6</sub> H <sub>30</sub>	65.42	9.15	—	65.13	9.36	—
X	–NHC <sub>6</sub> H <sub>5</sub>	–NHC <sub>6</sub> H <sub>5</sub>	–C <sub>6</sub> H <sub>5</sub>	C <sub>21</sub> N <sub>6</sub> H <sub>17</sub>	74.31	5.05	—	74.34	5.37	—
XI	–N(CH <sub>3</sub> ) <sub>2</sub>	–N(CH <sub>3</sub> ) <sub>2</sub>	–N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	C <sub>19</sub> N <sub>6</sub> H <sub>27</sub>	68.24	6.63	—	68.10	6.54	—
XII	–N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	–N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	–N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	C <sub>23</sub> N <sub>6</sub> H <sub>30</sub>	70.85	7.67	21.47	70.56	7.38	21.19
XIII	–N( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	–N( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	–N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	C <sub>27</sub> N <sub>6</sub> H <sub>38</sub>	72.61	8.58	18.82	72.69	8.42	18.71
XIV	–N( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	–N( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	–N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	C <sub>31</sub> N <sub>6</sub> H <sub>46</sub>	74.06	9.22	16.72	74.16	9.13	16.56
XV	–NC <sub>6</sub> H <sub>10</sub>	–NC <sub>6</sub> H <sub>10</sub>	–N(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	C <sub>25</sub> H <sub>6</sub> H <sub>30</sub>	72.43	7.29	20.28	72.53	7.51	20.02
XX	–SC <sub>6</sub> H <sub>11</sub>	–SC <sub>6</sub> H <sub>11</sub>	–SC <sub>6</sub> H <sub>11</sub>	C <sub>8</sub> N <sub>2</sub> H <sub>33</sub> S <sub>5</sub>	63.68	9.80	—	63.62	9.87	—
XXI	–OCH <sub>2</sub> (CF <sub>2</sub> ) <sub>4</sub> H	–OCH <sub>2</sub> (CF <sub>2</sub> ) <sub>4</sub> H	–OCH <sub>2</sub> (CF <sub>2</sub> ) <sub>4</sub> H	C <sub>18</sub> N <sub>3</sub> H <sub>9</sub> O <sub>3</sub> F <sub>24</sub>	28.02	1.19	5.43	28.70	1.20	5.21
XXIV	–OC <sub>6</sub> H <sub>5</sub>	–C <sub>6</sub> H <sub>5</sub>	–C <sub>6</sub> H <sub>5</sub>	C <sub>21</sub> N <sub>3</sub> H <sub>15</sub> O <sub>2</sub>	73.89	4.43	—	73.93	4.57	—
XXV	–SC <sub>6</sub> H <sub>5</sub>	–SC <sub>6</sub> H <sub>5</sub>	–C <sub>6</sub> H <sub>5</sub>	C <sub>21</sub> N <sub>3</sub> H <sub>15</sub> S <sub>2</sub>	67.55	4.05	—	67.63	4.11	—



A sample of triphenyl isocyanurate (XXVI) was prepared by the trimerization of phenyl isocyanate using triethylamine as a catalyst in acetonitrile solvent. The product was twice recrystallized from ethanol to yield colorless, birefringent, small rectangular prisms, m.p. 279.5–280°C. In some recovery crops a long needle form was found, m.p. 225–230°C., which recrystallized in the melt to yield the higher melting form.

Triphenyl-*s*-triazine (XXVII) was supplied by Dr. F. C. Schaefer, Central Research Division, American Cyanamid Company. 2,4-Diphenyl-6-methyl-*s*-triazine (XXVIII) was prepared by the Pinner synthesis.<sup>10</sup>

Table VIII gives analytical data for compounds not reported in references cited. Melting points are given in the tables of  $T_D$  values.

## 2. Borazine Derivatives

The borazine compounds XXIX through XXXII were supplied by Drs. T. F. McGrath, J. E. Milks and S. F. Stafiej, Central Research Division, American Cyanamid Company.

## 3. Biphenyl Derivatives

**a. 4-Biphenyl-4-biphenylcarboxylate (XXXV).** 4-Biphenylcarboxylic acid (25 g.) was refluxed with a 2–3-fold excess of thionyl chloride. The white acid powder became lavender, and after ca. 1 hr. reflux a deep red solution formed. The excess thionyl chloride was distilled off, and the resulting purple solid was purified by two vacuum sublimations to obtain a pure white solid, m.p. 112–113°C., of 4-biphenylcarbonyl chloride.

4-Biphenylcarbonyl chloride (25.8 g.) was dissolved in 400 ml. of chloroform. A slurry was prepared of 20.5 g. *p*-phenylphenol in 200 ml. of water containing 5 g. sodium hydroxide (completely soluble hot). Aqueous base was added to the chloroform solution and stirred overnight since no immediate reaction was apparent. A white, thixotropic product formed which was filtered and washed with ethanol and water. The product was recrystallized from benzene to yield a white product, m.p. 222–222.5°C.

ANAL. Calcd. for  $C_{26}H_{18}O_2$ : C, 85.69%; H, 5.18%. Found: C, 85.52%, H, 5.30%.

**b. Bis(4-biphenyl)carbonate (XXXVI).** The apparatus consisted of a phosgene cylinder with a gas line leading to a sulfuric acid scrubber through an

empty trap to the reaction vessel. From the reaction vessel the line was led to a trap containing benzene to serve as a bubble (rate) counter and finally through 28% ammonia.

*p*-Phenylphenol (20 g.) was slurried in aqueous sodium hydroxide (4 g., 10% excess base). Phenolphthalein was added as an indicator. Benzene (250 ml.) was added, and the phosgene was bubbled through at a temperature of 69–70°C. until the indicator color was discharged. The mixture was heated to reflux and air was bubbled through to remove excess phosgene. The yellow benzene layer was separated, cooled and evaporated to obtain an 81.6% recovery in two crops of crystals, m.p. 193.5–195.5°C.

ANAL. Calcd. for  $C_{26}H_{18}O_3$ : C, 81.95%; H, 4.95%. Found: C, 81.97%; H, 5.20%.

**c. 4-Biphenyl-4-biphenylcarboxamide (XXXVII).** The 4-biphenylcarbonyl chloride prepared previously (2.5 g.) was added to 25 ml. of benzene along with 0.8 g. of sodium azide freshly recrystallized from water-acetone. The mixture was refluxed 24 hr., cooled, and filtered. To the filtrate was added 10 ml. of concentrated HCl and the solution was heated to reflux for 3 hr. A voluminous precipitate formed. Water was added and the mixture filtered to obtain 1.4 g. of the 4-biphenylamine hydrochloride.

A small sample of this hydrochloride was slurried in water and neutralized with aqueous sodium hydroxide to obtain the free 4-biphenylamine, m.p. 53°C.

The hydrochloride, 1.4 g., was added to 50 ml. of benzene along with 1.4 g. of acid chloride. To the mixture was slowly added 20 ml. of aqueous NaOH (0.3 g.). Phenolphthalein was added and the mixture was heated with stirring. The pink color discharged at 60–65°C. At the end, 10 ml. 0.1*N* NaOH was added to give a permanent pink. The layers were separated, and the yellow benzene layer was evaporated to give 0.3 g. of a product, m.p. 314–315°C. The bulk of product (2.0 g.) of white powder was obtained at the interface (at first thought to be an emulsion). The product was recrystallized three times from dimethylformamide to obtain a pure white product, m.p. 315–315.5°C.

ANAL. Calcd. for  $C_{26}H_{19}NO$ : C, 85.93%; H, 5.48%. Found: C, 86.11%; H, 5.40%.

**d. Triphenylphosphine Oxide (XXXVIII).** Sample supplied by Dr. A. K. Hoffmann, Central Research Division, American Cyanamid Company.

**e. *p*-Quaterphenyl (XXXIV).** Sample supplied by Eastman Kodak Company and purified by sublimation and recrystallization from benzene.

**f. Tris(4-biphenyl)phosphate (XL).** This compound was prepared by the method of Britton and Bass.<sup>11</sup> Recrystallization from methyl cellosolve-water gave white needles, m.p. 140–141.5°C.

We are particularly indebted to Dr. R. Hermann and Mr. G. Yates of these laboratories for determining the decomposition temperature of the model compounds.

### References

1. Hammann, W. C., W.A.D.C. Technical Report 57-657, pp. 158–171 (1958); ASTIA Document No. AD-142285, Contract No. AF33(616)-3819.
2. Smith, A., and A. W. C. Menzies, *J. Am. Chem. Soc.*, **32**, 1412 (1910).
3. Lovelace, A. M., et al., W.A.D.C. Technical Report 59-453 (1959); *J. Polymer Sci.*, **50**, 270 (1959).
4. Sheehan, D., Microcell Ltd., 56 Kingsway, London W.C.2. British Patent Applications 8205/58, 8213/58.
5. Dale, et al., Monsanto Chemical Company, in a paper presented at the W.A.D.C. Symposium, Dayton, Ohio, May, 1959.
6. Thurston, J. T., *J. Am. Chem. Soc.*, **73**, 2981 (1951).
7. Kaiser, D. W., et al., *J. Am. Chem. Soc.*, **73**, 2984 (1951).
8. Dudley, J. R., et al., *J. Am. Chem. Soc.*, **73**, 2986 (1951).
9. Schaefer, F. C., et al., *J. Am. Chem. Soc.*, **73**, 2990 (1951).
10. Pinner, A., *Ber.*, **25**, 1414 (1892).
11. Britton, E. C., and S. L. Bass, U.S. Pat. 2,117,291.

### Synopsis

The thermal stability of a variety of derivatives of *s*-triazine, benzene, and borazine was determined with an isoteniscope. For the *s*-triazines the order of stability was

found to be aryl triazines > aryl melamines and benzoguanamines > methyl melamines > higher alkyl melamines > aryl cyanurates and thiocyanurates (with the exception of fluoroalkyl cyanurates). The borazines were poorer than the melamines but better than the cyanurates. Several di- and trifunctional linking groups were used to connect biphenyl groups which were known to be stable (from previous studies of *p*-quaterphenyl and polyphenyl ethers). The order of stability was found to be phosphate  $\cong$  phosphine oxide  $\cong$  ether > ester > amide > carbonate.

### Résumé

La stabilité thermique de différents dérivés de *s*-triazine, benzène et borazine a été déterminée à l'aide d'un isoteniscope. Pour les *s*-triazines on a trouvé l'ordre de stabilité suivant: aryle triazines > aryle mélamines et benzoguanamines > méthyl mélamines > homologues supérieurs des alkyles mélamines > cyanurates et thiocyanates d'aryle à l'exception des cyanates de fluoroalkyle. Les borazines sont inférieures aux mélamines mais supérieures aux cyanates. Plusieurs groupes de liaison di- et tri-fonctionnels ont été utilisés pour unir des groupes biphenylés qui sont connus comme étant stables (résultats d'études antérieures sur les éthers *p*-quaterphénylés et polyphénylés). L'ordre de stabilité est le suivant: phosphate  $\cong$  oxyde de phosphine  $\cong$  éther > ester > amide > carbonate.

### Zusammenfassung

Die thermische Stabilität verschiedener Derivate von *s*-Triazin, Benzol und Borazin wurde mit einem Isoteniscope bestimmt. Für *s*-Triazine wurde folgende Stabilitätsreihe gefunden: Aryltriazine > Arylmelamine and Benzoguanamine > Methylmelamine > höhere Alkylmelamine > Arylcyanurate und Thiocyanurate (ausgenommen Fluoralkylcyanurate). Bei den Borazinen ist die thermische Stabilität geringer als bei den melaminen, aber höher als bei den Cyanuraten. Einige bi- und trifunktionelle Kupplungsgruppen wurden zur Verkettung von Biphenylgruppen, die als stabil bekannt sind (aus früheren Untersuchungen von *p*-Quaterphenyl und Polyphenyläthern), verwendet. Folgende Stabilitätsreihe wurde gefunden: Phosphat  $\cong$  Phosphinoxyd  $\cong$  Ather > Ester > Amid > Karbonat.

Received January 11, 1961