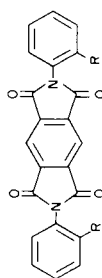




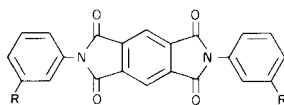
TABLE I  
*N,N'*-bis(*o*-Substituted Phenyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides (**2a-i**)



Compound	R	Yield %		M.p., °C	Empirical Formula	% C		% H		% N	
		Method A	Method B			Calcd.	Found	Calcd.	Found	Calcd.	Found
<b>2a</b>	H	52.0	65.0	330-420 (a)	C <sub>22</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub>	71.73	71.47	3.29	3.37	7.61	7.42
<b>b</b>	CH <sub>3</sub>	30.2	90.0	304-305	C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>	72.72	72.52	4.07	4.23	7.07	7.25
<b>c</b>	OH	72.5	---	400-403	C <sub>22</sub> H <sub>12</sub> N <sub>2</sub> O <sub>6</sub>	66.00	65.92	3.02	3.10	7.00	6.98
<b>d</b>	OCH <sub>3</sub>	25.5	50.8	335-336	C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>6</sub>	67.28	67.12	3.77	3.83	6.54	6.67
<b>e(b)</b>	F	59.5	---	339-341	C <sub>22</sub> H <sub>10</sub> F <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	65.35	65.54	2.49	2.65	6.93	7.07
<b>f(c)</b>	Cl	52.5	---	351-353	C <sub>22</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	60.43	60.45	2.31	2.31	6.41	6.32
<b>g(d)</b>	Br	29.0	---	368-369	C <sub>22</sub> H <sub>10</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	50.22	50.02	1.92	1.85	5.33	5.15
<b>h</b>	NO <sub>2</sub>	36.0	---	353-354	C <sub>22</sub> H <sub>10</sub> N <sub>4</sub> O <sub>8</sub>	57.65	57.70	2.20	2.36	12.22	12.00
<b>i</b>	COOH	73.5	---	370-390 (a)	C <sub>24</sub> H <sub>12</sub> N <sub>2</sub> O <sub>8</sub>	63.16	63.43	2.65	2.89	6.14	6.22

(a) Degradation range. (b) % F: Calcd. 9.40, Found 9.16. (c) % Cl: Calcd. 16.22, Found 16.39. (d) % Br: Calcd. 30.38, Found 30.62.

TABLE II

*N,N'*-bis(*m*-Substituted Phenyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides (**3a-h**)

Compound	R	Yield %	M.p., °C	Empirical Formula	% C		Analyses % H		% N	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
<b>3a</b>	CH <sub>3</sub>	48.0	344-345	C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>	72.72	72.63	4.07	3.93	7.07	7.11
<b>b</b>	OH	41.0	410-415	C <sub>22</sub> H <sub>12</sub> N <sub>2</sub> O <sub>6</sub>	66.00	65.78	3.02	3.24	7.00	7.28
<b>c</b>	OCH <sub>3</sub>	45.5	303-304	C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>6</sub>	67.28	67.31	3.77	3.94	6.54	6.59
<b>d</b> (a)	F	41.0	330-400 (b)	C <sub>22</sub> H <sub>10</sub> F <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	65.35	65.34	2.49	2.59	6.93	7.04
<b>e</b> (c)	Cl	60.0	391-392	C <sub>22</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	60.43	60.30	2.31	2.44	6.41	6.46
<b>f</b> (d)	Br	72.0	405-406	C <sub>22</sub> H <sub>10</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	50.22	50.32	1.92	2.01	5.33	5.39
<b>g</b>	NO <sub>2</sub>	19.5	387-388	C <sub>22</sub> H <sub>10</sub> N <sub>4</sub> O <sub>8</sub>	57.65	57.64	2.20	2.41	12.22	12.31
<b>h</b>	COOH	34.5	460-490 (b)	C <sub>24</sub> H <sub>12</sub> N <sub>2</sub> O <sub>8</sub>	63.16	63.09	2.65	2.93	6.14	6.21

(a) % F: Calcd. 9.40, Found 9.64. (b) Degradation range. (c) % Cl: Calcd. 16.22, Found 15.99. (d) % Br: Calcd. 30.38, Found 30.20.

Most of the *ortho* and *meta* substituted compounds (**2**, **3**) exhibit high but distinct melting points, the *meta* being higher melting than the corresponding *ortho* isomer (Table I and II). The *para* substituted compounds (**4**) and a few *meta*, such as *N,N'*-bis(*m*-carboxyphenyl)- and *N,N'*-bis(*m*-fluorophenyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides, possess outstanding thermal stability. They degrade at temperatures above 340° (Table III). The thermal degradation patterns, determined by thermogravimetric analysis (TGA), are characteristic with respect to the type of substituents in the phenyl ring (see Figure 1). These patterns not only indicate the temperature of the initial weight loss but also provide a semi-quantitative index of degradation mechanism types. The curves of the unsubstituted diimide and of the *p*-chloro derivative are simple and indicative of direct rapid degradation, while the curves of the other *para* substituted derivatives are more complex and show a stepwise weight loss as the temperature increases. The most gradual thermal degradation is shown by the dimethylamino derivative.

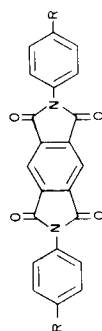
Intermolecular complex formation was observed when diimide **2d** was boiled with a large volume of solvents. Crude **2d** upon crystallization from benzene gave white crystals, which when heated at 290-300° transformed into larger golden yellow needles. This transformation product melted at 335-337° and when recrystallized from benzene reformed white crystals as above. The elemental analyses and the ir spectra show that the yellow product is diimide **2d** and the white product is a 1:1 complex of diimide **2d** with benzene. Similar complexes were formed with dioxane, tetrahydrofuran and acetonitrile.

The reaction of dianhydride **1** with aryl isocyanates was then applied to the formation of polymers. Condensation of diisocyanates, or prepolymers containing small amounts of diisocyanates, with various amounts of **1** gave polymers which show characteristics varying from those of soft elastomers to those of tough, brittle films, depending upon the amount of imide structure in the polymer chain. The polymer obtained by condensing equimolar amounts of **1** and methylenedi-*p*-phenylene diisocyanate showed properties identical to those of the polymer previously prepared from **1** and 4,4'-methylenedi-aniline (**7**).

#### EXPERIMENTAL

Melting points were determined in capillary tubes, employing an electric heated apparatus with a 500° thermometer (Mel-Temp, Lab. Devices, Cambridge, Mass.) and are uncorrected. Infrared spectra were taken on a Perkin-Elmer 137 "Infracord" Spectrophotometer, using the potassium bromide pellet technique. For detailed examination of the imide carbonyl bands a Perkin-Elmer 337 Grating Infrared Spectrophotometer was used. Thermogravimetric analyses (TGA) were conducted by means of a recording thermogravimetric balance (Aminco Thermo-Gray). Measurements were run in dry air from 0° to 900° on 100 mg. samples. The weight changes of a material were recorded as a function of temperature at a selected heating rate of 6°/minute. The degradation ranges were arbitrarily determined to be from the point of initial weight loss to a point on the linear temperature scale at 0% weight loss which is intersected by a tangent from the slope of the weight loss curve. Elemental analyses were performed by Dr. A. Bernhardt Microanalytische Laboratorium in Max Planck Institut für Kohlenforschung, Mülheim (Germany) and by Galbraith Laboratories, Inc., Knoxville, Tennessee.

TABLE III  
*N,N'*-bis(*p*-Substituted Phenyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides (**4a-l**)



Compound	R	Yield %		Degradation Ranges, °C	Empirical Formula	% C		Analyses % H		% N	
		Method A	Method B			Calcd.	Found	Calcd.	Found	Calcd.	Found
<b>4a</b>	CH <sub>3</sub>	58.0	60.6	390-417	C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>	72.72	72.49	4.07	4.20	7.07	7.01
<b>b</b>	OH	47.0	---	440-460	C <sub>22</sub> H <sub>12</sub> N <sub>2</sub> O <sub>6</sub>	66.00	65.86	3.02	3.20	7.00	7.12
<b>c</b>	OCH <sub>3</sub>	76.0	55.8	400-428	C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>6</sub>	67.28	67.42	3.77	3.76	6.54	6.46
<b>d(a)</b>	F	38.0	---	340-432	C <sub>22</sub> H <sub>10</sub> F <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	65.35	65.17	2.49	2.69	6.93	6.85
<b>e(b)</b>	Cl	28.0	42.9	370-446	C <sub>22</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	60.43	60.31	2.31	2.37	6.41	6.50
<b>f(c)</b>	Br	40.00	19.9	400-466	C <sub>22</sub> H <sub>10</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	50.22	50.46	1.92	2.06	5.33	5.20
<b>g(d)</b>	I	25.0	---	425-502	C <sub>22</sub> H <sub>10</sub> I <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	42.61	42.79	1.63	1.73	4.52	4.34
<b>h</b>	NO <sub>2</sub>	18.0	---	420-456	C <sub>22</sub> H <sub>10</sub> N <sub>4</sub> O <sub>8</sub>	57.65	57.38	2.20	2.19	12.22	12.29
<b>i</b>	CN	26.0	---	420-496	C <sub>24</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub>	68.90	68.80	2.41	2.40	13.39	13.26
<b>j</b>	COOH	28.0	---	430-470	C <sub>24</sub> H <sub>12</sub> N <sub>2</sub> O <sub>8</sub>	63.16	63.10	2.65	2.60	6.14	6.03
<b>k</b>	N=N-C <sub>6</sub> H <sub>5</sub>	17.0	---	430-495	C <sub>34</sub> H <sub>20</sub> N <sub>6</sub> O <sub>4</sub>	70.82	70.74	3.50	3.53	14.58	14.70
<b>l</b>	N(CH <sub>3</sub> ) <sub>2</sub>	53.0	---	348-358	C <sub>26</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub>	68.71	68.59	4.88	4.85	12.33	12.25

(a) % F: Calcd. 9.40, Found 9.62. (b) % Cl: Calcd. 16.22, Found 16.33. (c) % Br: Calcd. 30.38, Found 30.58. (d) % I: Calcd. 40.93, Found 40.78.

*N,N'*-bis(*o*-Substituted Phenyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides (**2a-i**).

#### Method A.

A solution of **1** (2.0 g., 0.01 mole) and the appropriate substituted aniline (0.025-0.03 mole) in dimethylformamide (25 ml.) was heated at 150-160° for 10-15 minutes. Approximately 50-75% of the solvent was evaporated, the concentrated solution was cooled and the crystals collected by filtration. Recrystallization was accomplished by using mixed solvent systems, such as dimethylformamide-benzene or dimethylformamide-methanol. The yields and melting points are listed in Table I. The infrared spectra show characteristic bands at 5.65 (sharp), 5.75 (strong and broad) and at 13.6-13.8  $\mu$ .

#### Method B.

A solution of **1** (2.0 g., 0.01 mole) and an excess of the appropriate isocyanate in dry dimethylformamide (20-25 ml.) was gradually heated. At 40-60° the solution developed a deep golden hue and at approximately 80° a noticeable amount of carbon dioxide was evolved. After 0.5 hour at 80° the reaction mixture was concentrated under vacuum to about half the original volume, cooled and the precipitate crystallized as described under Method A. The yields are listed in Table I. These compounds were found identical (mmp and ir spectra) to those prepared as described in Method A.

*N,N'*-bis(*m*-Substituted Phenyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides (**3a-h**).

These compounds were prepared following Method A above described for compounds **2a-i**. The yields and melting points are listed in Table II. The ir spectra are similar to those of compounds **2a-i**.

*N,N'*-bis(*p*-Substituted Phenyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimides (**4a-l**).

#### Method A.

These diimides were prepared following Method A above described for compounds **2a-i**, except only about 10% of the solvent was boiled off. The crystals were collected, washed with dimethylformamide, benzene, ether and dried in a vacuum oven. The yields and the decomposition ranges are listed in Table III. The ir spectra are similar to those of the above compounds **2a-i**.

#### Method B.

These diimides were prepared following Method B above described for compounds **2a-i**, with the difference that the reaction mixture after 0.5 hour at 80° was not concentrated, but cooled and diluted with benzene. The yields and the degradation ranges are listed in Table III. The ir spectra are identical to those of compounds **4a-l** prepared as described in the above Method A.

*N,N'*-bis(2,6-Diethylphenyl)-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimide.

A solution of **1** (2.1 g., 0.01 mole) in dimethylformamide (25 ml.) was added to 2,6-diethylaniline (4.2 g., 0.028 mole). The mixture was heated at 150-160° for 10-15 minutes and then concentrated until a slurry was obtained. The crystals were collected by filtration, washed with benzene, hexane and ether to give 2.5 g. (53%) of white powder, m.p. 282-292°.

*Anal.* Calcd. for C<sub>30</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>: C, 74.98; H, 5.87; N, 5.83. Found: C, 75.14; H, 5.74; N, 6.00.

*N,N'*-Diphenyl-1,2,4,5-benzenetetracarboxylic-1,2:4,5-diimide (**2a**) from **1** and Phenyl Isothiocyanate.

A solution of **1** (2.0 g., 0.01 mole) in dimethylformamide (25 ml.) was added to phenyl isothiocyanate (3.0 g., 0.02 mole) and the mixture was heated gradually while stirring. At about 50° an intense yellow solution was obtained and at 100° some bubbles of gas began to form. A moist lead acetate paper held above the mouth of the flask indicated evolution of carbonyl sulfide. The solution was heated at the boil for 1 hour, cooled, diluted with benzene (100 ml.) and the precipitate collected by filtration, washed with dimethylformamide (10 ml.), followed by benzene, hexane and ether to give 0.45 g. (13%) of **2a**. The ir spectra are identical to those of **2a** prepared from **1** and aniline and from **1** and phenyl isocyanate.

#### 1:1 Complex of Diimide **2d** with Benzene.

Crude **2d** (4.0 g.) was heated at reflux with ethanol (100 ml.). The insoluble product was crystallized from benzene (350 ml. for 0.4 g. of product) and dried *in vacuo* at 25° for 11 hours to give white crystals.

*Anal.* Calcd. for C<sub>30</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub> (1:1 complex of **2d** with benzene): C, 71.14; H, 4.38; N, 5.53. Found: C, 71.52; H, 4.56; N, 5.36.

This complex when heated at 290-300° gave **2d** as golden yellow needles, m.p. 335-337°, ir spectrum identical to that of **2d** prepared as above.

*Anal.* Calcd. for C<sub>24</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub>: C, 67.28; H, 3.77; N, 6.54. Found: C, 67.12; H, 3.83; N, 6.67.

This compound and the above complex with benzene showed practically identical infrared spectra. The yellow needles, when recrystallized from benzene, gave the above described white crystals.

#### 1:1 Complex of Diimide **2d** with Dioxane.

Crude **2d** was treated with ethanol as described above and crystallized from dioxane (100 ml. for 0.4 g. of product) to give 0.4 g. of fine white crystals. An analytical sample was kept at 25° *in vacuo* until constant weight.

*Anal.* Calcd. for C<sub>28</sub>H<sub>24</sub>N<sub>2</sub>O<sub>8</sub> (1:1 complex of **2d** with dioxane): C, 65.11; H, 4.68; N, 5.42. Found: C, 64.87; H, 4.73; N, 5.70.

This complex when heated at 298-310° gave **2d** as yellow needles, m.p. 336-337°, identical (m.m.p. and ir) with the above described yellow crystals obtained from the benzene complex.

Similar complexes were formed when crude **2d** was crystallized from tetrahydrofuran, acetonitrile, or *p*-xylene.

#### Polymer of **1** with an Isocyanate-Terminated Prepolymer.

To 20 g. of polyester-*o*-tolylene diisocyanate prepolymer (Vibrathane V-6008, U. S. Rubber., Naugatuck Chemical Division) containing 3.0% free isocyanate, determined by end group analysis with *n*-butylamine, was added while stirring a solution of dianhydride **1** (1.5 g., the stoichiometric amount required in this reaction) in dimethylformamide (20 ml.). A characteristic yellow color developed and a gradual release of gas was observed as the temperature was increased to 140°. After about 0.5 hour the polymer was removed from the flask and drawn into elastomeric films, which were air-cured at ambient temperature and then at 95° for several days.

A similar orange thermoplastic elastomer, which could be drawn into an elastic filament when hot, was obtained when in the above reaction a polyether-*o*-tolylene diisocyanate prepolymer ("Adiprene" L. 100, E. I. DuPont de Nemours Co.) was used in

place of the polyester-*o*-tolylene diisocyanate prepolymer and the mixture kept 3 hours at 120°.

An identical material was formed when the above reaction with "Adiprene" L. 100 was carried out in absence of solvent.

Polymer of **1** with Methylenedi-*p*-phenylene Diisocyanate and 1,4-Butanediol.

A solution of **1** (2.18 g., 0.01 mole) in dimethylformamide (30 ml.) was added to a fine slurry of methylenedi-*p*-phenylene diisocyanate (5.1 g., 0.02 mole) in dimethylformamide (10 ml.). The slightly cloudy yellow solution was stirred 10 minutes, anhydrous 1,4-butanediol (0.90 g., 0.01 mole) was added and the mixture heated gradually to about 120°. At 85° carbon dioxide started to evolve. The temperature rise levelled off at 120-122°, gas evolution ceased and the yellow solution became more viscous. Films of this solution were cast on glass plates and cured to a tack free film in 1.5 hours at 60°. After a post cure at 80° for 20 hours a tough, clear flexible film, soluble in hot dimethylformamide was obtained.

Polymer of **1** with Methylenedi-*p*-phenylene Diisocyanate.

Dimethylformamide (25 ml.) was added to an intimately blended mixture of **1** (2.18 g., 0.01 mole) and methylenedi-*p*-phenylene diisocyanate (2.5 g., 0.01 mole) and the slurry stirred to dissolve the reactants. The solution was heated at 80° for 10 minutes and then the golden liquid was cast on glass plates and heated at 100° for 2-4 hours. The brittle, flaky yellow film was removed as fine particles by scraping with a razor blade. The polymer was identical in appearance, brittle film character and ir spectrum to the polymer prepared from stoichiometric amounts of **1** and 4,4'-methylenedianiline (7).

#### Acknowledgment.

We gratefully acknowledge the valuable assistance of Dr. Mario F. Sartori in connection with this research.

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