2-Carbethoxy-2-fluorocyclopentanone (12) was obtained in 92% yield when **11** reacted with **1**: NMR δ 4.28 (2 H, q, J = 7.1 Hz), 2.6–2.05 (6 H, m), 1.34 (3 H, t, J = 7.1 Hz); ^{19}F NMR ϕ^* 164 (t, J = 20 Hz); MS; m/e 174 (M^+), 129 (M – OEt, base peak); IR 1780, 1725 cm^{-1}. Anal. Calcd for $C_8H_{11}FO_3$: C, 55.17; H, 6.32; F, 10.92. Found: C, 54.89; H, 6.60; F, 10.91.

Dimethyl fluoromalonate (14)[17] was prepared from dimethyl sodiomalonate (**13**): 52% yield; NMR δ 5.33 (1 H, d, J = 45 Hz), 3.88 (6 H, s); ^{19}F NMR ϕ^* 195.8 (d, J = 48 Hz); MS; m/e 150 (M^+, base peak).

Diethyl ethylfluoromalonate (16)[17] was obtained in 77% yield from diethyl ethylsodiomalonate (**15**): ^{19}F NMR ϕ^* 169.5 (t, J = 7.1 Hz); MS; m/e 177 [(M – Et)$^+$], 133 [(M – COOEt)$^+$], 105 [(CHFCOOEt)$^+$, base peak]. Compound **16** (650 mg) was refluxed in 50 cm^3 of HCl (6 N) for 48 h. The reaction mixture was extracted with ether, the ether layer dried, and the ether removed by distillation. A yield of 310 mg (92%) of α-fluorobutyric acid (**17**) was obtained: ^{19}F NMR ϕ^* 194.6 (dt, J_1 = 48, J_2 = 23 Hz).

Registry No. **1**, 78948-09-1; **2**, 108-56-5; **2a**, 40876-98-0; **3**, 392-58-5; **4**, 141-97-9; **4a**, 19232-39-4; **5**, 1522-41-4; **6**, 41302-34-5; **6a**, 56137-55-4; **7**, 84131-42-0; **8**, 874-23-7; **8a**, 72072-37-8; **9**, 74279-75-7; **10**, 84131-43-1; **11**, 13697-91-1; **12**, 84131-44-2; **13**, 18424-76-5; **14**, 344-14-9; **15**, 18995-13-6; **16**, 1578-75-2; **17**, 433-44-3; F_2, 7782-41-4; NaOAc, 127-09-3.

Thermally Induced Degradation of 2,3,5,6-Tetrachloroterephthalylidenebis(*o*-aminoaniline)

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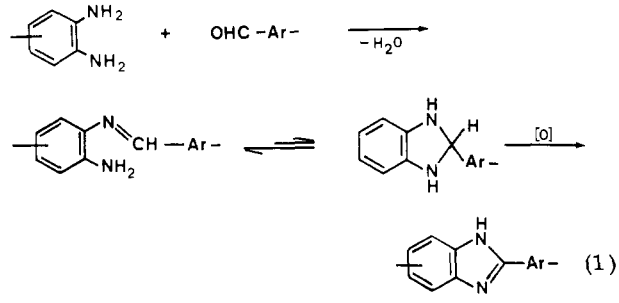
The bis(Schiff base) **1**, 2,3,5,6-tetrachloroterephthalylidenebis(*o*-aminoaniline), obtained by low-temperature solution condensation of *o*-phenylenediamine with 2,3,5,6-tetrachloroterephthalaldehyde, suffers fragmentation at 100 °C in dipolar aprotic solvent media under strictly anaerobic conditions, giving benzimidazole (**3**) and 1,2,4,5-tetrachlorobenzene (**4**). The same fragmentation of **1**, although accompanied by side reactions, is observed in refluxing ethanol or toluene. The reaction involves fission of the C–C bonds connecting the central tetrachlorophenylene segment with the outer two substituent groups and probably proceeds via the ring-tautomeric bis(imidazoline) form of **1**. Neither the bis(benzimidazole) **2**, 1,4-bis(benzimidazol-2-yl)-2,3,5,6-tetrachlorobenzene, in which the outer two substituent groups already exist in the aromatized state, nor the bis(Schiff base) **6**, terephthalylidenebis(*o*-aminoaniline), lacking the four bulky chloro groups at the center unit, undergo such C–C bond cleavage under the conditions indicated. These findings show that it is the combined effect of steric buttressing at the perchlorophenylene segment and imidazolation, i.e., aromatization, of the outer substituent groups which provides the driving force for the fragmentation observed. In a suitable oxidative environment, cyclodehydrogenation of the bis(Schiff base) **1** competes efficaciously enough with the degradative process to suppress the generation of the fragmentation products, and only the bis(benzimidazole) **2** is isolated.

It has been amply demonstrated[1-5] that aromatic Schiff bases possessing an additional amino group in the ortho position to the azomethine nitrogen atom undergo smooth oxidative cyclodehydrogenation, thereby converting to the corresponding benzimidazoles, and use of this aromatization process has been made[6] in polymerization studies aiming at the synthesis of linear polybenzimidazoles from open-chain polyazomethine precursors. The latter reaction, illustrated in eq 1 for a typical azomethine segment



(1)

(Ar = 1,3- or 1,4-phenylene, etc.), is catalytically assisted by certain transition-metal compounds and most likely proceeds via the imidazoline tautomer structure shown, hydrogen peroxide being the byproduct of oxidation.[4] Polyazomethines lending themselves as polybenzimidazole precursors in this type of reaction are generally accessible by anaerobic solution polymerization of aromatic bis *o*-diamines with aromatic dialdehydes in *N*,*N*-dimethylacetamide or related solvents at temperatures up to 100 °C.[6] However, attempts in our laboratory[7] to synthesize a chlorinated poly(Schiff base) in an analogous fashion from 3,3′-diaminobenzidine and 2,3,5,6-tetrachloroterephthalaldehyde over the temperature range –15 to +80 °C revealed grossly anomalous behavior: instead of the expected poly(Schiff base), low-molecular-mass fragments resulting from extensive chain cleavage were the main products isolated.

In an effort to shed some light on the causes underlying this unexpected chain scission, we investigated, and herein describe, the model reaction involving the solution condensation of *o*-phenylenediamine with 2,3,5,6-tetrachloroterephthalaldehyde at various temperatures in both oxidative and anaerobic environments.

Results

The low-temperature condensation behavior of the reactant pair, *o*-phenylenediamine and tetrachloroterephthalaldehyde, was investigated in an initial series of experiments in which the two reactants were allowed to undergo anaerobic condensation in a 2:1 molar ratio at –15 to +25 °C. *N*,*N*-Dimethylacetamide (DMAC), previously

(1) Weidenhagen, R.; Train, G. *Chem. Ber.* **1942**, *75*, 1936.
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(3) Stephens, F. F.; Bauer, J. D. *J. Chem. Soc.* **1949**, 2971; **1950**, 1722.
(4) Grellmann, K. H.; Tauer, E. *J. Am. Chem. Soc.* **1973**, *95*, 3104.
(5) Coville, N. J.; Neuse, E. W. *J. Org. Chem.* **1977**, *42*, 3485.
(6) Neuse, E. W. *Ind. Chem.* **1975**, 315.
(7) Unpublished results from this laboratory.

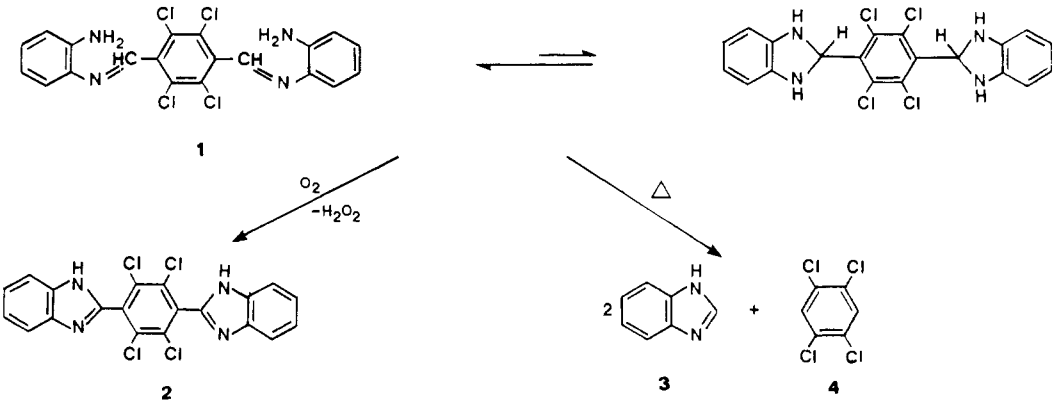
0022-3263/83/1948-0727$01.50/0

Table I. Condensation of o-Phenylenediamine with 2,3,5,6-Tetrachloroterephthalaldehyde and Related Reactions[a]

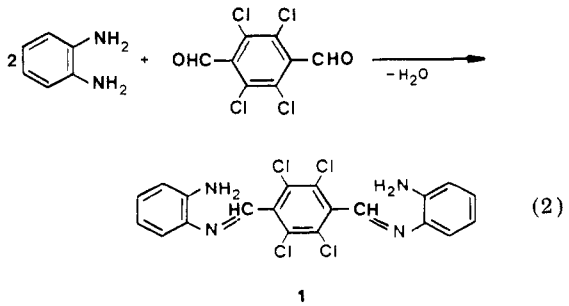
entry	reactants (molar ratio)	reaction conditions: first stage[b]	reaction conditions: second stage	isolated product yields,[c] %: 1	2	3	4	6	7
1[d]	OPD + TCT (2.1:1)	1 h at −10 °C, 4-h warmup to room temp, 5 h at room temp	immediate workup	94	e				
2[d]	OPD + TCT (2.1:1)	i	air introduced (10 L h^{-1}) for 12 h at room temp[f]		90	e	e		
3[g]	OPD + TCT (2.1:1)	i	10 h at 100 °C in absence of air	e	e	59 (91)	76 (87)		
4[g]	1		11 h at 100 °C in absence of air	e	e	52 (86)	72 (90)		
5	2		10 h at 100 °C in absence of air		91				
6	6		10 h at 100 °C in absence of air					93	4[h]

[a] Performed in N,N-dimethylacetamide unless otherwise stated. OPD = o-phenylenediamine; TCT = 2,3,5,6-tetrachloroterephthalaldehyde; room temp = ambient temperature (22 ± 3 °C). [b] Anhydrous and anaerobic conditions used throughout. Aldehyde solution added to amine solution at −15 °C. For details see the Experimental Section. [c] Mass spectrometrically assessed yields in parentheses; anthracene was added as an internal standard; results tabulated are averages of two independent runs. [d] Similar results in DMF, NMP, Me_2SO, THF, ethanol, and toluene. [e] Traces (by TLC), insufficient for preparative isolation. [f] Catalyzed by $FeCl_3$ (1.0 mol %). Similar results after 3.5 h at 50 °C or 35 min at 100 °C. [g] Similar results in DMF or NMP; imidazole 5 (4–8%) was additionally isolated in experiments performed in ethanol. [h] Probably formed from 6 during workup. [i] Same as for entry 1.

Scheme I



used in the analogous polymerization attempts,[7] was selected as the principal medium. A representative experiment, conducted over a period of 10 h, is summarized in Table I (first entry). Under the mild conditions chosen, the only product isolated in this and similar runs proved to be the expected bis(Schiff base) 1, 2,3,5,6-tetrachloroterephthalylidenebis(o-aminoaniline) (eq 2).[8] The same product resulted from experiments performed in other aprotic or protic solvents.



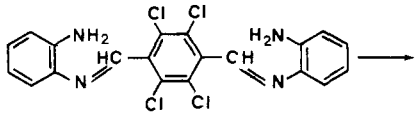
(2)

(8) Schiff bases of the benzal (o-aminoaniline) type represented in eq 1 can tautomerize to the corresponding imidazoline structure, although the high basicity of the amino group favors the open-chain azomethine form.[4] The prevalent, if not exclusive, open-chain structure 1 is supported by the ^{1}H NMR spectrum (see Experimental Section), which fails to exhibit the methine proton signal expected near δ 3.1 for an imidazoline structure,[9] while showing the azomethine proton peak at δ 8.8.

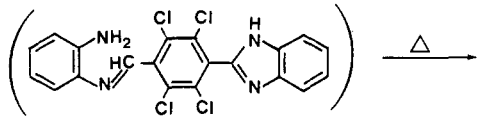
(9) Suzuki, H.; Ohashi, M.; Itoh, K.; Matsuda, I.; Ishii, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1922.

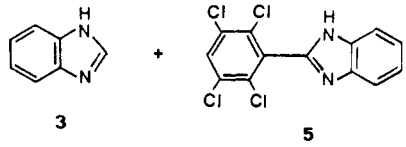
In subsequent experiments, 2:1 condensation of the two reactants was brought about in DMAC solution under anaerobic conditions as before; however, the bis(Schiff base) solutions so obtained were now further treated either by exposure to an oxidative environment or else by anaerobic heating under various conditions of time and temperature. Thus, in the second experiment tabulated, the solution was exposed for 12 h at room temperature to an air stream (10 L h^{-1}) in the presence of a catalytic quantity of iron(III) chloride. Under these conditions, the intermediate 1 behaved as the results of earlier work with nonchlorinated bis(Schiff bases) would suggest,[5] undergoing rapid cyclodehydrogenation to the bis(benzimidazole) 2 [1,4-bis(benzimidazol-2-yl)-2,3,5,6-tetrachlorobenzene, Scheme I]. Only trace quantities of other products were detectable by thin-layer chromatography (TLC). Raising the temperature to 50 (3.5 h) or 100 °C (35 min) gave substantially the same results, as did the replacement of the amide-type solvent by tetrahydrofuran, ethanol, or toluene. In the third experiment tabulated, exemplifying a series of runs performed ultimately at elevated temperatures, the solution containing 1 as obtained under the conditions of the first entry was heated in the absence of oxygen for 10 h at 100 °C. The workup afforded virtually no bis(benzimidazole) 2; instead, the simple benzimidazole (3) and 1,2,4,5-tetrachlorobenzene (4) were isolated as the sole products (Scheme I). Comparable results with respect to the formation of 3 and 4 were obtained in oxygen-free N,N-dimethylformamide or N-

methylpyrrolidone at the same temperature and, less cleanly, in refluxing deoxygenated toluene (50–60 h) or absolute ethanol (12–24 h), the monobenzimidazole 5 appearing as a byproduct in the last-named case (eq 3).[10]



1



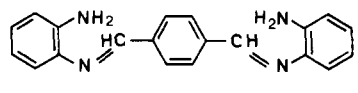


3 5 (3)

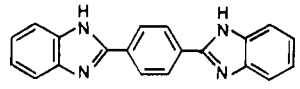
Isolated yields in these various experiments were not strictly reproducible owing to losses of volatile products during the workup. In several cases, therefore, a more realistic yield assessment was made by mass spectrometry using the crude product solution in the presence of anthracene as an internal standard. The yields so obtained are juxtaposed in Table I to the values of the isolated yields.

In order to ascertain whether the ultimate products of fragmentation (third entry) both originated from the common intermediate 1, as the formation of this bis(Schiff base) under the conditions of the first entry would suggest, several runs were conducted with 1 as the reactant in place of o-phenylenediamine and tetrachloroterephthaldehyde. Entry 4 exemplifies this series of experiments. In all instances, conforming to the results of the third entry, the degradation produces 3 and 4 proved to be the only isolable compounds. It may, hence, be concluded that it is indeed the bis(Schiff base) 1 which functions as the precursor of 3 and 4.

Several control experiments probing the degree of resistance of the cyclodehydrogenation product 2 to anaerobic thermal degradation were performed at 100 °C in DMAC solution, the purpose being to discount the possibility that 3 and 4 might have originated from the bis(Schiff base) via 2 rather than by direct fragmentation steps. Entry 5 (Table I) is representative. In no instance could the two fragmentation products be detected, and most of the bis(benzimidazole) employed was recovered unchanged in these efforts. In another type of control experiment, aimed at assessing the effect of the four chloro substituents in 1 on the compound's proneness to fragmentation, the chlorine-free bis(Schiff base) analogue 6[5] was subjected to the same anaerobic heat treatment in DMAC solution as employed in entry 4. The last entry in the table summarizes this experiment. The absence of 3 in the final reaction mixture and the almost quantitative recovery of 6 (in addition to the collection of a few percent of the cyclodehydrogenation product 7[5]) indicate that no



6



7

fragmentation of the kind suffered by 1 occurred in this case.

Our findings may be summed up as follows: (i) at temperatures not substantially exceeding 25 °C the anaerobic 2:1 condensation of o-phenylenediamine and tetrachloroterephthalaldehyde in various polar and nonpolar solvents, when conducted over sufficiently long reaction periods, proceeds smoothly to give the bis(Schiff base) 1 as the only isolable product; (ii) oxidative cyclodehydrogenation of 1 at 25–100 °C in an air stream, in both polar and nonpolar solvents, affords the corresponding bis(benzimidazole) 2 as the sole product isolated; (iii) the same bis(Schiff base) 1, when heated anaerobically in dipolar aprotic solvents at temperatures typically in the region of 70–100 °C, degrades cleanly, the ultimate products of this fragmentation being benzimidazole (3) and 1,2,4,5-tetrachlorobenzene (4); (iv) the same fragmentation, although proceeding in competition with other reactions, is observed in nonpolar solvents, e.g., toluene, or in protic solvents such as ethanol; (v) no fragmentation occurs on heating the analogous chlorine-free bis(Schiff base) 6 under the same conditions; (vi) contrasting with its precursor base 1, the bis(benzimidazole) 2 is resistant to thermal degradation under similar conditions.

Discussion

While the formation of the bis(Schiff base) 1 by low-temperature solution condensation of o-phenylenediamine with tetrachloroterephthalaldehyde (eq 2) is straightforward, its fate under more forcing conditions depends critically on both the temperature and the presence or absence of oxidants and also to some extent on the nature of the solvent. An oxidative environment at temperatures of 25–100 °C promotes clean and rapid cyclodehydrogenation in both protic and aprotic solvents, affording the bis(benzimidazole) 2. In the absence of oxygen or other oxidants, temperatures in the range of 70–100 °C bring about thermal fragmentation, giving rise to the formation of benzimidazole (3) and 1,2,4,5-tetrachlorobenzene (4, Scheme I). This cleavage process, which is highly efficient in a dipolar aprotic medium and somewhat less so in other solvent types, probably originates from the ring-tautomeric bis(imidazoline) and proceeds by fission of both C–C bonds connecting the perchlorinated phenylene center unit with the benzimidazoline rings and concomitant proton transfer from the two heterocycles to the central phenylene group.[11] The available evidence indicates that the expulsion of the α-carbon atoms from the xylylidene segment is a consequence of the combined effect of strain relief in the sterically crowded tetrachlorophenylene center unit and a gain in delocalization energy through aromatization of the two imidazoline

(10) In the protic ethanol medium dehydrogenation is sufficiently rapid even in the absence of oxygen to bring about occasional imidazole ring formation before C–C bond cleavage can occur at that site. Once imidazolized (as in 5), the heterocyclic substituent is no longer prone to elimination by fission of the connecting bond under the moderate thermal conditions of these experiments (see subsequent text).

(11) Although the C–C bond fission could be homolytic, thus requiring hydrogen transfer, we prefer to consider a mechanism involving bond polarization (induced by the electron-withdrawing halogen substituents) with sufficient electron density accumulated on the phenylene carbon atoms 1 and 4 to bring about heterolytic cleavage with concomitant proton transfer.

substituents. That neither factor alone suffices to cause the observed fragmentation into **3** and **4** is borne out by the results of the two control experiments involving the anaerobic heating of **2** and **6**. If steric crowding alone were a sufficient condition for C–C bond breaking, the bis(benzimidazole) **2** should have displayed some proneness to fragmentation, which it did not (entry 5). On the other hand, were aromatization of the imidazoline ring system the sole driving force, then the chlorine-free bis(Schiff base) **6** should have undergone some degree of C–C bond fission, which, again, was not observed (entry 6).

The chain scission and degradation suffered at elevated temperatures by the chlorinated poly(Schiff base) of the earlier polymerization work[7] is no longer unexpected when seen in the light of the results of the present model reaction study. Clearly, the same combined driving force of steric strain relief and heteroring aromatization as evidenced in the reaction of **1** must be operative in an analogous polymeric system comprising a tetrachlorophenylene-bridged bis(*o*-aminoazomethine) structure (and its ring-tautomeric form) in the recurring unit, in which, therefore, C–C bond fission will efficaciously compete with propagation at the higher temperatures employed. By judiciously restricting the polymerization temperature to a range not significantly exceeding 25 °C, it should be possible to suppress the bond breaking reaction in favor of polymerization. This topic is being pursued in our laboratory and will be discussed elsewhere.[12]

Experimental Section

Instrumentation. Melting points (uncorrected) were taken up to 300 °C in sealed capillaries. IR spectra were recorded on KBr pellets. Proton NMR spectra were recorded on a Varian HA-100 NMR spectrometer; δ values are given in parts per million relative to Me_4Si. Mass spectra (70 eV) were taken on Varian Mat-CH5 or Varian Mat-212 mass spectrometers at inlet temperatures of 25–150 °C. For quantitative assessment of product concentrations by mass spectrometry, an anthracene standard was dissolved in an aliquot volume of the crude reaction solution in a molar concentration comparable to those expected for the products **3** and **4**. The mass spectrum was then taken on this standard-containing aliquot, and the product concentrations were assessed by comparison of relative peak heights with those in reference spectra obtained by scanning equimolar solutions of **3**, **4**, and standard.

Solvents and Reagents. *N,N*-Dimethylacetamide (DMAC), *N,N*-dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), and tetrahydrofuran (THF) were dried by being refluxed over and distilled (under reduced pressure in the first three cases) from calcium hydride. Dimethyl sulfoxide (Me_2SO), predried over 4A molecular sieves, was distilled under reduced pressure. Benzene and toluene, predried over 4A molecular sieves, were distilled from sodium. Ethanol (absolute) was used as received, as was the monodeuterated carbinol. Solvents used for anaerobic experiments were saturated with prepurified nitrogen. *o*-Phenylenediamine was twice recrystallized from 96% ethanol under nitrogen.

2,3,5,6-Tetrachloroterephthalaldehyde was prepared by Pfitzner–Moffatt oxidation[13] of commercially available 2,3,5,6-tetrachloroxylylene-α,α'-diol with dicyclohexylcarbodiimide/Me_2SO. The method was found to give higher yields than the procedure described in the patent literature[14] involving $\alpha,\alpha,\alpha',\alpha'$,2,3,5,6-octachloro-*p*-xylene intermediacy. To the stirred solution of the xylylenediol (55.18 g, 0.2 mol) in 500 mL of Me_2SO and 250 mL of benzene, contained in a 2-L, round-bottomed flask equipped with a dropping funnel and secured with a drying tube, were added 31.6 g (0.4 mol) of pyridine and 16 mL (0.2 mol) of trifluoroacetic acid. Following the addition of dicyclohexylcarbodiimide (310 g, 1.5 mol), the exothermic reaction was allowed to proceed, the flask being submerged intermittently in ice–water. The mixture was stirred at room temperature for a total of 7 days, at which point the concentration of dialdehyde (monitored by TLC) had reached a stationary level. Ether (2.5 L) and then oxalic acid (135 g, 1.5 mol, dissolved in 1 L of methanol) were added to the reaction mixture. After the gas evolution had ceased (ca. 45 min), 2.5 L of water was stirred into the mixture, and the precipitated dicyclohexylurea was removed by filtration through glass wool. The residue was thoroughly extracted with ether (4 × 400 mL), as was the filtrate (4 × 600 mL). The combined ether extracts, concentrated to a volume of ca. 2 L, were washed with a 5% aqueous sodium hydrogen carbonate solution (2 × 600 mL) for removal of acidic oxidation products and then with brine (500 mL). After solvent removal from the dried organic phase, the remaining yellow solid (45 g), constituting a mixture of the dialdehyde with minor portions of the half-oxidized product 2,3,5,6-tetrachloro-4-formylbenzyl alcohol and unoxidized diol, was thoroughly extracted with hexane/chloroform (1:1), and the combined and concentrated extracts were chromatographed on Merck silica gel (0.05–0.2 mm) with benzene/chloroform as the eluent. Elution was monitored by TLC. The first major band gave 22 g (40.4%) of crude dialdehyde, which after recrystallization from hexane/chloroform was obtained as faintly yellowish fine crystals: mp 193–194 °C (lit.[14] mp 193 °C); IR (KBr) 2848 (w, ν_{C-H}), 1720 (s, d, $\nu_{C=O}$) cm^{-1}; MS (70 eV), *m/e* 270 (P^+, $C_8H_2{}^{35}Cl_4O_2$).

2,3,5,6-Tetrachlorophthalylidenebis(*o*-aminoaniline) (1; Entry 1, Table I). Under a gentle stream of nitrogen the solution of tetrachloroterephthalaldehyde (190 mg, 0.7 mmol) in 5 mL of DMAC was added over a period of 60 min to the stirred solution of *o*-phenylenediamine (159 mg, 1.47 mmol) in 3 mL of DMAC precooled to −15 °C. Stirring under a nitrogen blanket was continued for 1 h at −10 °C, for a further 4 h with gradual warming to 20 °C, and for an additional 5 h at ambient temperature. Overnight storage at 0 °C allowed a major fraction of the Schiff base **1** to crystallize as fine orange-red needles, which were removed by filtration. A second, microcrystalline portion, contaminated by traces of **2** (TLC, SiO_2, 25:1 ethyl acetate/acetic acid), was obtained by the addition of brine (15 mL) to the filtrate and allowing the mixture to stand in the cold as before. The combined product (297 mg, 93.8%) was recrystallized from deoxygenated THF: mp 182–184 °C (sealed under N_2); IR (KBr) 3460–3300 (w–m, ν_{N-H}, free and bonded), 1610–1590 (s, br, δ_{NH_2}, $\nu_{C=C,C=N}$), 750–740 (s, d, ν_{C-Cl}) cm^{-1}; NMR ($CDCl_3$) δ 8.78 (2 H, s, N=C—H), 7.3–6.7 (ca. 8 H, m, Ar H), 5.17 (4 H, br s, NH); NMR (Me_2SO-d_6) δ 8.80 (2 H), 7.3–6.6 (ca. 8 H), 5.18 (4 H); MS (70 eV), *m/e* 450 (P^+, $C_{20}H_{14}{}^{35}Cl_4N_4$). Anal. Calcd for $C_{20}H_{14}Cl_4N_4$: C, 53.12; H, 3.12; N, 12.39. Found: C, 52.89; H, 3.22; N, 12.01.

Analogous experiments conducted in ethanol, THF, or toluene afforded **1** in yields of 85–93%. The workup merely involved solvent removal by rotatory evaporation at <50 °C, followed by recrystallization in the absence of oxygen.

1,4-Bis(benzimidazol-2-yl)-2,3,5,6-tetrachlorobenzene (2; Entry 2, Table I). An experiment was initially conducted as described above for the preparation of **1**. After the 10-h stirring period at ultimately ambient temperature, anhydrous iron(III) chloride (1.1 mg, 0.007 mmol) was added, and some solid **1** which had deposited on the walls was returned by spatula into the liquid phase; this was then stirred for another 12 h at 22 ± 3 °C with air bubbled in at a rate of 10 L h^{-1}. During this treatment the solution's color changed gradually from red-orange to a grayish yellow, and a portion of the bis(benzimidazole) **2** crystallized from solution. The addition of brine (20 mL) completed the precipitation of **2** as a cream-colored solid. Extraction of the mother liquor with chloroform, back-washing of the extract with brine, and chloroform removal afforded a second crop of **2**, bringing the total yield up to 283 mg (90.2%). Traces of cleavage products **3** and **4** (no isolable quantities) were detected as contaminants by TLC (SiO_2, 99:1 chloroform/methanol). Recrystallization of the combined product fractions from DMF/water furnished off-white, fine crystals of the bis(benzimidazole): infusible at <300 °C; IR (KBr) 3100–2600 (m, br, ν_{N-H}), 1615 (w–m, $\nu_{C=C,C=N}$), 1425 (s, heterocycle), 745–735 (s, d, ν_{C-Cl}) cm^{-1}; NMR (Me_2SO-d_6) δ 13.0 (2 H, s, NH), 7.8–7.2 (ca. 8 H, m, Ar H); MS (70 eV), *m/e* 446 (P^+, $C_{20}H_{10}{}^{35}Cl_4N_4$). Anal. Calcd for $C_{20}H_{10}Cl_4N_4$): C, 53.60; H, 2.25; N, 12.50. Found: C, 53.33; H, 2.41; N, 12.37.

(12) Neuse, E. W.; Loonat, M. S. *Macromolecules*, in press.
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Experiments carried out as described except that the air treatment was performed at elevated temperatures (50 °C for 3.5 h or 100 °C for 35 min) gave **2** in yields of, respectively, 87% and 92%.

Benzimidazole (3) and 1,2,4,5-Tetrachlorobenzene (4). (a) From o-Phenylenediamine and 2,3,5,6-Tetrachloroterephthalaldehyde (Entry 3, Table I). An experiment was performed as described for the preparation of **1** except that, after the 10-h stirring period at −10 °C to ambient temperature, the mixture was heated for 10 h at 100 °C under N_2. During this period the color of the solution turned to a pale yellow. The volume of the reaction mixture was made up with DMAC to 8.00 mL, and two 0.50-mL aliquots were removed for mass spectrometric assessment of product yields. The remaining 7.00 mL of product solution was diluted with brine (15 mL). After a 12-h cooling period at 2 °C, the precipitated cream-colored solid, essentially a mixture of **4** (major) and **3** (minor; TLC, SiO_2, 99:1 chloroform/methanol), was collected by filtration and washed with water. Careful fractional extraction of the dried material (140 mg) with pentane removed **4**, of which 92 mg was recovered from the extract; mp 136–137 °C (hexane). The extraction residue, 25 mg, represented crude **3**, mp 168–171 °C (benzene), contaminated with traces of **1** and **2** (TLC). The aqueous filtrate, acidified (HCl) to pH ~4, was thoroughly extracted with ether, which took up the DMAC solvent together with some **4**, while leaving most of the imidazole as the hydrochloride in the brine. The combined extracts, after ether removal, were diluted with water (10 mL), giving a precipitate (7 mg) of crude **4**. The original acidic, aqueous phase was now treated with alkali (pH ~8) and extracted with large volumes (3 × 200 mL each) of ether and chloroform. The combined extracts, after solvent removal, yielded 67 mg of light brownish solid essentially consisting of **3** contaminated with **4**. The latter, more volatile component was removed by sublimation at 50 °C (0.01 torr), leaving 60 mg of **3** as a residue. Total isolated yields of **3** and **4** were, respectively, 85 (58.8%) and 101 mg (76.1%; percentage yields calculated for total products including aliquots removed for mass spectroscopy). Both compounds proved identical (IR, mixture melting point) with authentic samples.

A typical experiment performed with the same reactant quantities in 40 mL of boiling absolute ethanol (24 h) under N_2 was worked up by solvent evaporation under reduced pressure. This left a yellowish solid from which crude **4** (88 mg, 58%) was isolated by cold extraction with pentane and solvent removal. The residue, a mixture of **3** and **5** with traces of **2** (TLC), was carefully recrystallized from chloroform/benzene, giving 9 mg (3 mg upon recrystallization from DMF/H_2O) of the less soluble **5** [infusible at <300 °C; IR (KBr) 3500–2700 (m, br, ν_{NH}), 1615 (w–m, $\nu_{C=C,C=N}$), 1425–1410 (s, multiplet, heterocycle), 740 (s, ν_{C-Cl}) cm^{-1}; MS (70 eV), m/e 330 (P^+, $C_{13}H_6{}^{35}Cl_4N_2$)] and 122 mg (74%) of the somewhat more soluble **3**. An alternative workup, used in other experiments, involved precipitation from the concentrated product solution of the majority of **4** and **5** (71% combined) by the addition of excess water, followed by extraction of **3** (64%, contaminated with **5**) from the aqueous/alcoholic phase with chloroform.

Experiments similarly carried out in nitrogen-saturated toluene solvent (50 h, reflux) gave **3** (59%) and **4** (50%), in addition to an unidentified yellow product mixture and 5–10% of **1** and **2**.

(b) From Bis(Schiff Base) 1 (Entry 4, Table I). The solution of **1** (226 mg, 0.5 mmol) in 8 mL of DMAC was thoroughly deoxygenated and heated for 11 h at 100 °C with magnetic stirring under a blanket of nitrogen. A workup as in part a afforded **3** (52.2%) and **4** (71.9%) in addition to traces of **1** and **2** detected by TLC.

Anaerobic Heating of 2 (Entry 5, Table I). The bis(benzimidazole) **2** (112 mg, 0.25 mmol) was heated in 10 mL of DMAC for 10 h at 100 °C in the strict absence of oxygen. The milky suspension was diluted with 10 mL of water, and the insoluble solid, collected by filtration and washed with water, was found (TLC) to be pure unreacted **2**. Evaporation of the filtrate to dryness under reduced pressure gave a few more milligrams of **2**, bringing the total recovery to 102 mg (91%). No volatile matter (e.g., **4**) could be separated from the combined product fractions by sublimation.

Anaerobic Heating of 6 (Entry 6, Table I). A solution of terephthalylidenebis(o-aminoaniline) (**6**;[5] 200 mg, 0.65 mmol) in 10 mL of DMAC was heated for 10 h at 100 °C in the strict absence of oxygen. Storage at 0 °C overnight afforded a major fraction (128 mg) of unreacted **6** as reddish crystals. Addition of 20 mL of water resulted in the precipitation of another 58 mg of **6** as a fine-crystalline orange solid. Both fractions were shown (IR, TLC) to be free from contaminants. A small third fraction (8 mg) which separated out from the mother liquor upon overnight storage at 2 °C proved to be predominantly **7**, identified by TLC and spectroscopic comparison with the authentic[5] bis(imidazole).

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Registry No. **1**, 84057-62-5; **2**, 84057-63-6; **3**, 51-17-2; **4**, 95-94-3; **6**, 16524-60-0; 2,3,5,6-tetrachloroterephthalaldehyde, 3421-67-8; 2,3,5,6-tetrachloro-4-formylbenzyl alcohol, 84057-64-7; 2,3,5,6-tetrachloroxylylene-α,α'-diol, 7154-26-9; o-phenylenediamine, 95-54-5.